Variational quantum Monte Carlo simulation of the Helium atom

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In this paper, we compute the ground state energy of the helium atom via a variational quantum Monte Carlo simulation. Using a trial wave function with one variational parameter, the ground state energy of the helium atom is determined to be -2.8785 ± 0.0008, with a variance of 0.1145. This result is not in agreement with the experimentally determined value of -2.897. Additionally, the non-zero variance in the final result indicates that we, indeed, were not able to find the true ground state of helium using our current approach. It can, however, be concluded that the used approach can be used as a way of getting a fast crude estimation of an upper bound of the ground state energy of helium. Improvements upon this research are possible by employing more complicated trial wave functions, potentially with more variational parameters.

1. INTRODUCTION

In this paper we describe the use of the varational Monte Carlo [1] method to study the ground state energy of helium. This method is based on combining the variational principle [2] with the Monte Carlo method of evaluating integrals [3]. The variational principle is a very useful way of computing the ground state energies of systems when no analytical solutions exist, making use of a trial wave function. Furthermore, Monte Carlo integration is used as it yields a smaller error than standard numerical integration methods due to the high dimensionality considered in these problems [3].

Using the variational Monte Carlo method, the energies of particular quantum systems can be estimated by averaging over the local energy, by a random walk employed via the metropolis algorithm [3].

The present research first computes the analytically known ground state energies of the harmonic oscillator and the hydrogen atom using the variational Monte Carlo method as a proof of concept. Thereafter, the ground state energy of helium is computed and compared to known experimental values.

2. METHOD

A. Monte Carlo Integration

When numerically calculating the integral of a function $f(x)$, the usual approach is to calculate a weighted sum of values of the function, evaluated at a discretized set of N points on the relevant domain, say interval [a,b]. This standard procedure, as given by

$$\int_a^b f(x)dx \approx \sum_i^N w_i f(x_i), \tag{1}$$

uses weights, denoted by w_i, which depend on the integration scheme used. This way, common d-dimensional numerical integration methods of order k yield an error in the result that scales as $N^{\frac{k}{d}}$.

Monte Carlo integration uses a similar methodology, however, like other Monte Carlo techniques, it relies on random sampling for the evaluation of the function on interest. Furthermore, the weights, w_i in eq. 1, are set equal to 1. The error in the result for Monte Carlo integration is independent of the dimensionality of the problem, and scales with $\frac{1}{\sqrt{N}}$. We see that, in the case that $d > 2k$, Monte Carlo integration would be the preferred method of integration.

B. Importance sampling

The Monte Carlo integration method might yield large statistical errors if the function of interest is highly localized in space, while the random sampling is done homogeneously over space. For example, for Gaussian shaped functions, only few of the random samples over all of space would be within the domain where the function would give significant contributions to the integral.

This problem may be circumvented by using importance sampling, in which the sampling distribution takes on a similar shape as the integrated function. To clarify this method, we begin by introducing a normalized function $\rho(x)$ on the domain [a,b] which has more or less the same shape as $f(x)$, meaning that $\frac{f(x)}{\rho(x)}$ is approximately constant over [a,b]. The integral over $f(x)$ we now have is given as

$$\int_a^b f(x)dx = \int_a^b \rho(x)\left(\frac{f(x)}{\rho(x)}\right)dx, \tag{2}$$

in which the weight is given by $\rho(x)$. By defining $f(x)' \equiv \frac{f(x)}{\rho(x)}$, we can rewrite eq. 2 into the form of eq. 1, yielding

$$\int_a^b \rho(x)f(x)'dx = \frac{1}{N}\sum_i^N f(x_i)'. \tag{3}$$

Here x_i is distributed according to $\rho(x)$. Now the statistical error is significantly reduced, as the sampling is mainly done within the domain of interest. As a next task we now have to figure out how to find, and create, the distribution given by $\rho(x)$.

C. Variational Monte Carlo

The variational Monte Carlo method can be used to approximate the ground state of a particular quantum system [3]. Moreover, we shall see that the required probability density function for importance sampling can be found using the variational Monte Carlo method.

