

Variational Quantum Monte Carlo

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Abstract: The goal of this project is to compute an upper bound to the ground state energy for different quantum systems: the Harmonic Oscillator, the Hydrogen atom and the Helium atom. To do so, we make use of the variational principle and the integrals are performed using the so called Quantum Monte Carlo method, for which we will need to implement the Metropolis algorithm. Finally, the numerical simulations will be compared to analytical (if possible) and experimental results for each case. The results show a perfect accordance with other literature and experimental values.

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solutions are known) and the Helium atom.

The variational method

The variational method relies on the variational principle, which states that the ground state energy of a quantum system is always smaller than the energy of any other trial wave function [1]. With this mindset we can suggest a trial wave function in terms of a parameter α and minimize it. It is important to highlight that the energy that we find is an upper bound to the actual ground state energy. Comparing the variational energy with the one measured experimentally allows us to evaluate how correct is the trial wave function. The main disadvantage of this approach is obvious: we need a trial wave function which is, in general, very difficult to find and that relies in our physical intuition. This is opposite to perturbation theory, which is systematic and does not require any "guess". Apart from this weakness, the variational method has proved to be very useful when we lack of a good solution for an unperturbed Hamiltonian. In this case, the perturbation theory is less efficient.

The energy, $\langle E_T(\alpha) \rangle$ corresponding to the trial wave function, $\Psi_T(x, \alpha)$, is

$$\langle E_T \rangle = \frac{\langle \Psi_T | \hat{H} | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}, \quad (1)$$

where,

$$\langle \Psi_T | \hat{H} | \Psi_T \rangle = \int d\vec{x} \Psi_T^\dagger \hat{H} \Psi_T. \quad (2)$$

The variational method can become cumbersome specially if the integrals are difficult to compute. That is the reason why we will employ Monte Carlo integration, as it will be detailed in following sections.

II. MONTE CARLO INTEGRATION

In this section we will explain the Monte Carlo (MC) method to solve integrals numerically and how to implement such a methodology into our code. The basic idea

I. INTRODUCTION

The Schrodinger equation describes the temporal evolution of quantum systems. Therefore, it allows us to calculate physical quantities predicted by the quantum theory. Unfortunately, Schrodinger equation is not analytically solvable in the great majority of the cases. Some of the quantum systems that can be exactly solved are the Harmonic Oscillator, the infinite square potential well and the Hydrogen atom. For all of the cases for which not an exact solution of the Schrodinger equation exists, we can make use of different methods to find an approximated solution. Here we apply one of this approximation methods to find the energy of the ground state of the harmonic oscillator and the Hydrogen atom (for which exact

under MC integration is computing an integral numerically by using random numbers chosen within the volume of integration [2]. We can approximate a definite integral as:

$$\int_a^b f(x)dx = (b-a) \int_a^b p(x)f(x)dx \simeq \frac{b-a}{N} \sum_{i=1}^N f(x_i), \quad (3)$$

where x_i is a random number between a and b that follows a distribution given by $p(x)$, which in this case is $1/(b-a)$. Obviously, the more x_i we use (the bigger the N) the more accurate the result.

$$\int_a^b f(x)dx = \lim_{N \rightarrow \infty} \frac{b-a}{N} \sum_{i=1}^N f(x_i), \quad (4)$$

The random numbers we are using are uniformly distributed in the volume of integration, so the function is sampled homogeneously. However, it is very likely that the function is specially relevant in some region of the volume. This can bring up very large statistical errors since the function is being evaluated at the relevant region as many times as we evaluate it in regions where it is not. As a result, only few points will contribute to the integral significantly. To fix this problem we will use the so called *importance sampling*.

A. Importance sampling

This technique consists of choosing the points where we evaluate the function (x_i) to be concentrated in the relevant region (i.e. where the function in absolute value is larger), so the distribution of the random points is no longer homogeneous.

$$\int_a^b f(x)dx = \int_a^b dx \rho(x) \left(\frac{f(x)}{\rho(x)} \right). \quad (5)$$

Since $\rho(x)$ is the distribution function that samples the random points so that they are concentrated where $f(x)$ is more relevant, the quantity $F(x) = f(x)/\rho(x)$ is reasonably flat. This integral can now be rewritten as we did in equation (4) so that:

$$\int_a^b F(x)dx \simeq \frac{1}{N} \sum_{i=1}^N f(x_i), \quad (6)$$

Where $F(x) = \rho(x)f(x)$, which means that data points x_i follow a distribution given by $\rho(x)$.

Now that we have solved the problem of choosing the right distribution for the random points, it comes a new issue we need to address: how to sample ρ . To do so we employ the *Metropolis algorithm*.

B. Metropolis method

It is essential for the MC method that we properly sample the random points. The Metropolis method abandons the idea of generating random numbers that are uncorrelated. It makes use of Markov chains that consist of chains in which every element depends on the previous one.

We start our Markov chain with a random position inside the volume of integration. The next element of that chain will be correlated to this one.

Something important that we have to take into account is that the probability of going from one point to another has to be the same as the probability of taking the inverse step. That is called detailed balance.

