Variational Monte Carlo simulation of ground state energies of quantum systems

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Abstract

Determining the ground state energy of a given physical system is not only generally infeasible by analytical means, but also a computationally expensive task. In order to tackle this problem, a variety of methods have been proposed. In this report, we employ a variational quantum Monte Carlo algorithm, which allows us to approximate the ground state energies and wave functions of three different Hamiltonians: the one-dimensional harmonic oscillator, the Hydrogen atom and the Helium atom. A central component of this algorithm is the Markov Chain Monte Carlo (MCMC) algorithm, which is used to sample from the probability distribution defined by the respective wave function, and allows for efficient computation of energies. Our estimates agree with experimental results and literature, proving the effectiveness of the approach in solving high-dimensional problems.

1 Introduction

Finding the ground state energy of quantum systems is a challenging task. However, it has a wide variety of applications, especially in quantum chemistry. In particular, it enables numerically exact prediction of chemical reaction rates, gives insights into determining stable molecular structures and is essential in the design of new catalysts, pharmaceuticals and materials [1]. Whereas analytical solutions exist only in rare cases and for extremely small system sizes, a variety of methods for many-body systems has been proposed. In this paper, we investigate a variational Monte Carlo method (VMC), in which we iteratively minimize the energy of a trial wave function for a given Hamiltonian by means of Markov Chain Monte Carlo sampling.

We apply this algorithm for three different quantum systems: the one-dimensional quantum harmonic oscillator, the Hydrogen atom and the Helium atom. For the first two systems, the time-independent Schrödinger equation can be solved analytically, but we decided to solve them via VMC to validate our implementation. Regarding the Helium atom, it has been proven mathematically that an analytical solution can not exist. Consequently, we must rely on alternative approaches such as the variational method to find its ground state energy [2].

In this report, we first describe the Variational Monte Carlo method. Then, we present and discuss the results obtained for each of the quantum systems analyzed. We conclude by outlining the performance of our VMC simulation and summarizing the main findings.

2 Methods

In this section, we present the workflow of the Variational Monte Carlo algorithm, which consists of several interconnected subroutines. These subroutines are described in the following subsections in a logical order to help the reader understand the VMC algorithm as a whole.

2.1 Variational method

The Variational principle states that given an arbitrary wave function (not necessarily normalized), the expectation value of any Hamiltonian in that state is lower bounded by its ground state energy. The Variational method leverages this principle by proposing a trial wave function parametrization $\psi_T(\mathbf{r}, \alpha)$, and optimizing the variational parameters α to minimize the expectation value of the energy [3]:

$$E(\alpha) = \frac{\int d\mathbf{r}\psi_T^*(\mathbf{r}, \alpha)H\psi_T(\mathbf{r}, \alpha)}{\int d\mathbf{r}\psi_T^*(\mathbf{r}, \alpha)\psi_T(\mathbf{r}, \alpha)}, \qquad (1)$$

where the denominator is the normalization factor of the trial wave function. The trial wave functions used for each of the systems will be explained in Section 2.6. The helium atom has 6 degrees of freedom as it has 2 electrons moving in three dimensions, so the integral in Equation 1 is high-dimensional. Therefore, it is beneficial to solve it using Monte Carlo integration.

2.2 Monte Carlo integration

The integral in Equation 1 can be rewritten in the following way [4]:

$$E(\alpha) = \frac{\int d\mathbf{r}\psi_T^*(\mathbf{r}, \alpha)\psi_T(\mathbf{r}, \alpha)E_{loc}(\mathbf{r}, \alpha)}{\int d\mathbf{r}\psi_T^*(\mathbf{r}, \alpha)\psi_T(\mathbf{r}, \alpha)}, \qquad (2)$$

where the local energy $E_{loc}(\mathbf{r}, \alpha) = \frac{H\psi_T(\mathbf{r}, \alpha)}{\psi_T(\mathbf{r}, \alpha)}$ for the Quantum Harmonic Oscillator and Hydrogen atom is derived in Appendix 5.5. In this way, the energy $E(\alpha)$ can be interpreted as the expectation value of the local energy over the probability density $p_\alpha(\mathbf{r}) = \psi_T^*\psi_T / \int d\mathbf{r}\psi_T^*\psi_T$.

Monte Carlo integration consists of sampling N positions of the two electrons $\mathbf{r_i}$ from $p_\alpha(\mathbf{r})$ and approximating the integral as [4]:

$$E(\alpha) = \frac{1}{N}\sum_{i=1}^{N} E_{loc}(\mathbf{r_i}, \alpha) + O(N^{-1/2}) \qquad (3)$$

To sample positions from the probability density, we utilized the Metropolis algorithm.

2.3 Metropolis algorithm

In this section we will give a high level overview of the Metropolis algorithm, designed to produce samples of a desired distribution via a Markov chain. First, it starts from an initial state R_i, which for the case of the Helium atom is the position of the two electrons. Then, a trial move is performed, which for Helium is a random displacement of the two electrons within a cube of length d centered on their current positions. If the probability of the trial state R' is greater than the probability of the current state R, then the trial move is accepted, i.e., $R_{i+1} = R'$. However, if the opposite occurs, the trial move is accepted with probability $p(R')/p(R)$ and if it is rejected, we set $R_{i+1} = R$.

This procedure guarantees what is known in the literature as *detailed balance*. A derivation of why the Metropolis algorithm satisfies detailed balance can be found in Appendix 5.1. Furthermore, this condition ensures that the Markov chain converges to the desired probability distribution (a detailed proof for this statement is given in [4]).

Thus, we repeat the steps described for a burn-in period of 4000 steps and then start returning the Markov chain states until 30,000 positions have been sampled. Having obtained these samples, we can calculate the energy of the system with Equation 3.

Nevertheless, a key step of implementing the Metropolis algorithm efficiently is choosing the value of the maximum random trial move displacement d, which controls the portion of relevant space explored by the Markov chain. On the one hand, a large value will overshoot and end up in a low probability region, leading to a low acceptance ratio (ratio of accepted trial moves). On the other hand, if d is too low, the acceptance ratio will be high but a large portion of the relevant space will not be explored.

To choose the right value of d for our implementation, we tweaked it to find one that generates a Markov chain with an acceptance ratio of around 0.5. Moreover, we verified that the samples generated by the Metropolis algorithm indeed follow the desired probability density, as it is shown in Appendix 5.2. Finally, it is important to note that the main drawback of using Markov chains to generate samples of a probability distribution is that these are correlated. Inspired by the data-blocking method, our implementation samples one out of two Markov states (thinning factor = 2), which reduces the correlation without increasing the run time significantly.