The expectation energy of a system is given as

$$\langle E(\alpha)\rangle = \frac{\langle\psi(R,\alpha)|H|\psi(R,\alpha)\rangle}{\langle\psi(R,\alpha)|\psi(R,\alpha)\rangle}. \tag{4}$$

Here H is the Hamiltonian of the system ψ. R contains all spacial parameters on which ψ depends, whereas α contains all variational parameters. Note that in this paper all used wave functions are taken to only depend on one variational parameter. Now we define the local energy as

$$E_L(R,\alpha) \equiv \frac{H\psi(R,\alpha)}{\psi(R,\alpha)}, \tag{5}$$

where the wave function ψ is assumed to be real. The local energy is exact if ψ corresponds to an exact eigenfunction of Hamiltonian H. The more ψ corresponds to the exact eigenfunction, the less E_L will vary with position. Using $E_L(R)$, we can write eq. 4 as

$$\langle E(\alpha)\rangle = \frac{\int \psi(R,\alpha)^2 E_L(R,\alpha)dR}{\int \psi(R,\alpha)^2 dR}. \tag{6}$$

With this expression we have immediately found an equation in the form of eq. 3, although we got there in a different way than described. From this expression it becomes clear that the probability density function from eq. 3, required for importance sampling, is given as

$$\rho(R,\alpha) = \frac{\psi(R,\alpha)^2}{\int \psi(R,\alpha)^2 dR}. \tag{7}$$

Note, that for completeness the probability density function is normalized. Inserting eq. 7 into eq. 6 gives the final result,

$$\langle E(\alpha)\rangle = \int \rho(R,\alpha)E_L(R,\alpha)dR \approx \frac{1}{N}\sum_N E_L(R_i,\alpha), \tag{8}$$

where R_i is distributed according to eq. 7 and N is the amount of sampling points.

The wave function of the system we will be looking at, that of helium, cannot be solved analytically. Because of that we also do not know the exact form of the wave function ψ, required to generate the corresponding probability density function. Using the variational Monte Carlo method, combined with Monte Carlo integration, enables us to find the ground state of the studied quantum system by minimizing the energy of some introduced many particle trial wave function, $\psi_T(R,\alpha)$, that has the shape of the unknown exact wave function of the studied quantum system ψ.

Finding the ground state energy can now finally be achieved by varying α using some minimization algorithm. For this the damped steepest decent method is used, which will be explained further on in this paper. First, however, we need some way to actually acquire the probability distribution described by eq. 7.

D. Metropolis-Hastings algorithm

Creating the probability distribution function is done using the Metropolis-Hastings algorithm. The Metropolis algorithm works by generating correlated sequences of variables called Markov chains.

A Markov chain starts with the generation of a "walker" with random value X within the domain of integration. Subsequently, this walker is displaced with a random value, or in other words "walks", to a new value X', which depends on X. Important is that the so called detailed balance solution needs to be satisfied. This means that the acceptance ratio of going from $X \hookrightarrow X'$ needs to be same as going from $X' \hookrightarrow X$.

To fulfill detailed balance, the weights, $\rho(X)$ and $\rho(X')$ of the two positions X and X', are compared, and this way it is decided whether the walker is displaced or not. The algorithm is given here:

- if $\rho(X') > \rho(X)$, set $X_{i+1} = X'$
- if $\rho(X') < \rho(X)$, set $X_{i+1} = X'$ with probability $\frac{\rho(X')}{\rho(X)}$
- if $\rho(X') = \rho(X)$, set $X_{i+1} = X_i$

When the new position is accepted or rejected, start the algorithm again by letting this new position walk to another position and comparing the weights again.

Important is to first let the system equilibrate. The reason for this, is that the detailed balance solution is a steady state solution. To do this let the algorithm run for a certain amount of steps and then only use the steps after this equilibration for your computations.

These three steps above result in generating the probability distribution $\rho(x)$ as given in eq. 3. However, it is possible that a walker gets stuck in a local minimum. Therefore, it is useful to generate multiple Markov chains, i.e multiple walkers, and take the average value of all these walkers.

E. Minimization of the energy

The used minimization algorithm depends on minimizing the gradient of the energy with respect to the variational parameters. This will, however, give problems because the derivatives of stochastic variables are prone to large errors. To avoid this, we make use of the fact that we can sample the analytical derivative over the population of walkers. The derivative of the energy with respect to alpha is then given as [4]

$$\frac{dE}{d\alpha} = 2\left(\left\langle E_L \frac{d\ln\psi_T}{d\alpha}\right\rangle - E\left\langle \frac{d\ln\psi_T}{d\alpha}\right\rangle\right). \tag{9}$$

The optimal value of α is then computed using the damped steepest decent method, given as

$$\alpha_{new} = \alpha_{old} - \gamma\left(\frac{dE}{d\alpha}\right)_{old}. \tag{10}$$

Here gamma is a constant, which is taken to be 0.5. This value was found via trial and error. The optimal value for α is found when the difference between successive alphas is smaller than some set condition.