Therefore, we will first generate a new random position and compare the distribution function, $\rho(x)$, in both points. Based on the result we will accept or reject the new point.

- If $\rho(x_{i+i}) \geq \rho(x_i)$ we accept the point.
- If $\rho(x_{i+i}) < \rho(x_i)$ we accept the point with a likelihood of $\rho(x_{i+i})/\rho(x_i)$ (or reject with a likelihood of $[1 - \rho(x_{i+i})/\rho(x_i)]$)

In some cases, we can create the second point randomly within a shell around the first one. By doing this, we do not allow the random walker to take steps that are too large. We must make sure that the detailed balance property still holds.

The result is a collection of random points following a $\rho(x)$ distribution. With this, we have everything we need to know how to compute integrals with the MC method.

III. VARIATIONAL QUANTUM MC

In this section we are going to implement MC integration to the variational method. This discussion is followed by the particular cases of the Harmonic oscillator (HO), Hydrogen atom (H) and Helium atom (He).

We need to relate equations (1) and (6). In other words, we need to find $\rho(x)$ and $F(x)$. To do so we rewrite equation (1) as follows:

$$\begin{aligned} \langle E(\alpha) \rangle &= \frac{\int d\vec{r} \Psi_T^\dagger(\vec{r}, \alpha) \hat{H} \Psi_T(\vec{r}, \alpha)}{\int d\vec{r} \Psi_T^\dagger(\vec{r}, \alpha) \Psi_T(\vec{r}, \alpha)} \\ &= \frac{\int d\vec{r} \Psi_T^\dagger(\vec{r}, \alpha) \Psi_T(\vec{r}, \alpha) \frac{\hat{H} \Psi_T(\vec{r}, \alpha)}{\Psi_T(\vec{r}, \alpha)}}{\int d\vec{r} \Psi_T^\dagger(\vec{r}, \alpha) \Psi_T(\vec{r}, \alpha)} \\ &= \int d\vec{r} \rho(\vec{r}, \alpha) E_{Local}(\vec{r}, \alpha). \end{aligned} \quad (7)$$

So we need to evaluate

$$E_{Local}(\vec{r}, \alpha) = \frac{\hat{H} \Psi_T(\vec{r}, \alpha)}{\Psi_T(\vec{r}, \alpha)}, \quad (8)$$

following a distribution given by

$$\rho(\vec{r}, \alpha) = \frac{\Psi_T^\dagger(\vec{r}, \alpha) \Psi_T(\vec{r}, \alpha)}{\int d\vec{r} \Psi_T^\dagger(\vec{r}, \alpha) \Psi_T(\vec{r}, \alpha)}. \quad (9)$$

At this point we might encounter a reasonable difficulty if we need to find the norm of the trial wave function (which corresponds to the denominator of expression (9)). However, this will not be necessary since the Metropolis algorithm only compares the density distribution, $\rho(x)$, in two different points. Since the norm will only depend on α it will cancel out when we do the comparison. Its value is therefore not relevant for the Metropolis and we can completely take it out from the expression, yielding:

$$\rho(\vec{r}, \alpha) = \Psi_T^\dagger(\vec{r}, \alpha) \Psi_T(\vec{r}, \alpha). \quad (10)$$

The upper bound limit predicted by the variational principle is therefore given by the expression:

$$\langle E(\alpha) \rangle = \frac{1}{N} \sum_{i=1}^N E_{Local}(\vec{r}_i), \quad (11)$$

where N is the number of elements in the Markov chain and the positions \vec{r}_i follow a distribution given by equation (10).

In order to successfully implement Variational MC we need to find an explicit expression of the density distribution (10) and the local energy (8). These functions only depend on the trial wave function and the Hamiltonian, that encodes all the information of the evolution of the system. In the next Section, we will do this for the three particular cases. For both HO and H the exact solution is known.

Let us make a remark before going straight to the implementation. For the sake of simplicity we will be using reduced units in our computations. In the case of the H and He the mass will be measured in electron-masses. Also reduced Planck constant, \hbar , the electron charge e and $4\pi\epsilon_0$ are taken to be one. In the case of the HO, the frequency ω is taken to be the unit. This formalism is perfectly consistent and will make coding more simple.

A. Harmonic oscillator

The Hamiltonian of the 1D HO is given by:

$$\hat{H}_{HO} = -\frac{1}{2} \vec{\nabla}^2 + \frac{1}{2} x^2. \quad (12)$$

Where we are considering a unit mass particle.

As the variational method requires, we need to propose a trial wave function. For the HO we already know that the

exact solution of the Schrodinger equation is a Gaussian function [3], so we should get the exact result.

$$\Psi_T(x, \alpha) = e^{-\alpha x^2}. \quad (13)$$

The variational parameter is α (the one we minimize). There is no need of normalizing this function. The other functions we need for our calculation are the Local Energy and the density distribution. The latter is simply the square of the trial wave function.

$$\rho(x) = e^{-2\alpha x^2}. \quad (14)$$

Recalling equation (8), it is straightforward to compute the Local Energy:

$$E_{Local} = \alpha + x^2 \left(\frac{1}{2} - 2\alpha^2 \right). \quad (15)$$

As previously mentioned, we can compare this result easily with the exact one since this integration can be solved analytically. Particularizing equation (7) to the HO Hamiltonian we get the analytical solution for the local energy:

$$E_{Analytical} = \frac{1}{8\alpha} (4\alpha^2 + 1). \quad (16)$$

We can also solve analytically the expression for the variance of the energy:

$$Var(E)_{Analytical} = \frac{(1 - 4\alpha^2)^2}{32\alpha^2}. \quad (17)$$

To compute the integrals we have used Maple software.

