

A Variational Quantum Monte Carlo Study of the Helium Spectrum

Álvaro Bermejillo Seco (5579244), Daniel Bedialauneta Rodríguez (5567025), and Marc Serra Peralta (5623510)

ABSTRACT

We use the Variational Quantum Monte Carlo algorithm to estimate some of the spectral lines of the helium atom. The energies for the electronic states of He are calculated using the variational principle and Monte Carlo integration with importance sampling. We use the Metropolis-Hastings algorithm to sample from the corresponding probability distribution. Finally, the damped gradient descent method is used to minimize the expectation values of the energies with respect to the free parameters of the trial wave function. Our implementation is validated via comparison with the exact values of the quantum harmonic oscillator and the hydrogen atom. We then obtain the estimates for the eigenenergies of the helium atom for the ground and up to the fourth excited state, using 2 or even 3 free parameters in the trial wave function. The results show that the energy for the ground state has an error of $7 \cdot 10^{-3}\%$ compared to experimental data. The wavelengths for the allowed transitions in the He spectra have relative errors w.r.t the experimental data of 0.5%, 13.9% and 39.0%. Therefore, the followed method is found to be unreliable to compute spectral lines corresponding to transitions amongst excited states, but leads to satisfying results for the ground state energy and wavelength of the allowed transition from the ground to the first excited state.

I. INTRODUCTION

In 1868, Pierre-Jules-Cesar Janssen reported the discovery of a new element by measuring the absorption spectral lines of light coming from the sun. At that moment, it was only possible to tell that the measured spectrum did not match any other measured on earth, because they did not have the spectra of helium. In this report, we make use of the Variational Quantum Monte Carlo (VQMC) method to numerically compute the helium spectra, which would have unequivocally identified the element measured by Pierre.

To compute the exact He spectra, we need to solve the Schrödinger equation for two electrons in the presence of a two proton nucleus. This problem is not analytically solvable, in the same way as the classical three body problem. Therefore, we make use of numerical tools to get an approximate solution. In this work, we employ a numerical approach based on the combination of two ideas: the variational principle and Monte Carlo (MC) integration.

The variational principle states that the ground state energy of a quantum system is always smaller or equal to the average energy of any wave function, i.e. $\langle E \rangle_\Psi \geq E_g$ [1]. From this fundamental principle, it follows a simple algorithm that provides an upper bound to the ground state energy:

- 1) Construct a trial wave function $\Psi_T(\mathbf{r}, \alpha)$, with α a set of free parameters.

- 2) Compute the average energy corresponding to the trial wave function

$$\langle E(\alpha) \rangle = \frac{\langle \Psi_T(\alpha) | \hat{H} | \Psi_T(\alpha) \rangle}{\langle \Psi_T(\alpha) | \Psi_T(\alpha) \rangle}. \quad (1)$$

- 3) Minimize the energy with respect to α .

The choice of the trial wave function family $\{\Psi_T(\mathbf{r}, \alpha)\}$ is a problem of its own. We want the true ground state wave function to be included in this family (or at least to have a $\Psi_T(\mathbf{r}, \alpha)$ very similar to it) so that we can find the E_g (or an energy close to E_g) after the minimization step. For the choice of trial wave functions for the helium atom, we will follow the work of S. B. Doma *et al.* [2].

As we move on to slightly complicated Hamiltonians, such as that of the helium atom, computing the expectation value shown in Eq. (1) requires resorting to numerical schemes to calculate the integrals. To give a sense of the magnitude of the problem, consider the trial wave function of the helium atom for the ground state given by

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

with Hamiltonian for the He atom

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}, \quad (3)$$

where we assumed Hartree atomic units [3] (see subsection V-A), and compute the integral $\int d\mathbf{r}_1 d\mathbf{r}_2 \Psi_T^* H \Psi_T$.

In addition, these integrals are usually over a high dimensional space, namely, the positions of all the particles to be considered. In these situations, employing regularly spaced integration schemes becomes very inefficient. To be precise, these schemes usually result in an error of order $\mathcal{O}(\frac{1}{N^{k/d}})$, where k is the order of the integration method, d is the dimensionality of the integral and N is the number of points used [4]. On the other hand, the MC integration method gives an error of order $\mathcal{O}(\frac{1}{\sqrt{N}})$, which is independent of the dimensionality. Therefore, for large enough dimensionality $d > 2k$, the MC integration method outperforms other ordinary integration methods [4].

The helium atom integrals are of dimensionality $d = 6$, which accounts for the relative positions of the two electrons w.r.t. the nucleus of two protons. That means that, unless we use integration methods of 4th order or higher, MC integration is the way to go.

The aim of this report is to approximate the eigenenergies of the helium atom up to the fourth excited state using the VQMC method in order to assess how useful the method is for estimating some of the spectral lines of helium.

First, in section II, we describe the theoretical background of Monte Carlo Integration, including the Metropolis algorithm, as well as the numerical scheme used for the minimization of the energy. In section III, we show that the implemented algorithm works correctly by comparing its results with well-studied systems, such as the harmonic oscillator and the hydrogen atom. Then, we obtain the helium eigenenergies up to the fourth excited state, using 2 or 3 free parameters, and compare them with the literature. Finally, in section IV, we end with some conclusions.