The step size between successive α's will be larger if the values of α are further away from the optimal value. The step size gradually decreases when approaching the optimal value. This means that we can can choose an unknown value far away from the optimal value without losing a lot of computation time.

F. The Harmonic Oscillator

As a way of verifying the correctness of the variational method using a metropolis algorithm, we first study the harmonic oscillator. The reason is that the energy, corresponding to the used trial wave function, can be compared to known analytical values.

To start off we introduce the dimensionless Hamiltonian describing the harmonic oscillator,

$$H = -\frac{1}{2}\frac{d}{dx} + \frac{1}{2}x^2, \tag{11}$$

and a trial wave function of the form $\psi_{T,HO}(x)$ = exp(-αx^2) is assumed. The local energy is then obtained as described in the previous section, and can be written as

$$E_L(x,\alpha) = \alpha + x^2(\frac{1}{2} - 2\alpha^2). \tag{12}$$

The trial wave function is chosen to imitate the exact wave function, which is given by $\psi(x)$ = exp(-$\frac{1}{2}x^2$). Then, as a first check, we compute the ground state energies and their corresponding variance for different values of α and compare them to known analytical values aswell as values obtained by Thijssen [3]. The analytical energy is given by

$$E(\alpha) = \frac{1}{2}\alpha + \frac{1}{8\alpha} \tag{13}$$

and the analytical variance is given as

$$\mathrm{Var}\,(E(\alpha)) = \frac{(1-4\alpha^2)^2}{32\alpha^2}. \tag{14}$$

Next, by numerically minimizing the energy with respect to α, using the method explained in the previous section, a value of $\alpha = \frac{1}{2}$ should thus be obtained, together with a corresponding ground state energy of $\frac{1}{2}$ [3]. Furthermore, we know that the corresponding variance must be zero, based on the zero variance principle [5].

G. The Hydrogen atom

The next step in verifying the correctness of our model is by comparing our results to known analytical values, as well as those by Thijssen [3], for the energy of the hydrogen atom. The procedure for hydrogen goes along the same lines as for the harmonic oscillator, as the ground state energy of the hydrogen atom is also an exact known quantity.

The hydrogen atom consists of two particles, a nucleus and an electron. However, because the mass of the electron is negligible compared to that of the nucleus, we take the reference frame to be that of the center of mass, i.e. the nucleus. The Hamiltonian in this case is given, in atomic units, as

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r}. \tag{15}$$

The assumed trial wave function is of the form $\psi_{T,H}(R,\alpha)$ = exp(-αR), as the exact wave function is known to be $\psi(R)$ = exp(-R) [3]. The local energy corresponding to this Hamiltonian using this trial wave function is given as

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

The computed ground state energies can be compared to known analytical values for the energy give by

$$E = \frac{1}{2}\alpha^2 - \alpha, \tag{17}$$

and the analytical variance given as

$$var(E) = \alpha^2(\alpha-1)^2. \tag{18}$$

Numerically minimizing the energy with respect to α should now result in an α equal to 1, and a corresponding ground state energy of -0.5, again with zero variance.

Important to realize is that if we immediately try to solve this problem by reducing it to a 1-D problem, dependent only on r, we no longer comply with detailed balance. The reason is that the walkers prefer to walk outward since there are more possible positions to go to. Therefore, we first run the metropolis algorithm in 3-D using Cartesian coordinates to get the right distribution. Then, to compute the energies the problem is again reduced to a 1-D problem.

H. The Helium atom

In this section we finally arrive at what we truly wanna study, the ground state energy of the Helium atom. Helium consists of a nucleus and two electrons. Similarly as in the case for hydrogen, we take the center of mass frame to be that of the nucleus, as the mass of the electrons is negligible compared to that of the nucleus.

