Delft University of Technology

COMPUTATIONAL PHYSICS
AP3082

Variational Monte Carlo Simulations

Project 2

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Abstract

This project is focused on obtaining a numerical solution of the ground state energy of the simple harmonic oscillator, the hydrogen atom and the helium atom, using the variational Monte Carlo method. In the simulation the metropolis algorithm is used to obtain different distributions according to certain trial wave functions. A minimization algorithm which makes use of the simple damped steepest decent method is used to determine for which parameter of the trial wave function the energy is minimal. The simulation was successful in assessing the ground state energy of the simple harmonic oscillator and the hydrogen atom. For the helium atom a total of 19 steps were needed to find the energy $E = -2.8798 \pm 0.0003$ a.u. at an optimal variational parameter of $\alpha = 0.1433$. The obtained value for the ground state energy is not in agreement with the literature value of $E = -2.9037$ a.u. This is due to the fact that the trial wave function used in the variatonal Monte Carlo simulation is an approximation of the exact wave function for the helium ground state.

Keywords: *Computational Physics, Metropolis algorithm, Harmonic oscillator, Helium, Hydrogen*

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Contents

1 Introduction

In the field of quantum mechanics, only a select few problems have an analytical solution. Two of these few systems are the harmonic oscillator and the hydrogen atom, for which the solutions of the Schrödinger equation are well known. However, for most cases, only an approximation can be obtained by various methods and algorithms. The goal of this project is using such an algorithm, the variational Monte Carlo method, to find the ground state of the helium atom. The variational Monte Carlo method uses the Metropolis algorithm to find a set of samples according to a distribution function, depending on a trial wave function. Eventually, the ground state energy can be minimized by varying the parameter α for a certain trial wave function. In the first section of this paper the relevant theoretical background is presented. The variational Monte Carlo method is outlined and Monte Carlo integration is introduced. Then the quantum systems that have been simulated are discussed. In the computational method section the main numerical algorithms are explained; the Metropolis algorithm, bootstrapping and the minimization algorithm. The numerical results of our simulation and the performance results of the code are given in section 4. Section 5 includes a discussion and conclusion.

2 Theoretical background

In this section the theoretical background of the three quantum systems (the harmonic oscillator, the hydrogen atom and the helium atom), that have been simulated is introduced. First, in section 2.1 a brief outline of the Variational Monte Carlo method is given. In section 2.2 2.2 and 2.3 it is explained how the Monte Carlo with importance sampling is used. In sections 2.5, 2.6 and 2.7 the quantum systems for which the ground state energies are calculated are introduced.

2.1 Variational method for the Schrödinger equation

A variational method can be used to solve the Schrödinger equation of a many-body interacting system. The method consists of three main steps.

1. Construct a trial wave function $\Psi_T(\vec{r}, \alpha_1, ..., \alpha_n)$ where $\vec{r}$ is the variable containing the spatial coordinates of all interacting particles and α_* are the variational parameters of the wave equation of the system.
2. Calculate the expected energy of the trial wave function using the following relationship.

$$\langle E \rangle = \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \tag{1}$$

3. Vary the parameters α according to a minimization algorithm and return to step 1

The reason that calculating the ground state energy of quantum systems belongs to the field of Computational Physics is that for most quantum systems Eq. 1 can not be calculated analytically. How Monte Carlo integration with importance sampling can be used to calculate this integral is explained in the next two sections.

2.2 Monte Carlo method

The Monte Carlo method is a computational method for evaluating integals by computing a sum. The most straightforward technique "crude Monte Carlo" is to compute the sum over uniformly distributed random numbers between a and b:

$$I_{(\text{crude})} = \int_a^b f(x)\mathrm{d}x \approx \frac{(b-a)}{N} \sum_{i=1}^{N} f\left(x_i\right) \tag{2}$$

If the x_i's are uniformly distributed, the variance in f is given by:

$$\sigma^2_{(\text{crude})} = \frac{(b-a)}{N} \sum_{i=1}^{N} f^2\left(x_i\right) - \left[\frac{(b-a)}{N} \sum_{i=1}^{N} f\left(x_i\right)\right]^2 \tag{3}$$

Thus the error in the integration is given by:

$$\sigma_{\text{n(crude)}} = \sqrt{\frac{\sigma^2{}_{(\text{crude }})}{N}} = \frac{\sigma_{\text{ (crude)}}}{\sqrt{N}} \tag{4}$$

This results in the accuracy of crude Monte Carlo method being inversely proportional to the square root of the number of trials. Thus only two possible ways are available to reduce the error of this method. The first method is increasing the number of trials, which is not an effective way of reducing the error as it is computational very heavy and increases quadratically in time for reducing the error. The second method is decreasing the variation of the Monte Carlo method by importance sampling, which will be explained in the next section.