II. METHODOLOGY

A. MONTE CARLO INTEGRATION

As stated in section I, we make use of the MC integration to obtain $\langle E(\alpha) \rangle$, in particular we focus on the *importance sampling* method. This algorithm is based on sampling the random points for MC integration in such a way that they are concentrated in the regions where the integrated function takes its larger absolute values. The main advantage is that it reduces the computational run-time by sampling with higher frequency the values that have more impact on the integral.

Applying the *importance sampling* method to our case, the average energy of $\Psi_T(\mathbf{r}, \alpha)$ is approximated by

$$\langle E(\alpha) \rangle = \int d\mathbf{r} \rho(\mathbf{r}, \alpha) E_{\text{loc}}(\mathbf{r}, \alpha) \approx \frac{1}{N} \sum_{i=1}^N E_{\text{loc}}(\mathbf{r}_i, \alpha), \quad (4)$$

where $\rho(\mathbf{r}, \alpha) \equiv |\Psi_T(\mathbf{r}, \alpha)|^2 / \int d\mathbf{r} |\Psi_T(\mathbf{r}, \alpha)|^2$ is a probability distribution, $E_{\text{loc}}(\mathbf{r}, \alpha) \equiv (H\Psi_T(\mathbf{r}, \alpha))/\Psi_T(\mathbf{r}, \alpha)$, and the points $\{\mathbf{r}_i\}$ are sampled according to $\rho(\mathbf{r}, \alpha)$ [4].

B. METROPOLIS-HASTINGS ALGORITHM

The ingredient needed to compute $\langle E(\alpha) \rangle$ using Eq. (4) is to generate the points $\{\mathbf{r}_i\}$ following $\rho(\mathbf{r}, \alpha)$, which is implemented using the Metropolis algorithm. This method is

based on generating Markov chains and taking their steps as the points $\{\mathbf{r}_i\}$. The requirement for the Markov chain is that it fulfills the detailed balance: the probability of going from one point to the next one should be equal to the probability of taking the inverse step. The Metropolis algorithm to generate N points is as follows

- 1) Initialize the random walker in a random point \mathbf{r}_1
- 2) Repeat $M > N - 1$ times:
 - a) Generate \mathbf{r}' fulfilling the detailed balance
 - b) If $\rho(\mathbf{r}') > \rho(\mathbf{r}_i)$, set $\mathbf{r}_{i+1} = \mathbf{r}'$
If $\rho(\mathbf{r}') < \rho(\mathbf{r}_i)$, set $\mathbf{r}_{i+1} = \mathbf{r}'$ with probability $\rho(\mathbf{r}')/\rho(\mathbf{r}_i)$ or else set $\mathbf{r}_{i+1} = \mathbf{r}_i$

In our case, we generate \mathbf{r}' fulfilling the detailed balance as $\mathbf{r}' = \mathbf{r}_i + \sigma_{tm} N(0, 1)$, with $N(\mu, \sigma)$ corresponding to a Gaussian distribution and σ_{tm} being the trial move. Noteworthy, the trial wave function does not have to be normalized because we are working with ratios of ρ and E_{loc} does not depend on the normalization constant.

There are still some numerical details in the Metropolis algorithm that need to be solved. Firstly, we need to disregard the first steps of the Markov chain because the random walker has not reached equilibrium. We take out 4 000 steps, as done in [4]. Secondly, we run several random walkers instead of just one because this way we ensure that we cover all the space and not just a local minimum where the random walker has been stuck. Thirdly, we monitor the acceptance ratio of \mathbf{r}' in step 2(b) of the algorithm: if it is not close to 0.5, the sampling of the points has large errors, see subsection V-C.

In order to make the calculations more automatic, we include a function that finds the trial move σ_{tm} that makes the acceptance ratio close to 0.5 (with some specified tolerance). The description for finding the optimal σ_{tm} is explained in subsection V-C. The trial move is updated every time that the new value for α results in an acceptance ratio outside from the tolerance range, this way the total run-time of the algorithm is reduced.

C. ERROR IN THE MC INTEGRATION

As the sampling of $\{\mathbf{r}_i\}$ is based on generating Markov chains, the position of the walker is correlated in 'time' (steps) because the new positions that they land in depend on the previous position. However, each walker starts in a completely random and independent position from all other walkers, so the energies obtained by each walker are completely uncorrelated. Let $E_i(\alpha)$ be the estimate of the expected energy obtained by the i -th walker (with $i = 1, \dots, N_{\text{walkers}}$), then the mean, $E(\alpha)$, and its associated error, $\delta E(\alpha)$, are given by

$$E(\alpha) = \frac{1}{N_{\text{walkers}}} \sum_{i=1}^{N_{\text{walkers}}} E_i(\alpha), \quad \delta E(\alpha) = \frac{\sigma_E(\alpha)}{\sqrt{N_{\text{walkers}}}}, \quad (5)$$

where σ_E is the standard deviation of $\{E_i(\alpha)\}$.

