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Project 2

Variational Monte Carlo for the Helium Ground State

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Abstract

The Schrödinger equation can be solved analytically only for few simple cases. It is indeed not possible to find an exact solution for more complex systems; hence, in this study we used a variational Monte Carlo method to approximate the ground state energy of the Helium atom. We first validated our code by testing it on simple systems with known solutions, before proceeding to use it with the Helium atom. We then calculated the energy of the system using a trial wave function which depends on a variational parameter α ; by minimizing the energy with respect to α we then found an approximation of the ground state energy. The error is then found using data blocking, since the different values of the energy depend on correlated position steps, and are hence correlated. Our result for the ground state energy is $E = -2.9023 \pm 0.0007$, which is consistent with the literature value $E = -2.9037243771$ a.u. [1].

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1 Introduction

The Schrödinger equation can be solved analytically for only few cases, such as a harmonic oscillator or the Hydrogen atom. Instead, it is impossible to find an exact solution for more complex and interacting systems.

In this project we used a variational Monte Carlo method to approximate the ground state energy of the Helium atom. The idea behind this method is to find the energy of the system as a function of a variational parameter α , and then find the value of α that minimizes the energy. The choice of using Monte Carlo integration was made since this method works incredibly well with high-dimensional integrals, like those that are to be solved when integrating a Hamiltonian with six degrees of freedom, three degrees of freedom for each electron in Helium. In fact, dividing the integration interval in N sections, the error associated with ordinary numerical integration in one dimension is of the order $\frac{1}{N^k}$, with k the order of the integration method, and it becomes $\frac{1}{N^{k/d}}$ in d dimensions. On the other hand, the error using Monte Carlo integration is of the order of $\frac{1}{\sqrt{N}}$. Hence, the error associated with Monte Carlo is smaller for $d > 2k$, which is the case for the Helium atom.

The report begins with a detailed presentation of the methods used in the project. Preliminary tests of the variational Monte Carlo method on solvable systems (harmonic oscillator and Hydrogen atom) are then showed. The results of the simulation are then presented and analysed; to conclude, limitations of the project are discussed.

2 Methods

2.1 Random and Importance Sampling [2]

To introduce Monte Carlo integration and its usefulness, let us consider a probability distribution $\rho(x)$ of a random variable x . Then, we can compute the expectation value of a function $f(x)$ as:

$$\int \rho(x)f(x) dx \underset{\substack{x_i \text{ sampled} \\ \text{from } \rho(x)}}{=} \frac{1}{N} \sum_i f(x_i) + \mathcal{O}\left(\frac{1}{\sqrt{N}}\right) \quad (1)$$

This is random sampling, as we approximate the expectation of a function $f(x)$ by taking a finite sample x_i of the random variable x following the distribution $\rho(x)$.

However, a real wave function such that which we are going to sample, assumes very small values in large parts of configuration space, so that a straightforward procedure will fail, as sampling randomly and uniformly will in most cases sample an irrelevant configuration. To avoid this issue, we should not sample randomly, but according to a probability distribution that is concentrated in the physically relevant space. This is called *importance sampling*.

In the next section we will introduce the Metropolis Algorithm, which is a Monte Carlo method based on importance sampling.

2.1.1 Metropolis Algorithm

To sample exactly a probability distribution $p(R)$ we can use the so called Markov chain. According to the latter, we have a sequence of states $\{R_i\} = R_1, \dots, R_N$ for which the probability of

transitioning from a state R_i to a state R_{i+1} only depends on R_i and is defined as $T(R \rightarrow R')$. To make sure that we are sampling the correct probability function, we must ensure that the condition

$$p(R)T(R \rightarrow R') = P(R')T(R' \rightarrow R) \quad (2)$$

called *detailed balance* holds.

At the same time, to obtain the right probability distribution $p(R)$ we must make sure that we are choosing the right $T(R' \rightarrow R)$. This is done by the Metropolis algorithm, which is based on the ansatz:

$$T(R \rightarrow R') = \omega_{RR'} \cdot A_{RR'} \quad (3)$$

where, starting from a state R , we generate a candidate R' with a probability $\omega_{RR'}$, while the probability of moving from state R to state R' is $A_{RR'}$. This is the so called "trial move" and for this reason we define the *walkers* as the state moves from one to another. Since one walker might get stuck in a favourable region surrounded by barriers, it is wiser to use more than one to reduce this effect.