2.3 Importance sampling

Importance sampling is a method for improving the crude Monte Carlo method. This can be done by improving the crude Monte Carlo method, which samples the function homogeneously (uniform distribution). This method can be improved upon by sampling the parts of the integral with the highest significance. In this improved method, samples are chosen from a distribution resembling the function to be analysed. let such a function be defined as the function $g(x)$, a PDF on the interval $[a, b]$, which has a high resemblance to the desired function $f(x)$ to be assessed by the Monte Carlo method.

$$\frac{f(x)}{g(x)} \approx \text{constant} \tag{5}$$

With the following properties:

$$\int_a^b g(x)\mathrm{d}x = 1 \quad \text{and} \quad g(x) > 0, \quad \forall x \in [a, b] \tag{6}$$

This results in the original integral being transformed to:

$$\int_a^b f(x)\mathrm{d}x \rightarrow \int_a^b \left[\frac{f(x)}{g(x)}\right] g(x)\mathrm{d}x \tag{7}$$

After which the integral can be evaluated by using the new distribution function $g(x)$ and evaluating $\left[\frac{f(x)}{g(x)}\right]$ at these points. This leads to the following relationship:

$$\left\langle \frac{f(x)}{g(x)} \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \frac{f\left(x_i\right)}{g\left(x_i\right)} \tag{8}$$

This greatly reduces the error of the Monte Carlo simulation, if applied correctly with an appropriate distribution $g(x)$. A more intuitive explanation is provided in the figure below:

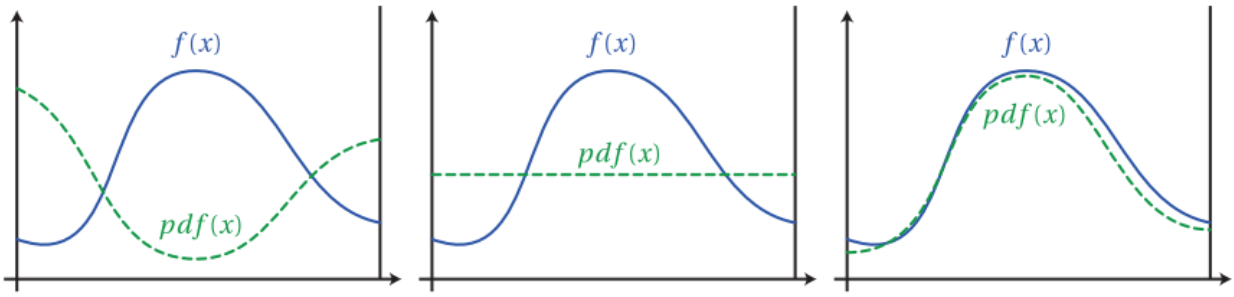


Figure 1: "A comparison of three probability sensity functions, The PDF on the right provides variance reduction over the uniform PDF in the center. However, using the PDF on the left would significantly increase the variance over simple uniform distribution" [1]

2.4 Local Energy

To use the Monte Carlo method with importance sampling we rewrite Eq. 1 as follows:

$$E = \int \rho(\vec{r}) E_{loc}(\vec{r})\mathrm{d}\vec{r} \tag{9}$$

Where E_{loc} denotes the local energy defined as:

$$E_{loc} = \frac{H\Psi(r, \alpha)}{\Psi(r, \alpha)} \tag{10}$$

and where the distribution $\rho(\vec{r})$ is given by:

$$\rho(\vec{r}) = \frac{|\psi_{\mathrm{T}}(R)|^2}{\int \mathrm{d}R' |\psi_{\mathrm{T}}\left(R'\right)|^2} \tag{11}$$

Therefore to use the Variational Monte Carlo method, a trial wave function and a expression for the local energy of a quantum system is needed. In the next three sections, these two formulas are given for the quantum systems researched.

2.5 Harmonic oscillator

One of the few systems with an analytically solution is the harmonic oscillator in one dimension with no external perturbation. The dimensionless Hamiltonian of this system is:[2]

$$H = -\frac{d^2}{dx^2} + \frac{1}{2}x^2 \tag{12}$$

For this system, the trial wave function $\Psi_T = e^{-\alpha x^2}$ was chosen as an initial educated guess for assessing the ground state of the system. As the exact solution for the system is known and is in the subset of $\Psi_T = e^{-\alpha x^2}$. This will result in the algorithm being able to find the exact solution of the system. The dimensionless local energy of the trial wave function is:

$$E_{loc} = \alpha + x^2\left(\frac{1}{2} - 2\alpha^2\right) \tag{13}$$

2.6 Hydrogen atom

The hydrogen atom is one of the few systems for which the Schrödinger equation has an exact solution. The hydrogen atom contains a nucleus and an electron, therefore the system can be described using six dimensions. Although the system can be simplified to a three-dimensional problem using the notation of the center of mass of the system. After which the problem is simplified even more by choosing $\hbar$, the mass of the electron and the magnitude of the electron charge e to all be one, which makes the Hamiltonian is made dimensionless. The dimensionless Hamiltonian corresponding to this system is:[2]

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r} \tag{14}$$

.