2.4 Optimization

In order to leverage the variational algorithm, it is essential to define an update rule for the variational parameter α. For simplicity, we resort to a generic gradient-based update rule: gradient descent. In particular, recalling that we are seeking to minimize the energy E, for a given step size η, we determine the new variational parameter as

$$\alpha_{new} = \alpha_{old} - \eta \left(\frac{dE}{d\alpha} \right)_{old}. \qquad (4)$$

As derived in Appendix 5.4, the energy gradient is given by

$$\frac{dE}{d\alpha} = 2 \left(\left\langle E_{loc} \frac{d\ln(\Psi_T)}{d\alpha} \right\rangle - E \left\langle \frac{d\ln(\Psi_T)}{d\alpha} \right\rangle \right). \quad (5)$$

Noting that E is obtained as the expectation value of the local energy $E_{loc} = \frac{H\psi}{\psi}$, we identify $\frac{dE}{d\alpha}$ to be the (scaled) covariance of E_{loc} and $\frac{d\ln(\psi)}{d\alpha}$. Computationally, we determine both expectation values $\left\langle E_{loc} \frac{d\ln(\Psi_T)}{d\alpha} \right\rangle$ and $\left\langle \frac{d\ln(\Psi_T)}{d\alpha} \right\rangle$ parallel to computing $E = \left\langle E_{loc} \right\rangle$ for a given iteration of the MCMC sampling. The particular analytical expressions for $\frac{d\ln(\Psi_T)}{d\alpha}$ over the three different Hamiltonians in question are derived in Section 2.6.

2.5 Convergence criteria

When running the MCMC simulation, it is crucial to provide a certain stopping criterion, i.e. a condition that, when fulfilled, determines that our result is good enough. A really simple but

powerful idea for the cases of the Quantum Harmonic Oscillator and the Hydrogen atom is to characterise the convergence of the standard deviation of the system's energy. Indeed, the trial wavefunctions that are used in those two cases actually give exact solutions for the ground state, and thus their energy standard deviation must be 0 (as their energy is well defined). This is exactly the way we implemented our stopping criterion: when the standard deviation falls below a certain threshold, we consider to have converged and the program stops, returning the obtained values.

Now, this same criterion cannot be used for the Helium atom. Indeed, the trial wavefunction does not necessarily need to be an eigenfunction of the Hamiltonian (in this case, it is not). We then need to come up with another criterion to stop the program. For that, we first note that the variational parameter α will converge to that value that minimises the energy, as can be seen from Equation (4). With this idea in mind, we can then apply the following stopping criteria: if α has not *changed much* in the last five iterations, we then say that the system has converged. How much the value of α has changed is quantified by the relative difference between the last two values of α. If this relative difference falls below a threshold, we say that α *has not changed much*.

2.6 Trial wavefunction

Let us recall that the Quantum Harmonic Oscillator is given by the Hamiltonian in Equation (6) in normalised units (see Appendix 5.6):

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2. \quad (6)$$

The eigenstates of this Hamiltonian are given by the wavefunctions $\Psi_{QHO}(x) = f(x)e^{-\frac{x^2}{2}}$, with $f(x)$ a function related to the Hermite polynomials. The ground state has $f(x) = \frac{1}{\sqrt{2\pi}}$, and its energy is given by $E_{GS,QHO} = -\frac{1}{2}$. Thus, the trial wavefunction for the 1d Harmonic oscillator is

$$\Psi_{T,1dHO}(x) = e^{-\alpha x^2}, \quad (7)$$

which gives rise to the local energy

$$E_{loc,1dHO} = \frac{H\psi_T(x)}{\psi_T(x)} = \alpha + x^2\left(\frac{1}{2} - 2\alpha^2\right), \quad (8)$$

as derived in Appendix 5.5. For the optimization step, we identify

$$\frac{d\ln(\Psi_T)}{d\alpha} = \frac{d}{d\alpha}(-\alpha x^2) = -x^2. \quad (9)$$

When it comes to the Hydrogen atom, its Hamiltonian is found to be, in atomic units:

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r}. \quad (10)$$

Without entering into the theoretical details, this Hamiltonian can be analytically solved, obtaining all its eigenstates and eigenenergies. The ground state eigenfunction is simply $\psi(r) \propto e^{-r}$, where r is the L2 norm of the position vector of the electron in three-dimensional Cartesian space. Its ground state energy is $-\frac{1}{2}$ in atomic units [4], which corresponds to -13.6 eV (see Appendix 5.6) [5]. It is then sensible to consider as a trial wavefunction in this case:

$$\Psi_{T,Hydrogen}(r) = e^{-\alpha r}. \quad (11)$$

This gives rise to the local energy

$$E_{loc,Hydrogen} = \frac{H\psi_T(r)}{\psi_T(r)} = -\frac{1}{r} + \frac{\alpha}{r} - \frac{\alpha^2}{2}, \quad (12)$$

as derived in Appendix 5.5. For the optimization step, we identify

$$\frac{d\ln(\Psi_T)}{d\alpha} = \frac{d}{d\alpha}(-\alpha r) = -r. \quad (13)$$

Finally, the Helium atom is described by the normalised Hamiltonian:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\vec{r_1} - \vec{r_2}|}. \quad (14)$$

Unlike the two previous systems, the Helium atom does not have an analytical solution, making a numerical solution a necessity. Experimental studies of Helium's ground state energy have found an approximate value of $E_{GS,He} \approx -79$ eV [5]. Accordingly, a *good* numerical approximation of Helium's ground state energy must

be around this value.

Skipping the details, the trial wavefunction in this situation will be composed of two terms: one being the Slater determinant, which describes the anti-symmetric behaviour of fermions, and a second encoding two-particle correlation effects [4]. This results in the trial wavefunction:

$$\Psi_T(\vec{r}_1, \vec{r}_2) = \exp\left[-2r_1 - 2r_2 + \frac{r_{12}}{2(1 + \alpha r_{12})}\right], \quad (15)$$

where $\vec{r}_1$ and $\vec{r}_2$ denote the vectorial positions of the two electrons, $r_{12} = \|\vec{r}_1 - \vec{r}_2\|$, and α the variational parameter. The local energy is given by the expression:

$$E_L(\vec{r}_1, \vec{r}_2) = -4 + (\hat{r}_1 - \hat{r}_2)(\vec{r}_1 - \vec{r}_2)\frac{1}{r_{12}(1 + \alpha r_{12})^2}$$
$$- \frac{1}{r_{12}(1 + \alpha r_{12})^3} - \frac{1}{4(1 + \alpha r_{12})^4} + \frac{1}{r_{12}}, \quad (16)$$

where $\hat{r}_1$ and $\hat{r}_2$ are the normalised unit vectors in the respective directions of $\vec{r}_1$ and $\vec{r}_2$.

To update the variational parameter α, we need to compute:

$$\ln(\Psi_T) = -2r_1 - 2r_2 + \frac{r_{12}}{2(1 + \alpha r_{12})}$$
$$\implies \frac{d\ln(\Psi_T)}{d\alpha} = -\frac{r_{12}^2}{2(1 + \alpha r_{12})^2}. \quad (17)$$

We then get that α is updated accordingly to the expression $\alpha_{new} = \alpha_{old} - \gamma\left(\frac{dE}{d\alpha}\right)_{old}$, where

$$\frac{dE}{d\alpha} = 2\left(\langle E_L\rangle\left\langle \frac{r_{12}^2}{2(1 + \alpha r_{12})^2}\right\rangle\right.$$
$$\left. - \left\langle E_L \cdot \frac{r_{12}^2}{2(1 + \alpha r_{12})^2}\right\rangle\right). \quad (18)$$

Jos Thijssen found in his book [4] the values shown in the Table 0.

