Project 5
Computational Physics
github.com/fariag

Faria Ghaffar

December 18, 2019

1 Abstract

The aim of this report is to study the properties of a quantum dots with two electrons in three dimensions, using the Variational Monte Carlo method to evaluate the ground state energy, relative distance between the electrons and expectation values of the energies. Using this method, we will compare the results with those obtained from an eigenvalue approach, and prove how Monte Carlo is way more effective.

2 Introduction

Quantum dots are nanoparticles made from semiconducting materials. The electrons inside of them are confined in all three spatial directions and, consequently, can only occupy defined energy levels. As a result of this, these tiny particles can have different optical and electrical properties to a large quantity of the same material, thus they are exceptionally useful in nanotechnology. Relevant applications of quantum dots cover medical imaging, lasers and quantum computing, among many others. These particles are a broad field of research nowadays, and therefore it is of our interest to study their behaviour. We are interested in a system of two electrons confined in a quantum dot. By using the Variational Monte Carlo method, based on the variational principle to approximate the ground state of a quantum system, we will evaluate the lowest energy state, the expectation values of the potential and kinetic energy and the relative distance between the two electrons considered in a stochastic way, comparing the results obtained to those acquired in project number two, where eigenvalue solvers were used. In the present report, we began by presenting the scheme theoretically. All of the vatiational method that has been used is expounded subsequently along with a brief guide of how to implement the code to resolve the desired problem. Results are critically discussed for the several subprob-

lems and a conclusion is presented at the end where we offer a summary of the outcomes.

3 Theory

The electrons confined in the quantum dots can be described as a system of electrons trapped in a three dimensional harmonic oscillator potential. For such a system, the Hamiltonian is given by the following expression.

$$H_0 = \Sigma_{i=1}^{N}(-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 r_i^2) \tag{1}$$

However, when considering electrons interacting with each other, it is also necessary to include the repulsive interaction between them, which is given by the extra term

$$H_1 = \Sigma_{i<j}\frac{1}{r_{ij}} \tag{2}$$

where $r_{ij} = \sqrt{r_1 - r_2}$ is the distance between the electrons. For a given electron i, the modulus of the positions of the electrons in three dimensions is given by $r_i = \sqrt{x_i^2 + y_i^2 + z_i^2}$ The total Hamiltonian of the system is the sum of both, the unperturbed H_0 and perturbed Hamiltonian H_1.

$$H = H_0 + H_1 \tag{3}$$

For two electrons in a harmonic oscillator with no repulsive Coulomb interaction, the Schrodinger equation is the following

$$(-\frac{\hbar^2}{2m}\frac{d^2}{dr_1^2} - \frac{\hbar^2}{2m}\frac{d^2}{dr_1^2} + \frac{1}{2}kr_1^2 + \frac{1}{2}kr_1^2)u(r_1, r_2) = E^{(2)}u(r_1, r_2) \tag{4}$$

where $u(r_1, r_2)$ is the two-electron wave function. Introducing a relative coordinate, $r = r_1 - r_2$ and the center of mass coordinate $R = \frac{1}{2}(r_1 + r_2)$ we may rewrite the Schrodinger equation as follows

$$(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - \frac{\hbar^2}{4m}\frac{d^2}{dR^2} + \frac{1}{4}kr^2 + kR^2)u(r, R) = E^{(2)}u(r, R) \tag{5}$$

The wave function may be separated in these two new coordinates, $U(r, R) = \psi(r)\phi(R)$. The energy is given by the sum of the relative energy and center of mass energy, $E^{(2)} = E_r + E_R$. In order to consider the repulsive interaction between the electrons now, we add the term

$$V(r_1, r_2) = \frac{1}{r_{12}} \tag{6}$$

so that the Schrodinger equation becomes

$$(-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{1}{2}kr^2 + \frac{1}{r_{12}})\psi(r) = E_r\psi(r) \tag{7}$$

Introducing a dimensionless variable, $\rho = \frac{r}{\alpha}$ and a new frequency which defines the strength of the oscillator potential,

$$\omega_r^2 = \frac{1}{4}\frac{mk}{\hbar^2}\alpha^4 \tag{8}$$

we can similarly resolve the equation. In light of this basic presentation of the theory corresponding to the problem that concerns us in this report, the methods used to study the desired system will be set forth in the following section.