If we assume that $\omega_{RR'} = \omega_{R'R}$, the detailed balance in eqn. (3) becomes:

$$\frac{A_{R'R}}{A_{RR'}} = \frac{p(R)}{p(R')} \quad (4)$$

with

$$A_{RR'} = \begin{cases} 1 & \text{if } p(R') > p(R) \\ \frac{p(R)}{p(R')} & \text{if } p(R') < p(R) \end{cases}$$

As we can see here, we are only interested in ratios of probabilities, which means we will not need to worry about normalizing $p(R)$.

It is important to verify detailed balance, which can be used to verify the validity of the code: at each step, one can check if $p(R)A_{RR'} - p(R')A_{R'R} = 0$ (rearrange eqn. (4)). These calculations were done for each of the three cases we will treat below (Harmonic oscillator, Hydrogen atom, Helium atom) and values yielded a maximum of $\sim 0.6 \times 10^{-17}$ which is essentially zero within python's error.

Finally, care must be taken about the choice of the trial move, and in particular of the distance from the original point to the new one (step size). In fact, we can define the acceptance ratio of the trial move as

$$a = \frac{\text{number of accepted moves}}{\text{number of total moves}} \quad (5)$$

If the step size is too big, a becomes very small and thus the Markov chain contains many repeated values and we only sample a few independent points, leading to strong correlation.

If the step size is too small, a gets close to 1 and almost every move gets accepted. Thus we only sample a small part of the probability distribution.

Hence, we need to make sure to choose the step size in such a way that $a \approx 0.5$

2.2 Variational Monte Carlo [3]

As stated in the introduction, the goal is to obtain the ground state energy for the Helium atom. To do so, we can use a variational method for which we consider a trial wave function $\psi_T(R, \alpha)$ where α is the variational parameter and R is a 6 dimensional parameter that indicates the position of the two electrons in the He atom. Before starting, it is worth noting that any energy we compute with this method will be equal or larger than the true one [4]. To find the ground state energy,

we want to minimize the energy $E(\alpha)$ with respect to α . To do so, we can compute the expectation value of the energy as [5]:

$$E(\alpha) = \frac{\int dR \psi_T(R, \alpha) H \psi_T(R, \alpha)}{\int dR |\psi_T(R, \alpha)|^2} \quad (6)$$

But since the integral in eqn. (6) cannot be solved analytically for the Helium atom, we will use the methods described in section 2.1.

The probability density to be sampled in our case will be stationary:

$$\rho(x) = \frac{|\psi_T(R)|^2}{\int dR' |\psi_T(R')|^2}$$

and our $f(x)$ will be the local energy E_L define as:

$$E_L(R, \alpha) = \frac{H \psi_T(R, \alpha)}{\psi_T(R, \alpha)} \quad (7)$$

Then, we will be able to compute the expectation value of the energy as:

$$E(\alpha) = \frac{\int dR |\psi_T(R, \alpha)|^2 E_L(R, \alpha)}{\int dR |\psi_T(R, \alpha)|^2} \quad (8)$$

The integral in eq. (8) can be solved using Monte Carlo integration with importance sampling.

2.3 1D - Harmonic Oscillator

Before we start doing calculations with the Helium atom, we consider the much simpler, one dimensional harmonic oscillator. For this problem we also know the wave function analytically and have an exact value for the energy, namely $1/2$ in Hartree units. We begin with the harmonic oscillator Hamiltonian in dimensionless units [3, 6]:

$$H\psi(x) = \left[-\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} x^2 \right] \psi(x)$$

We know its ground state wave function:

$$\psi(x) = \exp(-x^2/2)$$

We shall use the following form for the trial wave function:

$$\psi_T(x) = \exp(-\alpha x^2) \quad (9)$$

We use this form since it includes the correct wave function when $\alpha = 1/2$. When computing the energy for different values of α , we should expect a minimum in energy at the correct value of α . This minimum should also correspond to the true energy because we will have the correct wave function. After computing the local energy with eqn. (7) we will have all we need to begin our first simulation:

$$E_L = \frac{H\psi_T}{\psi_T} = \alpha + x^2 \left(\frac{1}{2} - 2\alpha^2 \right)$$

We begin by checking that the distribution sampled with the Metropolis algorithm is indeed the desired one (see fig. 1).