Helium atom		
α	$\langle E\rangle$	$\text{var}(\langle E\rangle)$
0.05	$-2.8713(4)$	$0.1749(2)$
0.075	$-2.8753(4)$	$0.1531(2)$
0.10	$-2.8770(3)$	$0.1360(2)$
0.125	$-2.8780(4)$	$0.1223(2)$
0.15	$-2.8778(3)$	$0.1114(2)$
0.175	$-2.8781(3)$	$0.1028(2)$
0.20	$-2.8767(4)$	$0.0968(2)$
0.25	$-2.8746(10)$	$0.0883(2)$

Figure 0: $\langle E\rangle$ and $\text{Var}(\langle E\rangle)$ in terms of the variational parameter α.

3 Results

3.1 1D Quantum Harmonic Oscillator

The 1-Dimensional Quantum Harmonic Oscillator (QHO) corresponds to the first and easiest model we can think of to implement and test our MCMC model on a quantum system. By only having one variable in the trial wavefunction, its numerical treatment is straightforward. Additionally, this system is analytically solvable, as seen in Subsection 2.6. With the trial wavefunction in (7) we expect to find the ground energy for the variational parameter $\alpha = \frac{1}{2}$. This is confirmed by our simulation, as visualised in Figure 1.
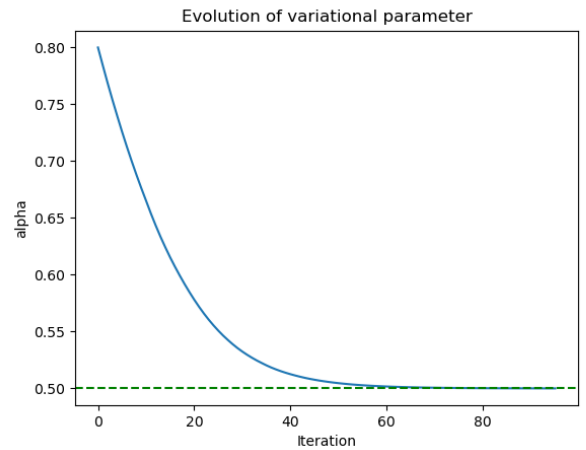

Figure 1: Evolution of the variational parameter in terms of the number of iterations performed in the case of the QHO. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d 1.7; GD_stepsize 0.25.

The expected ground state energy is $E_{GS,QHO} = -\frac{1}{2}$ (in normalised units), which is

also verified in the simulation as shown in Figure 2. These results confirm the correct functioning of our MCMC model, as it accurately finds the analytical result for the ground state energy of the 1D QHO.
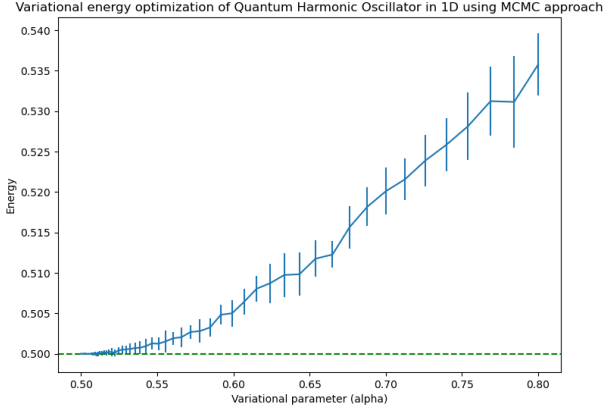

Figure 2: Evolution of the energy in terms of variational parameter for the QHO. The initial variational parameter is $\alpha = 0.8$. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d = 1.7; GD_stepsize 0.25.

3.2 Hydrogen atom

We are then ready to apply our MCMC model to a more complex system, the Hydrogen atom. This also provides a more interesting problem to study, as it presents a higher dimensionality than the QHO[1], while still being possible to obtain an analytical result to compare with.

The optimal variational parameter is found to be $\alpha = 1$ in our simulation, as can be seen in Figures 3 and 4. Note that the convergence is achieved either if we start with $\alpha < 1$ or $\alpha > 1$. This convergence coincides with the analytical result, as can be seen from the ground state wavefunction mentioned in Section 2.6.
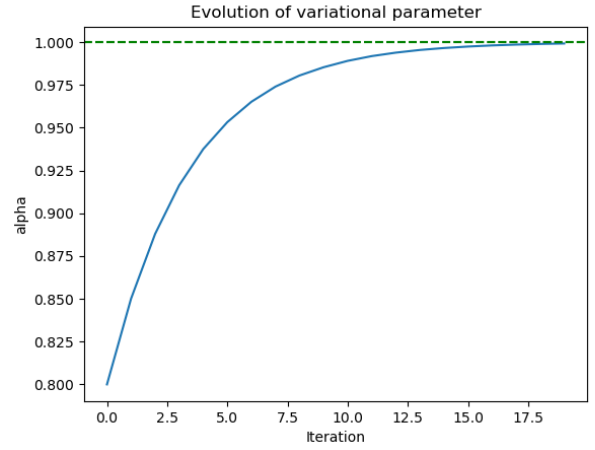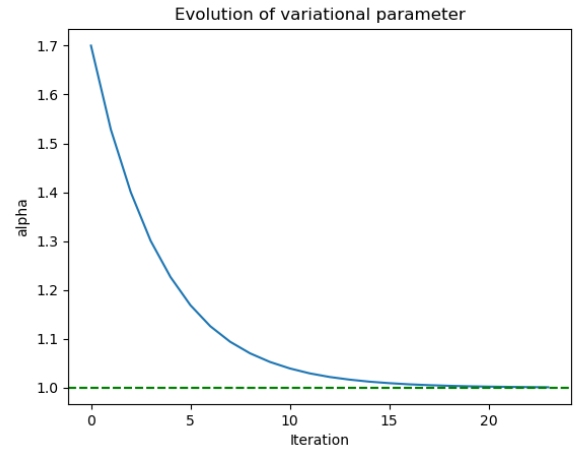

Figure 3: Evolution of the variational parameter in terms of the number of iterations performed in the case of the Hydrogen atom. The initial value was selected to be $\alpha = 0.8$. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d 1.45; GD_stepsize 0.25.

Figure 4: Evolution of the variational parameter in terms of the number of iterations performed in the case of the Hydrogen atom. The initial value was selected to be $\alpha = 1.7$. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d 1.45; GD_stepsize 0.25.

The energy is seen to converge to $-\frac{1}{2}$, as seen in Figures 5 and 4, resulting in the expected result. We numerically obtain the ground state energy $E_{GS,H} = (-2,1799 \pm 0,0033) \cdot 10^{-18} J = -13,607 \pm 0,025$ eV, which coincides with experimental results [5].

