

Variational Quantum Monte Carlo Method: A pedagogical approach

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1. Abstract

We present a report that describes the stochastic variational Monte Carlo method underlying ideas and techniques, such as the Metropolis Algorithm in a multi-dimensional space. We design Fortran codes that generates, according to Metropolis, random numbers with non-uniform density, to sample local energy and its squared. Then, we compute energy and energy squared as the average of their local partners and, from them, the variance. We enclose illustrative calculations on the Harmonic Oscillator, Hydrogen atom and Helium atom ground states.

2. Introduction

The twentieth century can be considered as one of the most hopeful for quantum chemistry. Until then, quantum mechanics had virtually the same limitations than classical mechanics. It was in 1946 when the first electronic computer showed up, also known as ENIAC (Electronic Numerical Integrator And Computer). Its first function was to carry out a series of calculations, related to neutron diffusion^[1] to assist in the design of the hydrogen bomb during the World War II. To this end, a new method based on random numbers sequences distributed evenly was developed. It was the beginning of the Monte Carlo (MC) method. Since this method uses random numbers, it is a stochastic procedure. Actually, it was along the World War II, and related to the development of nuclear weapons, when MC techniques were developed, mainly by scientist such as John Von Neumann, Enrico Fermi, S M Ulam and Nicholas Metropolis at Los Alamos National Laboratory, USA^[2]. With the development of electronic computers, a number of new investigations on numerical methods in quantum chemistry were developed (until then, only exact function could be calculated by solving the Schrödinger equation for very simple systems). Nowadays, we can carry out calculation of large molecules; we can even calculate ordered crystals.

The origins of quantum chemistry emerged many years ago, where some equations could be solve by standard analytical and numerical methods. These methods accounted for up to two-body problems. Prior to deal with the electronic part of the Schrödinger equation of standard atoms and molecules, it is worth starting with the simple system: the He atom. We must solve the Hamiltonian eigenvalue equation, $\hat{H} \cdot \varphi = \epsilon \cdot \varphi$, where $\varphi = \varphi(\tau_1, \tau_2)$ is the wave function, with $\tau = (r, \sigma)$, where r is the vector position and σ the spin. \hat{H} is the Hamiltonian, i.e., the energy operator and ϵ is the total energy of the system.

The He Hamiltonian can be expressed as $\hat{H}_{(1,2)} = \hat{H}_1 + \hat{H}_2 + V_{12}$ where $V_{12} = \frac{1}{r_{12}}$, being r_{12} the interelectronic distance. V_{12} is then singular (infinite) if $r_{12} = 0$. This means that the electron 1 and the electron 2 cannot be at the same position, i.e. $r_1 \neq r_2$. Therefore, the probability of finding both electrons at the same position $P(r_1 = r_2) = |\varphi_{(r_1=r_2)}|^2$ must be null.

The He atom is a three body problem. Then, it has not analytical solution. In order to solve the Schrödinger equation in an approximate manner, we can start with the *independent-particle mode*^[3]. This model disregards electron-electron repulsion. Then, $r_{12} = 0$ is not a hindrance for it. The *independent-particle* Hamiltonian can be written as $\hat{H}_{(1,2)} = \hat{H}_1 + \hat{H}_2$. Unfortunately, this model provides a very poor approximation of the real He energy and wave function (and in general of every poly-electronic atom and molecule).

To improve the model, the electron-electron repulsion must somehow be taken in. The self-consistent field SCF of Hartree-Fock method does it in an averaged way. Prior to deal with SCF we must say a few words on the Pauli's principle. Since permutation of identical particles commutes with the Hamiltonian, the Hamiltonian eigenfunctions must also be eigenfunctions of the permutation operator. In the simplest case of two particles, since a two-fold permutation is doing nothing, the squared of the permutation operator eigenvalue λ^2 must be the unity, then $\lambda = \pm 1$, i.e., we must have either symmetric $\varphi(\tau_1, \tau_2) = \varphi(\tau_2, \tau_1)$ or antisymmetric $\varphi(\tau_1, \tau_2) = -\varphi(\tau_2, \tau_1)$ functions. We call boson those particles with symmetric wavefunctions (e.g. photons) and fermions those with antisymmetric ones (e.g. electrons). Thus, the *independent-particle* model wave function of the He atom must be of the form: $\varphi_{(\tau_1, \tau_2)} = \varphi_1(\tau_1) \cdot \varphi_2(\tau_2) - \varphi_1(\tau_2) \cdot \varphi_2(\tau_1)$.

Another way to describe the anti-symmetric wave function is the so-called Slater determinant:

$$\phi_1(1) \cdot \phi_2(2) - \phi_1(2) \cdot \phi_2(1) = \frac{1}{2} \cdot \begin{vmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{vmatrix}$$

The exact N-body wave function of a system is not a single Slater determinant (this is the *independent-particle* model approximation to the exact wave function) but (due to the completeness of the Hilbert space of functions) it can always be written as a linear combination of (very many) Slater determinants.

Coming back to the Hartree-Fock method, it can be summarized in the so-called Hartree-Fock equation: $\hat{F}_i \phi_i = \epsilon_i \phi_i$, where \hat{F} is the Fock operator, ϕ_i the optimized orbital and ϵ_i the associated energy. The many-electron Hartree-Fock wave function is then written as the Slater determinant of the occupied lowest-lying orbitals.

Since, as stated above, the exact N-body wave function can always be written as a linear combination of Slater determinants, we can improve variationally the SCF wave function, as linear combinations of Slater determinants built out of Hartree-Fock orbitals. This method is referred to as *Configuration interaction (CI)*^[5] post-Hartree-Fock method. In the case of He atom, a *Configuration interaction* wave function will take the following form: $\varphi = a \cdot \det|1s(1)1\bar{s}(2)| + b \cdot \det|1s(1)2\bar{s}(2)| + c \cdot \det|1s(1)2\bar{p}_z(2)| + \dots$

The appearance of computers gave as a result the obtention in a short period of complex calculations. From there, different methods arose to obtain the exact energy of small atoms like He and H. But, how to verify that such results are correct? Kolos and Wolniewicz^[6] made variational methods for atoms with few electrons in order to calculate practically exact values of the energy that would serve as a reference. They took variational functions with thousands of parameters and simplified it so that they increasingly obtained a more sophisticated wave function. Its contribution to quantum chemistry is very important because it serves as a reference. Every time a new variational method comes up, we can compare the results to see how good the new method is.

One of the advantages of Monte Carlo method includes the possibility of solving different types of problems that can't be solved analytically. But sometimes the method also presents problems, for many-electron wave functions in order to obtain accuracy and exactly, it's necessary to apply the Jastrow correlation factor.

2.1. Jastrow correlation factor

Jastrow factor is used in atoms, molecules and solids. First Monte Carlo works were used with a two-body (electron-electron) Jastrow factor^[7]. In order to decrease the energy and avoid the fluctuations of the local energy, a three-body (electron-electron-nucleus) was studied.

The Jastrow factor equation^[8] includes both of them, but to make it easier, as a sum, Jastrow factor parameterizes the wave function equation in order to produce quality results and fairly accurately describe the electronic correlation. In Monte Carlo, in case of He atom, to prevent two particles from being in the same positions, i.e., $r_{12} = 0$, firstly the independent-particle model was introduced. As we said before, this model doesn't take in count the electron-electron repulsion, so the Hamiltonian would be $\hat{H}_{(1,2)} = \hat{H}_1 + \hat{H}_2$. In Monte Carlo, we can apply the Jastrow Factor that gives a better solution of the Hamiltonian due to that this factor doesn't reject the electron-electron repulsion. This equation would be $\phi_{(1,2)} = \varphi_1(r_i) \cdot \varphi_2(r_j) \cdot e^{-\frac{\alpha}{r_{ij}}}$, applying this factor the probability of finding the electron when $r_{i=j}$ would be $e^{-\frac{\alpha}{r_i-r_j}} = e^{-\frac{\alpha}{0}} = e^{-\infty} = 0 \rightarrow \varphi_1(r_i) \cdot \varphi_2(r_j) \cdot e^{-\frac{\alpha}{r_{ij}}} = 0$

In this chapter we introduce the basic parts of a variational Monte Carlo calculation and a simulation of the Schrödinger equation. We begin with an introduction of the Variation Principle where we present a Monte Carlo method for determining $E[\phi]$. After that, Metropolis Algorithm will show up. Then, we present the QMC calculations for different systems and finally, we end up presenting the essentials of Monte Carlo sampling and simulation.

3. Aim of the present work

The main objectives of this work are to show:

-First, an introduction of the variational theorem that begins with the Metropolis algorithm and the addition of random walkers for a multi-dimensional space.

-Second, the study of different systems such as the Harmonic Oscillator, the Hydrogen and the He atom.

-Finally, last but not least, the application and simulation of different systems in the Fortran program and its difference using the cusp conditions.

4. The Variational Principle

The aim of the Variational principle^[9] is to find an approximate solution to the Schrödinger's equation. It may be stated as follows: *The expectation value of a Hamiltonian, \hat{H} , calculated using a trial wave-function, ϕ_T , is never lower in value than the true ground state energy, ϵ_0 , which is the expectation value of \hat{H} calculated using the true ground state wave-function, ϕ_0* ^[10]. It also has to follow the next conditions: be continuous, differentiable, meet the boundary conditions etc...^[11]. Boundary conditions for bounded systems reads: $\phi(\infty) = \phi(-\infty) = 0$.

To explain the sentence we have to go back, starting first with the Schrödinger equation:

$$\hat{H} \cdot \phi = E \cdot \phi \quad (1)$$

Where ϕ is the wave function, \hat{H} is the Hamiltonian, the operator representing the energy of the system and E is the total energy of the system.