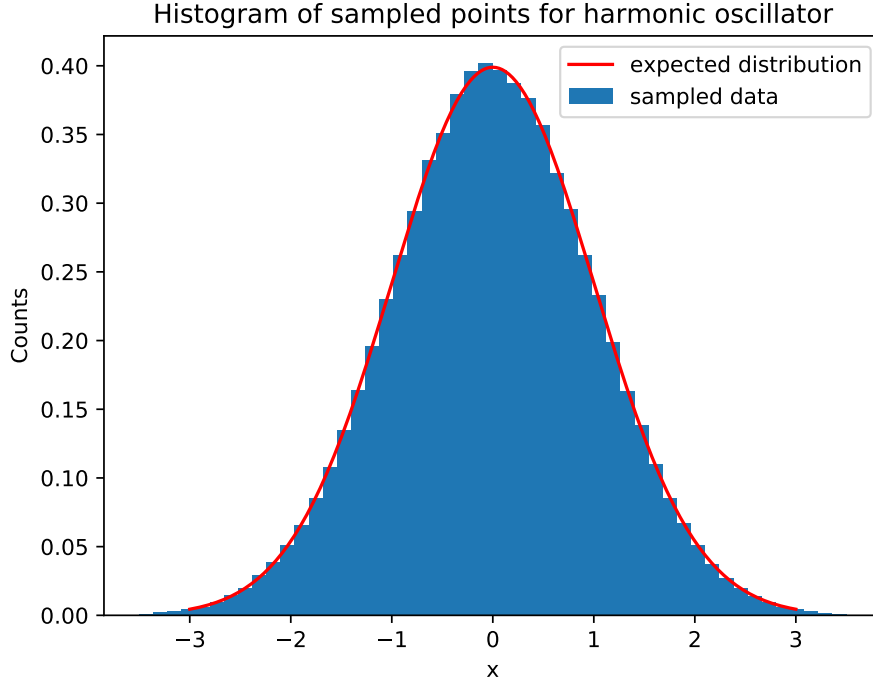


Figure 1: Validating that the sampled distribution for the harmonic oscillator's wave function matches the expected one of $|\psi_T|^2$ from eqn. (9) with $\alpha = 1/2$ (after normalizing).

Given the relative simplicity of the harmonic oscillator, we can even find an analytic expression for the energy and the variance as functions of α :

The analytic expression for the energy is obtained using eqn. (8):

$$E(\alpha) = \frac{1}{2}\alpha + \frac{1}{8\alpha} \quad (10)$$

Variance:

$$\sigma_E^2(\alpha) = \langle E_L^2 \rangle - \langle E_L \rangle^2 = \frac{(1 - 4\alpha^2)^2}{32\alpha^2} \quad (11)$$

Finally, in figure 2, we calculate the energy using eqn. (1) and the sampled points, the variance, and compare them to the analytical values given by eqn. (10) and 11.

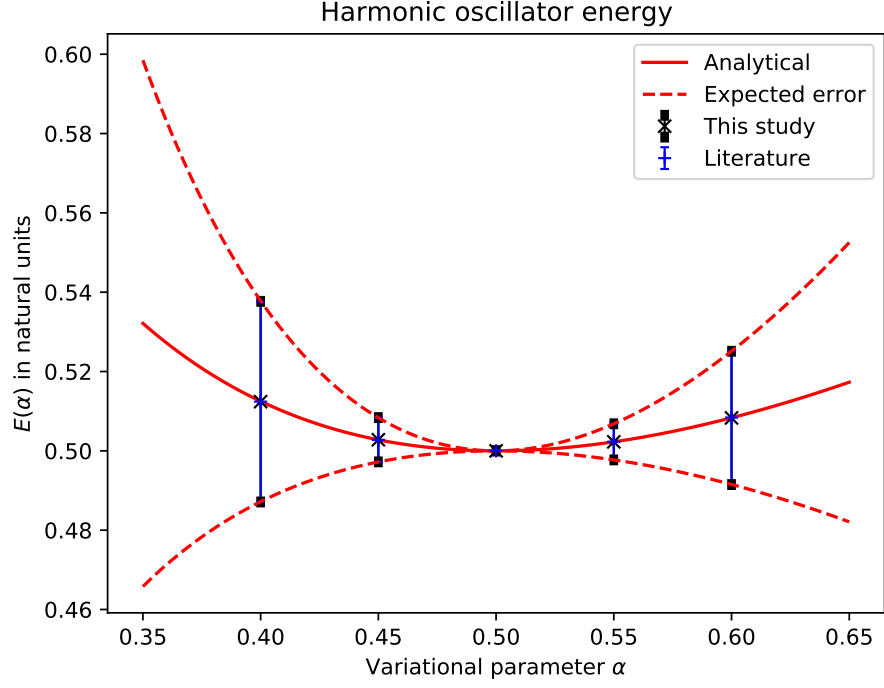


Figure 2: The variance in the sampled energies are taken as the error. The dashed red lines represent the analytical values of the variance as given in eqn. (11). Data from table 1.