B. Hydrogen atom

The Hydrogen atom is a system of two particles, an electron and a proton. Therefore, the configuration space is six dimensional. Since the proton is more massive than the electron, we can take the center of mass frame and then the problem becomes three dimensional. Then, the Hamiltonian in atomic units is:

$$H = -\frac{1}{2} \nabla^2 - \frac{1}{r}, \quad (18)$$

where \vec{r} is the relative coordinate of the electron with respect to the proton. Nevertheless, the problem can be reduced to one dimension if we use the Hamiltonian in spherical coordinates,

$$H = -\frac{1}{2} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] - \frac{1}{r}, \quad (19)$$

which only depends on the radial coordinate r . We will take a trial function of the following form [2]:

$$\Psi(\vec{r}, \alpha) = e^{-\alpha r^2}, \quad (20)$$

where $r = |\vec{r}|$. Then, the Local Energy is:

$$E_{Local} = -\frac{1}{2} \left[\alpha^2 - \frac{2\alpha}{r} \right] - \frac{1}{r}. \quad (21)$$

It is utterly important to note that using spherical coordinates is not a good strategy to follow. It may sound attractive since the problem is reduced to a one dimensional problem, but this comes at a price. In spherical coordinates the detailed balance is not ensured because the probability of going from a certain radius to a bigger one is definitely different from the other way around since the shells have different areas. That is the reason why it is preferable to produce three-dimensional points and then take the norm to compute the radius.

In the case of Hydrogen there exists an analytical solution for the ground state energy which corresponds to $\alpha = 1$ and $E_0 = -\frac{1}{2}$. Note that the expression for the local energy when $\alpha = 1$ does not depend on r .

$$E_{Local}(\alpha = 1) = -\frac{1}{2}. \quad (22)$$

Therefore for this value of α , the variance of the expectation value of the energy should be 0.

C. Helium atom

The Helium atom is a three particle problem: we have two electrons orbiting around the nucleus. Since the nucleus is much more massive than an electron, we can assume that it is at rest at the origin of the coordinate system. We will take the electrons to have positions \vec{r}_1 and \vec{r}_2 (six dimensional configuration space). Again using atomic units, the Hamiltonian of our system is as follows:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}, \quad (23)$$

where $r_{12} = |\vec{r}_1 - \vec{r}_2|$. Note that the Hamiltonian contains the two kinetic terms for each electron and the two potential (attractive) terms between each electron and the nucleus. Finally the term $\frac{1}{r_{12}}$ corresponds to the repulsive potential energy between the two electrons.

The choice of a wave function for this problem is complicated. In our case, we will use the Padé-Jastrow wave function, which consists of a product of two electron orbitals and a correlation term. It has the following form [2]:

$$\Psi(\vec{r}_1, \vec{r}_2) = e^{-2r_1} e^{-2r_2} e^{\frac{r_{12}}{2(1+r_{12}\alpha)}}. \quad (24)$$

This wave function consists of two exponentials, that would represent individual electrons, and an interacting term, characterized by the distance between the two electrons. It can be seen that when the distance between electrons is very big, the interacting term is just a constant larger than 1. However, when the electrons are close together the interacting term goes to 1. This feature is important since the square of Ψ gives as the probability density, so it ensures that the probability of finding the electrons close to each other will always be smaller than they being further apart, so we do not have to impose any extra conditions. Note that the parameter α has to be positive if we do not want the wave function to diverge for certain values of r_{12} .

For this trial wave function, the local energy given by [2] is:

$$E_{Local} = -4 + (\hat{r}_1 - \hat{r}_2)(\vec{r}_1 - \vec{r}_2) \frac{1}{r_{12}(1 + \alpha r_{12})^2} - \frac{1}{r_{12}(1 + \alpha r_{12})^3} - \frac{1}{4(1 + \alpha r_{12})^4} + \frac{1}{r_{12}}. \quad (25)$$

Finally, the density distribution is just the square of the trial wave function. Since there is no analytical solution for the case of Helium, we will not be able to compare our result with the exact solution.

IV. QUANTUM MC IMPLEMENTATION

In this section we discuss the steps taken to implement the code for the MC computation as well as issues that appear along the way.

Structure of the code. In our code, the very first functions define the trial wave function, the density probability and the local energy. These definitions are simple and do not deserve more explanation.

The only function left to talk about is the one that is performing the Metropolis algorithm following (which discussed in section II B). In the main program, some initial values are defined and the iteration to minimize the variational parameter, α , starts. Throughout this process, we compute the expectation value of the energy and the variance for each value of α .