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[1]Keep in mind that Monte Carlo methods offer a great advantage in large dimensional problems compared with integration methods, as the error always decreases with $\frac{1}{\sqrt{N}}$, independently on the dimensionality of the Hamiltonian.
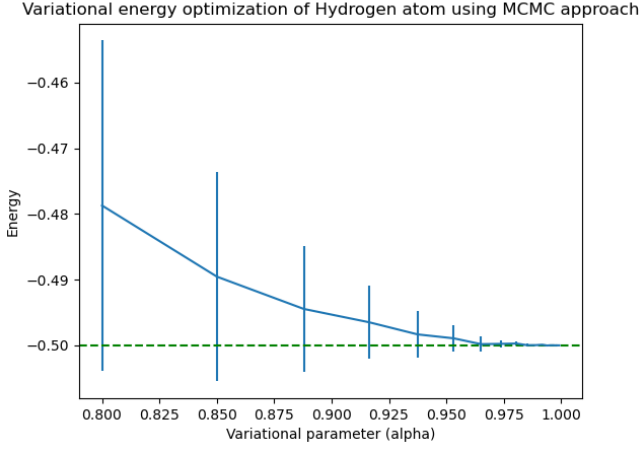
Figure 5: Evolution of the energy in terms of the variational parameter for the Hydrogen atom. The initial value was selected to be $\alpha = 0.8$. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d 1.45; GD_stepsize 0.25.
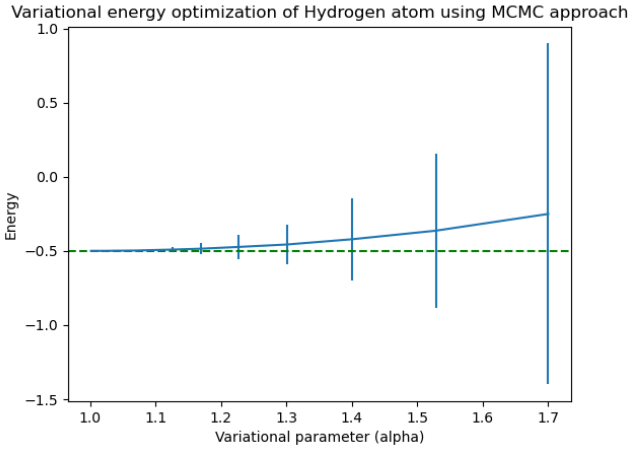

Figure 6: Evolution of the energy in terms of the variational parameter for the Hydrogen atom. The initial value was selected to be $\alpha = 1.7$. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d 1.45; GD_stepsize 0.25.

3.3 Helium atom

Having tested our MCMC simulation on systems that have analytical solutions to compare with, it is then interesting to use it on a system that does not have one. This is the case of the Helium atom. With the trial wavefunction discussed in 2.6 and with the convergence criteria explored in Section 2.5, we obtain the Figures 7 and 8, show-

ing the convergence of the variational parameter to a value around 0.148. This value may come as a surprise when compared to Figure 0, showing the values obtained by Thijssen. Indeed, he found that the value of α minimising the energy is 0.175, which slightly differs from our result.
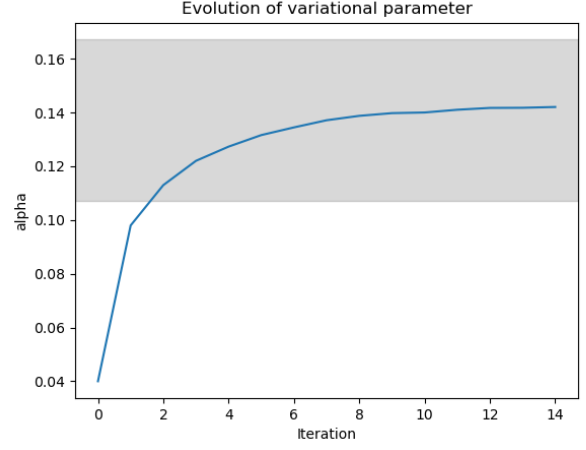

Figure 7: Evolution of the variational parameter in terms of the number of iterations performed in the case of the Helium atom. The initial value was selected to be $\alpha = 0.04$. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d 0.48; GD_stepsize 0.25.
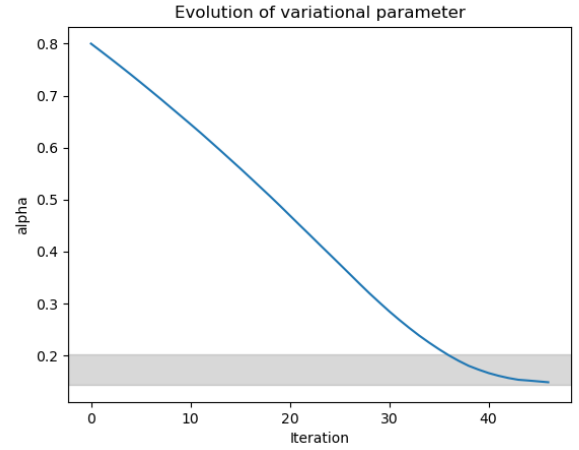

Figure 8: Evolution of the variational parameter in terms of the number of iterations performed in the case of the Helium atom. The initial value was selected to be $\alpha = 0.8$. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d 0.48; GD_stepsize 0.25.

However, before drawing any conclusion, it is worth taking a look at the evolution of the energy when varying the parameter α. This can be visualised in Figures 9 and 10. We can see

that energy presents a valley for values of α between 0.11 and 0.18 (approximately), where the energy is mostly the same. This coincides with the results from Thijssen, where the energies for $\alpha = 0.125$, 0.15 and 0.175 are almost the same. In this sense, we can say that we are in accordance with his results.
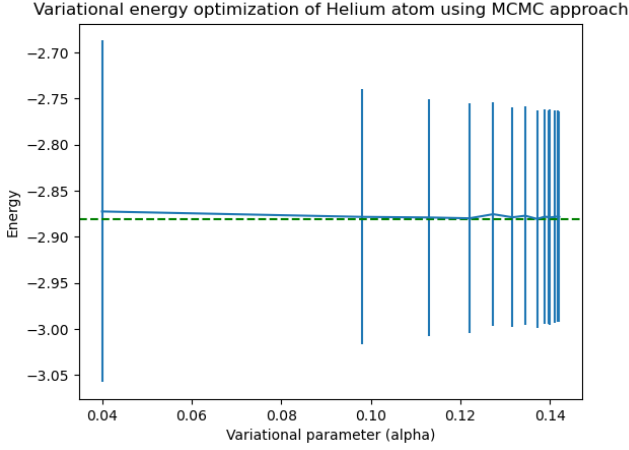