This error does not tell much about how far our trial wave function is from the true ground state. It is an error in the computation of the expected energy. As such, the more steps

each walker takes and the more walkers we average over, the smaller this error will be, as is shown in subsection V-B. In the scenario that our trial wave function is indeed an eigenstate, though, this error will be zero (with some machine error). Note that if $\Psi_T(\alpha_0)$ is an eigenstate for some α_0 with energy E_0 , then from the definition of the local energy, $E_{\text{loc}}(\mathbf{r}, \alpha_0) = E_0, \forall \mathbf{r}$. Therefore, from Eq. (4), $\langle E(\alpha) \rangle$ will give E_0 for all walkers, thus $\sigma_E(\alpha_0) = 0$. The total error of the estimation of the ground state energy comes from two sources: the numerical error in the integration, which can be decreased by taking larger number of steps and walkers, and the intrinsic error in the variational principle when choosing the trial wave function, which can be decreased by choosing a better trial wave function. Noteworthy, even though we can expect that as we get closer to the true eigenstate the error will diminish, a small error does not tell you how close you are to the true ground state. To assess this later error, we use the quantum mechanical uncertainty of the energy, defined as

$$\Delta E(\alpha) = \sqrt{\langle E^2(\alpha) \rangle - \langle E(\alpha) \rangle^2}, \quad (6)$$

because it is a measure for how close you are to an eigenstate that does not depend on the number of steps and walkers [4]. If its value is zero for α_0 , then $\Psi_T(\alpha_0)$ is an eigenstate of the Hamiltonian. However, we will not treat this quantity in the report because we already know that our trial wave functions for He are not eigenstates of \hat{H} .

Finally, another error source to be taken into account is the numerical second derivative of the trial wave function w.r.t. \mathbf{r} used to calculate $E_{\text{loc}}(\mathbf{r}, \alpha)$ for the case of the helium system. Specifically, we use the second order central formula to compute the laplacian of the kinetic term. We have taken this numerical approach because the analytical expression for $E_{\text{loc}}(\mathbf{r}, \alpha)$ was too complex when using the trial wave functions of the excited states. To minimize this source of error, we selected an appropriate derivative step h . By comparing the values obtained for the local energy of the helium ground state through the analytic and numerical methods, a value of $h = 10^{-5}$ was found to be optimal.

D. NUMERICAL MINIMIZATION OF $\langle E(\alpha) \rangle$

Once we can calculate the expectation value of the energy for a certain parameter α , we minimize it w.r.t. α . For this, we will use the damped gradient descent algorithm.

The basic idea is to find a parameter $\alpha^{(N)}$, by updating α according to the following relation

$$\alpha^{(k+1)} = \alpha^{(k)} - t_k \vec{\nabla} E(\alpha^{(k)}), \quad k = 0, \dots, N-1, \quad (7)$$

for which the norm of the gradient $\|\vec{\nabla} E(\alpha)\|$ is sufficiently low, i.e. close to a minimum due to the minus sign. The closer $\alpha^{(k)}$ gets to $\alpha^{(\min)} \approx \alpha^{(N)}$, the smaller $\|\vec{\nabla} E(\alpha)\|$ becomes. Ideally, then, we would expect $\|\alpha^{(k+1)} - \alpha^{(k)}\|$ to also become smaller as we keep updating α . However, this is not always the case, as the algorithm could get stuck oscillating around $\alpha^{(\min)}$ without getting close to it. This is where the damping parameter t_k comes in. By making it smaller, we can damp these oscillations and get closer to $\alpha^{(\min)}$.

E. PARALLELIZATION FOR MC INTEGRATION

The structure of the Metropolis algorithm allows to take advantage of parallel computation to speed-up the calculation of $\langle E(\alpha) \rangle$. Dividing the number of random walkers (N_{walkers}) into N_{cores} cores decreases (ideally) the the total time of the algorithm by a factor of N_{cores} . Moreover, depending on the architecture used, it is also possible to reduce the size of RAM memory needed for each core to perform the calculations as it scales with N_{walkers} .

Our goal of implementing multi-core computation is to show that the algorithm is suitable for parallel computation by proving that the run-time decreases when using more than one core. We use the *multiprocessing* Python library to achieve such objective. Nevertheless, it has been reported that the speed-up when using this library kicks off when using more than 24 cores [5], and our available computers have less than 24 cores. There are more specialized libraries (e.g. Ray [6]) that already show a good speed-up when using more than 2 cores, but their implementation is beyond the scope of our goal regarding parallelization.

III. RESULTS

A. VALIDATION OF THE CODE

Before computing the results for the helium atom, we first address a series of checks to show that the code works correctly.

Firstly, we monitor the acceptance ratio and verify that the trial move is chosen correctly. In the studied case, the acceptance ratio for each random walker follows a Gaussian distribution centered around 0.525 and they are all inside the tolerance range (see Figure 4 in subsection V-C). This proves that the procedure to set the acceptance ratio to 0.5 ± 0.05 works properly.