A. Implementation of the Metropolis algorithm

The Metropolis function builds a Markov Chain that is used to integrate the energy expectation value and other parameters that will be needed for the computation of the variance and the minimization algorithm. Firstly, we would like to discuss the values of the typical length that we have chosen to build the Markov chain.

For the case of HO, since the trial wave function is a Gaussian, we have chosen to account for three times the typical length (given by the variance of the Gaussian dis-

tribution), which is

$$\sigma = \frac{1}{\sqrt{2\alpha}}. \quad (26)$$

Taking a larger integration region would be less efficient since the density distribution quickly decays and we would be generating random points in position where the trial wave function is not relevant at all. Nevertheless, if we take enough data the result should be the same.

For the case of Hydrogen, the maximum radial distance we will consider is the Bohr radius, which in our unit system is the unit. In our computations, we will use twice the Bohr radius as the typical length. However, the trial wave function strongly depends on α . We can see that the larger the α value, the narrower the density distribution is, and therefore it would make sense to restrict the maximum possible value of the distance to be inversely proportional to α . Therefore, we could generate the Markov chain to have radial distances up to $2/\alpha$. This is not necessary but it makes the convergence to the minimum faster and the variance becomes smaller.

For He the trial wave function is more complicated and there are more features that we need to take into account. Since it involves the wave function of the independent electrons and a term accounting for the interaction we will apply a similar reasoning as for H and use a constant typical length of $L = 1$ in this case.

We are working with a six dimensional problem, so in each metropolis iteration we have six walkers. Nevertheless, three account for the position of one of the electrons and three for the other. That is why we will just move one electron at a time: we will randomly chose whether to move \vec{r}_1 or \vec{r}_2 for each step of the metropolis algorithm. Finally, we will get rid of the first points of the Metropolis iteration. In this way, we ensure that when we start computing the energy the walkers are already in the relevant probability region.

As explained in Section II B, there is the possibility of considering at each step a small box around the previous position instead of doing each step randomly within the typical length. This procedure ensures that the random walkers do not take too large steps.

In order to know how the Metropolis algorithm is performing we will compute, for each value of α , the Rejection ratio, which is the ratio of points X that were rejected divided by the number of steps taken by the random walker. The Rejection ratio should be around 10 – 40%. If it is smaller, that tells us that we are being very strict taking points. The contrary would imply that the points are less correlated and that could take more steps to reach the region of maximum probability.

Finally, a general important feature to take into account when constructing the Metropolis algorithm is to con-

sider more than one random walker. That is because the Metropolis algorithm might get stuck at some point and start giving the same value of x for all following steps. This means that the random walker will not move around the probability distribution and therefore our results will not be reliable. If instead we initialize the metropolis algorithm more than once, we will start at a different point each time and the probability that all random walkers get stuck is much lower.

B. Minimizing the variational parameter

The goal of this project is to find the minimum value of the energy, which is in terms of the parameter α . Therefore, we are interested in using a minimum finder. Methods like the Newton algorithm use the gradient of the function that we want to minimize. This is a problem since the derivatives of stochastic variables can lead to large numerical errors [2]. Instead, what we can do is compute the derivative over the population of walkers and then take the average [2]:

$$\frac{dE}{d\alpha} = 2 \left(\left\langle E_L \frac{d \ln \Psi_T}{d\alpha} \right\rangle - E \left\langle \frac{d \ln \Psi_T}{d\alpha} \right\rangle \right). \quad (27)$$

Then,

$$\alpha_{new} = \alpha_{old} - \gamma \left(\frac{dE}{d\alpha} \right), \quad (28)$$

where $\alpha \in (0, 1]$ is a parameter that we can choose. We will take it to be 0.9 for the harmonic oscillator and 0.5 for both the Helium and the Hydrogen atoms. We have fixed this values by trial and error.

V. RESULTS

For each case, we show will the energy in terms of the parameter α , which allows us to see where the minimum is located. We will also show the minimizing process where the algorithm in (28) has been used, in which we plot the evolution of the parameter α , the expectation value of the energy and the variance of the energy. We will compare the results with Table IV, which is obtained from [2].

A. Harmonic Oscillator

For the case of the Harmonic oscillator we can easily compare the numerical and the analytical results (Section III A). The results obtained are plotted in the Appendix (Fig. 1 and Fig. 2 show the minimization process for Energy and variance; and Fig. 3 that shows the dependence of the energy with α). We show a summary of the values near the minimum in Table I.

α	$\langle E \rangle$	$Var(E)$	$E_{analytical}$	$Var(E)_{analytical}$
0.45	0.5039	0.0061	0.5028	0.0056
0.5	0.5	0	0.5	0
0.55	0.5006	0.0053	0.5023	0.0046

TABLE I: Table with the results for the Harmonic Oscillator. This table shows the values closer to the minimum.

The results we have obtained are almost equivalent to the ones in Table IV. Notice that for $\alpha = 1/2$ we get the exact solution as expected, with a vanishing error.