On the other hand, to calculate the energy for any given choice of trial function, φ_T , will follow as:

$$E = \frac{\langle \varphi_T | \hat{H} | \varphi_T \rangle}{\langle \varphi_T | \varphi_T \rangle} \quad (2)$$

As the sentence said, the energy for φ_T will never be lower than the true ground state energy, E_o , then,

$$E_o \leq E ; E_o \leq \frac{\langle \varphi_T | \hat{H} | \varphi_T \rangle}{\langle \varphi_T | \varphi_T \rangle} \quad (3)$$

To demonstrate it, the trial function can be expressed as a linear superposition:

$$\varphi_T = \sum_n C_n \cdot \phi_n , \text{ where } n \in 1,2,3, \dots \quad (4)$$

Where ϕ_n is the true normalized eigenfunctions and $\sum_n |C_n|^2 = 1$

With the equation (2) and (4):

$$E = \frac{\langle \varphi_T | \hat{H} | \varphi_T \rangle}{\langle \varphi_T | \varphi_T \rangle} = \frac{\sum_{nm} c_n^* c_m \langle \phi_n | \hat{H} | \phi_m \rangle}{\sum_{nm} c_n^* c_m \langle \phi_n | \phi_m \rangle} = \frac{\sum_n |c_n|^2 E_n \langle \phi_n | \phi_n \rangle}{\sum_n |c_n|^2 \langle \phi_n | \phi_n \rangle} = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} \geq \frac{\sum_n |c_n|^2 E_o}{\sum_n |c_n|^2} = E_o \quad (5)$$

To make it simpler, imagine that E_o is the ground state or lower state energy, for $E_n > E_o$:

$$E = \sum_n |c_n|^2 E_n \geq \sum_n |c_n|^2 E_o \geq \frac{(\sum_n |c_n|^2) E_o}{(\sum_n |c_n|^2) = 1} = E_o \quad (6)$$

In order to determine E_o , the wave function corresponds to the true ground state wave function, ϕ_o :

$$E_o = \langle \phi_o | \hat{H} | \phi_o \rangle \quad (7)$$

The Variational procedure starts by adjusting a set of parameters that φ_T contains. The best choice of the value of these parameters for the trial wave function will minimize E_o . We can write φ_T as:

$$\varphi_T = \varphi_T(x, y, z, \alpha, \beta, \gamma, \dots) \quad (8)$$

The main goal in VMC is to find the minimum value of E that depends on equation (2). Moreover, we will find a set of parameters in order to obtain that low energy. Furthermore, for greater efficiency we will use the Metropolis Algorithm, its random walker and the thermalization explained in the next points. Last but not least, we will focus in the calculation of the variance and comparing it with the value of the energy because when

the variance is closer to zero it means that we are closer to the exact value of the wave function, therefore one of our objectives is to search the minimum value of the variance.

One of the advantages of having variational^[5] method in front of the non-variational method is that the first one, the calculated energy is always higher or equal to the exact energy for the ground state. For example the calculation of the energy for the ground and the excited state will always produce an error in the same direction in front of the exact energy solution and thus, as both errors are in the same direction, the difference in errors is small. However, the second case, the calculated energy can be higher or lower than the exact energy. Following the same example, the energy of the ground and the excited state can produce errors in different directions. Therefore, the difference may combine instead of cancelling.

5. Variational Monte Carlo Method

The variational method is one of the most productive approaches for finding approximate solutions of the electronic Schrödinger equation ^[5].

The expected value of the energy is the following

$$\langle E \rangle = \frac{\int dR \varphi_{(R;\alpha)}^* \hat{H}(R) \varphi_{(R;\alpha)}}{\int dR |\varphi_{R;\alpha}|^2} \quad (9)$$

Where $R = (r_1, r_2, \dots, r_N)$ are the positions of the particles in the system and $\alpha = (\alpha_1, \alpha_2, \dots, \alpha_s)$ is a set of variational parameters in question which the trial wave function $\varphi_{T,\alpha}$ depends.

The efficient way to calculate the minimum expectation value of $\langle E \rangle$ is to search and after that, vary the α parameters.

The procedure to obtain the minimum value of the energy is the next one:

1. Construct a trial wave function $\varphi_{T,\alpha}$ with the correspondent variational parameters.
2. Calculate $\langle E \rangle$.
3. Vary the set of parameters in order to minimize the energy.

We will introduce the Metropolis Algorithm in the next paragraph.

5.1. Metropolis Algorithm

The straightforward application to obtain the minimum energy comes from choosing a trial wave function $\varphi_{T,\alpha}$, this one serves as a mean to define the probability density^[12]

$$\int_a^b |\varphi_T(x; t)|^2 dx \quad (10)$$

This is called the probability density for a one particle in the system.

The probability density is interpreted as the probability of finding the particle between the position a and b in a t time.

As we will work with normalized functions, these ones have to accomplish the next condition:

$$\int_{-\infty}^{\infty} |\varphi_T(x; t)|^2 dx = 1 \quad (11)$$

Then, $|\varphi_T(x; t)|^2$ represents the probability of finding the particle in our system state in a x position.

After that, from the equation of the energy we can observe that another way to interpret its equation (9) is

$$\langle E \rangle = \frac{\int dR \varphi_T^* \hat{H} \varphi_T}{\int dR |\varphi_T|^2} = \int dR \frac{\hat{H} \varphi_T}{\varphi_T} \frac{|\varphi_T|^2}{\int dR |\varphi_T|^2} = \int dR E_L(R) \rho(R) = \langle E_L(R) \rangle_\rho \quad (12)$$

Where ρ is a distribution function.

Then we define the local energy to be:

$$E_L(R) = \frac{\hat{H} \varphi_T(R)}{\varphi_T(R)} \quad (13)$$

Therefore, the more improvement of the trial wave function, the better expected value of the local energy E_L we will obtain and thus, a closer possibility to the exact energy E.

Then, another way to express the energy following the VMC from the local energy is

$$\langle E \rangle = \frac{\int |\varphi_T|^2 E_L dR}{\int |\varphi_T|^2 dR} \quad (14)$$

In order to simplify, the equation (14) can be expressed as an approximation

$$\langle E \rangle = \frac{\sum |\varphi_T|^2 E_L}{\sum |\varphi_T|^2} \quad (15)$$

This new equation will be used to calculate the energy.

On the other hand, we calculate the sample of the local energy E_L and the sample E_L^2 in order to get $\langle E_L^2 \rangle$, this is used to calculate the variance

$$\sigma_{E_L}^2 = \langle E_L^2 \rangle - \langle E_L \rangle^2 \quad (16)$$

In probability theory, a continuous uniform distribution describes that the probability is the same at any point of the interval, therefore, the mean of the distribution is $E = \frac{1}{n} \sum E_i$.

For a non-uniform distribution like the harmonic oscillator the mean depends on the probability, e.i. $E = \sum_i P_i \cdot X_i$

Then the equation to calculate E is a mix of both equations

$$E = \frac{1}{n} \sum_{k=1}^n E_L(x_k) \quad (17)$$

Where x_k are the points at which the local energy is sampled E_L , and n are the number of sample points.

The main objective of the Metropolis Algorithm is to perform what is called a sampling of importance in the configurational space, e.i., sampling not all the space of configurations, but only that important area. Therefore, areas of very high and low probability are not treated on equal foot. Then the sampling distribution will be lead by a random numbers uniformly distributed to a non-uniform distributed histogram.

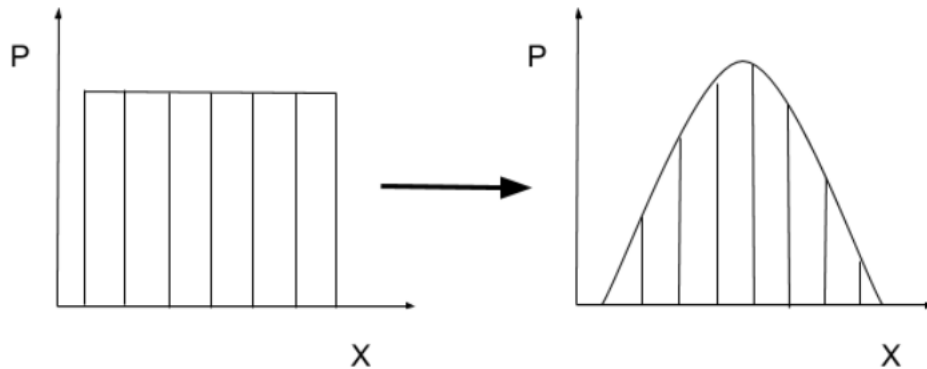


Figure 1. Probability distribution function for the Metropolis Algorithm.

In order to sample only the important areas, the Metropolis algorithm starts by a random step. Once the electron is moved from its original position R to the new position R' we have to calculate the probability of each one and then, calculate the ratio, i.e. $w = \frac{P(R')}{P(R)}$.

The Metropolis algorithm tells us that if

$$w > 1$$

Then we have to accept the new position. But if $w < 1$, in order to know if the new position R' should be discarded or not, it will be compared with a random number that will range from 0 to 1 which are the uniform distributions that most computers generate. If the probability is greater than the probability of R' , then the position R' will be discarded while if the probability is lower then it will be accepted.

5.1.1. Thermalization

Once we start generating random numbers, to be sure that we have reached all the possible positions, we must include the term *thermalization*.

It's important that the entire area is sampled, that is, that it goes to both low and high probability areas. To ensure that the random walkers have sampled the entire area, half of the steps will be determined to be good and the other half, bad. In order to know that a step is good, a random number will be asked and if it has a high probability then it will be accepted, while if the probability is low, the step will be discarded.

This term doesn't reject totally a bad step, i.e., we will introduce an equation which adjust every step to accept at least 50% of the probability that the particle is within our acceptance area.

$$Step = step * m_i / (0,5d0 * cont) \tag{18}$$

Where the step is the maximum step-length in the random walk.