We see that our code is capable of reproducing the expected results. We are now in a position to proceed to a higher dimensional problem.

2.4 3D - Hydrogen Atom

As an intermediate step between the harmonic oscillator and the Helium atom, it is sensible to consider the Hydrogen atom, a three dimensional system which also has known analytical solutions. The procedure is exactly the same as for the harmonic oscillator. We begin by writing down the Hamiltonian in dimensionless units [3, 6]:

$$H = -\frac{1}{2}\nabla^2 - 1/r$$

The correct ground state wave function is known:

$$\psi(r) = \exp(-r)$$

But we shall use the following trial wave function:

$$\psi_T(r) = \exp(-\alpha r) \tag{12}$$

Next, we confirm that the code has been properly promoted to 3D problems by checking that the sampled distribution indeed matches the desired one as is shown in figure 3.

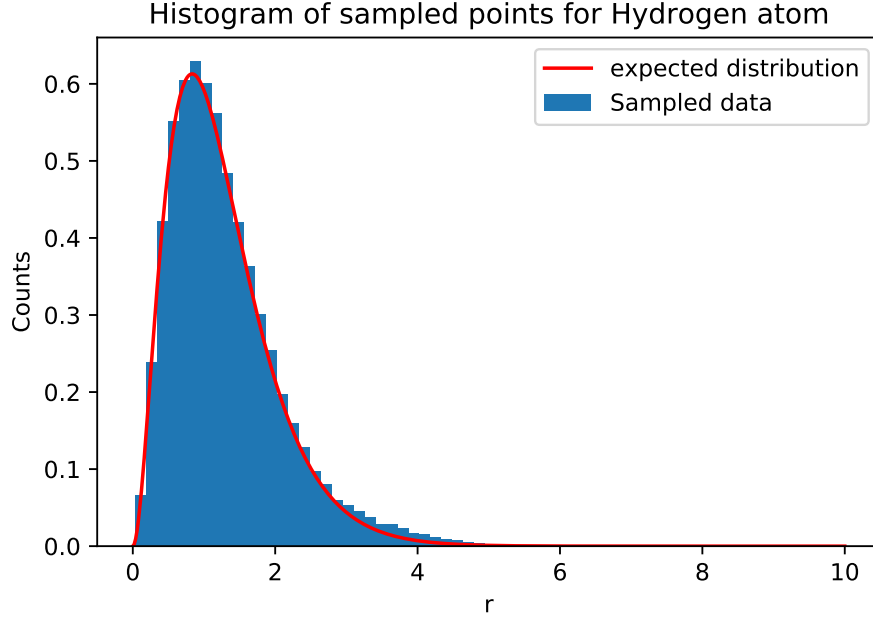


Figure 3: Validating that the sampled distribution for the hydrogen wave function matches the expected one of $4\pi r^2 |\psi_T|^2$ (after normalizing and multiplying by the Jacobian since we are in spherical coordinates).

Local energy:

$$E_L(r) = -\frac{1}{r} - \frac{1}{2}\alpha \left(\alpha - \frac{2}{r} \right) \quad (13)$$

We could describe the problem in spherical coordinates and exploit symmetry, however, we want to exploit the fact that the Metropolis sampling is powerful in high dimensional problems and switch to Cartesian coordinates.

$$r = \sqrt{x^2 + y^2 + z^2}$$

The energy as a function of α is calculated with eqn. (8):

$$E(\alpha) = \frac{1}{2}\alpha^2 - \alpha \quad (14)$$

The variance is calculated as:

$$\sigma_E^2(\alpha) = \langle E_L^2 \rangle - \langle E_L \rangle^2 = \alpha^4 - 2\alpha^3 + \alpha^2 \quad (15)$$

Again, we gather all the information given above in figure 4.