Where r is the length of the difference between the coordinates of the electron $\vec{r}_e$ and the nucleus $\vec{r}_p$, $r = |\vec{r}_e - \vec{r}_p|$. The Hamiltonian of this problem can be reduced to an one dimensional problem with the Hamiltonian operator:

$$H = -\frac{1}{2}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right] - \frac{1}{r} \tag{15}$$

Which has the know ground state wave function $\Psi = e^{-r}$ with a corresponding ground state energy of $E_0 = -0.5$. The trial wave function used for this system is $\Psi_T(r, \alpha) = e^{-\alpha r}$, which gives the following relationship for the dimensionless local energy:

$$E_{loc}(r, \alpha) = -\frac{1}{r} - \frac{1}{2}\alpha\left(\alpha - \frac{2}{r}\right) \tag{16}$$

2.7 Helium atom

A more complex system for which the variational Monte Carlo method is an effective method of solving the ground state is the helium atom. The helium atom consists of two protons accompanied with 2 neutrons and two electrons with mass m_e and electric charge e. The nucleus in this system can be assumed to be at rest, resulting in 2 relative electron coordinates $\vec{r}_1$ and $\vec{r}_2$. In this problem, the Hamiltonian is made dimensionless by setting all units to one($\hbar = m_e = e = 1$). This gives the following relationship for the Hamiltonian:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \tag{17}$$

In this formula, $r_{12} = |\mathbf{r}_{12}| = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the 2 electrons, $r_1 = |\mathbf{r}_1|$ and $r_2 = |\mathbf{r}_2|$ are respectively the length of the vector coordinate of electron 1 and 2. The following trial wave function was used in the variational Monte Carlo method for solving the ground state:[2]

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-2r_1}e^{-2r_2}e^{\frac{r_{12}}{2(l+\alpha r_{12})}} \tag{18}$$

Where the same definitions for r_{12}, r_1 and r_2 are used as above. The local energy of the trial wave function is calculated with the following relationship:

$$\begin{aligned} E_{\mathrm{L}}(\mathbf{r}_1, \mathbf{r}_2) = -4 + (\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2)\cdot(\mathbf{r}_1 - \mathbf{r}_2)\frac{1}{r_{12}(1+\alpha r_{12})^2} \\ -\frac{1}{r_{12}(1+\alpha r_{12})^3} - \frac{1}{4(1+\alpha r_{12})^4} + \frac{1}{r_{12}} \end{aligned} \tag{19}$$

Where $\hat{\mathbf{r}}$ is a unit vector of $\mathbf{r}$ and r_{12} corresponds to the distance between the two electrons.

3 Computational method

In sections 3.1 and 3.3 the two main numerical algorithms used are explained on how to perform the Metropolis algorithm and how to find the correct α corresponding with the ground state. In section 3.2 the bootstrap method is explained.

3.1 Metropolis algorithm

Still one of the biggest problems of importance sampling is using an appropriate density function $g(x)$, as this is most of the time easy to obtain in a one dimensional problem, but gets very complicated if not nearly impossible for higher dimensional problems, which are used in the Variational Monte Carlo method of Quantum systems, and the density function should be invertible, which sometimes can be very hard to obtain analytically. One such method to obtain this density function is the Metropolis algorithm, which is listed as one of the top 10 algorithms of the 20th century.[3] The way the Metropolis algorithm operates is by generating a set of points:

$$x_i, \ i \in \mathbb{N} \tag{20}$$

After which the following steps are executed to let the set of points randomly walk all over the function space:

- Choose a fixed maximum of the step-size h.
- Generate a new trial point x_{trial} in the interval $[x_i - h/2, x_i + h/2]$
- calculate the acceptance ratio defined as: $\alpha = f\left(x_{trial}\right)/f\left(x_i\right) \sim p\left(x_{trial}\right)/p\left(x_i\right)$
- Accept or reject the new trial point by picking a number from an uniform distribution u on $[0, 1]$
- if $u \leq \alpha$ then accept the new point and $x_i = x_{trial}$, else reject it and $x_i = x_i$

Intuitively this will converge to the desired density function, if this is done for a large number of points and for an large number of steps. But one of the difficulties is to pick a step-size h, which is not too small nor too large. As for a step-size too large, the system will be very crude and most point might randomly walk far away from the desired region of the function. Take one too small and there is an incredible large numbers of steps needed for the random walkers to walk a significant distance. This is why for most Metropolis algorithms the following rule of thumb is applied:[4][5]

$$\text{Acceptance ratio } = \frac{\text{No. of steps accepted}}{\text{Total number of trial steps}} \sim 0.5 \tag{21}$$

3.2 Bootstrapping

Bootstrapping is a resampling method that is used to calculate the expectation value of correlated data and the error in the expectation value. We modify the bootstrapping algorithm to calculate the error of the average energy, the variance, and the error in the variance. The first step is to take N random data points from the data generated. Of these N data points the variance is calculated. This procedure is repeated n times, giving n variances. Of these n variances, the average and standard deviation is calculated. The error of the energy is calculated by taking n times the mean of the N data points and then taking the standard deviation of the n averages.