4 Methods

4.1 Variational Method

Sometimes, when wanting to calculate the ground state energy of a system described by a specific Hamiltonian, but solving the time-independent Schrodinger equation can be tricky. Picking any normalised wavefunction ψ, the Variational Principle states that the expectation value of the Hamiltonian H in that arbitrary state ψ is certain to overestimate the ground state energy E_{gs}.

$$E_{gs} \leqslant \langle \psi | H | \psi \rangle \tag{9}$$

This principle is extraordinarily powerful, and easy to use. Simply by writing a trial function and calculating the expectation value of the Hamiltonian in that state, it is possible to get a very accurate upper limit for the energy of the lowest state. Of course, the more similar the trial wavefunction is to the actual one, the better upper bound that is obtained. The Variational Method is applied as follows. First, a trial state $\psi_T(\alpha)$ is chosen, that depends on one or more variational parameters α. Next, the trial energy is calculated. It is given by

$$E_{tr}(\alpha) = \frac{\langle \psi_\alpha | H | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \tag{10}$$

Once the energy is obtained, it needs to be minimised with respect to the variational parameter α. This minimum trial energy will be the upper limit of the ground state energy we are looking for. The Variational Monte Carlo algorithm is strongly based on this method. It constructs a trial wavefunction $\alpha_T(r;\alpha)$ for a system of N particles located in the positions $r = (r_1...r_N)$ that depends on α variational parameters. Next, it evaluates the expectation value of the Hamiltonian

$$\langle H \rangle = \frac{\int dr \psi_{T^*}(r;\alpha) H(r) \psi_T(r;\alpha)}{\int dr \psi_{T^*}(r;\alpha) \psi_T(r;\alpha)} \tag{11}$$

And the variational parameter is varied through a loop in order to find the best value of α that gives the trial energy closest to the ground state energy of the system. Normally, H is a sum of kinetic energy, involving a second derivative, and two potentials, one depending on the specific body we are considering and

other depending on the interaction between the particles. It could be written as

$$H = -\frac{\hbar}{2m}\Sigma_{i=1}^{N} \bigtriangledown_i^2 + \Sigma_{i=1}^{N}V_{body}(r_i) + \Sigma_{i<j}^{N}V_{int}(|r_i - r_j|) \tag{12}$$

Then, the trial energy we consider must have the form

$$E_T(r;\alpha) = \frac{1}{\psi_T(r;\alpha)}(-\frac{\hbar}{2m}\Sigma_{i=1}^{N} \bigtriangledown_i^2 + \Sigma_{i=1}^{N}V_{body}(r_i) + \Sigma_{i<j}^{N}V_{int}(|r_i - r_j|))\psi_T(r;\alpha) \tag{13}$$

In the following subsection, we discuss how this method is implemented to the specific problem that concerns us in this project.

4.2   Implementation

In the present subsection, a brief summary of the code implementation is presented. We consider two trial wave functions, ψ_{T_1} and ψ_{T_2}, that depend on variational parameters α and β.

$$\psi_{T_1}(r_1, r_2) = C exp - \alpha\omega(r_1^2 + r_2^2)/2 \tag{14}$$

$$\psi_{T_2}(r_1, r_2) = C exp(-\alpha\omega(r_1^2 + r_2^2)/2) exp(r_{12}/2(1 + \beta r_{12})) \tag{15}$$

These functions give closed form expressions for the local energy, which will be the expressions used for developing the program. This code begins with defining the variational parameters α, β, and γ values. Next, it finds a suitable step length δ, chosen for each variational parameter, in order to get approximately a 50% of accepted moves in each cycle. Then, it starts the Variational Monte Carlo calculation, whose moves are given by

$$R^{\cdot} = R + \delta + \gamma \tag{16}$$

where r is a random number from the uniform distribution. The Metropolis Algorithm uses a sampling rule to accept or reject the proposed moves. It chooses wave functions for the configurations, employing a random number generator to accept or reject the moves. If accepted, it increases the acceptance count by one and makes this the new wave function. If not, it continues with the previous one. Then, the local energy is calculated and added to the total energy and the total energy squared, which adds up all the results from the Monte Carlo cycles. It then repeats this process for all the Monte Carlo cycles, using the configuration found in the previous cycle. The code and results can be found in the Github address provided.