Secondly, we perform the same procedure that we are going to use for helium to two systems from which we know the analytic solution, in particular the 1D harmonic oscillator and the hydrogen atom. The family of trial wave functions used for both cases includes the true ground state of the system, thus in this way we can check that $\delta E = 0$ for the true ground state and that, upon numerical optimization, the values of α and $\langle E(\alpha) \rangle$ get closer to the analytic solutions.

We start with the harmonic oscillator. The trial wave functions are shown in subsection V-D. First, we make use of a wave function with single variational parameter a and solve the usual Hamiltonian $H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} x^2$, with units described in subsection V-A. We perform a scan of a that includes the value of the true ground state, i.e. $a_{GS} = 1/2$ with $E(a_{GS}) = 1/2$. As expected, the scan shows a minimum in $a = 1/2$, see Figure 1, and we also verify that $\delta E(a = 1/2) = 0$.

Additionally, we also use a two parameter wave function from Eq. (11) to check the performance of the numerical optimization with multiple free parameters. The computation resulted in $E(0.503, -0.032) = 0.5004(3)$, which is very close to the exact value $E(a = 0.5, b = 0) = 0.5$. In

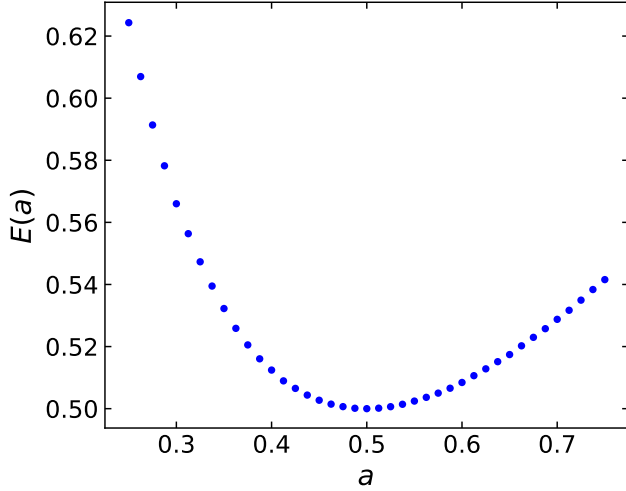


FIGURE 1: $\langle E(a) \rangle$ as a function of the free parameter a for the 1D harmonic oscillator with trial wave function shown in subsection V-D. The error bars are too small to be visible in the plot ($\sim 10^{-4}$). The minimum corresponds to $E(a = 1/2) = 1/2$. The number of random walkers is 400 with 30000 steps each. The units are described in subsection V-A.

conclusion, the code has passed the checks for the harmonic oscillator.

For the case of the hydrogen atom, the Hamiltonian is $H = -\nabla^2/2 - 1/r$ and the trial wave function is given by Eq. (12). The true ground state corresponds to $\alpha_{GS} = 1$, with $E(\alpha_{GS}) = -1/2$. Setting the initial guess of α to 0.75, we get $E(0.9978) = -0.499996(4)$ after 14 optimization cycles with three damping resets, i.e. from $t = 0.25$ to 0.01, and with energy tolerance of 10^{-5} . Therefore, the code has passed the check for the hydrogen atom.

For all these checks, we use 400 random walkers with 30 000 steps per walker, from which we skip the first 4 000. As the numerical optimization seems to work and the error is low enough, we will use the same configuration as a starting point to study the helium system.

Noteworthy, in the case of 2 or more free parameter trial wave functions, e.g. the 2-parameter harmonic oscillator mentioned above, it is not easy to obtain the result of the minimization process in one go. What we do is, first, set some initial free parameters with a certain damping factor t . After some iterations, we can take the parameters that gave the lowest energy as new initial parameters, and lower the damping factor t to scan a smaller region. These steps can then be repeated until we obtain a satisfactory answer.

B. HELIUM GROUND STATE

The helium atom has a significant difference with respect to the previous shown cases: we do not know the exact ground state of the system. For this reason the choice of the trial wave functions plays a major role in solving the problem via the VQMC. As commented before, we follow the work by Doma *et al.* [2]. Their choice of wave functions is the standard one when dealing with multi-electronic atoms. They are

TABLE 1: Results for the ground state energy of helium computed with the trial wave function, Ψ_T , in Eq. (13) with one single variational parameter (β), where the effective charge (z_1) is fixed to the nucleus charge 2, and with two variational parameters where the effective charge is added as a parameter. Results from the literature are shown for comparison.

Ψ_T	z_1	β	$E(z_1, \beta)$	E literature
1 param.	2	0.1367	-2.8783(5)	-2.8781(5) [4]
2 param.	1.839	0.36	-2.8904(1)	-2.903591(37) [2]

TABLE 2: Results from the first four excited levels of helium. The first two are computed with three variational parameters, three and four with parameters taken from [2]. Results from [2] are shown for comparison.