Figure 9: Evolution of the energy in terms of the variational parameter for the Helium atom. The initial value was selected to be $\alpha = 0.04$. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d 0.48; GD_stepsize 0.25.
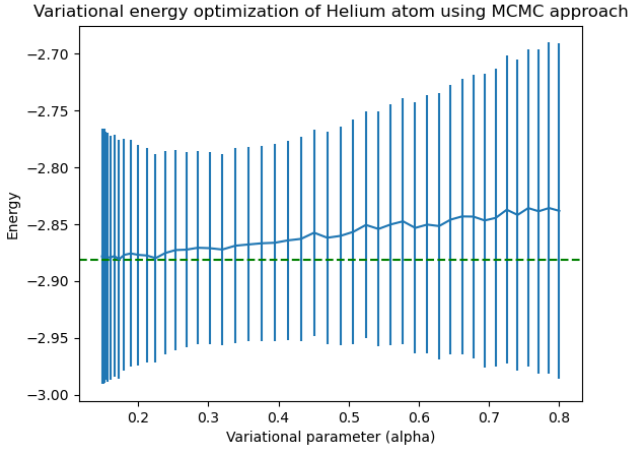

Figure 10: Evolution of the energy in terms of the variational parameter for the Helium atom. The initial value was selected to be $\alpha = 0.8$. Parameters: 30000 samples; burn_in_period 4000; thinning_factor 2; d 0.48; GD_stepsize 0.25.

On the other hand, a difference appears when we compare the values for the energy. In normalised units, we found a ground state

energy of -2.8809, which deviates from Thijssen's result of -2.8781. Nevertheless, if we take into account the standard deviations, we find that the values match between our simulation and Thijssen's table. Indeed, we find a standard deviation of 0.34 (i.e. a variance of 0.1156), in concordance with Thijssen's variance. Additionally, accounting for this standard deviation, the value -2.8781 is inside the range -2.8809 ± 0.34, signifying that our simulation is indeed in agreement with Thijssen.

Furthermore, if we convert our ground state energy to SI units, we obtain $E_{GS,He} = (-1.26 \pm 0.14) \cdot 10^{-17} J = -78.4 \pm 9.4$ eV. Consequently, our simulation correctly predicts the experimental result of -79 eV [5].

3.4   Performance Analysis

In order to gauge how well our variational quantum algorithm performs in terms of efficiency, we compare the runtime of different numbers of MCMC samples used for the Metropolis algorithm. Since the generation of such samples displays the highest computational cost, we expect the runtime of the entire program to scale with the time complexity of sample generation, which is linear. Indeed, as Figure 11 verifies, the simulation time scales favourably from $5,000$ to $30,000$ samples.
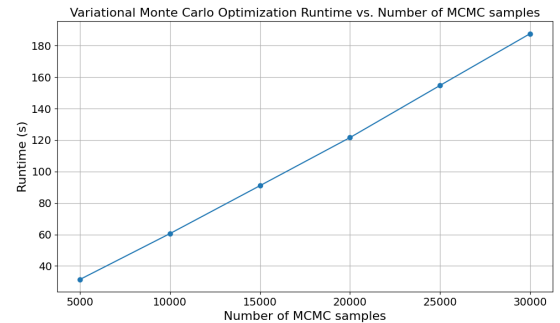

Figure 11: Simulation time per number of MCMC samples in variational quantum MC simulation: Hydrogen Atom Ground State, 20 samplers, burn-in period 10%, lr $= 0.1$, d $= 1.45$, convergence_crit $= 1e - 3$, thinning_factor=1.

4   Conclusion

In this report, we presented the implementation of the Variational Monte Carlo (VMC) method to obtain the ground state energy of three quantum mechanical systems: the quantum harmonic oscillator, the Hydrogen atom, and the Helium atom. The first two systems allow for analytical solutions for their eigenenergies and eigenfunctions, making them suitable for testing and debugging the algorithm. After verifying that the program is well-functioning, we studied the Helium atom, a more complex system with a larger number of degrees of freedom. By studying the convergence of the energy, we were able to reproduce the results found by J. Thijssen [4], as well as obtain a ground state energy that is in agreement with experimental values [5].

With this model in place, future research could focus on its use for even more complex atoms, such as Lithium, Carbon, or Fluorine atoms. Another possible line of investigation could be the implementation of the VMC method to problems other than ground state calculation, such as phase transition in different materials [6] or for exoplanet observation in astrophysics [7].

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5 Appendix

5.1 Derivation of detailed balance for Metropolis algorithm

In order to see why the Metropolis acceptance rule leads to detailed balance, first recall the general requirement of detailed balance:

$$p(R)T(R \mapsto R') = p(R')T(R' \mapsto R).$$

Now the Metropolis transition rate is defined as

$$T(R \mapsto R') = w_{RR'} A_{RR'}, \tag{19}$$

where the trial move probabilities satisfy $w_{RR'} = w_{R'R}$, and the acceptance ratio is defined via cases as

$$A_{RR'} = \begin{cases} 1, & \text{if } p(R') > p(R) \\ \frac{p(R')}{p(R)}, & \text{if } p(R') < p(R). \end{cases} \tag{20}$$

Hence, we consider the two cases separately.

Firstly, if $p(R') > p(R)$, then we have

$$p(R)T(R \mapsto R') = p(R)w_{RR'} A_{RR'} = p(R)w_{RR'} = p(R')w_{RR'}\frac{p(R)}{p(R')} = p(R')w_{R'R}A(R'R)$$
$$= p(R')T(R' \mapsto R), \tag{21}$$

where we have multiplied by $\frac{p(R')}{p(R')} = 1$ for equality 3, used symmetry of trial moves as well as the acceptance rule $A_{R'R}$ (with $p(R') > p(R)$) for equality 4, and applied the definition of the transition rate to obtain the final term. The chain of equalities verifies that detailed balance is satisfied with the given Metropolis update in the first case.

Secondly, if $p(R') < p(R)$, then we have

$$p(R)T(R \mapsto R') = p(R)w_{RR'} A_{RR'} = p(R)w_{RR'}\frac{p(R')}{p(R)} = p(R')w_{RR'} = p(R')w_{R'R}A(R'R)$$
$$= p(R')T(R' \mapsto R), \tag{22}$$

where we have used that $A(R'R) = 1$ for the case that $p(R') < p(R)$. Hence, detailed balance is satisfied in the second case as well.

As shown above, detailed balance is satisfied for both cases, completing the proof that the Metropolis algorithm, and in particular its acceptance rule, satisfies this principle.

5.2 Validation of the Metropolis algorithm

To validate the correctness of our implementation of the Metropolis algorithm, we had to verify two aspects. First, we ensured that the maximum random displacement d yielded an acceptance ratio γ close to 0.5 for the initial variational parameter α. The optimal values of d and the corresponding acceptance ratios for each of the quantum systems are:

- Quantum Harmonic oscillator: $d = 1.7$, $\alpha = 0.8 \implies \gamma = 0.488$

- Hydrogen atom: $d = 1.45$, $\alpha = 0.8 \implies \gamma = 0.517$

- Helium atom: $d = 0.48$, $\alpha = 0.12 \implies \gamma = 0.502$

Secondly, we ensured that th e positions sampled by the Metropolis algorithm follow the desired probability distribution. To verify this, we generated histograms of the sampled positions for the quantum harmonic oscillator and the Hydrogen atom [2]. For the latter, we sample 3D Cartesian coordinates, but in the histogram we can represent the probability distribution of the electron being at a distance r. It is important to note that this probability density is not given by $|\psi|^2$ but by the radial probability density in spherical coordinates $4\pi r^2 |\psi|^2$, where the trial wave function ψ of each system is described in section 2.6. Figure 12 shows that for both systems, the Metropolis algorithm samples follow the desired distribution, where we have used 60000 samples and a burn-in period of 8000 steps.