3.3 Minimization algorithm

The final step for finding a solution of the system is minimizing the energy of the system. This can be done using a finite difference calculation of the gradient, but these are bound to fail: the derivatives of stochastic variables are subject to large numerical errors. Thus an analytically derivative is obtained from the trial wave function with respect to α, which gives the following derivative:

$$\frac{\mathrm{d}E}{\mathrm{d}\alpha} = 2\left(\left\langle E_{\mathrm{L}}\frac{\mathrm{d}\ln\psi_{\mathrm{T}}}{\mathrm{d}\alpha}\right\rangle - E\left\langle\frac{\mathrm{d}\ln\psi_{\mathrm{T}}}{\mathrm{d}\alpha}\right\rangle\right) \tag{22}$$

After which an iteration process can be used to find the minimum of the system, using this exact derivative in combination with a " simple damped steepest decent method":

$$\alpha_{\mathrm{new}} = \alpha_{\mathrm{old}} - \gamma\left(\frac{\mathrm{d}E}{\mathrm{d}\alpha}\right)_{\mathrm{old}} \tag{23}$$

In which the γ is a small constant which will be predefined in the algorithm. In this project the γ was chosen to be 0.5 and the process will keep repeating itself until the the tolerance is met or the maximum number of iteration is crossed. In the appendix a flow chart is given which illustrates how the code works. In this figure one can observe which files contribute to which part of the code for the minimization algorithm.

4 Results

This section will discuss the numerical obtained data for the harmonic oscillator, hydrogen atom and the helium atom. This data will be compared to the data from the paper of Jos Thijssen [2], as a guideline of validity. All the results were obtained by using the VMC with 30.000 steps and 400 random walkers.

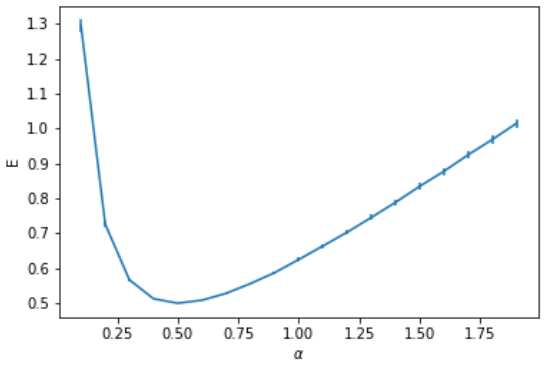
4.1 Harmonic oscillator

The energy of the ground state of the harmonic oscillator is well known and has a exact solution, which is used to validate if the Metropolis algorithm is implemented correctly. This is done by comparing the data from the simulation with the literature values obtained from the paper produced by Jos Thijssen.[2] The results of this comparison are given in the table below:

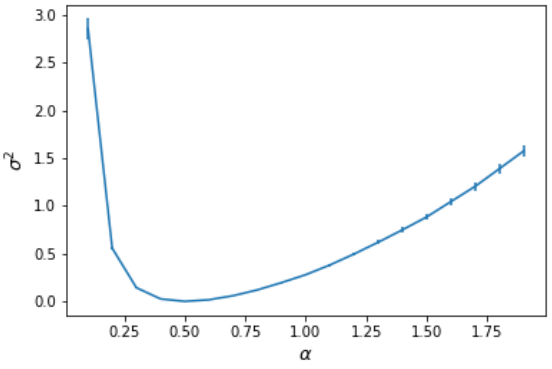
Table 1: Data from the simulation of the harmonic oscillator and compared to the paper of Jos Thijssen.[2] This is done by comparing the energy and the variance of the energy for given α. α and and the ground state energy E are all given in dimensionless units. The analytical values for the energies and variance are also given (E_v and $var(E)_v$). The algorithm was executed with 30.000 steps and 400 walkers.