The Hamiltonian, in atomic units, for the Helium atom is given as [3]

$$H = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - 2\left(\frac{1}{r_1} + \frac{1}{r2}\right) + \frac{1}{r_{12}}, \tag{19}$$

where r_1 and r_2 are the positions of electrons 1 and 2 with respect to the nucleus, and r_12 is the (absolute) distance between the two electrons. The chosen trial wave function is given as

$$\psi_{T,He}\left(\underline{r}_1,\underline{r}_2\right) = e^{-2\cdot r_1}e^{-2\cdot r_2}e^{r_{12}/[2(1+\alpha\cdot r_{12}]}. \tag{20}$$

α cannot be negative, as this could lead to divergence if αr_{12} = -1. The form of this wave function belongs to a class of wave functions known as Padé–Jastrow wave functions [6], using this wave function and the helium Hamiltonian results in the following local energy:

$$E_{L,He}(\underline{r}_1, \underline{r}_2) = -4 + \frac{(\underline{r}_1 - \underline{r}_2) \cdot (\underline{r}_1 - \underline{r}_2)}{r_{12}(1 + \alpha \cdot r_{12})^2} + \frac{1}{r_{12}} - \frac{1}{r_{12}(1 + \alpha \cdot r_{12})^3} - \frac{1}{4(1 + \alpha \cdot r_{12})^4}. \quad \textbf{(21)}$$

Even though no analytical solutions exist, the validity of the results can still be verified by comparing them to values obtained by Thijssen [3].

Finally, we minimize the ground state energy using the damped steepest decent method earlier explained and compare the result to the known experimental value of -2.897 [2].

Note, that again the metropolis algorithm is first run in 3-D Cartesian coordinates to ensure detailed balance after which the energy computation is again reduced to only depend on r_1, r_2 and r_{12}.

3. RESULTS & DISCUSSION

A. Harmonic oscillator

The expectation energies for the 1D harmonic oscillator have been computed using the metropolis algorithm for 30000 steps per walker, for 400 walkers. Equilibrium was assumed to have been reached after 4000 steps. These numbers for the amount of steps, walkers and equilibrium steps were used for all computations, including the minimization of both the harmonic oscillator and the hydrogen atom. The computed values are compared to the values obtained by J. Thijssen, who used the same values for the input parameters [3]. Results for the energies and variances for different values for α are presented in table 1, along with the analytical values. We see that the computed values are in good agreement with both the values obtained by J. Thijssen and the analytical values, strengthening the validity of the used method.

To further exemplify the correspondence of the simulation with the analytically known values, figure 1 shows the results for the energy and the variance, for different values of α, together with the analytical values.

The damped steepest decent minimization method was used to minimize the ground state energy of the harmonic oscillator as a function of variational parameter α. The tolerance for successive alphas was set to 0.001, i.e. once the difference between successive alphas is less than 0.001, the minimization was complete. The minimization yielded the theoretical value of 0.5 for α. The theoretical minimal energy of 0.5 was found with negligible uncertainty. The found zero variance further confirmed the finding of the ground state, based on the zero variance principle [5]. The acceptance ratio of displacing a walker was found to be 50% for α equal to 0.5, satisfying detailed balance.

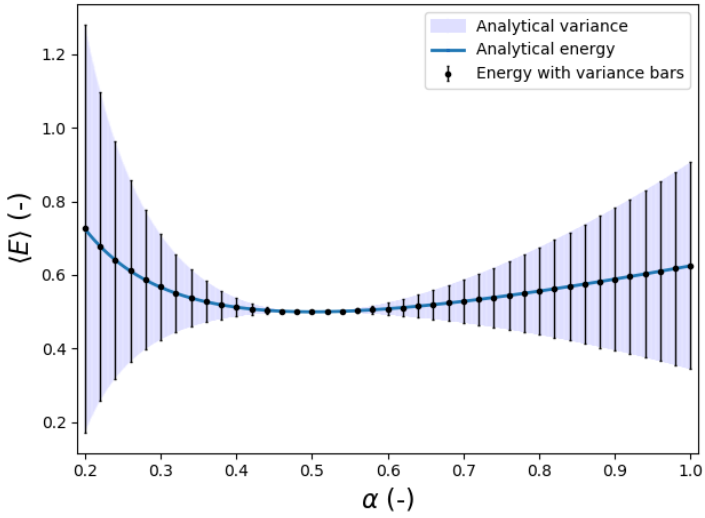

Fig. 1. Computed values for the energy and the variance of these energies for a harmonic oscillator, for the same parameters as described before. Results are plotted together with the analytical values. Computed values are observed to to be largely consistent with analytical values.