5.1.2. Metropolis random walkers

To introduce the Metropolis random walker^[13] applied by Metropolis in 1953 we will consider a one dimension random walker. R for the probability of moving to the right and L to the left. The walker starts at $x=0$, where x is the position, then, the walker can jump as we mentioned before, either to the left or to the right. Moreover, the walker can remain at the same position, but we won't consider this situation. Finally, the length of every step is $\Delta x = l$.

As easy illustration to understand the example is the following

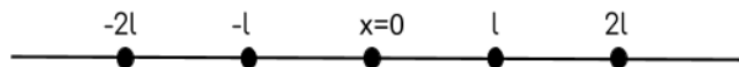


Figure 2. One dimensional walker

In case of complex problems, one random walker is not enough due to the great time it would be and the difficulty of finding all the peaks of the distribution. For that reason, it's more useful to start with a large number of independent random walkers which will start from different random points in the configuration space.

On the other hand, in case of multi-dimensional space it's convenient to use a large number of random walkers in order to obtain a better accuracy of the peaks of the distribution.

We will introduce the random walkers into the "main" program which will be explained in the next points.

```
t0=secnds(time) %Initial time.

energia=0.d0 %Initial energy which is zero.
energia2=0.d0 %Initial square of energy.
do kk=1,walkers

    call walk_scan %Run a walk.
    energia=energia+ene1 %Energy for this walk.
    energia2=energia2+ene2 %Square energy for this walk.
enddo

temps=secnds(time)-t0 %Time to do the calculations.

energia=energia/walkers %Average of the energies.
energia2=energia2/walkers %Average of the square energies.
variancia=energia2-energia**2 %Average of the variance.
```

5.2. Cusp conditions

The development and continued research of analytics wave functions is making problems easier in order to solve problems in atomic physics. The variational approach has achieved a very high level of accuracy on the calculation, for example the He atom that we will see in the next paragraphs.

The energy eigenfunction

$$H^N \phi(r_i) = E \phi(r_i) \quad (19)$$

And considering the Hamiltonian for N-electron atoms and ions is

$$H = T + V \quad (20)$$

Where

$$T = -\sum_{i=1}^N \frac{1}{2m_i} \nabla_i^2 ; V = \sum_{i<j}^N \frac{z_i z_j}{r_{ij}}$$

$r_{ij} = |r_i - r_j|$ and T,V are the kinetic and potential energy operators.

The potential contains singularities at the set of points $\{r_{ij} = 0\}$, that is, at the coalescence of any two (or more) particles, then the $\phi(r_i)$ cannot satisfy the cusp condition.

In other words, cusp conditions, as the name says, are conditions that are applied to an equation, in our case the local energy, in order to avoid obtaining infinite and therefore, an infinite cusp.

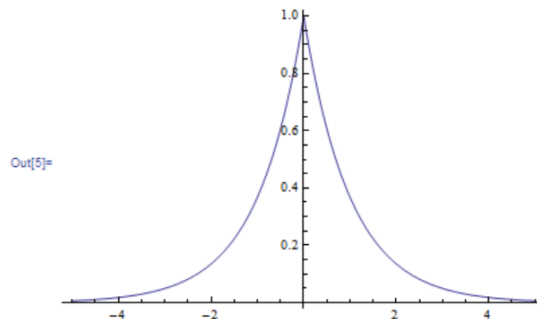


Figure 3. Representation of an infinite cusp.

As an easy example we can introduce the hydrogen atom, its local energy is $E_L(r) = -\frac{1}{r} - \frac{\alpha}{2} \left(\alpha - \frac{2}{r} \right)$ which will be explained in the next sections. When we consider

$r=0$, the local energy tends to infinite and therefore, the cusp. To avoid this, we have to apply the cusp condition, which is the introduction of a condition that despite the fact that r continues to be 0, the result does not tend to infinity. Looking at the equation, the condition that is imposed is that $\alpha = 1$. Then, although $r=0$, the result of the equation is no longer 0, but $-\frac{1}{2}$.

H.S.Patil^[14] develops simple wave functions for 2 and 3 electrons and ions in order to deduce fairly accurate values for the energies by adjusting the wave function in front of the position.

Nevertheless, cusp conditions do not work for all situations. For example, when the hydrogen atom is confined, its wave function is no longer the same and therefore, it no longer has the same cusp conditions. Another way to explain it is when the boundary conditions are natural, the cusp conditions can be applied, but when altering them, the differential equations are modified and therefore, the cusp conditions change.

5.3. Fortran's code

We are going to use the FORTRAN 95^[15]. The name FORTRAN comes from FORMula TRANslation, as it the name says, it was designed in order to solve numerical tasks for physics and mathematical sciences mostly.

In this section we are going to introduce the different codes, parameters and variables that afterwards, will be written into the program.

First of all, we have to know how is going to be the structure of the program. This structure has a principal program called "main".

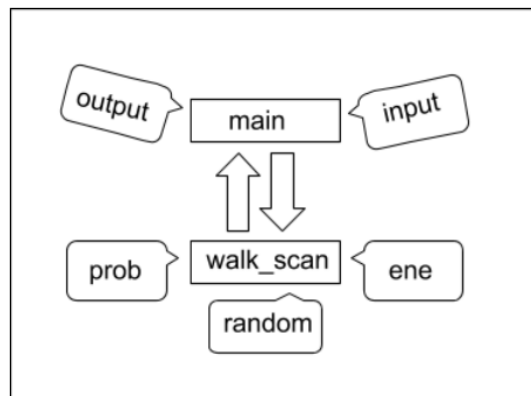


Figure 4. Structure of the Fortran program.

This *main* program works from the values we introduce to the *input* and at the same time, the *main* interacts with a routine that we call *walk_scan* where all the calculations are made. In order for this routine to be able to perform all the calculations, it needs a series of functions: *prob*, *ene* and *random/funtion_ran2*.

In the first one, it refers to probability, *prob*, where the probability function for each case is introduced. The next one is the *ene*, referring to the local energy function and the last one, the program *funtion_ran2* where we will established the random numbers.

A code has been developed for the Fortran program.

Table 1. Parameters used in the VMC.

Parameter	Variable name
Initial position	x_0
Length of the coordinate domain	r_0
Random number	Rand2(idum)
Probability at the initial position	p_0
Number of stages	m

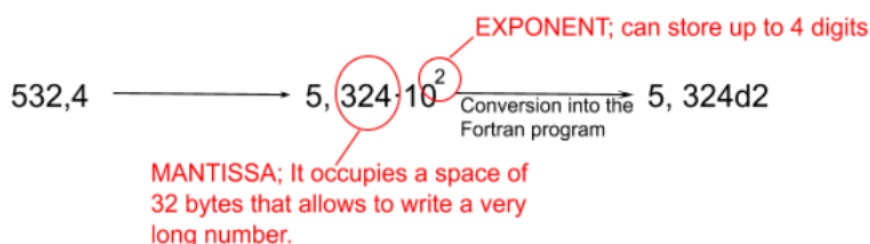
As a complex program the Fortran is, it's very important to define everything, so first of all, before defining the different functions, we have to introduce some terms:

The *Integer* term, as its name says, it's a number that can be written without a fractional component and therefore, the space it occupies in the computer memory is relatively small, specifically 4 bytes.

The *Integer* term is computed as:

```
integer:: walkers, m, mi, mf
```

On the other hand, in all fields of science there is the Double Precision term. This term works with real numbers, as an example of a real number is the following:



Therefore, real numbers need more precision than integers. In case of different real numbers we have to introduce the Double Precision in order to distinguish them.

The *Double Precision* term for the local energy function is computed as

```
double precision function ENE(x)
```

Another way to introduce the term in order to simplify the operator's work is called the *Implicit double precision* term

```
Implicit double precision(a-h,o-z)
```

This term defines that the variable that begins with the letters a-h and o-z will be double precision while the other letters, i-r will be an integer.

Now we will define the different functions as the local energy, probability and random walker. As the energy and probability will be different to each case, in this chapter we will only define the random walker in a program called *function_ran2*.

```
double precision function ran2(idum)
  Implicit double precision(a-h,o-z)
  call random_number ( x_scalar )
  ran2=x_scalar
  return
end
```

These 3 programs will be executed into the *walk_scan* program, which in the first place, the thermalization is performed.

```

subroutine walk_scan
Implicit double precision(a-h,o-z)
double precision:: alpha,r0,pas
integer:: cont,walkers, m, mi, mf
common/dades1/alpha,r0,pas
common/dades2/walkers, m, mi, mf,hits
common/results/ene1,ene2

x=r0*(2*ran2(idum)-1)
p0= prob(x)

! thermalization

cont=0
do i=1,mi
cont=cont+1
1 continue
pastemx=pas*(2*ran2(idum)-1)

xb=x+pastemx

p1=prob(xb)

w=ran2(idum);

IF(p1/p0>w) THEN
x=xb
p0=p1
ELSE
cont=cont+1
goto 1
ENDIF

enddo

! write(*,*) "initial step ",pas
pas=pas*mi/(hits*cont);
! write(*,*) " fitted step ",pas

```

%x random starting point.

%Calls the probability function and calculate it at the initial position.

! thermalization

%We start a loop.

cont=0

do i=1,mi

%Counter to know how many steps we perform.

cont=cont+1

%STEP 1.

1 continue

pastemx=pas*(2*ran2(idum)-1)

%Actual step, it allows that the random number can be either positive or negative.

xb=x+pastemx

%New position.

p1=prob(xb)

%New probability.

w=ran2(idum);

%Calling a random number ($0 < w < 1$).