α	$\langle E \rangle$	var($\langle E \rangle$)	$\langle E \rangle_{lit}$	var($\langle E \rangle)_{lit}$	E_v	$var(E)_v$
0.40	0.512(2)	0.0247(9)	0.5124(1)	0.02521(5)	0.5125	0.02531
0.45	0.5026(7)	0.0056(2)	0.50276(4)	0.00556(2)	0.50278	0.00557
0.50	0.5(0)	0	0.5	0	0.5	0
0.55	0.5022(7)	0.0046(2)	0.50232(6)	0.00454(1)	0.5022727	0.0045558
0.60	0.508(1)	0.0170(6)	0.5084(1)	0.0168(4)	0.508333	0.0167056

The results obtained from the simulation are nearly identical to the literature values from Jos Thijssen [2] as can be seen in table 1. This suggests that the Metropolis algorithm was implemented correctly. This was done by choosing the trial wave function correctly. The trial wave function was chosen to be an Guassian integral, Which was already known to be the correct solution to the Harmonic oscillator. The solution for which the variance of the wave function went to zero was at $\alpha = 0.5$, with a corresponding energy of $E = 0.5$. The results of the variational Monte Carlo simulation can be seen in the figures below.



(a) This figure shows the ground state energy E for different α with an error bar. It can be observed that the energy is minimized for $\alpha = 0.5$, which is in agreement with the exact ground state wave function of the harmonic oscillator.



(b) This figure shows the variance for the given trial wave function for varying α. The variance is minimal for $\alpha = 0.5$, which also agrees with the minimum α found for the ground state energy.

Figure 2: The results for the harmonic oscillator obtained from the simulation. vmc_oscillator.py

The results seem plausible as the minimum are close to $\alpha = 0.5$. A minimization algorithm was used to check if the minimization was indeed in line with the exact solution of the system. As can be seen in figure 3. In the minimization algorithm, an initial alpha is chosen at $\alpha = 1.2$ and a value for $\gamma = 0.5$. The minimization algorithm is converting to a single solution of α as the algorithm gives a minimum of $\alpha = 0.5$ after 8 steps.

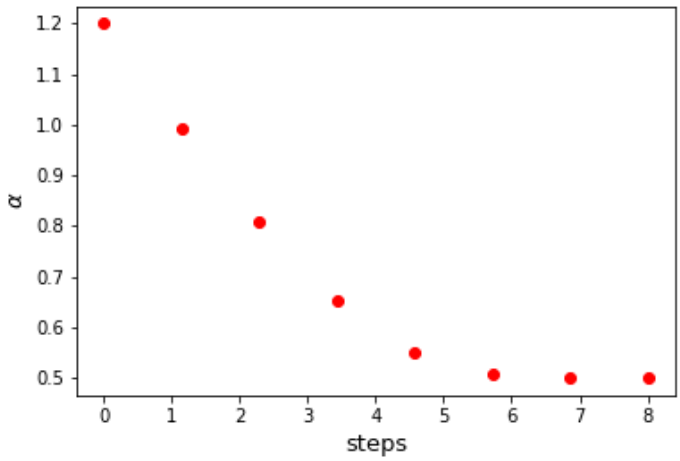


Figure 3: The minimization algorithm at work, using a simple damped steepest decent method. This graph shows the number of iterations needed to find the minimum of the trial wave function. A total of 8 steps were needed to find a solution to the system at $\alpha = 0.5$, which is precisely the exact solution. minimal_energy_oscillator.py

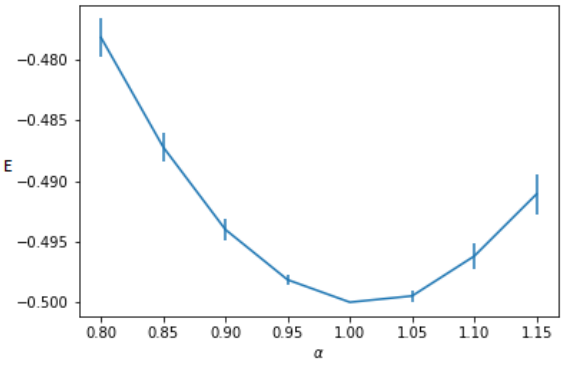
4.2 Hydrogen atom

The energy of the ground state of the hydrogen atom is one of the few quantum systems with an exact solution and thus a correct trial wave function was used to approach the solution of the hydrogen atom. The data obtained from the simulation are compared to the results in the paper produced by Jos Thijssen.[2] The results of this comparison are in the table below:

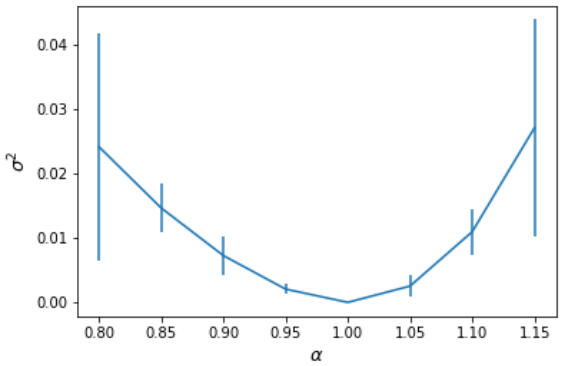
Table 2: This table contains the data from the simulation of the Hydrogen atom and compares it to the paper of Jos Thijssen.[2] This is done by comparing the ground state energy E and the variance of the energy for given α. α and E are all given in dimensionless units.The algorithm was executed with 30.000 steps and 400 walkers.