B. The Hydrogen atom

The expectation energies for the 1D harmonic oscillator have been computed using the metropolis algorithm, again for 30000 number of steps, 400 walkers and 4000 steps untill equilibrium. Similarly as for the harmonic oscillator, the computed values are compared to the values obtained by J. Thijssen, who again used the same values for the parameters [3]. Results for the energies and variances for different values of α are presented in table 1, along with the analytical values. We see that the computed values are in good agreement with both the values obtained by J. Thijssen and the analytical values, again strengthening the validity of the used method. A reason for the small deviations is due to the statistical nature of computing the energies and variance. Small deviations are always possible when computing the same energy multiple times.

Again, to further show the correspondence of the simulation with the analytically known values, figure 2 depicts the results for the energy and the variance, for different values of α, together with the analytical values.

The simulation computed the energy minimizing to be equal to 1, together with a ground state energy equal to -0.5. Both these values were in perfect correspondence with the theoretical values. The found variance of 0 was also in agreement with the zero variance principle [5]. For α equal to 1, the acceptance ratio of displacing a walker was found to be 50%, satisfying detailed balance. Based on these results we again conclude that method used is viable for computing the ground state energy of particular quantum systems.

Table 1. The expectation energies harmonic oscillator computed using the simulation $\langle E \rangle$ along with their variance var($\langle E \rangle$) for different values of α. 400 walkers were used with 30000 steps, with an equilibration period of 4000 steps. Computed values are compared to the obtained values by J. Thijssen [3] ($\langle E \rangle_T$) and the analytical values (E). The computed values are shown to be in good agreement with both.

α	$\langle E \rangle$	Var ($\langle E \rangle$)	$\langle E \rangle_T$	Var($\langle E \rangle_T$)	E	Var(E)
0.4	0.5127 ± 0.0004	0.025255	0.5125	0.025313	0.5125	0.0253
0.45	0.5026 ± 0.0002	0.00558	0.5028	0.00557	0.50278	0.00557
0.5	0.5	0	0.5	0	0.5	0
0.55	0.5021 ± 0.0002	0.0045695	0.5023	0.0045558	0.5023	0.0045556
0.6	0.5083 ± 0.0003	0.0168234	0.5083	0.0168056	0.05083	0.0168056

Table 2. The expectation energies $\langle E \rangle$ for the hydrogen atom, calculated using the simulation, along with their variance Var($\langle E \rangle$) for different values of α. 400 walkers were used with 30000 steps, with an equilibration period of 4000 steps. Computed values are compared to the obtained values by J. Thijssen [3] ($\langle E \rangle_T$) and the analytical values (E). The computed values are, again, shown to be in good agreement with both.

α	$\langle E \rangle$	Var ($\langle E \rangle$)	$\langle E \rangle_T$	Var($\langle E \rangle_T$)	E	Var(E)
0.8	-0.4800 ± 0.0004	0.0252	-0.4796	0.0243	-0.48	0.0256
0.9	-0.4948 ± 0.0002	0.0079	-0.4949	0.0078	-0.495	0.0081
1.0	-0.5	0	-0.5	0	-0.5	0
1.1	-0.4948 ± 0.0003	0.0118	-0.4951	0.0121	-0.495	-0.0121
1.2	-0.4811 ± 0.0006	0.056	-0.4801	0.058	-0.48	-0.0576

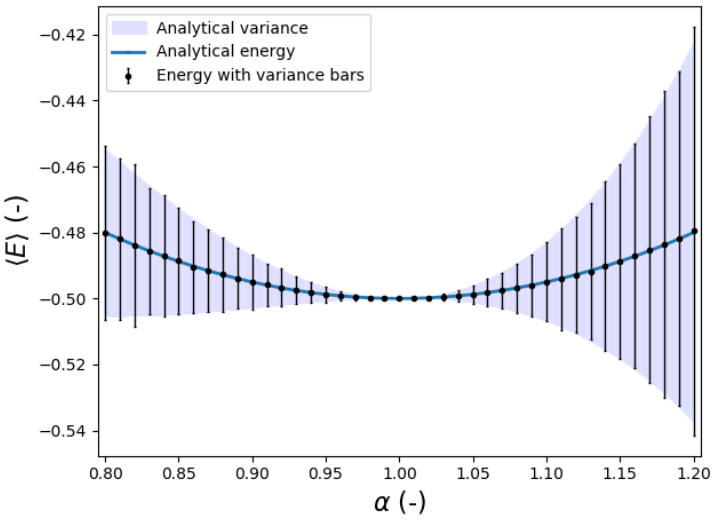

Fig. 2. Computed values for the energy and the corresponding variance for helium, computed using 30000 steps, 400 walkers and an equilibration period of 4000 steps. Results are plotted together with the analytical values. Again, computed values can be seen to to be largely consistent with analytical values.