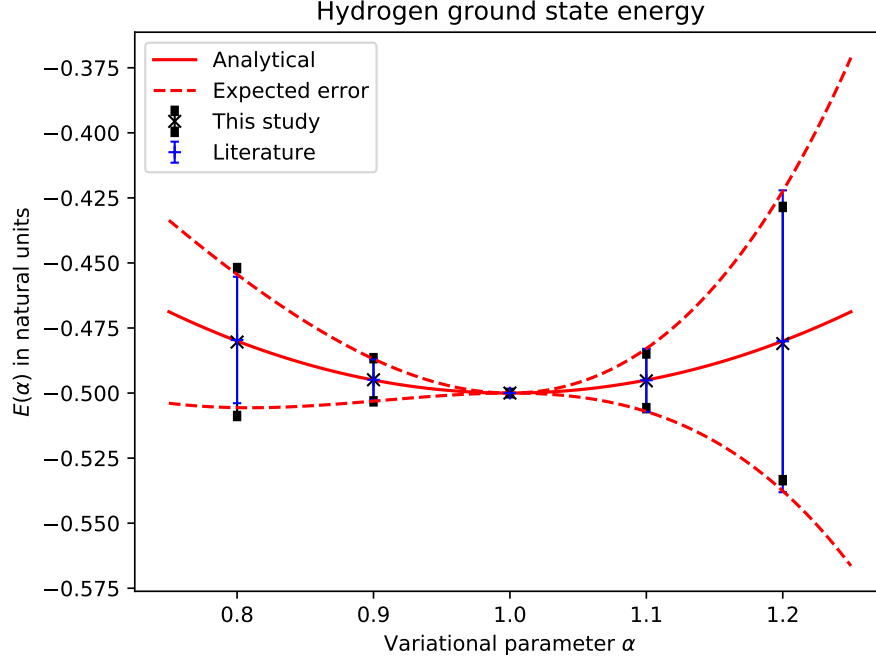


Figure 4: The variance in the sampled energies are taken as the error. The dashed red lines represent the analytical values of the variance as given in eqn. (15). Data from table 2.

2.5 Helium Atom

After validating the code with the Harmonic oscillator and the Hydrogen atom, which have known solutions, we start implementing the code to compute the ground state energy of the Helium atom. First of all, we have the Hamiltonian in dimensionless units [6, 4]:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (16)$$

Then, we have the trial wave function consisting of the product of individual electron wave functions times a correlation term:

$$\psi_T(\mathbf{r}_1, \mathbf{r}_2) = e^{-2r_1} e^{-2r_2} e^{r_{12}/[2(1+\alpha r_{12})]} \quad (17)$$

with $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

Finally, the local energy is:

$$E_L(\mathbf{r}_1, \mathbf{r}_2) = -4 + (\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2) \frac{1}{r_{12}(1 + \alpha r_{12})^2} - \frac{1}{r_{12}(1 + \alpha r_{12})^3} - \frac{1}{4r_{12}(1 + \alpha r_{12})^4} + \frac{1}{r_{12}} \quad (18)$$

Having the trial wave function and the local energy, we promote the code from 3D to 6D in the same way that we did before, to make sure that we are doing it correctly, after which we can compute the expectation value of the energy as well as the variance. The results are presented in table 3 and in section 3.

2.6 Minimization

Minimizing the energy with respect to the variational parameter α gives the following general expression:

$$\frac{dE(\alpha)}{d\alpha} = 2 \left(\left\langle E_L \frac{d \ln \psi_T}{d\alpha} \right\rangle - E \left\langle \frac{d \ln \psi_T}{d\alpha} \right\rangle \right) \quad (19)$$

To find the appropriate α we use the following simple steepest descent method:

$$\alpha_{\text{new}} = \alpha_{\text{old}} - \gamma \left(\frac{dE(\alpha)}{d\alpha} \right)_{\text{old}} \quad (20)$$

with a damping factor chosen such that α changes slowly. To compute eqn. (19) we need to know $d \ln \psi_T / d\alpha$. We shall do this for the Hydrogen (eqn. (21)) and the Helium (eqn. (22)) atoms:

$$\frac{d \ln \psi_T}{d\alpha} = \frac{d}{d\alpha} (-\alpha r) = -r \quad (21)$$

Helium:

$$\begin{aligned} \frac{d \ln \psi_T}{d\alpha} &= \frac{d}{d\alpha} (-2r_1 - 2r_2 + r_{12}/[2(1 + \alpha r_{12})]) \\ &= - \frac{r_{12}^2}{2(1 + r_{12}\alpha)^2} \end{aligned} \quad (22)$$

With the above relations and E_L (eqn. (13) for Hydrogen and eqn. (18) for Helium) one can proceed to minimize the energy. Below, in figure 5, is a plot on a logarithmic scale where α is plotted over the number of iterations of the formula in eqn. (20). The value α is chosen initially at 38. We see that α indeed converges at 1:

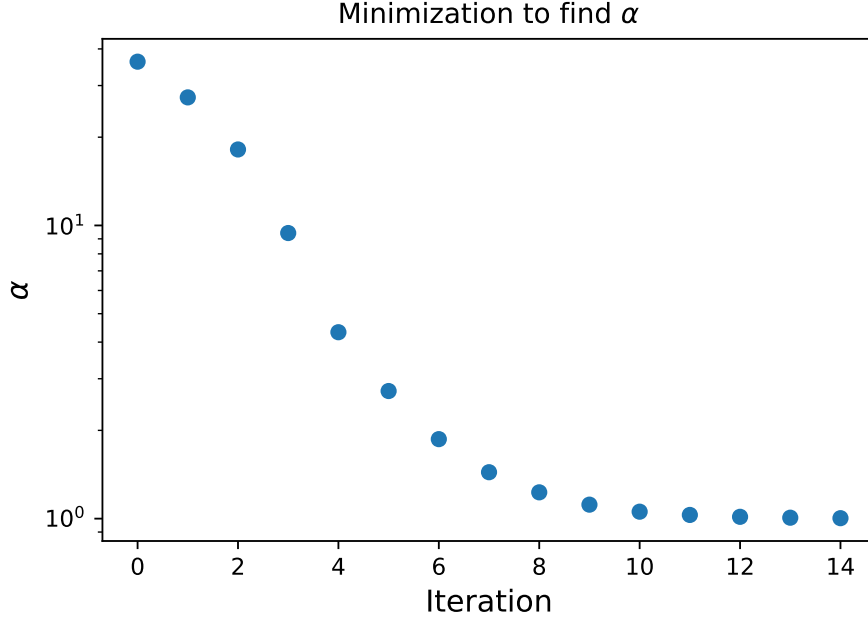


Figure 5: Minimization of the Hydrogen ground state energy by correcting α by means of eqn. (20). 40 walkers, each taking 3000 steps, with 1000 steps left out for equilibration have been used. The iterations are repeated until $\frac{dE}{d\alpha}$ is below 0.001. The damping factor is $\gamma = 0.5$. The run-time was 26 seconds.

2.7 Error with data blocking

The positions found with the mcmc algorithm are correlated and so are the energies, since they depend on the positions. Hence, in order to estimate the error on the energy, we used data blocking. The idea behind data blocking is to group the values of the energy at different steps in bins of increasing size, and find the average energy for each bin. When the bin size becomes bigger than the correlation length we can compute the error as [7]:

$$\sigma_A(b) = \sqrt{\frac{1}{N_b - 1} (\langle a^2 \rangle - \langle a \rangle^2)} \quad (23)$$

with b the size of the bins and N_b the number of bins. Once the size of the bins is large enough, σ_A has an almost constant value, which is the error associated with the energy.

3 Results

Figure 6 shows a comparison with the literature value [3] of the Helium ground state energy as a function of the variational parameter α .

Below, in figure 7, the minimization is presented. The initial value of α was 1 and it began to converge at $\alpha = 0.2115$ after 23 iterations. Next, the energy was computed (with eqn. (6)) for this value of α with 30 walkers taking 30000 steps each (minus 1000 for equilibration). As expected, the error in figure 8 converges. It does so at around 0.0007 hence the final result for the energy is $E(\alpha = 0.2115) = -2.9023 \pm 0.0007$ a.u..

It is also worth mentioning that different numbers of walkers and steps taken have been tested for the minimization. The following observations could be made: by taking 40 walkers with 30000 steps and demanding $dE(\alpha)/d\alpha < 0.001$, the computation took 26 minutes and yielded $\alpha = 0.209769$. Another trial with 40 walkers taking 3000 steps gave $\alpha = 0.2168$ and ran for 140 seconds. All of these had an initial value of $\alpha = 0.8$ and 1000 steps were removed per walker for equilibration. In addition, the time taken for the integral of the energy with 400 walkers each taking 30000 steps for the final value of alpha was about one minute.