α	$\langle E \rangle$	var($\langle E \rangle$)	$\langle E \rangle_{lit}$	var($\langle E \rangle_{lit}$
0.8	-0.479(1)	0.023(9)	-0.4796(2)	0.0243(6)
0.9	-0.4937(6)	0.007(2)	-0.4949(1)	0.0078(2)
1.0	-0.5	0	-0.5	0
1.1	-0.4962(7)	0.011(2)	-0.4951(2)	0.0121(4)
1.2	-0.480(8)	0.05(1)	-0.4801(3)	0.058(2)

The results and the literature values of the Jos paper do agree and are of the same order. This suggests that the Metropolis alogrith was implemented correctly, which makes sense as the exact solution is an exponential and the algorithm tried to find a trial wave function of the same form. The exact solution matched for $\alpha = 1$, which corresponds with an energy of $E = -0.5$, both for the literature values as well as for the simulation. This was to be expected. The results of the trial wave function can be seen below:



(a) This figure shows the ground state energy E for each α with an error bar. It can be observed that the energy is minimized for $\alpha = 1$, which agrees with the alpha needed for the correct trial wave function.



(b) This figure shows the variance for the given trial wave function for varying α. The variance is minimized for $\alpha = 1$, and has a value of $\sigma^2 = 0$ at the minimum.

Figure 4: The results for the trial wave function of the Hydrogen atom obtained from the algorithm. *vmc_hydrogen.py*

In the following figure different steps from the minimization algorithm described in section 3.4 are shown. As can be seen, the minimization algorithm is converging to a value of $\alpha = 1$. Also in this simulation, an initial alpha is chosen at $\alpha = 1.2$ and a value for $\gamma = 0.5$.

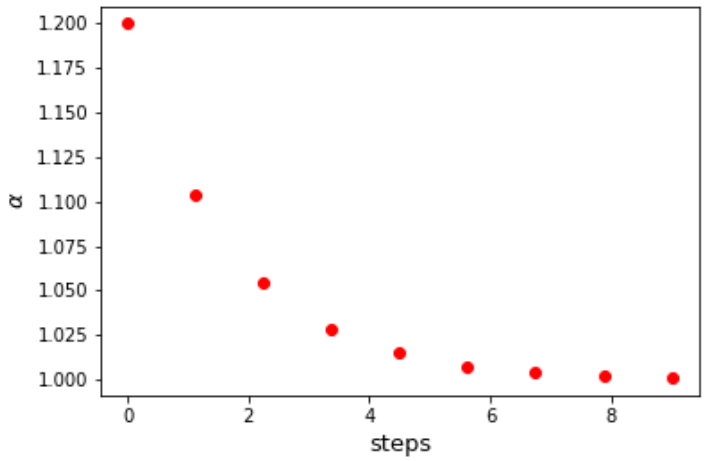


Figure 5: The minimization algorithm at work, using a simple damped steepest decent method. This graph shows the number of iterations needed to find the minimum ground state energy for the hydrogen atom. A total of 9 steps were needed to find the ground state energy $E = -0.5$ at an alpha of $\alpha = 1.001$. *minimal_energy_hydrogen.py*

4.3 Helium atom

The last goal of the project was evaluating the ground state of the helium atom, which has no exact solution, but was determined experimentally at an value of 2.9037 *a.u.* [2]. The results of the project will be compared with the values provided in the paper of Jos Thijssen.[2]:

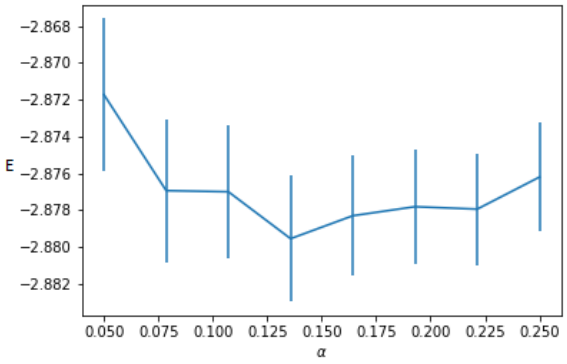
At last the helium atom was evaluated. There is no exact solution for the helium atom, but the ground state energy is experimentally determined and was valued at 2.9037 a.u. [Thijssen, 2007]. Again the results of the simulation can be compared with literature [Thijssen, 2007]. Which is done in table 3.

In the next figures the ground state energy and variance calculated with the variational Monte Carlo simulation is plotted against the variational parameter α.