5   Results

5.1   Non-interacting System

The wavefunction for each electron in a three dimensional harmonic oscillator where electrons are not interacting with each other is

$$\psi_{n_x,n_y,n_z}(x, y, z) = A(H_{n_x}(\sqrt{\omega}x)H_{n_y}(\sqrt{\omega}y)H_{n_z}(\sqrt{\omega}z)) \tag{17}$$

where the functions H_{n_i} are Hermite polynomials, which are orthogonal polynomials that give rise to the eigenstates of the quantum harmonic oscillator. The wavefunction of the ground state, corresponding to $n_x = n_y = n_z = 0$ is given by

$$\psi(r_1, r_2) = C exp(-\omega(r_1^2 + r_2^2)/2) \tag{18}$$

Because a pair of electrons in the same energy level must have opposite spins, the quantum number m must be 0. Then, the possible values for the spin s could be either 0 or 1, given a singlet or a triplet state. In the singlet state, there are no unpaired electrons, while in the triplet state all electrons are unpaired. According to Hund's rules, for a given electron configuration, the term with maximum multiplicity has the lowest energy. Because the multiplicity is equal to 2s + 1, the state with spin s = 1 has lowest energy, corresponding to the ground state.

5.2 Interacting System

Performing the Variational Monte Carlo calculation for the first trial wave function we considered,

$$\psi_{T_1}(r_1, r_2) = C exp(-\alpha\omega(r_1^2 + r_2^2))/2 \tag{19}$$

$$E_{L_1} = \frac{\omega^2}{2}(r_1^2 + r_2^2)(1 - \alpha^2) + 3\omega\alpha + \frac{1}{r_{12}} \tag{20}$$

the energy and its variance are plotted as functions of the variational parameter α, in order to study their behavior and obtain an upper bound for the actual ground energy, making use of the variational method. It is done for different values of the frequency ω. According to the Variational Principle, the minimum value of the energy on these graphs is the best approximation of the true energy of the system, and the associated value of α, is the best value for the adjustable parameter. In Figure (1,2 & 3), we can observe the behaviour of the energy for
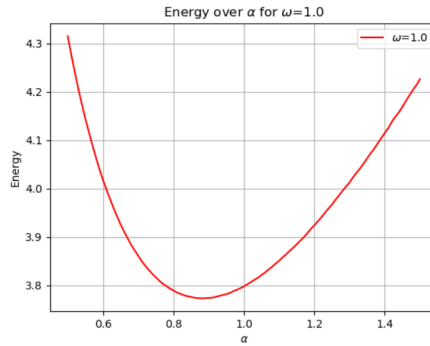

Figure 1: Plots for the energy as a function of the variational parameter α for different values of $\omega = 1.0$
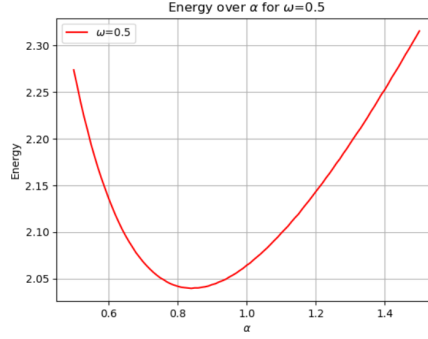
Figure 2: Plots for the energy as a function of the variational parameter α for different values of $\omega = 0.5$
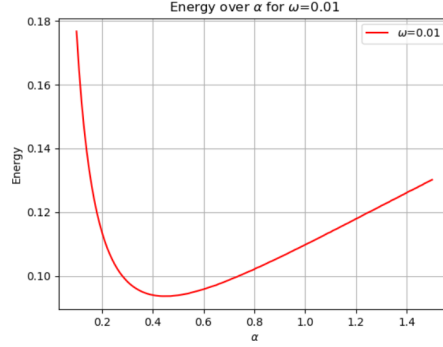

Figure 3: Plots for the energy as a function of the variational parameter α for different values of $\omega=0.01$

a certain range of variational parameters. All of the figures show a similar trace, reaching a minimum for a certain value of the energy and of α, which are the values we are interested in. It is readily observed how, when taking a smaller value of the frequency, smaller values for the minimum energy and minimum adjustable parameter are also reached, due to the fact that the energy has a dependence on the square of the frequency. Our purpose is to find this minimum energy, so as to give the lowest upper bound possible for the real ground state energy of the system. The minimum energy with respect to the adjustable parameter can be found by taking the derivative of the energy with respect to that parameter, setting the resulting expression equal to zero, and solving for the parameter α. These results are displayed in Table 1. Plotting the energy variance as a function of the variational parameter, in Figure (4,5 & 6), it is precisely observed how the variance will also reach a minimum value, corresponding to a certain value of α. Due to the fact that the variance describes how much a variable differs from its expected value, the smaller it is, the closer we are to

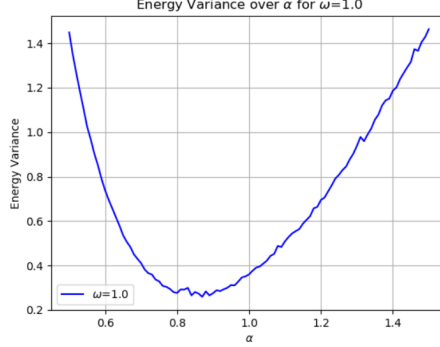the real value of the energy. In Table 1 and 2, the values corresponding to the