In figure 1 we can see the process of minimization of the value of the energy, in which the parameter α converges to the value $1/2$. The error bars, which correspond to the square root of the variance of the energy, are considerably large at the beginning but the decrease as the minimum is reached. The same behaviour is also seen for VII, where the variance clearly decreases as the minimizing α evolves.

For this case, to ensure points are reasonably correlated, every time we generate a new point in the Markov chain we consider a box of size 40% the size of the integrating volume about the previous point. This results in a rejection ratio of the 30%.

B. Hydrogen

For the case of the Hydrogen, we have not compared the results to the analytic solution for every value of the parameter α as it has been done for the Harmonic Oscillator case. Nevertheless, we know the minimum value of the energy and to which parameter α it corresponds (22).

The results obtained in our simulation can be found in the Appendix (Fig. 4, Fig. 5). We show a summary of the values near the minimum in Table II. We clearly see that the minimum corresponds to $\alpha = 1$, and energy 0.5 as expected, for which the variance is zero.

For Hydrogen the rejection rate is within 10% (for small values of α) and 30% (for larger values of α). In this case the points in the Markov chain are generated in a box of 20% the size of the integrating volume.

α	$\langle E \rangle$	$Var(E)$
0.95	-0.4972	0.0019
1.0	-0.5	0.000
1.05	-0.4921	0.0024

TABLE II: Table with the results for the Hydrogen. This table shows the values closer to the minimum.

The results we have obtained are almost equivalent to the ones in Table IV.

In figure 4 we can see the process of minimization of the value of the energy, in which the parameter α converges to the value 1. The error bars, which correspond to square root of the variance of the energy, are con-

siderably large at the beginning but the decrease as the minimum is reached.

C. Helium

For the case of the Helium, the problem becomes a little bit more complicated. Firstly, we cannot compare the results to an analytical solution, but we know that the experimental value of the ground state energy of an Helium atom is -2.9037 . We can also compare it with the values obtained with other numerical simulations, such as Hartree-Fock (-2.8617) or Density functional theory (DFT) (-2.83) or the ones found in Table IV where they also use Quantum MC. Other value for the ground state found in literature is -2.90372 , see [4]. This value is in agreement with the one found by us using the QMC method.

The experimental value is -2.9034 as found in NIST database [5]. The results obtained using our simulation are found in the Appendix (Fig. 6, Fig. 7). We show a summary of the values near the minimum in Table III. We can see that there is a minimum for $\alpha = 0.15$, which corresponds to an energy of -2.87 .

α	$\langle E \rangle$	$Var(E)$
0.05	-2.8717	0.1752
0.1	-2.8767	0.1361
0.15	-2.8789	0.1111
0.2	-2.8764	0.0962
0.25	-2.8753	0.0885

TABLE III: Table with the results for the Helium. This table shows the values close to the minimum.

The results we have obtained are almost equivalent to the ones in Table IV, both for the value of the energy and the values of the variance.

In figure 6 we can see the process of minimization of the value of the energy, in which the parameter α converges to the value 0.15. The variance is around 0.1 throughout the whole process of minimization and does not decrease to zero as happened with H and HO. Nevertheless, this agrees with the Table IV.

Markov chains for Helium are generated considering new points to be around 50% of the size of the integration volume. This results in a rejection ratio of 38%. It is bigger than for the other cases but still reasonable and the results are very satisfactory.

VI. CONCLUSION

In this project we have obtained an approximation to the ground state energy of three different systems using the variational principle and we have integrated using the Monte Carlo method.

The harmonic oscillator was the simplest case. An analytical solution to this problem exists and the choice of a trial wave function is clear. The results match the analytical solution almost perfectly.

On the other hand, Hydrogen and Helium are more complicated systems. For Hydrogen, the ground state energy can also be solved analytically and we see that the result of the numerical calculations matches the expected value. The minimization procedure also converges to the minimum.

As for Helium, no analytical solution exists and the choice of the trial wave function is more subtle: some

approximations need to be made and there are different opinions about which expression to use. By using the expression in [2] and taking into account a series of features when performing the MC integration we managed to obtain a minimum with matches the expected value. The minimization process also converges to the minimum. All the values obtained agree with others found in experiments and literature. We cannot conclude but the Quantum Monte Carlo is an excellent estimator for an upper bound to the ground state energy, at least for the systems considered in this report.