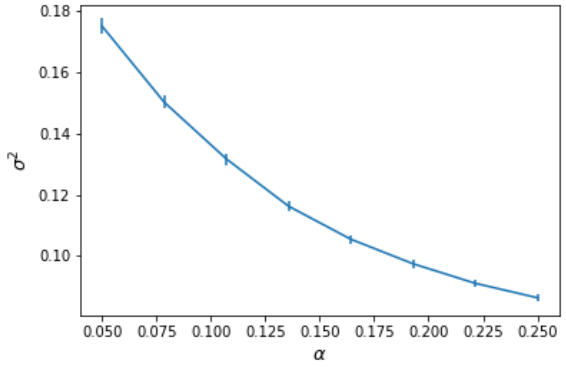
Table 3: This table contains the data from the simulation of the helium atom and compares it to the paper of Jos Thijssen.[2] This is done by comparing the energy and the variance of the energy for given α. α and E are all given in dimensionless units. The algorithm was executed with 30.000 steps and 400 walkers.

α	$\langle E \rangle$	var($\langle E \rangle$)	$\langle E \rangle_{lit}$	var($\langle E \rangle)_{lit}$
0.05	-2.872(4)	0.176(2)	-2.8713(4)	0.1749(2)
0.075	-2.875(4)	0.150(2)	-2.8753(4)	0.1531(2)
0.10	-2.878(4)	0.131(2)	-2.8770(3)	0.1360(2)
0.125	-2.880(3)	0.117(2)	-2.8780(4)	0.1223(2)
0.15	-2.880(3)	0.105(1)	-2.8778(3)	0.1114(2)
0.175	-2.879(3)	0.097(1)	-2.8781(3)	0.1028(2)
0.20	-2.878(3)	0.091(1)	-2.8767(4)	0.0968(2)
0.25	-2.877(3)	0.086(1)	-2.8746(10)	0.0883(2)

From the data given in table 3, one can see that the values obtained with the simulation are in agreement with the data found in the papers of Jos Thijssen.



(a) This figure shows the ground state energy E for each α with an error bar. It can be observed that the energy has multiple local minimum for different values of α.



(b) This figure shows the variance for the given trial wave function for different values of α. The variance is decreasing for an increasing $\alpha = 1$.

Figure 6: The results for the trial wave function of the helium atom obtained from the simulation.These figures can be obtained by executing file *vmc_helium.py*

It is hard to obtain an numerical solution for the ground state for the helium atom according to the graphs as the variance of the energy is quite large compared to the change in the local energy. This means that there might be a lot of local minimums which due to the high uncertainty are impossible to obtain. A better result can be obtained by improving the trial wave function.

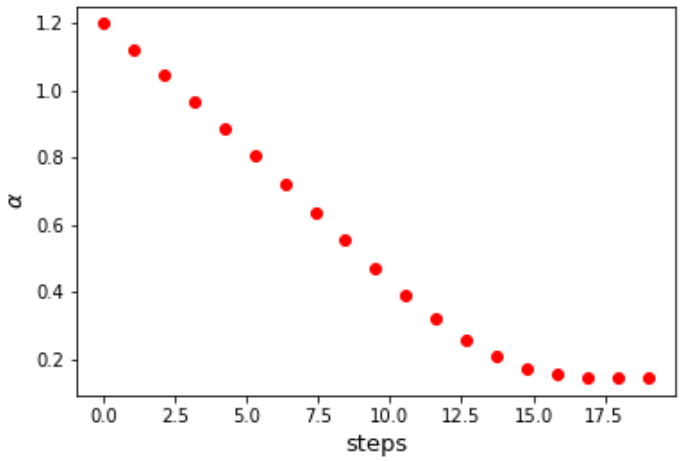


Figure 7: The minimization algorithm at work, using a simple damped steepest decent method. This graph shows the number of iterations needed to find the minimum ground state energy for the helium atom. A total of 19 steps were needed to find the ground state energy $E = -2.8798$ at an alpha of $\alpha = 0.1433$. for the trial wave function of the helium atom obtained from the simulation. minimal_energy_helium.py

The minimazation algorithm shows that the ground state of the system is converging to an $\alpha = 0.1433$, which corresponds with an energy of $E = -2.8798$.

4.4 Performance

The algorithm was optimized and tested for the simple harmonic oscillator and was tested on a **Asus laptop, with an "intel core I7-6500 CPU at 2.5 Ghz** , the run-time is shown below:

Table 4: In this table the run-time was measured of the Monte Carlo algorithm for the hydrogen atom. m is the number of steps and n is the number of walkers used in the Metropolis algorithm.

m/n	**40**	**200**	**400**
10000	30,38	49,71	54,8
20000	41,75	50,27	59,74
30000	46,34	64,26	77,078

The run-time of the code seems to increase for increasing walkers and increasing number of steps, as is expected as this would results in more calculations to be performed to finish the algorithm. Matlab was used to obtain a linear relationship for time with a dependency on the number of walkers and the number of steps, according to the following relationship:

$$t(N_{steps}, N_{walkers}) = (21.54 \pm 5.25) + (0.068 \pm 0.013)N_{walkers} + (0.00081 \pm 0.00021)N_{steps} \tag{24}$$

This means that the current code can be expanded to larger numbers of walkers or steps and still be usefull for simulations as the time needed to run this would still be manageable. The code was optimized by using as little for-loops as possible, although the focus of further improvements should be directed to improving the trial wave function as this would greatly improve the accuracy of the results without making the code computational heavy.