(a) Quantum Harmonic Oscillator
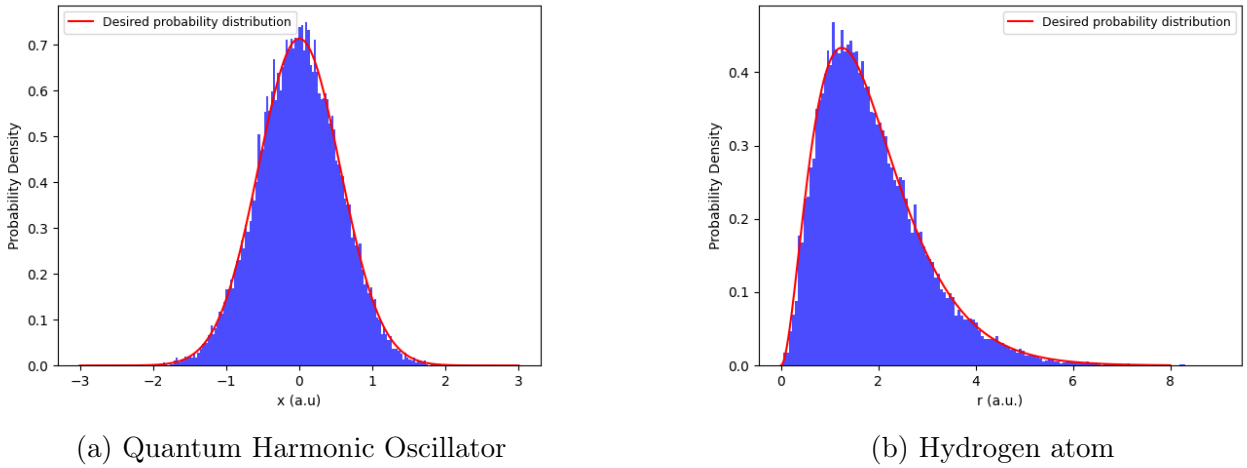
(b) Hydrogen atom

Figure 12: Histogram of the positions sampled by the Metropolis algorithm for a) Quantum Harmonic Oscillator, and b) Hydrogen atom. The red line represents the desired probability density.

5.3 Profiler information for performance analysis

This is the (truncated) profiler output of our Metropolis algorithm to find the ground state energy of the Hydrogen atom, with $20,000$ samples, sorted by decreasing internal execution time, as described in Section 3.4. We find that the Metropolis sampling is the most compute-intensive function, as expected.

```
  ncalls  tottime  percall  cumtime  percall filename:lineno(function)
   309/1    0.002    0.000  195.560  195.560 {built-in method builtins.exec}
       1    0.155    0.155  195.559  195.559 <string>:1(<module>)
    1060   66.361    0.063  141.474    0.133 .functions.py:58(metropolis)
44522120   41.419    0.000   66.171    0.000 .numpy/linalg/_linalg.py:2575(norm)
23321060   20.003    0.000   64.964    0.000 .functions.py:8(trial_wavefunction)
    1060    7.429    0.007   53.301    0.050 .functions.py:177(energy)
21200000   11.818    0.000   43.581    0.000 .functions.py:129(local_energy)
44521061   11.484    0.000   11.484    0.000 {method 'dot' of 'numpy.ndarray' objects}
23321060   10.121    0.000   10.121    0.000 .functions.py:42(probability_density)
23321060    8.538    0.000    8.538    0.000 {method 'astype' of 'numpy.generic' objects
```

[2]The higher dimensionality of the Helium atom makes it less convenient for visualization.

```
44521065    4.780    0.000    6.112    0.000 .numpy/linalg/_linalg.py:128(isComplexType)
44521062    3.863    0.000    3.863    0.000 {method 'ravel' of 'numpy.ndarray' objects}
89054227    2.890    0.000    2.890    0.000 {built-in method builtins.issubclass}
44522120    2.143    0.000    2.143    0.000 .numpy/linalg/_linalg.py:2571(_norm_dispatc
44522161    1.632    0.000    1.632    0.000 {built-in method numpy.asarray}
42442855    1.179    0.000    1.179    0.000 {method 'append' of 'list' objects}
    9342    1.057    0.000    1.057    0.000 {built-in method numpy.asanyarray}
```

5.4   Derivation of energy gradient

In the following, we derive that the energy gradient is given by the formula

$$\frac{dE}{d\alpha} = 2\Big(\langle E_{loc}\frac{d\ln(\Psi_T)}{d\alpha}\rangle - E\,\langle\frac{d\ln(\Psi_T)}{d\alpha}\rangle\Big). \tag{23}$$

Firstly, note that we have

$$E_\alpha(r) = \frac{\int \Psi_T^*(r)H\Psi_T(r)dr}{\int \Psi_T^*(r)\Psi_T(r)dr} = \frac{\int |\Psi_T(r)|^2 E_{loc}dr}{\int |\Psi_T(r)|^2 dr}. \tag{24}$$

Then we can apply the quotient rule to write (dropping the function arguments and indices for convenience)

$$\frac{dE}{d\alpha} = \frac{d}{d\alpha}\frac{\int |\Psi|^2 E_{loc}dr}{\int |\Psi|^2 dr} = \frac{\left(\frac{d}{d\alpha}\int |\Psi|^2 E_{loc}dr\right)\int |\Psi|^2 dr - \int |\Psi|^2 E_{loc}dr\left(\frac{d}{d\alpha}\int |\Psi|^2 dr\right)}{(\int |\Psi|^2 dr)^2}. \tag{25}$$

Justified by the dominated convergence theorem, we may interchange the order of operators in the numerator to write

$$\begin{aligned}
\frac{dE}{d\alpha} &= \frac{\left(\int \frac{d}{d\alpha}(|\Psi|^2 E_{loc})dr\right)\int |\Psi|^2 dr - \int |\Psi|^2 E_{loc}dr\left(\int \frac{d}{d\alpha}|\Psi|^2 dr\right)}{(\int |\Psi|^2 dr)^2} \\
&= \frac{\left(\int(\frac{d}{d\alpha}|\Psi|^2)E_{loc} + |\Psi|^2(\frac{d}{d\alpha}E_{loc})dr\right)\int |\Psi|^2 dr - \int |\Psi|^2 E_{loc}dr\left(\int \frac{d}{d\alpha}|\Psi|^2 dr\right)}{(\int |\Psi|^2 dr)^2} \\
&= \frac{\int(\frac{d}{d\alpha}|\Psi|^2)E_{loc}dr}{\int |\Psi|^2 dr} + \frac{\int |\Psi|^2(\frac{d}{d\alpha}E_{loc})dr}{\int |\Psi|^2 dr} - \frac{\int |\Psi|^2 E_{loc}dr\left(\int \frac{d}{d\alpha}|\Psi|^2 dr\right)}{(\int |\Psi|^2 dr)^2},
\end{aligned} \tag{26}$$

where we further applied the product rule to the first term of the expression. Next, we use two lemmas that will help us to further simplify Equation 26.