IF(p1/p0>w) THEN

%If $p1/p0 > w$ then we accept the new step.

x=xb

%The random walker change its position from x to xb. Go to STEP 2.

p0=p1

ELSE

cont=cont+1

%If $p1/p0 < w$ then we go back to STEP 1 and get a new random position.

goto 1

ENDIF

enddo

! write(*,*) "initial step ",pas

pas=pas*mi/(hits*cont);

! write(*,*) " fitted step ",pas

```

ene1=0.d0
ene2=0.d0

i2=i

cont=0

do i=i2,m
    cont=cont+1;
    continue
    pastemx=pas*(2*ran2(idum)-1)

    xb=x+pastemx

    p1=prob(xb)

    w=ran2(idum);

    IF(p1/p0>w) THEN

        aux=ene(xb)
        ene1=ene1+aux
        ene2=ene2+aux**2
        x=xb
        p0=p1

    ELSE

        cont=cont+1
        goto 2

    ENDIF

enddo
ene1=ene1/mf
ene2=ene2/mf
return
end

```

2

%STEP 2.

%We generate a new position.

%New probability.

%Calling a random number ($0 < w < 1$).

%Calls the local energy function, then calculate the energy and finally collect all the energies (ene1).
%Collect all the squared of local energies (ene2)

%LAST STEP.

%Average of energies.

%Average of squared of energies.

The last step is to define our main program in which all the instructions must be written in order to obtain the results we need, which in this case is the value of alpha, the energy and the variance.

```

Implicit double precision(a-h,o-z)
integer:: walkers, m, mi, mf
common/dades1/alpha,r0,pas
common/dades2/walkers, m, mi, mf, hits
common/results/ene1,ene2

pi=dacos(-1.d0)

open (unit=10, file='input.data')
read(10,*)
read(10,*) r0,m,walkers,hits
read(10,*)
read(10,*) alphai,alphaf,alphap
close(10)

open(unit=40,file='out.data')
write(40,*) "r0, m, walkers, hits"
write(40,*) r0," ",m," ",walkers," ",hits

write(40,*) "alphai, alphaf, alphap"
write(40,*) alphai, alphaf, alphap

write(40,*) "{alpha,energy,variance}"

mi=2*m/10
mf=m-mi

pas = r0/2

t1=secnds(time)

do alpha=alphai,alphaf,alphap

t0=secnds(time)

```

%Value of pi.

%The program opens the *input* file.

%The program reads the first line of the *input* file.

%It reads the values of r0, m, walkers and hits.

%The program reads the third line.

%It reads the values of alphai, alphaf and alphap.

%The program closes the *input* file.

%The program opens a new file called *out.data*.

%We write r0,m,walkers,hit in the first line and the values of the variables in the second line of our *out.data*

%We write alphai, alphaf, alphap in the fourth line and its values in the next line.

%Alpha, energy, variance is written in the fifth line.

%Defining the initial step.

%We will calculate the time the program will take to perform all calculations.

```

energy=0.d0
energy2=0.d0
do kk=1,walkers
    call walk_scan
    energy=energy+ene1
    energy2=energy2+ene2
enddo

temps=secnds(time)-t0

    energy=energy/walkers
    energy2=energy2/walkers
    variance=energy2-energy**2

write(*,*) "{",alpha,"",energy,"",variance,"",
write(40,*) "{",alpha,"",variance,"",variance,"",
write(40,*)
enddo

temps=secnds(time)-t1
write(40,*) "computation time",time
close(40)
write(*,*) "computation time",time
stop
end

```

%Initial value of energy.
%Initial value of squared energy.
%The program goes to the *walk_scan* file.
%Sum of all energies.
%Sum of all squared energies.

%The best energy.
%The best squared energy.
%Average of variance of the walks.

%alpha, energy, variance is written in the program.
%The values calculated are written in the program.

%At the end of the out.data file, the computation time, i.e., the time that the program takes to obtain all the calculations.

As the *main*, *walk_scan* and *funtion_ran2* programs are the same for all our examples, we only have to define the *ene* (local energy) and *prob* (probability) programs and varying the values of the *input* for each case.

We will start with the simplest case, the monodimensional harmonic oscillator following by the hydrogen atom to finish with the helium atom.

5.4. Harmonic Oscillator

A little reminder of what a harmonic oscillator is reflected in the simplest example out there: the movement of a mass "m" attached to a massless spring that moves in a one-dimensional way around an equilibrium point.

We can adapt this model to a system of two atoms joined by a bond that assimilates to the spring by shortening and stretching from its equilibrium position^[16].

On the other hand, the Hamiltonian for the harmonic oscillator in one dimension is the following^[18]

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad (21)$$

Where m is the mass of the particle and k is the force constant for the Harmonic oscillator. In order to simplify the calculation, we will consider $m=k=\hbar=1$. Then, the equation is rewritten as^[16]

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{x^2}{2} \quad (22)$$

The harmonic oscillator energy eigenvalue is

$$\begin{aligned} H\phi &= E\phi \\ \left[-\frac{1}{2} \frac{d^2}{dx^2} + \frac{x^2}{2} \right] \phi &= E\phi \end{aligned} \quad (23)$$

To calculate the exact wave function for the ground state, we consider then $E_0 = 1$, so the exact wave function for the ground state is the following

$$\phi_0(x) = \frac{e^{-\frac{x^2}{2}}}{\pi^{\frac{1}{4}}} \quad (24)$$

Since we want to make a pedagogical approach to the VMC method, then we have to follow the instructions we determined in point 4. First of all, we have to choose a trial function and it has to accomplish some conditions: Meet the boundary conditions, be continuous, differentiable, etc...

Therefore, our chosen trial function is the following:

$$\phi_T(x) = e^{-\alpha x^2} \quad (25)$$

From the equation (22) and (25), we insert both equations in equation (13) in order to obtain the local energy, E_L :

$$E_{L,\alpha}(x) = \alpha + x^2 \left(\frac{1}{2} - 2\alpha^2 \right) \quad (26)$$

The calculation of the local energy will be shown at Appendix 1.

So we have to introduce the local energy into the Fortran program, calling it *ene*. We will implement it in a few lines

```
double precision function ENE(x)
Implicit double precision(a-h,o-z)
    common/dades1/alpha,r0,pas

    ENE =alpha+(0.5d0-2*alpha**2)*x**2

    return
end
```

Figure 5. *Ene* for the harmonic oscillator.

After that, an easy step is to define the probability density of Eq. (10), we obtain the following expression for the probability density

$$|\phi_T(x)|^2 = |e^{-\alpha x^2}(x)|^2 \quad (27)$$

Finally, we obtain

$$p(x) = e^{-2\alpha x^2} \quad (28)$$

Once we have our probability, it's time to introduce it into the program, calling *prob* to the probability density

```
double precision function prob(x)
Implicit double precision(a-h,o-z)
    common/dades1/alpha,r0,pas

    prob = exp(-2*alpha*x**2)

    return
end
```

Figure 6. *Prob* for the harmonic oscillator.

We define the values for the different variables of the *input*. In this calculation we set 10.000 points and 300 walkers.

Table 2. Selected values for the different variables of the *input*.

r0	0,25
M	10.000
Walkers	300
hits	0,5
Alpha i	0,4
Alpha f	0,8
Alpha p	0,05

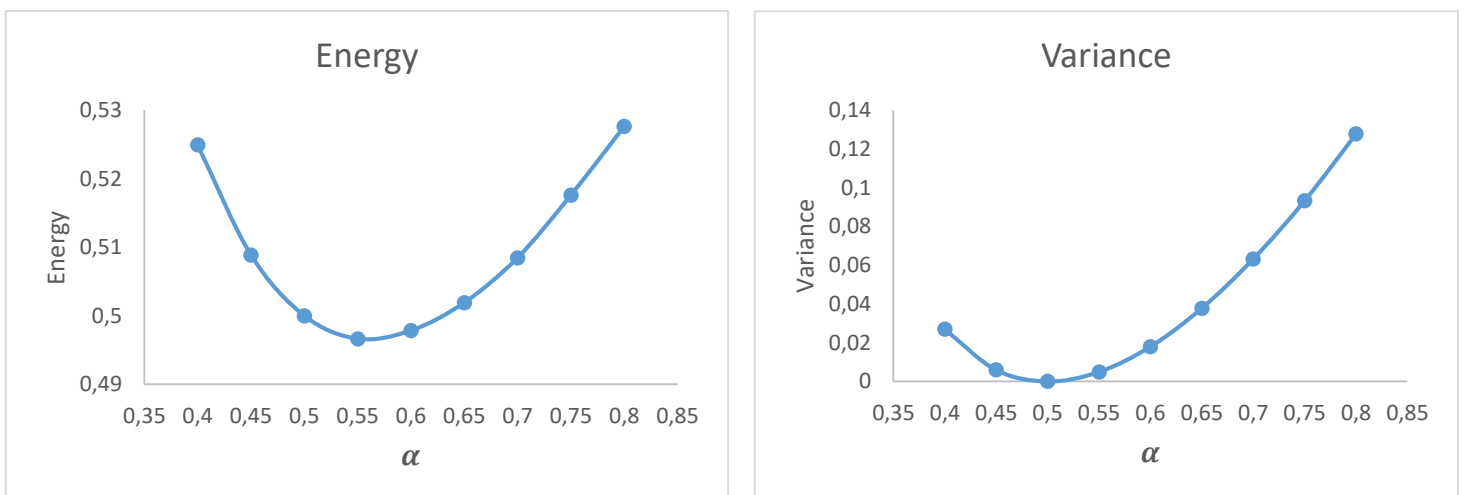
From the input program we obtain the values of the energy and the variance.

Table 3. Results for the energy and the variance of the harmonic oscillator with 10.000 points and 300 walkers from Fortran program.