5 Discussion and Conclusion

With the variational Monte Carlo simulation, the ground state energy is assessed for the harmonic oscillator, the hydrogen atom and the helium atom. The values obtained for the harmonic oscillator and the hydrogen atom are in agreement with literature values of analytical solutions. This is due to the simple ground state wave function needed for the calculations. The trial wave function is an eigenfunction of the Hamiltonian when the trial wave function is equal to the exact wave function of the ground state of the system. In this case, the local energy defined in formula (3) is a constant function and consequentially will result in a variance equal to zero. For the harmonic oscillator, the ground state energy is calculated for values of alpha from 0.1 to 2. The minimum of the variational parameter can be observed at $\alpha = 0.5$. The corresponding ground state energy found with the simulation is equal to $E = 0.5$. For the hydrogen atom, the same conditions apply as for the harmonic oscillator. The trial wave function for the hydrogen atom is equal to the exact ground state wave function for a value of $\alpha = 1$. For this system, the corresponding ground state energy found is $E = -0.5$. The minimization algorithm for both the harmonic oscillator and the hydrogen atom confirm this minimum at the given variational parameter α. The data obtained from the papers of Jos Thijssen also validate the other results, as can be seen in table 1 and 2. The values for the energy of the ground state and the variance are in agreement with the literature values when the uncertainty is taken into account.

The simulation for the helium atom is a different matter, in this case, the construction of the trial wave function is a problem of its own. For the trial wave function, the simple Padé-Jastrow function is used. Although this trial wave function won't give an exact solution to the system for any value of α. This will result in the variance of the system not going to zero nor will it give a clear minimum for the ground state of the helium atom.

The variance obtained from the simulation decreases for an increasing alpha. This result can also be observed in figure(6) and table 3. The ground state energy has multiple minima for different values of α in the range of (0.05-0.25). With the minimization algorithm an optimal alpha is obtained of $\alpha = 0.1433$ with a corresponding ground state energy of $E = -2.8798 \pm 0.0003$. The ground state energy obtained from the simulation is compared to different literature values, such as the Hartree Fock energy of $E = -2.8617$ a.u. and the exact value of $E = -2.9037$ a.u.[2] These values differ from the optimum value obtained with the variational Monte Carlo simulation more than the error range. A reason for this is the incorrect trial wave function which can be improved in further projects. For example, considering the case where one electron is further away from the nucleus than the other electron. In this case, the wave function should see an effective charge of $Z = 1$, as one of the electrons shields of one unit charge. This should be adjusted in the trial wave function. furthermore, the values obtained for the variance and the ground state energy are compared to the data from Jos Thijssen. These values do agree and therefore it can be concluded that the Metropolis algorithm and the variational Monte Carlo simulation are programmed correctly.

6 Group work

In the beginning of the project we all did some research about the variational monte carlo method and made a general plan of who was going to make which part of the code. What often happened was that one of us wrote a function and someone else debugged it, made it more efficient, or made the function more general such that it could be used for the different systems. Therefore in this section we have written down who made the biggest contribution to each code and report section:
Coen:

- Code contributions
  - 1D Metropolis algorithm
  - code performance
  - minimization algorithm
  - bootstrap
- report contributions
  - abstract
  - introduction
  - theoretical background
  - results 4.1, 4.2, 4.4
  - performance
  - conclusion

Vincent:

- Code contributions
  - minimization algorithm
  - 6d metropolis algorithm for helium atom
  - variational monte carlo simulation helium atom
  - running the simulation to create different plots used in results
- Report contributions
  - abstract
  - theory 2.5 2.6 2.7
  - results
  - figures 1-7
  - conclusion and discussion

Peter-Jan:

- Code contributions
  - variational Monte Carlo simulation harmonic oscillator
  - variational Monte Carlo simulation hydrogen
  - metropolis algorithm
  - error calculation/bootstrap algorithm
  - overall code structure
- Report contributions
  - theoretical background 2.1 2.2
  - computational method
  - table 1, 2 and 3
  - Appendix

6.1 Work organization

At the start of the project, we all read additional papers about the project and made a plan on how to devide the work and who was going to make which part of the code. At the lectures on Wednesday morning we all looked at the progress made, and helped each other if there were problems. We also prepared questions the day before the lectures to achieve the optimal result.

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7 Appendix