Lemma 5.1.

$$\frac{d}{d\alpha}|\Psi|^2 = 2|\Psi|^2\frac{d}{d\alpha}\ln(\Psi). \tag{27}$$

Proof. Assuming that Ψ is real for simplicity,[3] we have

$$\frac{d}{d\alpha}|\Psi|^2 = \frac{d}{d\alpha}\Psi^*\Psi = 2\Psi\frac{d}{d\alpha}\Psi = 2\Psi^2\frac{\frac{d}{d\alpha}\Psi}{\Psi} = 2\Psi^2\frac{d}{d\alpha}\ln(\Psi) = 2|\Psi|^2\frac{d}{d\alpha}\ln(\Psi). \tag{28}$$

$\square$

---

[3]This restriction is not necessary, but simplifies the argument. Also note that all wave functions considered in this paper are real-valued.

Lemma 5.2.

$$\frac{d}{d\alpha}E_{loc} = \frac{H\frac{d}{d\alpha}\Psi}{\Psi} - E_{loc}\frac{d}{d\alpha}\ln\Psi. \tag{29}$$

Proof. This lemma follows directly by applying the quotient rule and noting that $\frac{d}{d\alpha}\ln(\Psi) = \frac{\frac{d}{d\alpha}\Psi}{\Psi}$, as in the previous lemma. $\qquad\square$

Using the lemmata, we proceed to analyze the three terms in Equation 26 separately. Firstly, by Lemma 27, we have

$$\frac{\int(\frac{d}{d\alpha}|\Psi|^2)E_{loc}dr}{\int|\Psi|^2dr} = \frac{\int 2|\Psi|^2\frac{d\ln(\Psi)}{d\alpha}E_{loc}dr}{\int|\Psi|^2dr} = 2\int\frac{|\Psi|^2}{\int|\Psi|^2dr}\frac{d\ln(\Psi)}{d\alpha}E_{loc}dr = 2\left\langle\frac{d\ln(\Psi)}{d\alpha}E_{loc}\right\rangle. \tag{30}$$

It should be noted that this is not a quantum-mechanical, but a statistical expectation value in the limit of the MCMC sampling procedure.

Secondly, by Lemma 29, we have

$$\begin{aligned}
\frac{\int|\Psi|^2(\frac{d}{d\alpha}E_{loc})dr}{\int|\Psi|^2dr} &= \frac{\int|\Psi|^2(\frac{H\frac{d}{d\alpha}\Psi}{\Psi} - E_{loc}\frac{d}{d\alpha}\ln(\Psi))dr}{\int|\Psi|^2dr} = \frac{\int|\Psi|^2(\frac{H\frac{d}{d\alpha}\Psi}{\Psi} - \frac{H\Psi}{\Psi}\frac{d}{d\alpha}\ln(\Psi))dr}{\int|\Psi|^2dr} \\
&= \frac{\int|\Psi|^2(\frac{1}{\Psi}(H\frac{d}{d\alpha}\Psi - H\Psi\frac{\frac{d}{d\alpha}\psi}{\Psi}))dr}{\int|\Psi|^2dr} = \frac{\int|\Psi|^2(\frac{1}{\Psi}(H\frac{d}{d\alpha}\Psi - H\Psi\frac{\frac{d}{d\alpha}\Psi}{\Psi}))dr}{\int|\Psi|^2dr},
\end{aligned} \tag{31}$$

where we write $\frac{d}{d\alpha}\Psi = f_\alpha\Psi$ for some coefficient function f_α.[4] It follows that

$$\frac{\int|\Psi|^2(\frac{d}{d\alpha}E_{loc})dr}{\int|\Psi|^2dr} = \frac{\int|\Psi|^2(\frac{1}{\Psi}(Hf_\alpha\Psi - H\Psi\frac{f_\alpha\Psi}{\Psi}))dr}{\int|\Psi|^2dr} = \frac{\int|\Psi|^2(\frac{1}{\Psi}(Hf_\alpha\Psi - Hf_\alpha\Psi))dr}{\int|\Psi|^2dr} = 0, \tag{32}$$

such that the second term in Equation 26 vanishes.

Lastly, by Lemma 29 again, we have

$$\begin{aligned}
\frac{\int|\Psi|^2E_{loc}dr\left(\int\frac{d}{d\alpha}|\Psi|^2dr\right)}{(\int|\Psi|^2dr)^2} &= \frac{\int|\Psi|^2E_{loc}dr\left(2\int|\Psi|^2\frac{d}{d\alpha}\ln(\Psi)dr\right)}{(\int|\Psi|^2dr)^2} = 2\frac{\int|\Psi|^2E_{loc}dr}{\int|\Psi|^2dr}\frac{\int|\Psi|^2\frac{d}{d\alpha}\ln(\Psi)dr}{\int|\Psi|^2dr} \\
&= 2\int\frac{|\Psi|^2}{\int|\Psi|^2dr}E_{loc}dr\int\frac{|\Psi|^2}{\int|\Psi|^2dr}\frac{d\ln(\Psi)}{d\alpha}dr = 2\left\langle E_{loc}\right\rangle\left\langle\frac{d\ln(\Psi)}{d\alpha}\right\rangle,
\end{aligned} \tag{33}$$

where the last expression is again a statistical expectation value.

Combining the three parts terms of Equation 26, we find

$$\frac{dE}{d\alpha} = 2\left\langle\frac{d\ln(\Psi)}{d\alpha}E_{loc}\right\rangle - 2\left\langle E_{loc}\right\rangle\left\langle\frac{d\ln(\Psi)}{d\alpha}\right\rangle = 2\left(\left\langle\frac{d\ln(\Psi)}{d\alpha}E_{loc}\right\rangle - E\left\langle\frac{d\ln(\Psi)}{d\alpha}\right\rangle\right), \tag{34}$$

as desired.

5.5   Derivation of local energies

In the following, we derive the expressions for the local energy for the cases of the 1D Harmonic Oscillator and the Hydrogen atom. We recall that the local energy is given by

$$E_{loc} = \frac{H\Psi_T}{\Psi_T}. \tag{35}$$

---

[4]This is of course not justified in general, but since we are working with exponential trial function, we employ this rather strong assumption in order to get traction on simplifying the expression.