Figure 4: Plots for the energy as a function of the variational parameter α for different values of $\omega = 1.0$
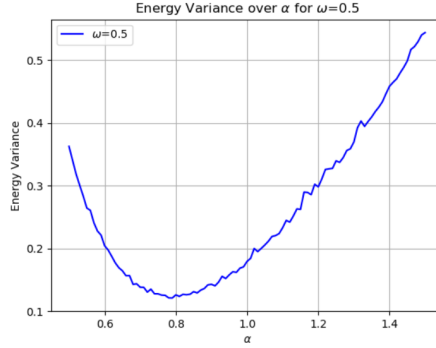

Figure 5: Plots for the energy as a function of the variational parameter α for different values of $\omega = 0.5$

minimum energy, minimum variance, and their corresponding minimum variational parameter are shown for the different values of the frequency considered, using a number of 10^7 Monte Carlo cycles to carry out the calculations. The smaller the energy variance is, the better our approximation is with respect to the real ground state energy of the system. Thus it is possible to see how the values obtained corresponding to the smaller frequency, $\omega = 0.01$, give the best upper bound for the ground state energy of the system. The minumum variance and every are not expected to have the same minimum adjustable parameter α because two different integrals were computed to obtain these values, for the reason that the trial wave function that is being used is not the exact wave function of the system. Were we to use the exact wavefunction, the variance would be expected to be zero.
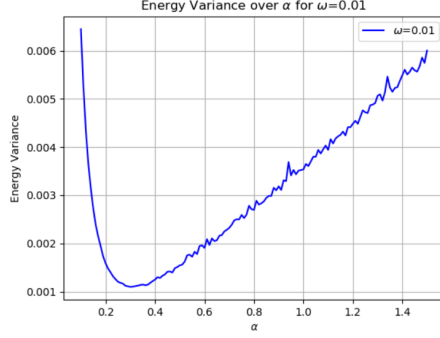
Figure 6: Plots for the energy as a function of the variational parameter α for different values of ω=0.01

ω	E_{min}	α_{min}
1	3.7728	0.88
0.5	2.0397	0.84
0.01	0.0936	0.46

Table 1: Minimum values of the energy and variational parameter α for different ω

ω	σ^2_{min}	α_{min}
1	0.2593	0.87
0.5	0.1215	0.79
0.01	0.0011	0.30

Table 2: Minimum values of the variance and variational parameter α for different ω

It is important to mention how the expectation value of the mean distance at the energy minimum varies for the different values of the frequency. For bigger values of ω, the electrons are closer together, creating a stronger well. In Project 2, we saw this graphically, representing the position of the particles for different values of the frequency. As we increased ω, we got sharper and narrower curves, meaning that the electrons were closer together. In Table 2, the expectation values of the mean distance for different values of the frequency, corresponding to the energy minimum, are displayed, proving what was anticipated.

ω	r_{12}
1	1.7015
0.5	2.4627
0.01	23.5331

Table 3: Expectation values of the mean distance at the minimum for different values of ω

In what follows, the second trial wave function is used,

$$\psi_{T_2}(r_1, r_2) = Cexp(-\alpha\omega(r_1^2 + r_2^2)/2)exp(r_{12}/2(1 + \beta r_{12})) \qquad (21)$$

where there is an extra exponential term, corresponding to the Jastrow factor, whose purpose will be discussed afterwards. The corresponding energy is

$$E_{L_2} = E_{L_1} + \frac{1}{2(1 + \beta r_{12})^2}(\alpha\omega r_{12} - \frac{1}{2(1 + \beta r_{12})^2} - \frac{2}{r_{12}} + \frac{2\beta}{1 + \beta r_{12}}) \qquad (22)$$

Finding the optimal parameters for the ground state wave function, α and β, the expectation values of the energy and variance are obtained for the three different frequencies that are being considered $\omega = 1$, $\omega = 0.5$, $\omega = 0.01$, as well as the expectation value mean distance between the electrons at the mean minimum, just as it was done for the first trial wave function. The results obtained are displayed in Table (4). It is remarkable how these values are more accurate than the ones obtained with the first wavefunction. This is due to the addition of the Jastrow factor. This term plays an important role in quantum Monte Carlo calculations. It helps obtain highly accurate correlation wave functions, resulting in the achievement of a very high percentage of the total correlation energy in a Variational Monte Carlo calculation.