C. The Helium atom

Having verified the computation method, firstly, the expectation energies of helium are computed for different values values of α and compared by results obtained by Thijssen [3]. These results are presented in table 3. We see that the are mostly in good agreement with each other, except for some small deviations, f.e. the case of $\alpha = 0.2$. The small deviation can be blamed on the statistical nature of the way the energies and variance are computed, i.e. successive computations for the same α result in slightly different energies.

Table 3. The expectation energies $\langle E \rangle$ for the helium atom, computed using the simulation, along with their variance var($\langle E \rangle$) for different values of α. These values are compared to the values obtained by Thijssen [3] ($\langle E \rangle_T$).

α	$\langle E \rangle$	var ($\langle E \rangle$)	$\langle E \rangle_T$	var($\langle E \rangle_T$)
0.05	-2.873 ± 0.001	0.1767	-2.871	0.1749
0.075	-2.8743 ± 0.001	0.1535	-2.8753	0.1531
0.10	-2.8754 ± 0.0009	0.1361	-2.8770	0.1360
0.125	-2.8783 ± 0.0009	0.1224	-2.8780	0.1223
0.15	-2.8779 ± 0.0008	0.1113	-2.8778	0.1114
0.175	-2.8768 ± 0.0008	0.1024	-2.8781	0.1028
0.20	-2.8776 ± 0.0008	0.0963	-2.8767	0.0968
0.25	-2.8749 ± 0.0007	0.0884	-2.8746	0.0883

To find the ground state of the helium atom, the steepest decent method was used. In a preliminary run the minimization was done using 30000 steps, 400 walkers and an equilibration

period of 4000 steps. In figure 3, results are depicted for two different minimizations, one starting from a value for α of 0.1 and one starting from a value for α of 1.0. Both resulted in a value of α of approximately equal to 0.1433, a value which we always ended up approximating doing the minimization this way. Trying to find a more accurate result for the energy minimizing α using that we expect a minimum around 0.1433, we did multiple minimizations using 50000 steps, 5000 walkers and an equilibration period of 5000 steps. The result for two minimizations using these parameters and starting values of α of 0.1 and 0.2, is depicted in figure 4. Like before, an energy minimizing value of α of approximately 0.1433 was found by both minimizations.

Looking at figure 4, we can see that far away from the found minimum value of α, the difference between succeeding α values is relatively constant. Only when nearing the minimum value, as can be seen in figure 3, we start observing a slowdown in the difference between succeeding α values. For the minimization process for the harmonic oscillator and the hydrogen atom, however, the further away from the minimum the current α value was, the larger the difference in the succeeding value was. The failure for the helium minimization in taking larger steps when far away from the minimum, significantly influences the minimization time.

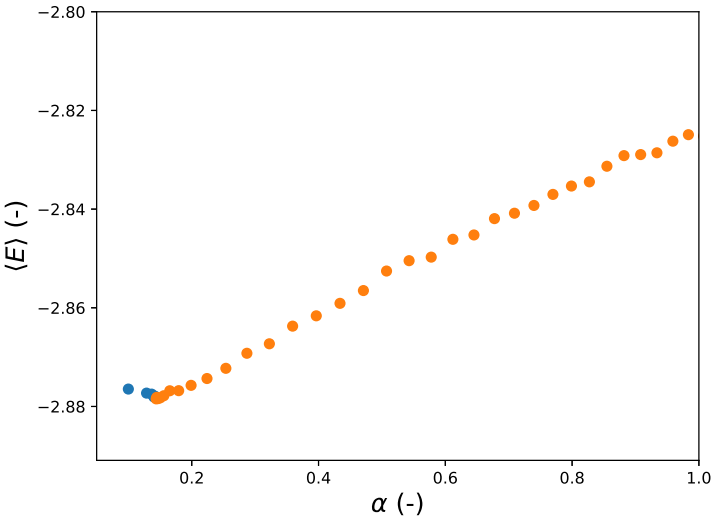

Fig. 3. Alpha minimization of helium using 30000 steps, 400 walkers and an equilibration period of 4000 steps. Results are depicted for two different minimizations, one starting from a value for α of 0.1 (from the left, in blue) and one starting from a value for α of 1.0 (from the right, in orange).