5.5.1   1d Harmonic oscillator

The 1d Harmonic oscillator is characterized by the Hamiltonian

$$H_{1dHO} = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{1}{2}x^2. \tag{36}$$

As trial wave function, we employ

$$\Psi_{T,1dHO}(x) = e^{-\alpha x^2}, \tag{37}$$

where we know by analytical results that the true ground state wave function lies in the subspace of this parameterized family of functions. Then we can write

$$
\begin{aligned}
E_{loc} &= \frac{H\Psi_T}{\Psi_T} = \frac{\left(-\frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{1}{2}x^2\right)e^{-\alpha x^2}}{e^{-\alpha x^2}} = \frac{-\frac{1}{2}\left(-2\alpha e^{-\alpha x^2} + 4\alpha^2 x^2 e^{-\alpha x^2}\right) + \frac{1}{2}x^2 e^{-\alpha x^2}}{e^{-\alpha x^2}} \\
&= \alpha + x^2\left(\frac{1}{2} - 2\alpha^2\right).
\end{aligned} \tag{38}
$$

5.5.2   Hydrogen atom

The Hydrogen atom is characterized by the Hamiltonian

$$H_{Hydrogen} = -\frac{1}{2}\nabla^2 - \frac{1}{r}. \tag{39}$$

As trial wave function, we use

$$\Psi_{T,Hydrogen}(r) = e^{-\alpha r}. \tag{40}$$

Again, the true ground state wave function lies in the subspace of this parameterized family of functions. Then we can write

$$
\begin{aligned}
E_{loc} &= \frac{H\Psi_T}{\Psi_T} = \frac{\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)e^{-\alpha r}}{e^{-\alpha r}} = \frac{\left(-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{1}{r}\right)e^{-\alpha r}}{e^{-\alpha r}} \\
&= -\frac{1}{2}\left(-\frac{\alpha}{r} + \frac{\alpha x^2}{r^3} + \frac{\alpha^2 x^2}{r^2} - \frac{\alpha}{r} + \frac{\alpha y^2}{r^3} + \frac{\alpha^2 y^2}{r^2} + -\frac{\alpha}{r} + \frac{\alpha z^2}{r^3} + \frac{\alpha^2 z^2}{r^2}\right) - \frac{1}{r} \\
&= -\frac{1}{2}\left(-\frac{3\alpha}{r} + \frac{\alpha}{r^3}r^2 + \frac{\alpha^2}{r^2}r^2\right) - \frac{1}{r} = -\frac{1}{r} + \frac{\alpha}{r} - \frac{\alpha^2}{r},
\end{aligned} \tag{41}
$$

where the fourth equality follows directly from applying, without loss of generality, the following equality on all three Cartesian components:

$$
\begin{aligned}
\frac{\partial^2}{\partial x^2}e^{-\alpha r} &= \frac{\partial^2}{\partial x^2}e^{-\alpha(x^2+y^2+z^2)^{1/2}} = \frac{\partial}{\partial x}\left(-\alpha x(x^2+y^2+z^2)^{-1/2}e^{-\alpha(x^2+y^2+z^2)^{1/2}}\right) \\
&= e^{(x^2+y^2+z^2)^{1/2}}\left(-\alpha(x^2+y^2+z^2)^{-1/2} + \alpha x^2(x^2+y^2+z^2)^{-3/2} + \alpha^2 x^2(x^2+y^2+z^2)^{-1}\right) \\
&= e^{-\alpha r}\left(-\alpha r^{-1} + \alpha x^2 r^{-3} + \alpha^2 x^2 r^{-2}\right).
\end{aligned} \tag{42}
$$

5.6   Normalised units

Henceforth, a variable $\tilde{A}$ will denote its expression in SI units, while A will represent its dimensionless counterpart.

5.6.1 1D Quantum Harmonic Oscillator

The 1D QHO is characterised by the Hamiltonian:

$$\tilde{H} = -\frac{\hbar^2}{2m}\frac{d^2}{d\tilde{x}^2} + \frac{1}{2}m\omega^2\tilde{x}^2 \tag{43}$$

As a consequence of its physical meaning, the Hamiltonian clearly has units of energy. On the other hand, $[\hbar] = J \cdot s$ and $[\omega] = s^{-1}$. Then, defining the normalised Hamiltonian $H = \frac{\tilde{H}}{\hbar\omega}$, and the normalised position as $x = \sqrt{\frac{m\omega}{\hbar}}\tilde{x}$, we obtain the expression (44)

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2. \tag{44}$$

5.6.2 Hydrogen and Helium atoms

Let us first take a look at the case of the Hydrogen atom. Its Hamiltonian is given by equation (45).

$$\tilde{H} = -\frac{\hbar^2}{2m}\tilde{\nabla}^2 - \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{\tilde{r}}. \tag{45}$$

In order to normalise this Hamiltonian, let us recall the fine-structure constant $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$, a dimensionless quantity, and the Bohr radius $a_0 = \frac{\hbar}{m_e\alpha c}$, with dimensions of distance. With these two constants, we can rewrite equation (45) as:

$$\tilde{H} = -\frac{1}{2}\alpha c a_0 \hbar \tilde{\nabla}^2 - m_e \alpha^2 c^2 a_0 \cdot \frac{1}{\tilde{r}}. \tag{46}$$

Then, defining the atomic distances $x = \frac{\tilde{x}}{a_0}$, $y = \frac{\tilde{y}}{a_0}$ and $z = \frac{\tilde{z}}{a_0}$, we also then obtain $r = \frac{\tilde{r}}{a_0}$, $\frac{\partial^2}{\partial x^2} = \frac{1}{a_0^2}\frac{\partial^2}{\partial \tilde{x}^2}$ and analogously for y and z. Therefore, the Hamiltonian can be rewritten as

$$\tilde{H} = -\frac{1}{2}\frac{\alpha c\hbar}{a_0}\nabla^2 - \frac{\alpha c\hbar}{a_0}\frac{1}{r}. \tag{47}$$

By expressing $\eta = \frac{\alpha c\hbar}{a_0}$, and defining the normalised Hamiltonian $H = \frac{1}{\eta}\tilde{H}$, we finally come to the dimensionless expression of the Hydrogen Hamiltonian:

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r}. \tag{48}$$

The case of the Helium atom is completely analogous. Indeed, its Hamiltonian is given by:

$$\tilde{H} = \tilde{H}_1 + \tilde{H}_2 + \tilde{V}_{int}, \tag{49}$$

where H_1 and H_2 are the individual non-interacting Hamiltonians of each electron, mathematically represented as:

$$\tilde{H}_j = -\frac{\hbar^2}{2m}\tilde{\nabla}_j^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_j}, \quad j \in \{1, 2\}, \tag{50}$$

where Z is the atomic number. In the case of Helium $Z = 2$. The additional term $\tilde{V}_{int} = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|}$ symbolises the electron-electron interaction of the Hamiltonian. By comparing the expressions (45) and (49), we can straightforwardly deduce that we can use the same normalised variables used for the Hydrogen case for the Helium system. Accordingly, the Helium Hamiltonian in normalised units is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}. \tag{51}$$

Note on authorship: All three authors contributed equally to the project, with tasks clearly defined and split as documented in the weekly journals. This is also reflected in consistent commits of all team members.