α	Energy	Variance
0,40	0,524916496	0,026953987
0,45	0,508872421	0,005961365
0,50	0,5	0
0,55	0,496636257	0,004921188
0,60	0,497831078	0,017943971
0,65	0,501905206	0,037806655
0,70	0,508463951	0,06320927
0,75	0,517605294	0,093264883
0,80	0,527625781	0,127739564

We represent the energy and the variance. In order to know if our solution is more accurate or not, we have checked that the minimum of both the energy and the variance are the same.

Figure 7. The figures show a variational plot of the harmonic oscillator with 10.000 points and 300 walkers. The figure on the left shows the energy from the α parameter, while the figure on the right shows the variance from the α parameter.



As we can see the minimum of both clearly differs and do not coincide. One way to decrease this minimum is to increase the number of points or walkers so this later can sample better the entire area.

Then, to get accurate results, we will increase the number of points from 10.000 to 50.000, and to be completely safe, we will also increase the number of walkers from 300 to 500.

Table 4. Selected values for the different variables of the *input*.

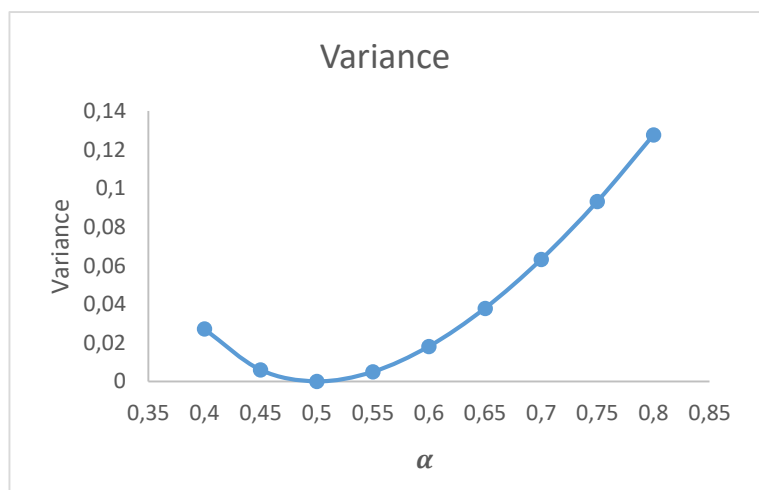
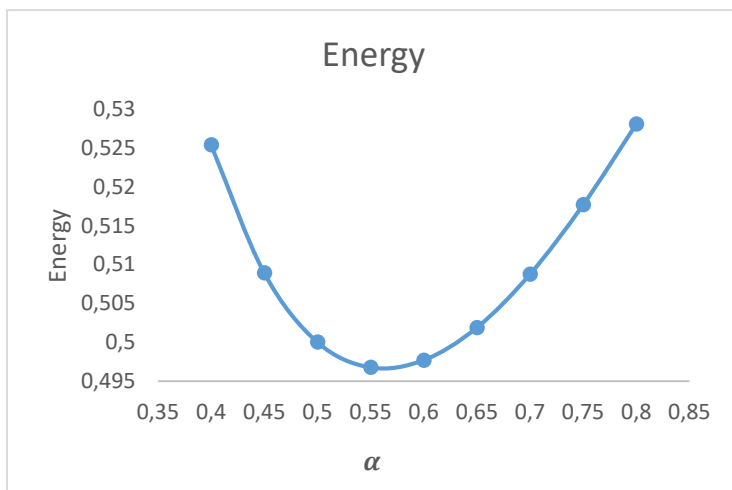
r0	0,25
M	50.000
Walkers	500
hits	0,5
Alpha i	0,4
Alpha f	0,8
Alpha p	0,05

From the input program we obtain the values of the energy and the variance.

Table 5. Results for the energy and the variance of the harmonic oscillator with 50.000 points and 500 walkers from Fortran program.

α	Energy	Variance
0,40	0,525373939	0,027130826
0,45	0,508906586	0,005980667
0,50	0,5	0
0,55	0,496754412	0,004888279
0,60	0,497689099	0,018059323
0,65	0,501871152	0,037827525
0,70	0,508736349	0,063095214
0,75	0,517671771	0,093110174
0,80	0,528055042	0,127541426

Figure 8. The figures show a variational plot of the harmonic oscillator with 50.000 points and 500 walkers. The figure on the left shows the energy from the α parameter, while the figure on the right shows the variance from the α parameter.



As we can see, the result of the graphs is the same even though we have modified the variables. This means that a good "sample" has been achieved and therefore, we do not need to calculate more.

In this point, we have to mention that as we said in the chapter 4, the energy for ϕ_T will never be lower than the true ground state energy, E_o , i.e. $E_o \leq E$. In our case, we have obtain for the harmonic oscillator some energies that its values are lower than E_o , this does not fulfill the variational principle. The cause is due to an imperfect sampling that can lead to an incorrect prediction regarding the optimal parameter and energy. In order to solve this, we will compare at the end of this work, our result with the true ground state energy.

5.5. Hydrogen atom

A system with two particles, a heavy nucleus (consisting of a single proton) and an electron, known as the hydrogen atom, has the following Hamiltonian^{[12][19]}

$$H = -\frac{\hbar^2}{2mr^2} \left[\left(\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \right) - \frac{L^2(\theta, \varphi)}{\hbar^2} \right] - \frac{1}{r} \quad (29)$$

For states with $l=0$ and $h=m=1$, the equation is simplified as follows

$$H_{l=0} = -\frac{1}{2r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \right] - \frac{1}{r} \quad (30)$$

Then, our chosen trial function is the next one

$$\phi_T(r) = e^{-\alpha r} \quad (31)$$

From the equation (13), we use the equations (30) and (31) to obtain the local energy

$$E_L(r) = -\frac{1}{r} - \frac{\alpha}{2} \left(\alpha - \frac{2}{r} \right) \quad (32)$$

Where the calculation of the local energy will be shown at Appendix 1.

And the probability is the square of the local energy multiplied by the spherical coordinates, that is, the volume element $dv = r^2 \cdot \sin\theta \, drd\theta d\varphi$

$$p(r) = r^2 \cdot e^{-2\alpha r} \quad (33)$$

Now, it's time to introduce the local energy and the probability to the Fortran.

```
double precision function ENE(x)
Implicit double precision(a-h,o-z)
common/dades1/alpha,r0,pas

ENE = -(1.d0/x) - (alpha/2.d0)*(alpha - 2.d0/x)

return
end
```

Figure 9. *Ene* for the hydrogen atom.

```
double precision function prob(x)
Implicit double precision(a-h,o-z)
common/dades1/alpha,r0,pas

prob = dexp(-2*alpha*x)*x**2

return
end
```

Figure 10. *Prob* for the hydrogen atom.

As in the case of the harmonic oscillator, the variables are defined in the *input*. This time we will start with smaller values so that the calculation time is also shorter. In this calculation we set 5.000 points and 50 walkers.

Table 6. Selected values for the different variables of the *input*.

r0	4
M	5.000
Walkers	50
hits	0,5
Alpha i	0,4
Alpha f	1,5
Alpha p	0,1

We change in the *Main* program the value of Pas:

```
pas = r0/4.d0
```

In order to avoid negative regions because the domain in the case of hydrogen goes from 0 to r while for the harmonic oscillator the values were from $-\alpha$ to $+\alpha$.

Another change we have introduced is the *Random shoots* which substituted the *Random walks*. The difference between these two are that the first one, the random walk scans all regions, including all low probability zones, while the random shoot only scans

more specific regions and avoids low probability zones. The random shoot is used above all for more complicated systems, therefore, we will use the random shoot for the system following that of hydrogen, the helium atom.

```
xb=r0*ran2(idum)
```

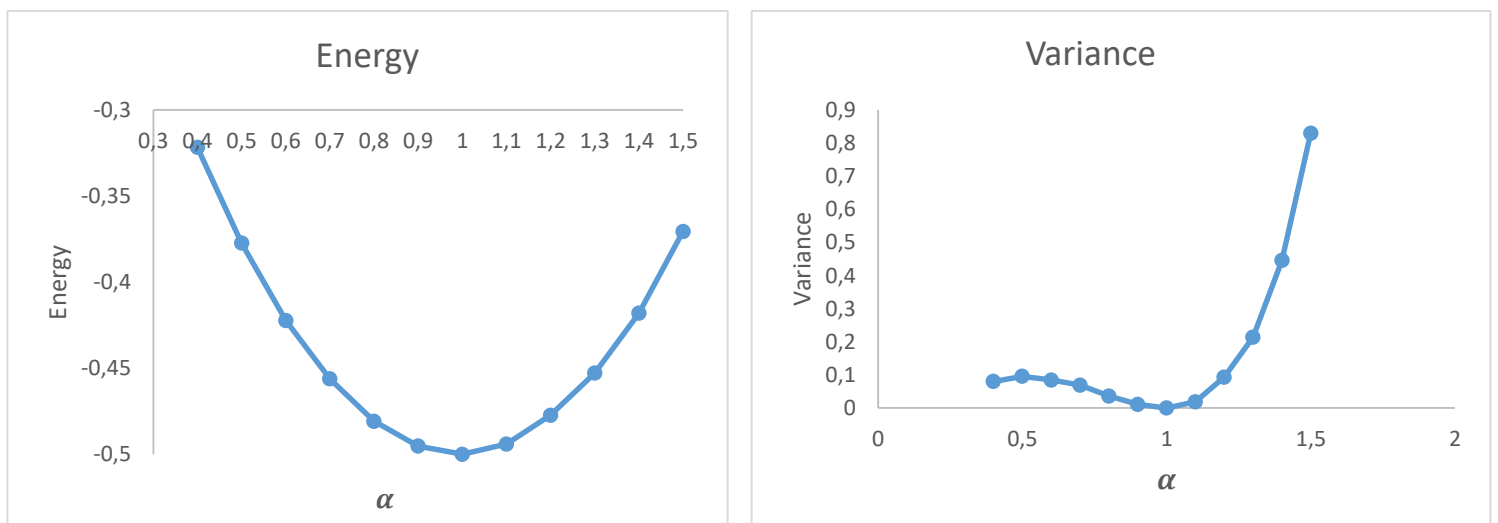
We assure that the value obtained at random is positive because as we mentioned before, the domain for the hydrogen atom is from 0 to r.