VII. APPENDIX

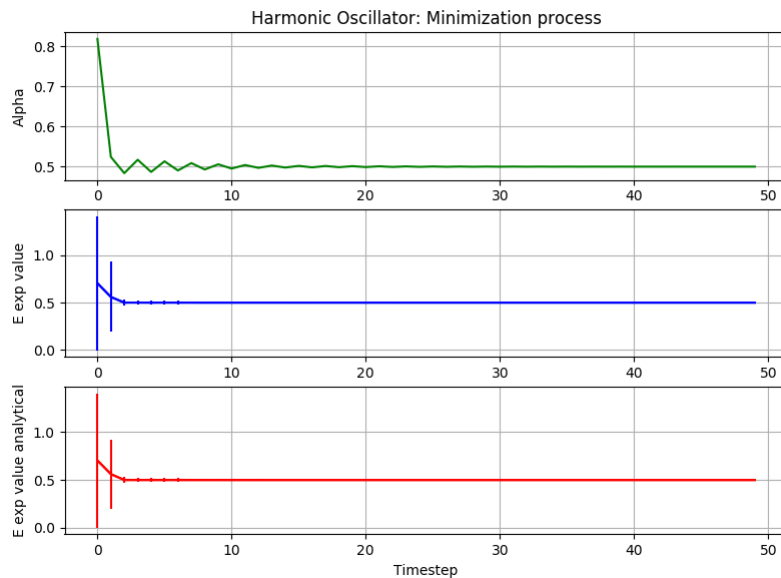


FIG. 1: This figure corresponds to the Harmonic Oscillator case. In it, we can observe the minimization of the parameter α starting at $\alpha = 1.2$ and the behaviour of the numerical and the analytical computation of expectation value of the energy. We see that the behaviour for the two computations is almost equivalent. The errors shown in the figure correspond to $\sqrt{\text{var}(E)}$, for the variance computed numerically and analytically in each case. The minimum value of $\alpha = 0.5$ is reached approximately within the first ten steps. For this figure we have taken 50 steps in the value of the parameter α , 500 iterations in the Metropolis algorithm and 200 random walkers. The typical length has been taken to be $L = 3/\sqrt{2\alpha}$.

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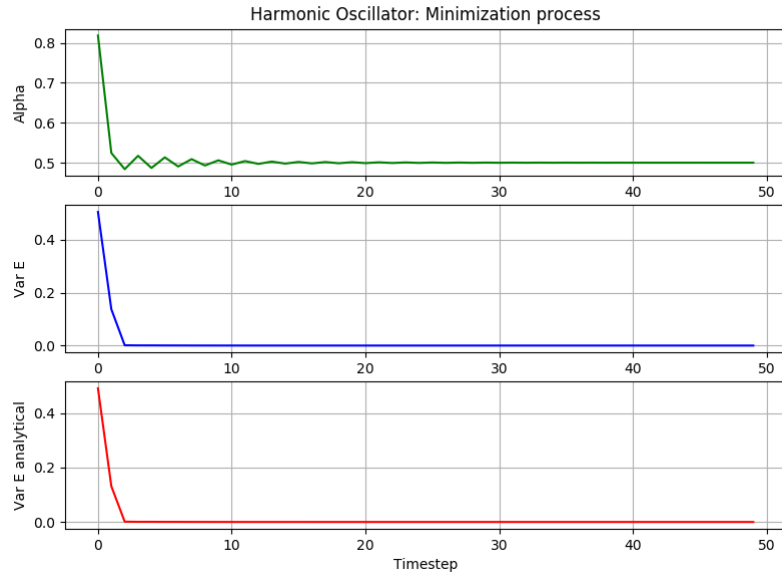


FIG. 2: This figure corresponds to the Harmonic Oscillator case. In it, we can observe the minimization of the parameter α starting at $\alpha = 1.2$ and the behaviour of the numerical and the analytical computation of variance of the energy. We see that the behaviour for the two computations is almost equivalent. For this figure we have taken 50 steps in the value of the parameter α . Nevertheless, the variance becomes almost zero within the first time steps. For this figure we have taken 50 steps in the value of the parameter α , 500 iterations in the Metropolis algorithm and 200 random walkers. The typical length has been taken to be $L = 3/\sqrt{2\alpha}$.

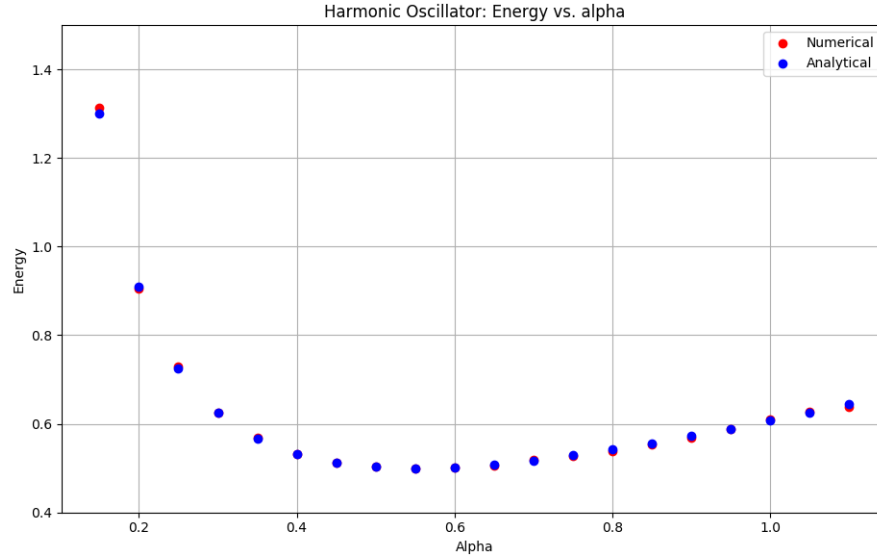


FIG. 3: This figure corresponds to the Harmonic Oscillator case. In it we can observe the dependence of the energy in the parameter α , both for the numerical and the analytical computation. To obtain it, we have iterated equally spaced values of α from 0.1 to 1. We can clearly see that there is a minimum for $\alpha = 0.5$, as it was expected, and that both computations present almost the same behaviour. For this figure we have taken 10 values of α , 500 iterations in the Metropolis algorithm and 200 random walkers. The typical length has been taken to be $L = 3/\sqrt{2\alpha}$.