State	z_1	z_2	β	$E(z_2, \beta)$	E from [2]
2^3S	1.962	1.638	0.282	-2.1681(3)	-2.168902(15)
2^1S	1.99	1.5	0.25	-2.1396(3)	-2.145965(20)
2^1P	2	1.00	1.00	-2.12366(8)	-2.123401(4)
2^3P	2	1.2	0.4	-2.13116(6)	-2.131104(6)

composed of single orbitals of the hydrogen atom allowing for a different effective charge, followed by a correlation term that introduces the electron–electron interaction. These items are combined such that they respect fermionic statistics and cusp conditions such that statistical fluctuations are avoided. All the wave functions employed are explicitly shown in subsection V-D.

Firstly, we are going to focus on the ground state of the helium atom. For that we are going to consider two different trial wave functions, one with a single variational parameter, β , in the correlation function and another with two variational parameters, z_1 and β , that gives freedom in the effective charge, which is actually screened giving a lower value than the nuclear charge. The results are shown in Table 1. It can be observed how the obtained values are in good agreement with the literature. In addition, due to the two parameter trial wave function being a more general function, we observe a better approximation of the ground state energy compared to the one with just one free parameter, as expected.

C. HELIUM EXCITED STATES

Next, we can make use of the trial wave functions corresponding to the first four excited states, Eq. (14)-(17), to compute their corresponding energies. To find energies corresponding to excited states we use families of trial wave functions that are orthogonal to the ground state. In this way we can still apply the variational principle. However, for excited states, the method is more unreliable than for the ground state because we do not know the true ground state and thus we cannot make true orthogonal states. In such case, the corresponding energies are not an upper bound of the true excited energies.

The results are shown in Table 2 and they are in agreement with the literature. It is of importance to say that we did not use the minimization algorithm to obtain the last two energies. The shape of this orbitals is more complex, which leads to a much smaller trial move and the characteristics of the computation vary significantly. For that reason the minimization algorithm used previously could not approach

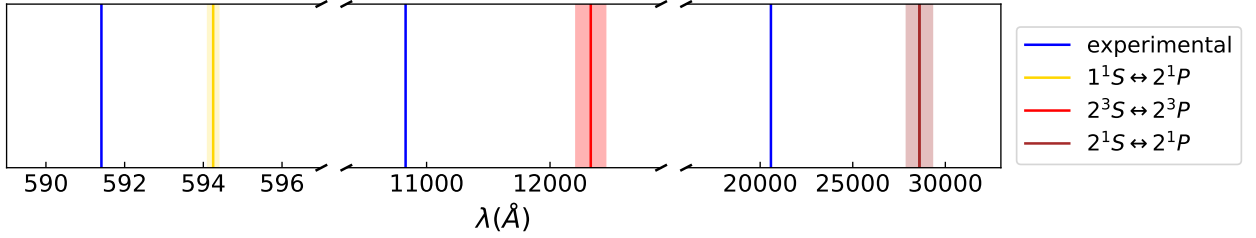


FIGURE 2: Spectral lines of helium computed from the energy differences shown in Table 1 and Table 2. In blue experimental data from [7] and in yellow ($\lambda = 594.3(1)$), red ($\lambda = 12300(100)$) and brown ($\lambda = 28600(700)$) our estimations. Note that the horizontal axis is divided in three different sections.

the minimum efficiently (see caption of Table 2).

It was stated before that the configuration for the VQMC would follow from that used in the checks, in instance $N_{\text{steps}} = 30\,000$, $N_{\text{walkers}} = 400$ and $N_{\text{skip}} = 4\,000$. However, in order to get higher accuracy, these parameters have been changed throughout the whole process. For instance, in order to obtain the value for the 2^3P energy we used $N_{\text{steps}} = 30\,000$, $N_{\text{walkers}} = 3\,000$ and $N_{\text{skip}} = 2\,000$.

D. HELIUM SPECTRA

Transitions between these electronic levels give raise to a singular emission spectrum that characterizes any element. From all the possible transitions, we first need to find which are permitted by the selection rules [8]. In this case they correspond to

$$1^1S \leftrightarrow 2^1P, \quad 2^1S \leftrightarrow 2^1P, \quad 2^3S \leftrightarrow 2^3P.$$

From the energy difference between these levels computed in subsection III-C, we can easily compute these spectral lines and their uncertainty. The outcomes and a comparison with experimental values from [7] are shown in Figure 2.

We observe that except for the transition that includes the ground state, the values do not match the experimental data. This is due to the energy closeness between the excited states and the accuracy of our results. VQMC has some fundamental flaws, i.e. you cannot know how good your result is, unless it is perfect. Even if we can compute the integrals very accurately, the result is completely dependent on the choice of trial wave function family. With the numerical results reported in [2], with an error of one order of magnitude less, the spectral lines still differ substantially from the experimental results.