Once we set our programs, we run to get the local energy values as well as the variance.

Table 7. Results for the energy and the variance of the hydrogen atom with 5.000 points and 50 walkers from Fortran program.

α	Energy	Variance
0,40	-0,321810293	0,080184078
0,50	-0,377410661	0,095604285
0,60	-0,422280888	0,084647283
0,70	-0,456201855	0,069366411
0,80	-0,480884415	0,036492927
0,90	-0,495284114	0,011216274
1	-0,5	0
1,10	-0,494071739	0,019136482
1,20	-0,477377539	0,093244951
1,30	-0,452900871	0,213963741
1,40	-0,418080273	0,445612216
1,50	-0,370605775	0,829475343

Figure 11. The figures show a variational plot of the hydrogen atom with 5.000 points and 50 walkers. The figure on the left shows the energy from the α parameter, while the figure on the right shows the variance from the α parameter.



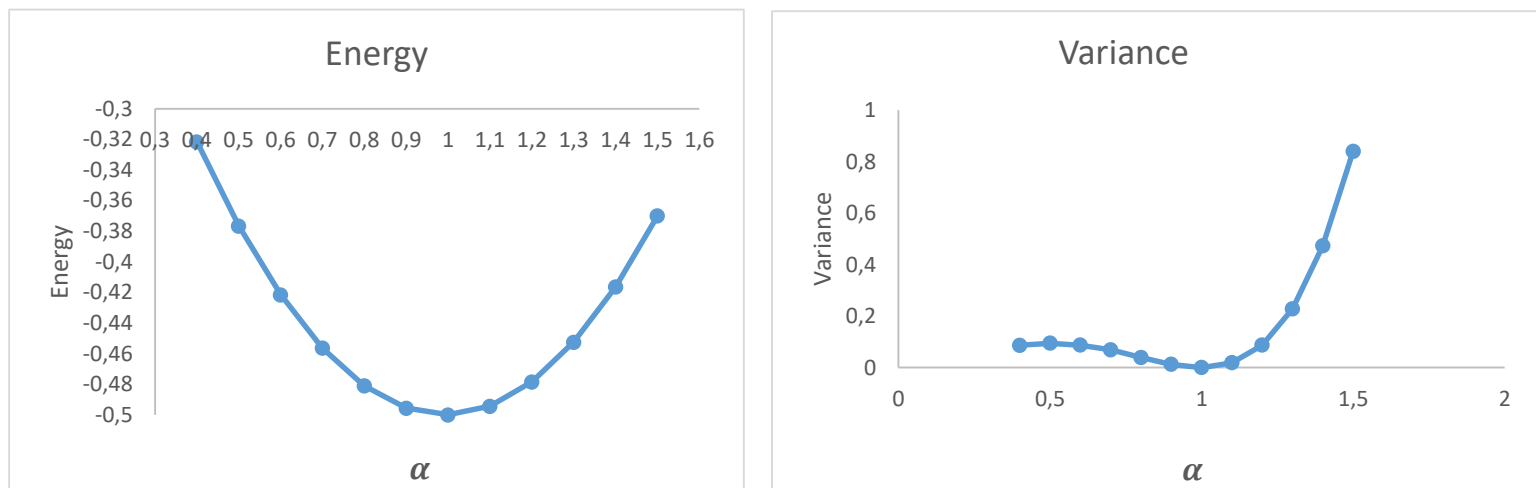
The lowest point cuts at 1, to ensure that, we will increase the number of points or walkers so this later can sample better the entire area.

Therefore, we will increase the number of points from 5.000 to 50.000, and the number of walkers from 50 to 1.000.

Table 8. Results for the energy and the variance of the hydrogen atom with 50.000 points and 1.000 walkers from Fortran program.

α	Energy	Variance
0,40	-0,321607826	0,0863487398
0,50	-0,376617125	0,0948691017
0,60	-0,421554304	0,0870296316
0,70	-0,456403722	0,0689179719
0,80	-0,481016514	0,0390292970
0,90	-0,495591857	0,0125427519
1	-0,5	0
1,10	-0,494294980	0,0188894181
1,20	-0,478406828	0,0870331950
1,30	-0,452546498	0,2281680587
1,40	-0,416430534	0,4726736834
1,50	-0,370034575	0,8394580725

Figure 12. The figures show a variational plot of the hydrogen atom with 50.000 points and 1.000 walkers. The figure on the left shows the energy from the α parameter, while the figure on the right shows the variance from the α parameter.



The difference between the figure 11 and figure 12 is practically null. As the minimum of the energy and the variance is the same, we have obtained a good "sample".

5.6. Helium atom

The He atom, the simplest polyelectronic system, has the following Hamiltonian^{[12][20]}

$$H(r_1, r_2) = -\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (34)$$

Where Z is the nuclear charge of the electron i , ∇_i^2 is the laplace operator that derives the (x_i, y_i, z_i) coordinates, r_i is the distance between the nucleus and the electron i and finally, r_{12} is the interelectronic distance.

We want to perform a VMC calculation of the ground state of the helium atom^[19], then we are going to define our trial function that fulfills the cusp conditions,

$$\phi(r_1, r_2) = e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+\alpha r_{12}}} \quad (35)$$

Being α and β the variational parameters.

From the equation (13), we consider the equations (34) and (35) to obtain the local energy equation

$$E_L(r_1, r_2) = -Z^2 + \frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{r_{12}} \left[1 - \frac{2\beta}{(1+\alpha r_{12})^2} \right] + \frac{2\alpha\beta}{(1+\alpha r_{12})^3} - \frac{\beta^2}{(1+\alpha r_{12})^4} + \frac{Z\beta(r_1+r_2)}{r_{12}(1+\alpha r_{12})^2} \cdot \frac{1-r_1 r_2}{r_1 r_2} \quad (36)$$

The calculation of the local energy will be shown at Appendix 1.

And the probability is $|\phi(r_1, r_2)|^2$

$$P(r_1, r_2) = e^{-2Zr_1} e^{-2Zr_2} e^{\frac{2\beta r_{12}}{1+\alpha r_{12}}} \quad (36)$$

Once we have define our local energy and our probability, it's time to introduce them to the Fortran program.

```
double precision function ENE(dist, r1, r2, x1, x2, y1, y2, z1, z2)
Implicit double precision(a-h,o-z)
common/dades1/Z,beta,alpha,r0,pas

dist=sqrt((x1-x2)**2+(y1-y2)**2+(z1-z2)**2)
pol = 1 + alpha*dist

ENE = -Z**2 + (Z-2.d0)/r1 + (Z-2.d0)/r2 + (1/dist)*(1.d0 - (2*beta)/pol**2) + &
(2*alpha*beta)/pol**3 - beta**2/pol**4 + Z*beta*(r1 + r2)/(dist*pol**2)*(1.d0-(x1*x2 + y1*y2 + z1*z2)/(r1*r2))

return
end
```

Figure 13. *Ene* for the helium atom.

```

double precision function prob(r1,r2,dist)
Implicit double precision(a-h,o-z)
common/dades1/Z,beta,alpha,r0,pas

prob = exp(-Z**2*r1 - Z**2*r2 + (2*beta*dist)/(1 + alpha*dist))

return
end

```

Figure 14. *Prob* for the helium atom.

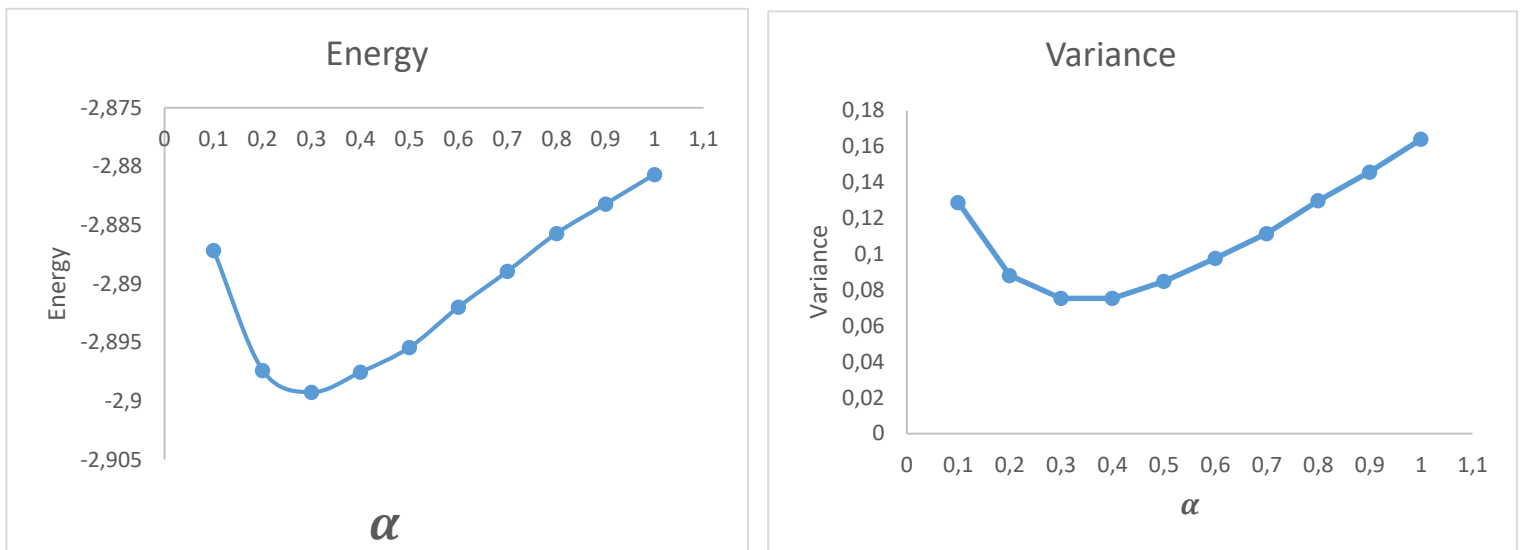
We define the value of $Z=2$ and $\beta=0,5$ and then define the variables, as we did before for the harmonic oscillator and the hydrogen atom, in the *input*.