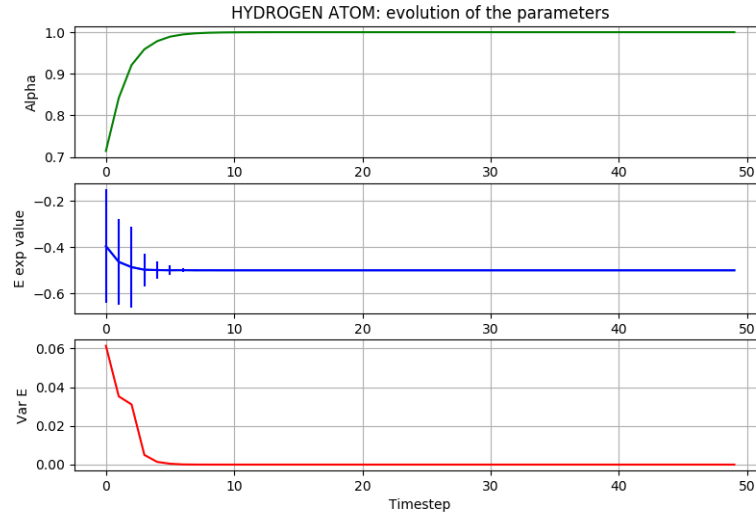


FIG. 4: This figure corresponds to the Hydrogen case. In it, we can observe the minimization of the parameter α starting at $\alpha = 0.5$ and the behaviour of the expectation value of the energy. The errors shown in the figure correspond to $\sqrt{\text{var}(E)}$. The variance is also plotted in the figure. The minimum value of α , which is expected to be around 1 is reached. We see that the energy converges to 0.5 and the variance to zero, as it was predicted. For this figure we have taken 50 steps in the value of the parameter α , 500 iterations in the Metropolis algorithm and 200 random walkers. The typical length has been taken to be $L = 2$.

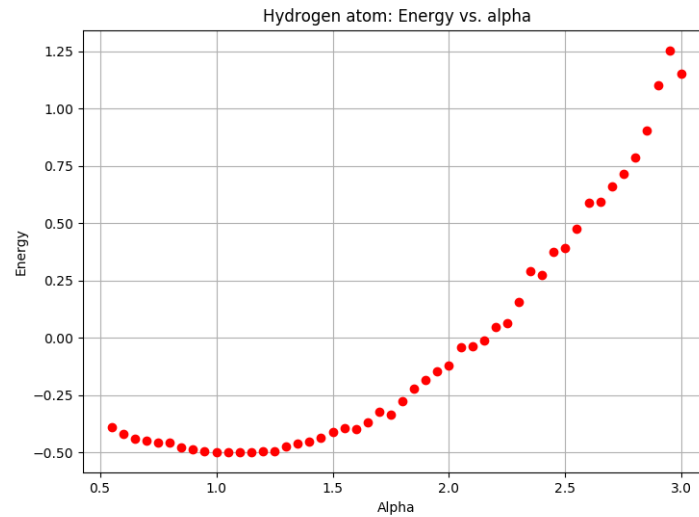


FIG. 5: This figure corresponds to the Hydrogen case. In it we can observe the dependence of the energy in the parameter α . To obtain it, we have iterated equally spaced values of α from 0.5 to 1.5. We can clearly see that there is a minimum around $\alpha = 1$. The minimum value of the energy is around 0.5 as expected. For this figure we have taken 500 iterations in the Metropolis algorithm and 200 random walkers. The typical length has been taken to be $L = 2$.