Using the found value of α, the acceptance ratio was approximately 50%, satisfying detailed balance. Furthermore, a ground state energy of -2.8785 $\pm$ 0.0008 is found with a variance of 0.1145. The fact the variance is non-zero means that this is not the true ground state, based on the zero variance principle [5]. Our result is not in agreement with the experimental value of -2.897 [2]. Therefore, we conclude that the used approach is merely a method of obtaining a quick crude upper bound of the ground state energy. To improve upon this, more complex trial wave functions can be used that depend on more variational parameters, like the one used by Kinoshita et. al. [7]. Their

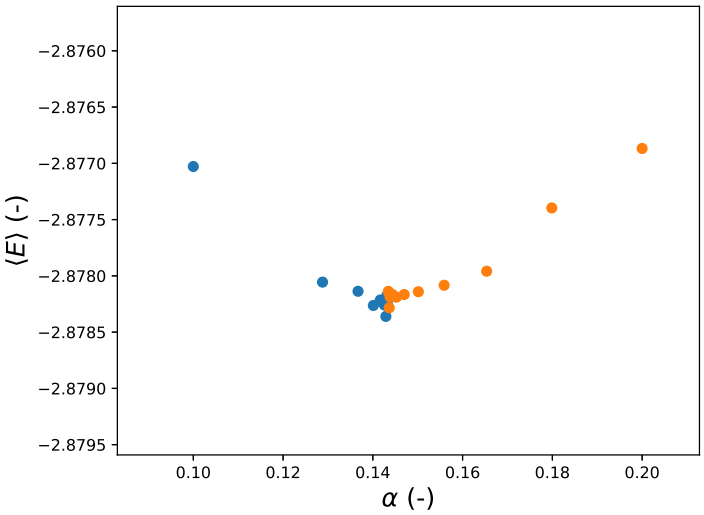

Fig. 4. Alpha minimization of helium using 50000 steps, 5000 walkers and an equilibration period of 5000 steps. Results are depicted for two different minimizations, one starting from a value for α of 0.1 (from the left, in blue) and one starting from a value for α of 0.2 (from the right, in orange).

approach resulted in a ground state energy of -2.903. However, the trade off is that the whole process becomes more complex as well as more time consuming. In figure 5, a plot of computed energies of helium for different values of α is given, together with its variance. Indeed, a minimum in the energy can be observed around a value for α of 0.1433.

D. Code performance

In figure 6 the simulation time of an energy calculation as a function of the product of the amount of walkers and the amount of steps used for a helium simulation. The used simulation makes use of two for loops. One loop is used to cover all different walkers, and one nested loop over all steps. Using these loops within Python, combined with required calculations for all six spacial degrees of freedom for helium, makes up for a less than fully optimized running of the script.

As discussed, the failure for the helium minimization in taking larger steps between succeeding α values when far away from the minimum, significantly influences the minimization time. Therefore it is highly recommended for further research to make use of a different minimization algorithm that converges faster.

To partially optimize the script, we used Numba. For helium calculations, this approximately sped up the simulation by a factor 60. For increased performance of the source script we could have looked for ways to vectorize the script, but using Numba, simulation times weren't considered too long to pursue further running time optimization. To enable further research using f.e. more variables it would, however, be recommended to try to optimize script performance by looking looking into ways to vectorize the script, look for other optimization modules or doing the computations in another language all together, to allow for faster computation times. Time, unfortunately, limited us in further improving upon the used script.