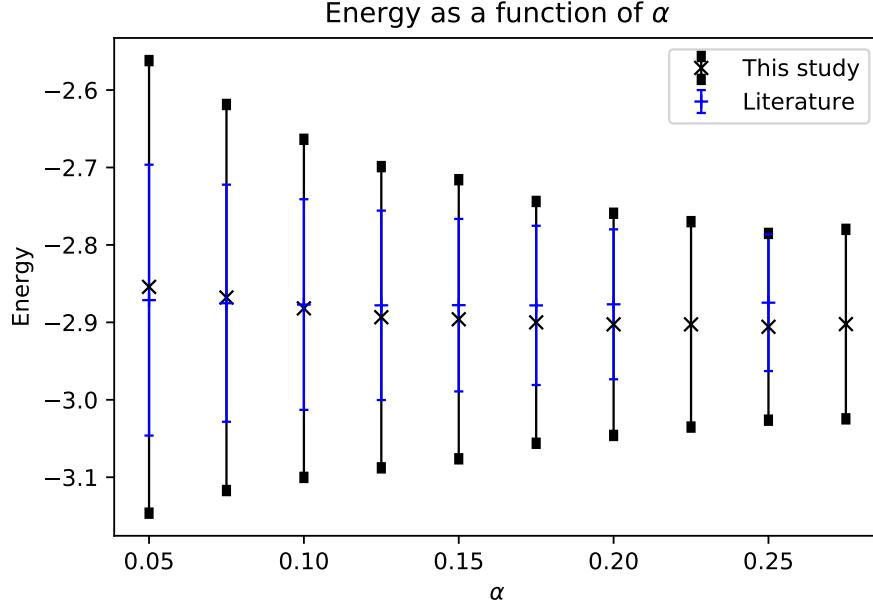


Figure 6: Plot of the energy for the He atom ground state as a function of α compared to [3]. Data from table 3.

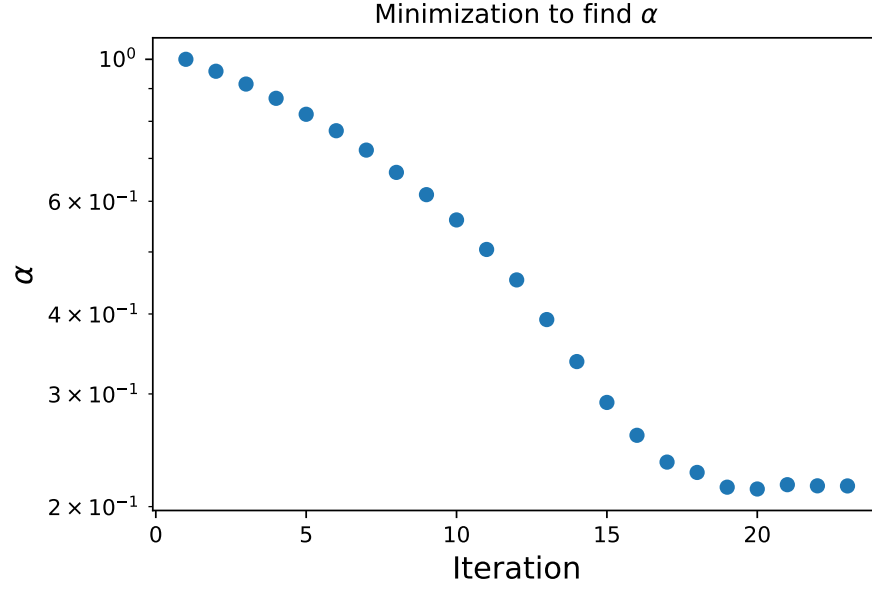


Figure 7: Using eqn. (20) over enough iterations for α to converge. Each time, 30 walkers taking 20000 steps minus 1000 for equilibration are used to compute the energy and its error. The runtime was 20 minutes.

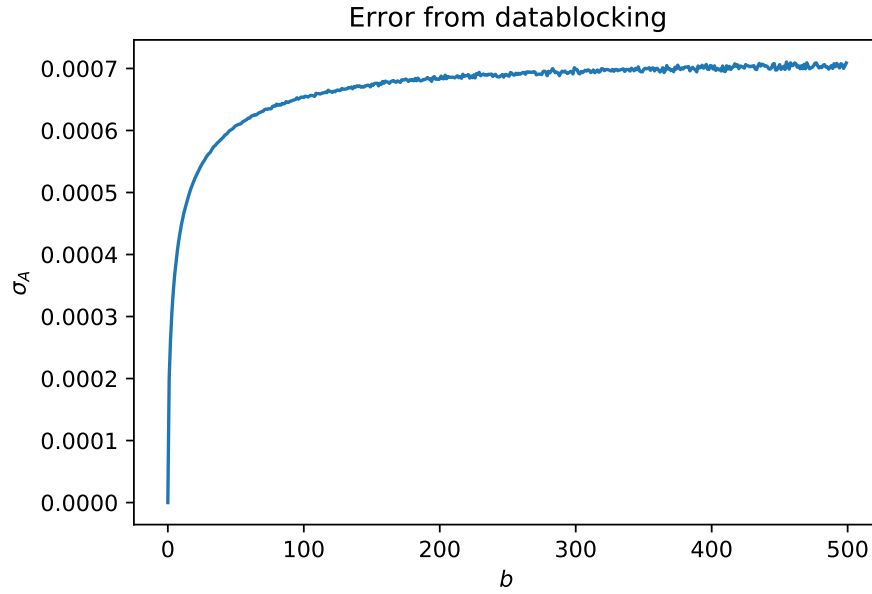


Figure 8: Error in the energy of the He atom ground state computed with data blocking. Computed with eqn. (23).