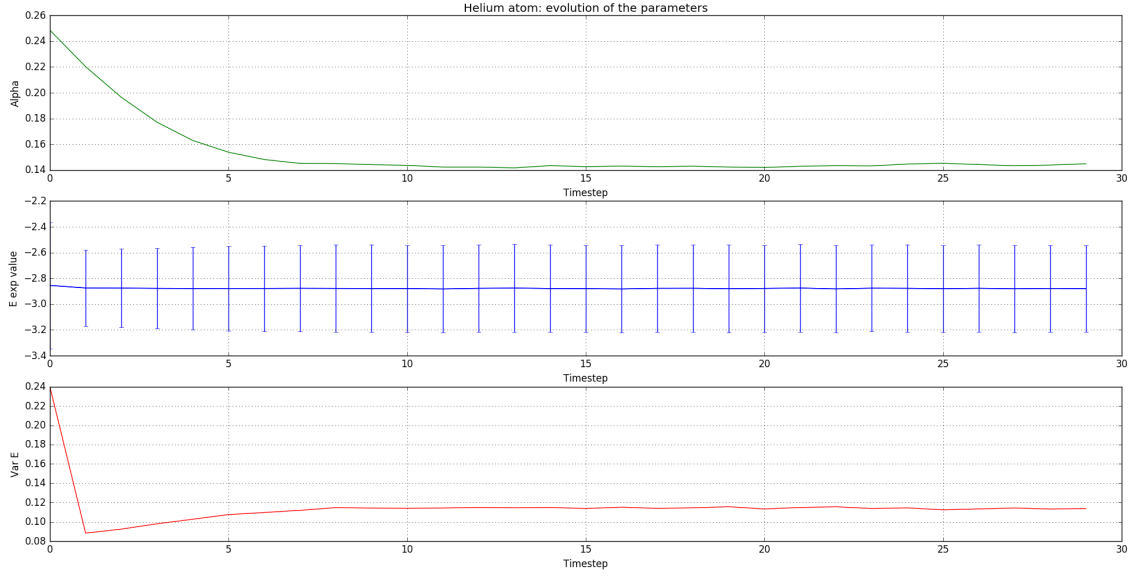


FIG. 6: This figure corresponds to the Helium case. In it, we can observe the minimization of the parameter α starting at $\alpha = 0.05$ and the behaviour of the expectation value of the energy. The errors shown in the figure correspond to $\sqrt{\text{var}(E)}$, for the variance, which can also be plotted in the figure. For this figure we have taken 30 steps in the value of the parameter α . The minimum value of α , which is expected to be around 0.15 is reached. We see that the energy converges to approximately -2.88 and the variance is around 0.1 and does not decrease to zero in this case. For this figure we have taken 5000 iterations in the Metropolis algorithm, but the first 5000 were discarded. We have also considered 200 random walkers. The typical length has been taken to be $L = 1$.

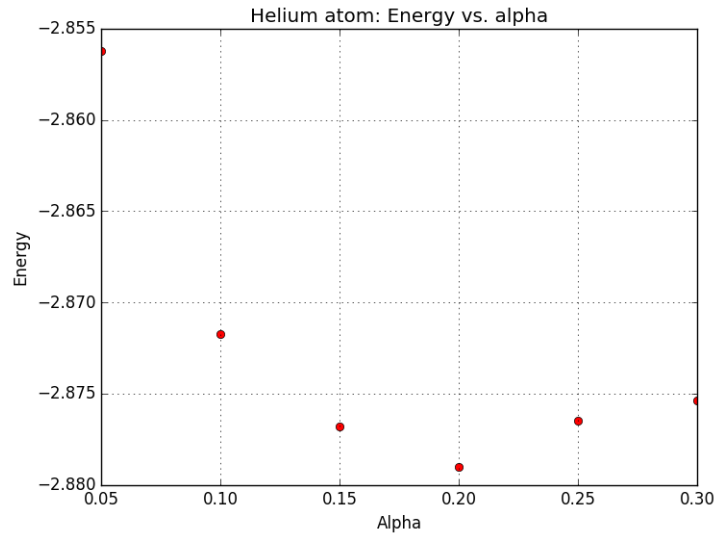


FIG. 7: This figure corresponds to the Helium case. In it we can observe the dependence of the energy in the parameter α . To obtain it, we have iterated equally spaced values of α from 0 to 0.3. We can clearly see that there is a minimum around $\alpha = 0.2$. The minimum value of the energy is around -2.87 as expected. For this figure we have taken 10000 iterations in the Metropolis algorithm, but the first 1000 were discarded. We have also considered 200 random walkers. The typical length has been taken to be $L = 1$.

Harmonic oscillator				
α	$\langle E \rangle$	$\text{var}(\langle E \rangle)$	E_v	$\text{var}(E)_v$
0.4	0.5124(1)	0.02521(5)	0.5125	0.0253125
0.45	0.50276(4)	0.00556(2)	0.50278	0.00557
1/2	1/2	0	1/2	0
0.55	0.50232(6)	0.00454(1)(1)	0.5022727	0.0045558
0.6	0.5084(1)	0.0168(4)	0.508333	0.0168056

Hydrogen atom			Helium atom		
α	$\langle E \rangle$	$\text{var}(\langle E \rangle)$	α	$\langle E \rangle$	$\text{var}(\langle E \rangle)$
0.8	-0.4796(2)	0.0243(6)	0.05	-2.8713(4)	0.1749(2)
0.9	-0.4949(1)	0.0078(2)	0.075	-2.8753(4)	0.1531(2)
1.0	-1/2	0	0.10	-2.8770(3)	0.1360(2)
1.1	-0.4951(2)	0.0121(4)	0.125	-2.8780(4)	0.1223(2)
1.2	-0.4801(3)	0.058(2)	0.15	-2.8778(3)	0.1114(2)
			0.175	-2.8781(3)	0.1028(2)
			0.20	-2.8767(4)	0.0968(2)
			0.25	-2.8746(10)	0.0883(2)

TABLE IV: Table of values obtained from [2]. It displays the values of the energy and the variance of the energy that they obtained for the three cases that we have taken into account.