Table 9. Selected values for the different variables of the *input*.

m	10.000
Walkers	30
hits	0,5
Alpha i	0,1
Alpha f	0,5
Alpha p	0,1

Once we set our programs, we run to get the local energy values as well as the variance.

Figure 15. The figures show a variational plot of the helium atom with 10.000 points and 30 walkers. The figure on the left shows the energy from the α parameter, while the figure on the right shows the variance from the α parameter.



As we did in the previous cases, the number of walkers should be increased as well as points, to ensure that we obtain a good sample.

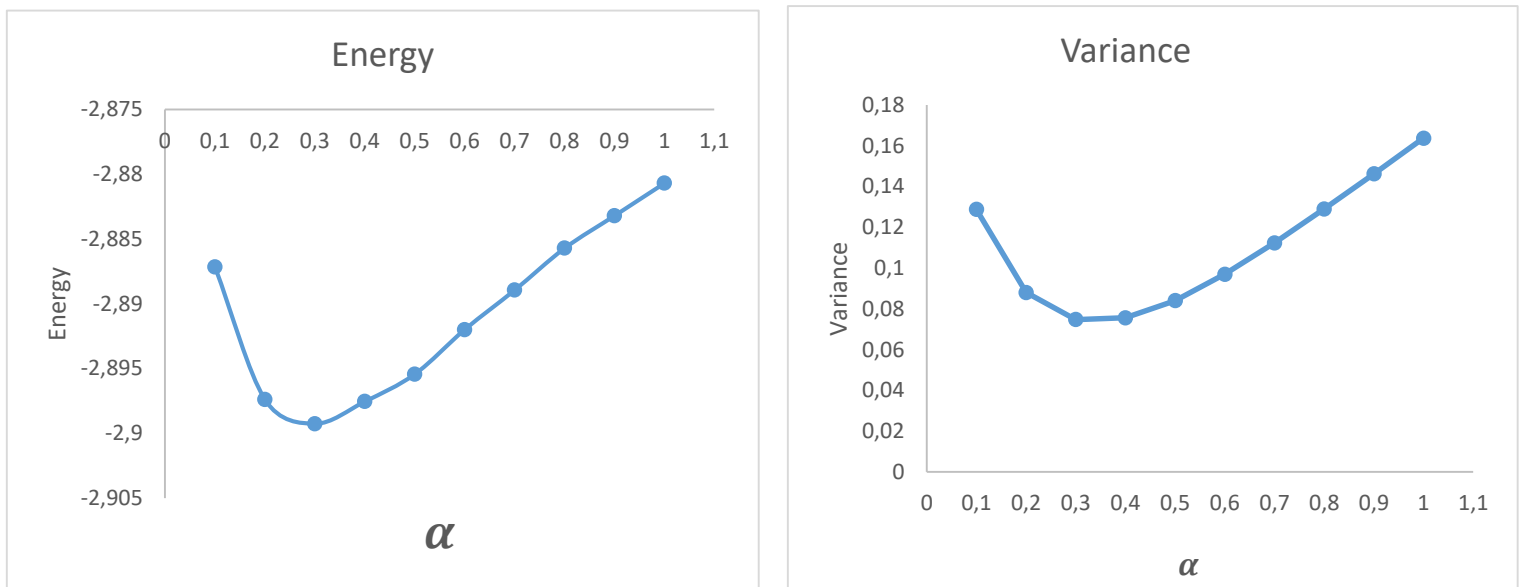
Table 10. Selected values for the different variables of the *input*.

m	100.000
Walkers	300
hits	0,5
Alpha i	0,1
Alpha f	0,5
Alpha p	0,1

Table 11. Result for the energy and the variance of the helium atom with 100.000 points and 300 walkers from Fortran program.

α	Energy	Variance
0,10	-2,8871720201	0,1288254790
0,20	-2,8973993333	0,0880324597
0,30	-2,8992661283	0,0747072885
0,40	-2,8975571739	0,0755853980
0,50	-2,8954444381	0,0840059018
0,60	-2,8920013138	0,0969516939
0,07	-2,8889521874	0,1123684394
0,08	-2,8857201686	0,1289611364
0,09	-2,8832081431	0,1461683652
1,00	-2,8806966216	0,1636861969

Figure 16. The figures show a variational plot of the helium atom with 100.000 points and 300 walkers. The figure on the left shows the energy from the α parameter, while the figure on the right shows the variance from the α parameter.



As we can see, the figure 15 and 16 have almost no difference, the minimum point cuts by approximately 0,3, therefore we can confirm that we have obtained a good sample.

6. Conclusions

In this final degree work, a pedagogical approach has been carried out on the Monte Carlo variational method and its subsequent illustrative calculations such as the harmonic oscillator and the hydrogen atom from the Fortran program in order to estimate the ground state energy of the systems.

As the first application of the method, the variational principle has been studied and then delved into the variational method of Monte Carlo (VMC).

After that, the Fortran's code was developed in order to accomplish the Fortran's language. The code uses the Metropolis Algorithm and the random walkers.

Once we have obtained the results of our different systems, we have seen that the code we have developed produces good results, as we can see as the table below

Table 12. The table shows the energy comparison. Energies are in units of Hartree.

Energy comparison		
Atom	Reference energy ^[21]	VMC results by Fortran Energy
Harmonic oscillator	0,5	0,5
Hydrogen	-0,5	-0,5
Helium	-2,86168	-2,89927

Comparing our results with the reference energies we can clearly see that our results are pretty accurate, a perfect result for the harmonic oscillator and the hydrogen atom. On the other hand, we observe that the result of the helium energy with that of the reference is very close, so we can conclude that VMC is a very precise method.

We have to emphasize that one of the drawbacks of the Fortran program is that the calculation time is much longer for more complex systems, where a clear increase in time has been noticed in the calculation of helium compared to that of the harmonic oscillator.

To finish, we can conclude that VMC produces very good results when developing a good code, besides that it is a quick and easy method to use, although it must be taken into account that it only works for very simple systems since the calculation time can increase considerably.

7. Bibliography

- [1] Thomas J. Bergin "50 years of Army computing: From ENIAC to MSRC" ARL Technical Publishing Branch, September 2000 (ISBN 0-9702316-1-X).
- [2] Sukanta Deb "Variational Monte Carlo Technique", *Ground State Energies of Quantum Mechanical Systems*. August 2014 (715-716).
- [3] John C. Morrison "Many-Electron Atoms" *Modern Physics*, 2010.
- [4] Attila Szabo, Neil S. Ostlund, "Modern quantum chemistry", *Introduction to Advanced Electronic Structure Theory*, Dover Publications, INC, 2006.
- [5] B.L. Hammond, W.A. Lester, Jr, P.J. Reynolds, "Monte Carlo Methods in Ab Initio Quantum Chemistry", World Scientific, 1994.
- [6] Kolos W & Wolniewicz L., "This Week's Citation Classic", *CC/NUMBER* 33, August 17, 1981.
- [7] M.P. Nightingale & C.J. Umrigar, "Quantum Monte Carlo Methods in Physics and Chemistry", *NATO Science Series*, Vol.525, 12-14 July 1998.
- [8] N.D. Drummond, M.D. Towler & R.J. Needs, "Jastrow Correlation factor for atoms, molecules, and solids", February 2, 2008.
- [9] Havard Sandsdalen, "Variational Monte Carlo studies of Atoms", Thesis for the degree of Master of Science, June 2010.
- [10] Andrew Williamson "The variation principle" *TCM*, University of Cambridge, 1996.
- [11] Josep Planelles, "Noves notes de Química Quàntica", Universitat Jaume I, 2010.
- [12] Morten Hjorth-Jensen, "Computational Physics", University of Oslo, Fall 2010.
- [13] Morten Hjorth-Jensen, "Computational Physics", University of Oslo, Fall 2010. Chapter 9.
- [14] S.H. Patil, "Wave functions for two- and three- electron atoms and isoelectronic ions", Department of Physics, Indian Institute of Technology, 27 November 1998.
- [15] Dennis Dunn, "Computational Physics", Unit 3phss, 2003.
- [16] Guillermo Cruz Quesada, "Determinación experimental de la constante de dimerización del ácido cetopírico en un medio moderadamente polar mediante espectroscopía FTIR", TFG, Universidad de Jaén, Julio 2016.

[17] Srinivasan S.Iyengar, "Atomic and Molecular Quantum Theory", Indiana University, 2003.

[18] Farshid Mehrdoust, Hossein Aminikhah, Mohammad Ghamgosar, "Variational Monte Carlo algorithm for solving one dimensional harmonic oscillator problem", The Journal of Mathematics and Computer Science, December 2011.

[19] Morten Hjorth-Jensen, "FYS4411", University of Oslo, Spring 2013.

[20] S.B.Doma, M.O.Shaker, A.M.Farag, F.N.El-Gammal, "Applications of the Variational Monte Carlo Method to the Ground States of the Lithium Atom and its Ions up to $Z=10$ in the Presence of Magnetic Field", Alexandria University, Tanta University, Menofia University.