IV. DISCUSSION

In this report, we have implemented the Variational Quantum Monte Carlo algorithm, which allows to estimate the eigenenergies of quantum systems given the Hamiltonian and an appropriate trial wave function. After validating our code with the Quantum harmonic oscillator and the hydrogen atom exact solutions, we are able to obtain an approximation for the ground state energy and for the first four excited states of the helium atom. The numerical result for the ground state $E = -2.8904(1)$ is in very close to the experimental

value $-2.90338583(13)$ [9], with an error of less than 0.01%. However, the transition wavelengths $\lambda_{1^1S-2^1P} = 594.3(1)$, $\lambda_{2^1S-2^1P} = 12\,300(100)$ and $\lambda_{2^3S-2^3P} = 28\,600(700)$ present errors of 0.5%, 13.9% and 39.0% w.r.t. the experimental data [7].

The computed transitions between excited states do not correctly reproduce the experimental data. In the next paragraph, we will comment the possible reasons of such problem. For now, we can focus on the fact that the spectral line lying in the visible range appears to be more precise. This points out that it could be worthwhile studying transitions from excited states to the ground state. For instance, if we find appropriate trial wave functions for the 3^1P and 4^1P states, we could find with reasonable accuracy the visible range of the helium spectrum.

As stated before, in general, our implementation of the variational method is not suitable for calculating the spectral lines of atoms and identifying them with the corresponding level transitions. Indeed, regardless of the computational power available to calculate the integrals, the choice of trial wave function is a limiting factor. Even if the trial excited states are orthogonal to our trial ground state, it does not imply they are orthogonal to the real ground state. As a result, an upper (or lower) bound for the energies of the excited states does not exist, unlike for the ground state. In any case, the variational method is still useful to validate our understanding of the main characteristics of the ground state of a system. For the more precise calculation of atom and molecule electronic levels, other methods exist, such as Hartree-Fock or Density Functional Theory [8].

During our computations, we noticed that the minimization algorithm we used is prone to get stuck oscillating or even jump away from the equilibrium point when the number of free parameters is greater than one. This is because the computationally obtained energy $E(\alpha)$ fluctuates for the same α due to Monte Carlo integration. If the true function $E(\alpha)$ is very slowly varying, then the calculated gradient could sometimes be in one direction and other times in the opposite for the same α . The more free parameters there are, the more directional derivatives have to be calculated and the more chances these fluctuations slow down or break the convergence of the minimization process. Therefore, either improving or replacing this minimization algorithm is one of

the key points to make our implementation of VQMC more reliable.

An alternative to decrease these fluctuations is to reduce the numerical error, for which we need to increase the number of steps and number of walkers. At first sight, this can look impractical since it will greatly increase the computation time. However, we have shown that it is possible to parallelize the random walkers. In particular, we have obtained a $2\times$ speedup for large number of walkers despite not using a large number of cores or the most advanced parallelization libraries. Therefore, the possibility of running the code in specific architectures tailor made for parallelization, such as clusters or supercomputers, leaves plenty of room for improving the results.

In conclusion, we have seen that the Variational Quantum Monte Carlo algorithm works well to estimate the ground state energy of systems from which we have a good understanding of the shape of their wave function. For the case of the excited states, the trial wave functions may not be close enough to the real ones, which leads to large differences between the numerical and experimental values. The code implemented in this report is general enough to be used for other systems such as ionized atoms and small molecules. In addition, it can be upgraded with better parallelization libraries which would allow to increase the number of random walkers and thus solve the previously mentioned problems.

REFERENCES

- [1] D. J. Griffiths, Introduction to Quantum Mechanics (2nd Edition), 2nd ed. Pearson Prentice Hall, Apr. 2004.
- [2] N. A. E. Salah Badawi Doma, Mahmoud Ahmed Salem, "Applications of the variational quantum monte carlo method to the two-electron atoms,," International Journal of High Energy Physics, vol. 6, no. 2, pp. 42–53, 2019.
- [3] D. R. Hartree, "The wave mechanics of an atom with a non-coulomb central field. part i. theory and methods," Mathematical Proceedings of the Cambridge Philosophical Society, vol. 24, no. 1, p. 89–110, 1928.
- [4] J. Thijssen, Computational Physics, 2nd ed. Cambridge University Press, 2007.
- [5] "10x faster parallel python without python multiprocessing." [Online]. Available: <https://towardsdatascience.com/10x-faster-parallel-python-without-python-multiprocessing-e5017c93cce1>
- [6] "Ray 1.12.0." [Online]. Available: <https://docs.ray.io/en/latest/index.html>
- [7] W. C. Martin, "Energy levels of neutral helium (4he i)," Journal of Physical and Chemical Reference Data, vol. 2, no. 2, pp. 257–266, 1973. [Online]. Available: <https://doi.org/10.1063/1.3253119>
- [8] P. Atkins, P. W. Atkins, and J. de Paula, Physical Chemistry. Oxford university press, 2014.
- [9] D. Z. Kandula, C. Gohle, T. J. Pinkert, W. Ubachs, and K. S. Eikema, "Extreme ultraviolet frequency comb metrology," Physical Review Letters, vol. 105, no. 6, p. 063001, 2010.
- [10] R. P. Brent, Algorithms for minimization without derivatives. Englewood Cliffs, 1973.

V. SUPPLEMENTARY INFORMATION

A. UNITS

The units used for the Hamiltonians of all the systems described in the report are summarized in Table 3.