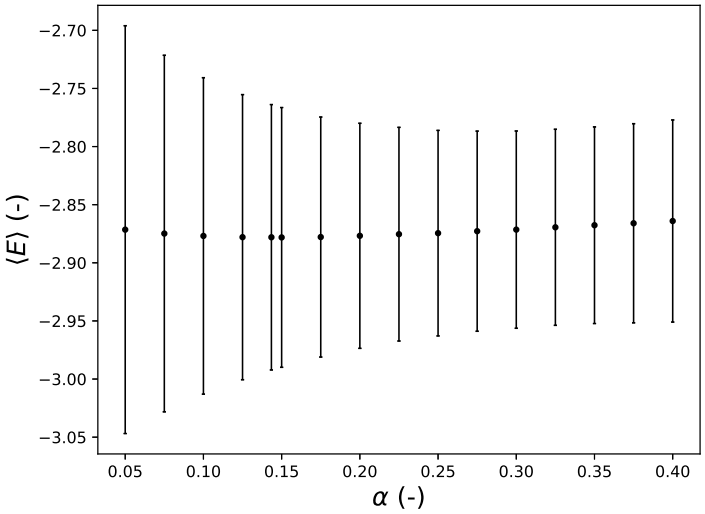

Fig. 5. Computed energies of helium for different values of α, with the corresponding values for the variance. In line with the minimization results, a minimum in the energy can be observed around a value for α of 0.1433. We also observe a non-zero value for the variance for all α's, indicating that using this trial wave function we were not able to find the actual ground state of the system.

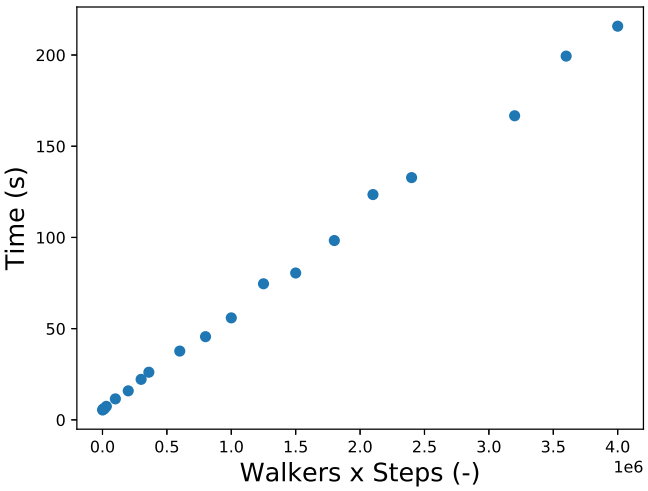

Fig. 6. Average simulation time for the calculation of the ground state energy of the helium atom for some particular value for α as a function of the amount of the product of the amount of used steps and walkers. As can be seen, the simulation time increases linearly with the amount of particles. Simulation was performed with 8 GB of RAM and an Intel® Core™ i7-6700HQ CPU @2.6 GHz.

4. CONCLUSION

The ground state energies of the harmonic oscillator and hydrogen atom have been determined using the variational Monte Carlo method. Results were largely consistent with the analytical values. Using the same method, the ground state energy of the helium atom was determined to be -2.8785 ± 0.0008, with a variance of 0.1145. This result does not correspond with the experimentally determined value of -2.897 [2]. Additionally, the non-zero variance in the final result indicates that we, indeed, were not able to find the true ground state of helium using our current approach. It can, however, be concluded that the used approach can be used as a way of getting a fast crude estimation of an upper bound of the ground state energy of helium.

Improvements upon this research are possible by employing more complicated trial wave functions with more variational parameter, this does, however, make the computations more complex and time consuming.

REFERENCES

1. D. Ceperley, G. V. Chester, and M. Kalos, "Monte carlo simulation of a many-fermion study," Phys. Rev. B **16**, 3081 (1977).
2. D. J. Griffiths and D. F. Schroeter, *Introduction to quantum mechanics* (Cambridge University Press, 2018).
3. J. Thijssen, *Computational Physics* (Cambridge University Press, Kavli Institute of Nanoscience, Delft University of Technology, 2007). ISBN-13 978-0-521-83346-2.
4. X. Lin, H. Zhang, and A. M. Rappe, "Optimization of quantum monte carlo wave functions using analytical energy derivatives," The J. Chem. Phys. **112**, 2650–2654 (2000).
5. J. Gubernatis, N. Kawashima, and P. Werner, *Quantum Monte Carlo Methods* (Cambridge University Press, 2016).
6. R. Jastrow, "Many-body problem with strong forces," Phys. Rev. **98**, 1479 (1955).
7. T. Kinoshita, "Ground state of the helium atom," Phys. Rev. **105**, 1490 (1957).