4 Conclusions

After running our simulation multiple times with different numbers of walkers and different numbers of steps, we are satisfied with the results. Figure 6 shows good agreement with literature, in fact, the value obtained for the ground state energy of $E = -2.9023 \pm 0.0007$ a.u. is extremely close to the one in literature $E = -2.9037243771$ a.u.. Our value is slightly above the true one, as it should be since we used a variational method (see section 2.2). Also, the energy being close to the true one, means that the trial wave function is really well chosen and resembles the true Helium wave function almost perfectly.

Regarding minimization, we could only get the value of $\frac{dE}{d\alpha}$ down to approximately 0.001, but this still gives accurate results.

The error of ± 0.0007 a.u. found with data blocking is indeed quite small, but this is possible since the values obtained for the energy are extremely close to the literature ones.

Finally, to take a look at performance, we were able to run simulations with 40 walkers and 30000 steps for each. This kind of simulation took 20-30 minutes to run, giving accurate results. The most time consuming task was the minimization of the energy, while computing the integral itself took just about 60 seconds. At the same time, a simulation with 40 walkers and 3000 steps for each, took only about 2 minutes to run completely and still had a very similar output to the previous one. In conclusion, we were able to run the simulations needed and even more.

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A Data in tabular form

Table 1: Results for the harmonic oscillator’s ground state energy from this study compared to those from [3]. This study used one walker with 15 million displacements while the literature value was obtained for 400 walkers with 30 000 displacements.

Harmonic Oscillator	This study		Literature	
α	$\langle E \rangle$	$\text{var}(\langle E \rangle)$	$\langle E \rangle$	$\text{var}(\langle E \rangle)$
0.40	0.5124	0.02529	0.5124(1)	0.02521(5)
0.45	0.50280	0.00558	0.50276(4)	0.00556(2)
1/2	1/2	0	1/2	0
0.55	0.50227	0.00455	0.50232(6)	0.00454(1)(1)
0.60	0.5083	0.0168	0.5084(1)	0.0168(4)

Table 2: Results for the Hydrogen atom’s ground state energy from this study compared to those from [3]. This study used 400 walkers with 30 000 displacements each, out of which 4000 are omitted for equilibrium to be reached, just like the literature did.

Hydrogen atom	This study		Literature	
α	$\langle E \rangle$	$\text{var}(\langle E \rangle)$	$\langle E \rangle$	$\text{var}(\langle E \rangle)$
0.8	-0.4804	0.0284	-0.4796(2)	0.0243(6)
0.9	-0.49489	0.0083	-0.4949(1)	0.0078(2)
1	-1/2	0	-1/2	0
1.1	-0.495293	0.01051	-0.4951(2)	0.0121(4)
1.2	-0.4810	0.05250	-0.4801(3)	0.058(2)

Table 3: Results for the Helium atom’s ground state energy from this study compared to those from [3]. This study used 40 walkers with 30 000 displacements each, out of which 4000 are omitted for equilibrium to be reached, just like the literature did. Acceptance ratio: 0.5039

Helium atom	This study		Literature	
α	$\langle E \rangle$	$\text{var}(\langle E \rangle)$	$\langle E \rangle$	$\text{var}(\langle E \rangle)$
0.05	-2.87121	0.25489	-2.8713(4)	0.1749(2)
0.075	-2.88064	0.21708	-2.8753(4)	0.1531(2)
0.10	-2.88924	0.19348	-2.8770(3)	0.1360(2)
0.125	-2.89676	0.17349	-2.8780(4)	0.1223(2)
0.15	-2.90050	0.15663	-2.8778(3)	0.1114(2)
0.175	-2.90165	0.14246	-2.8781(3)	0.1028(2)
0.20	-2.90354	0.13189	-2.8767(4)	0.0968(2)
0.25	-2.90236	0.11452	-2.8746(10)	0.0883(2)