TABLE 3: Units for the quantum harmonic oscillator (QHO) and Hartree atomic units (HA). Here, ω is the characteristic frequency of the oscillator defined by its Hamiltonian.

Dimension	QHO	HA
Length	$\sqrt{\hbar/(m\omega)}$	a_0
Energy	$\hbar\omega$	$E_h \equiv \hbar^2/(m_e a_0^2)$

B. DEPENDENCE OF THE ERROR WITH THE NUMBER OF STEPS AND WALKERS

In Figure 3, we show the dependence of $E(\alpha)$ both on the amount of walkers N_{walkers} and the amount of steps N_{steps} each walker takes, for the ground state trial wave function of the helium atom with $z_1 = 1.84$ and $\beta = 0.35$, as defined in Eq. (12) and Eq. (20).

From the curves with a large number of walkers, we see that the dependence of the error with N_{steps} is $\Delta E \propto 1/\sqrt{N_{\text{steps}}}$. The same dependence was found for the quantum harmonic oscillator and the hydrogen atom.

Interestingly, in order to reduce the error, there is no preference for increasing N_{steps} or N_{walkers} . For instance, taking $N_{\text{steps}} = 10^4$ and $N_{\text{walkers}} = 10^2$ gives a very similar error as $N_{\text{steps}} = 10^2$ and $N_{\text{walkers}} = 10^4$. However, other factors, such as the parallelization of walkers, could make increasing one of the two more computationally advantageous.

C. ACCEPTANCE RATIO

A parameter of relevance when assessing the correct sampling of a function via the Metropolis algorithm is the acceptance ratio, defined as

$$A = \frac{\text{accepted moves}}{\text{total attempted moves}}. \quad (8)$$

The acceptance ratio of a walker is determined by the trial move, which in our implementation of the Metropolis algo-

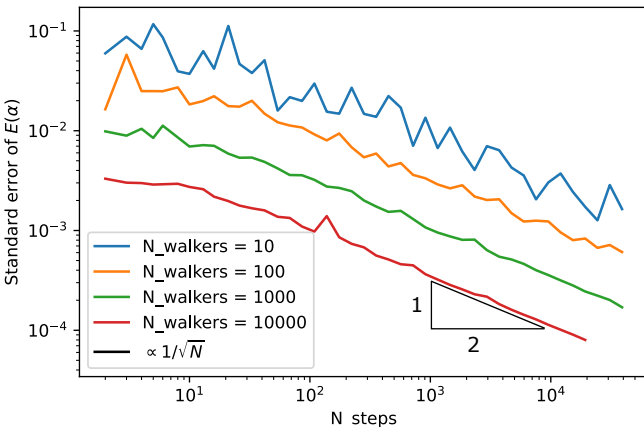


FIGURE 3: Standard error of $E(\alpha)$ as a function of N_{steps} and N_{walkers} for the ground state of the helium atom with parameter $\alpha = (1.84, 0.35)$.

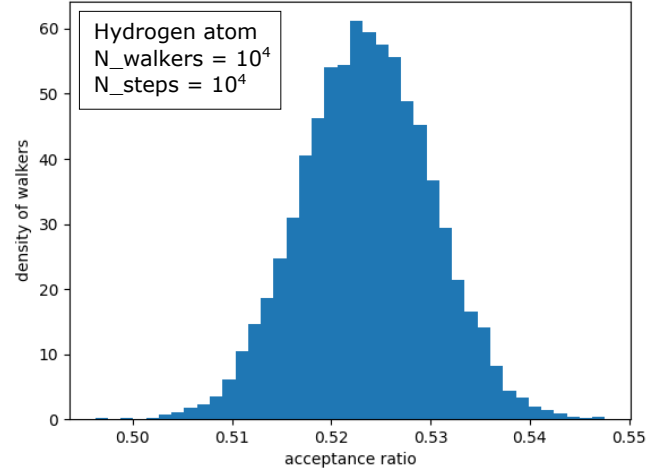


FIGURE 4: Density of walkers as a function of the acceptance ratio. It can be seen that all them fall in the range of 0.50 ± 0.05 , as ensured with the routine employed. This analysis is performed for a sampling of the density of probability corresponding to the hydrogen atom, for 10 000 walkers and 10 000 steps.

rithm is chosen according to a normal distribution. The trial move is then represented by the standard deviation of the normal distribution, σ_{tm} .

In general, an acceptance ratio of approximately 0.5 will ensure a correct sampling. To fulfil this requisite, we implemented a routine that, prior to any computation, finds an optimal σ_{tm} such that the acceptance ratio is in $0.5 \pm \text{tol}$, where tol is a tolerance set to 0.05 in all of our computations.

The routine is based in finding the root of the function

$$f(\sigma_{tm}) = \text{acceptance_ratio}(\sigma_{tm}) - 0.5, \quad (9)$$

via Brent's method [10]. The success of this routine is shown in Figure 4 for the sampling of the hydrogen atom.

D. TRIAL WAVE FUNCTIONS

The trial wave functions are taken include the exact solutions for the case of the harmonic oscillator and hydrogen atom and for the ground state and excited states of the helium atom they are extracted from [2]. We enumerate them hereunder.