ω	E	σ^2	r_{12}	α	β
1	3.7302	0.000264	1.8147	0.99	0.29
0.5	2.0001	0.000135	2.6802	0.99	0.21
0.01	0.0793	0.000005	29.565	0.99	0.04

Table 4: Expectation values of the energy, variance and distance between electrons for different values of the frequency ω

In Project 2, we resolved this very same problem by an eigenvalue approach, obtaining certain values for the ground state energy of the system. Table (5) compares the values obtained using each method, conclusively proving the superiority of the Variational Monte Carlo method.

ω	E VMC	E Eigenvalue Solver
1	3.7302	9.9127
0.5	2.0007	6.1239
0.01	0.0793	2.1462

Table 5: Results comparison between eigenvalue solvers and Variational Monte Carlo

The exact ground state energy for $\omega = 1$ is 3.558 a.u. Variational Monte Carlo gave a value of 3.7302, which is an exceedingly good upper limit, considering the wave function used is not the exact wave function of the system. Within the two Monte Carlo calculations that were performed with the two different trial wave functions, the second one, which included a term accounting for electron correlation, gave a more precise result.

5.3   Virial Theorem

The Virial Theorem states that, the relation between the kinetic T and potential energy V of a system of two particles at a distance r when the potential has the form V(r) = ar^n is given by

$$2\langle T \rangle = n \langle V \rangle \qquad (23)$$

In particular, for a pure harmonic oscillator, it happens that

$$\langle T \rangle = \langle V \rangle \qquad (24)$$

In the following plot, we present the expectation values of these two energies with and without repulsive interaction, in a range of frequency $\omega \; \epsilon \; [0.01, \; 1]$ to see how they behave. When we do not consider repulsive interaction between
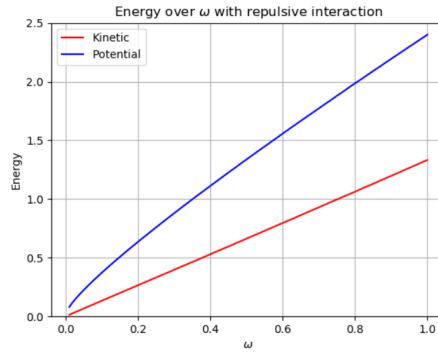

Figure 7: Plots of the expectation values of the potential and kinetic energy with and without Coulomb interaction for different values of ω

electrons, we can observe in the left plot of Figure (7) how the expectation values of both energies practically overlap each other, getting nearly the same values for the given range of ω, consequently, fulfilling Virial's Theorem. However, when taking into account Coulomb interaction, there will be an extra term added to the potential energy, which will have a dependence with the distance between the electrons, being this the reason why the rise is slightly faster for smaller values of the frequency. When plotting the ratio $\langle T \rangle / \langle V \rangle$ as a function of ω, in Figure (8), it is straightforward to observe whether Virial's Theorem is satisfied or not. Without Coulomb repulsion, the pattern obtained is a straight line, very close to 1, which proves conclusively the theorem. Nonetheless, when considering electron-electron repulsion, for smaller values of the frequency, corresponding to the electrons being further away from each other, it does not obey the theorem exactly, but as higher frequencies are considered, this ratio eventually adopts a constant value.
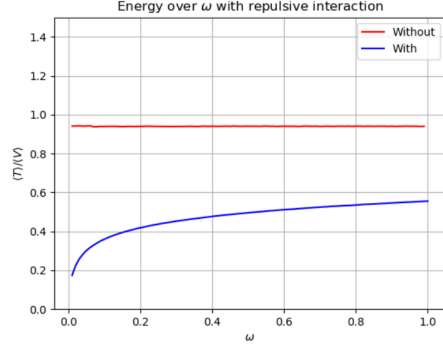
Figure 8: Plot of the ratio $\langle$ T $\rangle/\langle$ V $\rangle$ for different values of ω

6   Conclusion

Using the Variational Monte Carlo method to approximate the ground state of a system of two electrons in a three dimensional quantum dot, very satisfactory results were obtained. These values were compared to the ones acquired in Project 2, where the problem was carried out by an eigenvalue approach, giving results that are not entirely accurate when contrasting them to the exact ground state energy. Consequently, it can be concluded that Variational Monte Carlo is more effective and, from our personal opinion, easier to implement.

7   Reference

1. Hjorth-Jensen, M. Computational Physics. Lecture Notes 2015. University of Oslo, 2015.

2. Griffiths, David J. Introduction to Quantum Mechanics. Cambridge University Press, 2017.