[21] "Atomic Structure Calculations. Hartree-Fock Energy Results for the Elements Hydrogen to Lawrencium", Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico.

8. Appendix

APPENDIX 1

Local energy for a 1D harmonic oscillator

The Hamiltonian for the harmonic oscillator in one dimension is the following:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad (\text{A.1})$$

We can simplify the calculation and choose $m=k=\hbar=1$. Then the equation would be:

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{x^2}{2} \quad (\text{A.2})$$

As we mention before, we chose a trial function that accomplish some conditions (Meet the boundary conditions, be continuous, differentiable, etc...):

$$\phi_T(x) = e^{-\alpha x^2} \quad (\text{A.3})$$

Now we introduce the local energy, E_L :

$$E_L(R) = \frac{\hat{H}\phi_T(x)}{\phi_T(x)} \quad (\text{A.4})$$

Therefore, from the local energy equation and taking into account the equations (A.3) and (A.4) we obtain the equation of the local energy that afterwards will be introduced in the Fortran program.

$$E_{L,\alpha}(x) = \frac{\left(-\frac{1}{2} \frac{d^2}{dx^2} + \frac{x^2}{2}\right) e^{-\alpha x^2}}{e^{-\alpha x^2}} \quad (\text{A.5})$$

$$\begin{aligned} E_{L,\alpha}(x) &= \left(-\frac{1}{2 \cdot e^{-\alpha x^2}} \frac{d}{dx} \cdot \left(\frac{d}{dx} e^{-\alpha x^2} \right) \right) + \left(\frac{x^2}{2 \cdot e^{-\alpha x^2}} \cdot e^{-\alpha x^2} \right) = \\ &= \left(-\frac{1}{2 \cdot e^{-\alpha x^2}} \frac{d}{dx} \cdot ((-2\alpha x) \cdot e^{-\alpha x^2}) \right) + \left(\frac{x^2}{2 \cdot e^{-\alpha x^2}} \cdot e^{-\alpha x^2} \right) = \\ &= \left(\frac{\alpha}{e^{-\alpha x^2}} \frac{d}{dx} \cdot (x \cdot e^{-\alpha x^2}) \right) + \frac{x^2}{2} = \frac{\alpha}{e^{-\alpha x^2}} \cdot (1 - 2\alpha x^2) \cdot e^{-\alpha x^2} + \frac{x^2}{2} = \\ &= \alpha - 2\alpha^2 x^2 + \frac{x^2}{2} \end{aligned}$$

Then the local energy finally remains as follows:

$$E_{L,\alpha}(x) = \alpha + x^2 \left(\frac{1}{2} - 2\alpha^2 \right) \quad (\text{A.6})$$

Local energy for the hydrogen

The Hamiltonian of the hydrogen atom is the following:

$$H = -\frac{\hbar^2}{2mr^2} \left[\left(\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \right) - \frac{L^2(\theta, \phi)}{\hbar^2} \right] - \frac{1}{r} \quad (\text{A.7})$$

In order to simplify the equation we take into account when $l=0$, and $\hbar=m=1$, then the equation ends as:

$$H_{l=0} = -\frac{1}{2r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \right] - \frac{1}{r} \quad (\text{A.8})$$

Having the trial function equation:

$$\phi_T(r) = e^{-\alpha r} \quad (\text{A.9})$$

We can solve both equations from the local energy equation:

$$E_L(R) = \frac{\hat{H}\phi_T(x)}{\phi_T(x)} \quad (\text{A.10})$$

The steps to obtain the local energy equation is the following:

$$\begin{aligned} E_L(r) &= \frac{1}{e^{-\alpha r}} \cdot \left(-\frac{1}{2r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \right] - \frac{1}{r} \right) \cdot e^{-\alpha r} = \frac{1}{e^{-\alpha r}} \cdot \left(-\frac{1}{2r^2} \left[\frac{d}{dr} \left(r^2 \cdot e^{-\alpha r} \frac{d}{dr} \right) \right] - \frac{e^{-\alpha r}}{r} \right) = \\ &= \frac{1}{e^{-\alpha r}} \left(\frac{-2\alpha r \cdot e^{-\alpha r} + \alpha^2 r^2 \cdot e^{-\alpha r}}{2r^2} - \frac{e^{-\alpha r}}{r} \right) = \frac{-2\alpha r}{2r^2} + \frac{\alpha^2 r^2}{2r^2} - \frac{1}{r} = \\ &= -\frac{2\alpha}{2r} + \frac{\alpha^2}{2} - \frac{1}{r} \end{aligned}$$

Then the local energy finally remains as follows:

$$E_L(r) = -\frac{1}{r} - \frac{\alpha}{2} \left(\alpha - \frac{2}{r} \right) \quad (\text{A.11})$$

In order to check that the calculations made are correct, they are verified in the program *Mathematica*.

```
In[1]:= R[x_] = Exp[-a * x];
In[5]:= (-1/(2 x^2) (D[(x^2 D[R[x], x]), x]) - R[x]/x) / R[x] // Simplify // Expand
Out[5]= -a^2/2 - 1/r + a/r
```

Local energy for the Helium

The simplest system beyond the hydrogen is the helium atom, who has the following Hamiltonian

$$H(r_1, r_2) = -\frac{1}{2} \nabla_{r_1}^2 - \frac{1}{2} \nabla_{r_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (\text{A.12})$$

Defining the trial function

$$\phi(r_1, r_2,) = e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} \quad (\text{A.13})$$

It's time to solve both equations from the local energy equation:

$$E_L(R) = \frac{\hat{H}\phi_T(x)}{\phi_T(x)} \quad (\text{A.14})$$

Writing out the kinetic energy term in the spherical coordinates of electron 1 and 2, we arrive at the following expression for the local energy^[12]

$$E_L(r_1, r_2) = \frac{1}{e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}}} \cdot \left(-\frac{1}{2} \frac{d^2}{dr_1^2} - \frac{1}{r_1} \frac{d}{dr_1} - \frac{1}{2} \frac{d^2}{dr_2^2} - \frac{1}{r_2} \frac{d}{dr_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} \quad (\text{A.15})$$

$$E_L(r_1, r_2) = \frac{1}{e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}}} \cdot \left(-\frac{1}{2} \frac{d}{dr_1} \left(\frac{d}{dr_1} e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} \right) - \frac{1}{r_1} \frac{d}{dr_1} \left(e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} \right) - \frac{1}{2} \frac{d}{dr_2} \left(\frac{d}{dr_2} e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} \right) - \frac{1}{r_2} \frac{d}{dr_2} \left(e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} \right) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \quad (\text{A.16})$$

$$E_L(r_1, r_2) = \frac{1}{e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}}} \cdot \left(-\frac{1}{2} \left(\frac{2\alpha^2 \beta (r_1+r_2)}{(1+ar_{12})^3} - \frac{2\alpha\beta}{(1+ar_{12})^2} \right) \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} + \left(\frac{\beta}{1+ar_{12}} - \frac{\alpha\beta(r_1+r_2)}{(1+ar_{12})^2} - Z \right)^2 \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} - \frac{1}{r_1} \left(\frac{\beta}{1+ar_{12}} - \frac{\alpha\beta(r_1+r_2)}{(1+ar_{12})^2} - Z \right) \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} - \frac{1}{2} \left(\frac{2\alpha^2 \beta (r_1+r_2)}{(1+ar_{12})^3} - \frac{2\alpha\beta}{(1+ar_{12})^2} \right) \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} + \left(\frac{\beta}{1+ar_{12}} - \frac{\alpha\beta(r_1+r_2)}{(1+ar_{12})^2} - Z \right)^2 \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} - \frac{1}{r_2} \left(\frac{\beta}{1+ar_{12}} - \frac{\alpha\beta(r_1+r_2)}{(1+ar_{12})^2} - Z \right) \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} - \frac{1}{r_1} \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} - \frac{Z}{r_2} \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} + \frac{1}{r_{12}} \cdot e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{1+ar_{12}}} \right) \quad (\text{A.17})$$

$$E_L(r_1, r_2) = -\frac{1}{2} \left(\frac{2\alpha^2 \beta (r_1+r_2)}{(1+ar_{12})^3} - \frac{2\alpha\beta}{(1+ar_{12})^2} \right) + \left(\frac{\beta}{1+ar_{12}} - \frac{\alpha\beta(r_1+r_2)}{(1+ar_{12})^2} - Z \right)^2 - \frac{1}{r_1} \left(\frac{\beta}{1+ar_{12}} - \frac{\alpha\beta(r_1+r_2)}{(1+ar_{12})^2} - Z \right) - \frac{1}{2} \left(\frac{2\alpha^2 \beta (r_1+r_2)}{(1+ar_{12})^3} - \frac{2\alpha\beta}{(1+ar_{12})^2} \right) + \left(\frac{\beta}{1+ar_{12}} - \frac{\alpha\beta(r_1+r_2)}{(1+ar_{12})^2} - Z \right)^2 - \frac{1}{r_2} \left(\frac{\beta}{1+ar_{12}} - \frac{\alpha\beta(r_1+r_2)}{(1+ar_{12})^2} - Z \right) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (\text{A.18})$$

Simplifying the equation we arrive at the following expression for the local energy

$$E_L(r_1, r_2) = -Z^2 + \frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{r_{12}} \left[1 - \frac{2\beta}{(1+ar_{12})^2} \right] + \frac{2\alpha\beta}{(1+ar_{12})^3} - \frac{\beta^2}{(1+ar_{12})^4} + \frac{Z\beta(r_1+r_2)}{r_{12}(1+ar_{12})^2} + \frac{1-r_1 \cdot r_2}{r_1 \cdot r_2} \quad (\text{A.19})$$