For the one dimensional harmonic oscillator the exact solution is given by a gaussian

$$\Psi_{HO,1}(x) = N \exp(-ax^2), \quad (10)$$

with $a = 1/2$, but we also employ a 2 parameter (a, b) wave function to test the minimization algorithm with multiple parameters

$$\Psi_{HO,2}(x) = N \exp(-ax^2 - bx). \quad (11)$$

The exact solution for the hydrogen ground state is also known

$$\psi_{1s}(r) = N \exp(-z_1 r), \quad (12)$$

with $z_1 = 1$. For the helium atom, we use the wave functions corresponding to the ground state (1^1S) and the first four excited states ($2^3S, 2^1S, 2^1P, 2^3P$)

$$\Psi_{1^1S}(r_1, r_2) = N \psi_{1s}^1 \psi_{1s}^2 f(r_{12}), \quad (13)$$

$$\Psi_{2^3S}(r_1, r_2) = N [\psi_{1s}^1 \psi_{2s}^2 - \psi_{1s}^2 \psi_{2s}^1] f(r_{12}), \quad (14)$$

$$\Psi_{2^1S}(r_1, r_2) = N [\psi_{1s}^1 \psi_{2s}^2 + \psi_{1s}^2 \psi_{2s}^1] f(r_{12}), \quad (15)$$

$$\Psi_{2^1P}(r_1, r_2) = N [\psi_{1s}^1 \psi_{2p}^2 + \psi_{1s}^2 \psi_{2p}^1] f(r_{12}), \quad (16)$$

$$\Psi_{2^3P}(r_1, r_2) = N [\psi_{1s}^1 \psi_{2p}^2 - \psi_{1s}^2 \psi_{2p}^1] f(r_{12}). \quad (17)$$

They are composed of single hydrogen orbitals

$$\psi_{2s}(r) = (1 - z_2 r/2) \exp(-z_2 r/2), \quad (18)$$

$$\psi_{2p}(r) = r \exp(-z_2 r/2) (z/r), \quad (19)$$

and the correlation function

$$f(r_{12}) = \exp\left(\frac{r_{12}}{\alpha(1 + \beta r_{12})}\right). \quad (20)$$

The superscripts make reference to the electrons 1 or 2 (evaluated in r_1 or r_2), N is a normalization constant, z_1 , z_2 and β are the variational parameters, and α is a parameter that allows to fulfil the cusp conditions, which equals 2 for unlike spins ($2^1S, 2^1P$) and 4 for like spins ($2^3S, 2^3P$).

E. CODE EFFICIENCY AND PARALLELIZATION

The performance analysis of the code and parallelization has been done calculating $\langle E(a) \rangle$ for the harmonic oscillation with $a = 0.65$ and $\sigma_{tm} = 1.2222$ (optimized such that the acceptance ratio is 0.5). The run-time has been studied as a function of the number of steps in the random walkers (N_{steps}), the number of random walkers (N_{walkers}), and the number of cores (N_{cores}). The results are shown in Table 4 and Table 5.

TABLE 4: Run-time as a function of the number of steps and the number of cores. The number of random walkers is fixed at $N_{\text{walkers}} = 1\,000$ (top) and $2\,000$ (bottom).

N_{steps}	time [s] (1 core)	time [s] (4 cores)	speed-up factor
2 500	0.43	0.51	0.84
25 000	3.59	3.16	1.14
50 000	6.58	5.74	1.15
75 000	9.80	8.61	1.14
100 000	15	12.7	1.18
N_{steps}	time [s] (1 core)	time [s] (4 cores)	speed-up factor
2 500	0.76	0.55	1.38
25 000	6.13	4.97	1.23
50 000	14.0	10.5	1.33
75 000	18.9	15.6	1.21
100 000	28.3	19.7	1.43

The speed-up factor as a function of N_{steps} is low and does not increase with the number of steps used. The explanation for these values is that the bottleneck of the function `random_walkers` is given by the number of steps and not

the number of random walkers, because the first one is implemented in a `for` loop, while the second one is implemented using `numpy`. However, the speed-up factor shows an increase as a function of N_{walkers} , which is higher than a $2\times$ factor. We can also observe that there is a decreasing tendency of the run-time with the number of cores and with the number of N_{walkers} . Therefore, it is possible to take advantage of parallel computation to reduce the run-time of the calculations. As stated in section II, there are more advanced libraries that allow better parallel performance, but as the computers used in this report are not suitable for multi-core processing, we would not be able to use all the power of such libraries.

TABLE 5: Run-time as a function of the number of random walkers and the number of cores. The number of steps is fixed at $N_{\text{steps}} = 25\,000$.

N_{walkers}	time [s] (1 core)	time [s] (4 cores)	speed-up factor	time [s] (8 cores)	speed-up factor
250	2.34	2.22	1.05	2.80	0.84
1 000	4.12	2.91	1.42	3.16	1.30
4 000	9.94	5.17	1.92	4.52	2.20