

## Project 2

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SCHRÖDINGER'S EQUATION FOR TWO ELECTRONS IN A THREE-DIMENSIONAL  
HARMONIC OSCILLATOR WELL

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# Introduction

In this project we studied the energies of a system consisting of two electrons in a three-dimensional harmonic oscillator well. This is an interesting topic cause it can better our understanding about quantum dots. *'A quantum dot is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons (bound pairs of conduction band electrons and valence band holes) in all three spatial directions'*. From what I understand, the quantum dot is a crystal structure, which has conductive electrons (in a range of 1-100)<sup>1</sup>. What is special is that their motion is confined, and their energies are quantized. The fact that its energies are quantized has given the quantum dot the nickname 'artificial atom'<sup>2</sup>, since this a known property of atoms. The size of the quantum dot decides the allowed energy states it can have.

In this project we have also confined the motion of the electron(s). We have a well potential. We know from quantum mechanics that the energies the three-dimensional oscillator possess is quantized and that we find these by finding the eigenvalues of its Hamiltonian. For each of the particles isolated this is no big task. We find that

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \rho^2\psi(\rho) = \lambda\psi(\rho).$$

However when considering the coulomb repulsion between them it's more complicated. The potential energy of each electron will then not only depend on its own position in the oscillator, but the other ones as well. After series of changes of variables we ended up with the Schrödinger's equation:

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \omega_r^2\rho^2\psi(\rho) + \frac{1}{\rho} = \lambda\psi(\rho).$$

Where now the dependence is on  $\rho = r/\alpha$ , where  $r = r_1 - r_2$ , and  $\omega_r$  is the oscillator frequency. This is a one-dimensional problem, but it describes a three-dimensional system. The last term on the lefthand side is the potential energy of the system due to the repulsion between the electrons.

These eigenvalue equations we solved by constructing a matrix for the Hamiltonian, and obtained the energies (eigenvalues of the Hamiltonian) by using Jacobi's rotation method.

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<sup>1</sup>[http://www.sciencedaily.com/articles/q/quantum\\_dot.htm](http://www.sciencedaily.com/articles/q/quantum_dot.htm)

<sup>2</sup><http://www.sigmaaldrich.com/materials-science/nanomaterials/quantum-dots.html>

## Jacobi's rotation method

This method is rather simple to understand and is well presented in the textbook. The basics of it is this: We have a real symmetric matrix  $A$ . This matrix obviously has the eigenproblem

$$\hat{A}\psi = \lambda\psi \quad (1)$$

Where  $\lambda$  is the eigenvalue of  $\hat{A}$  with corresponding eigenvector  $\psi$ . We define a matrix  $\hat{B}$  and  $\hat{S}$  such that

$$\hat{B} = \hat{S}^T \hat{A} \hat{S} \quad \hat{S}^T \hat{S} = \hat{S}^{-1} \hat{S} = \hat{I} \quad (2)$$

We now multiply with  $\hat{S}^T$  on both sides of (1), getting

$$\begin{aligned} \hat{S}^T \hat{A} \psi &= \hat{S}^T (\lambda \psi) \\ \hat{S}^T \hat{A} \psi &= \lambda (\hat{S}^T \psi) \end{aligned}$$

Multiplying  $\hat{I}$  with something won't change anything, and therefor we can do this on either side, without worries. We end up with

$$\begin{aligned} \hat{S}^T \hat{A} (\hat{S} \hat{S}^T) \psi &= \lambda (\hat{S}^T \psi) \\ \hat{S}^T \hat{A} \hat{S} (\hat{S}^T \psi) &= \lambda (\hat{S}^T \psi) \\ \hat{B} (\hat{S}^T \psi) &= \lambda (\hat{S}^T \psi) \end{aligned} \quad (3)$$

We call  $\hat{B}$  a simmilarity transformation of  $\hat{A}$ . As we can see thay share the same eigenvalues  $\lambda$ , however the eigenvector/eigenfunction may differ.

Jacobi's rotation method takes advantage of equation (3) , by making sure that for each rotation the new matrix  $\hat{B}$  is more diagonal than the the matrix previous to the rotation,  $\hat{A}$ . By more diagonal i mean that the sum of all non-diagonal elements of matrix  $\hat{B}$  is less then the sum of all non-diagonal elements of matrix  $\hat{A}$ . With repeated rotations we should thus progress toward a diagonal matrix. This matrix has to have the eigenvalues along the diagonal!

This is the main idea behind Jacobi's rotation method. An important part is obviously to define matrices  $\hat{S}$  that satisfies (2) and makes the transformed matrix  $\hat{B}$  more diagonal than  $\hat{A}$ .

In this project we let

$$\hat{S} = \begin{pmatrix} 1 & 0 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ 0 & 1 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \cos \theta & 0 & \cdots & 0 & \sin \theta \\ 0 & 0 & \cdots & 0 & 1 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 0 & 0 & \cdots & 1 & 0 \\ 0 & 0 & \cdots & -\sin \theta & 0 & \cdots & 0 & \cos \theta \end{pmatrix} \quad (4)$$

If we now consider the matrix  $\hat{B} = \hat{S}^T \hat{A} \hat{S}$  its elements will consist of

$$\begin{aligned} b_{ii} &= a_{ii} \quad , i \neq k, i \neq l \\ b_{ik} &= a_{ik} \cos \theta - a_{il} \sin \theta \quad , i \neq k, i \neq l \\ b_{il} &= a_{il} \cos \theta + a_{ik} \sin \theta \quad , i \neq k, i \neq l \\ b_{kk} &= a_{kk} \cos^2 \theta - 2a_{kl} \cos \theta \sin \theta + a_{ll} \sin^2 \theta \\ b_{ll} &= a_{ll} \cos^2 \theta + 2a_{kl} \cos \theta \sin \theta + a_{kk} \sin^2 \theta \\ b_{kl} &= (a_{kk} - a_{ll}) \cos \theta \sin \theta + a_{kl}(\cos^2 \theta - \sin^2 \theta) \end{aligned}$$

The angle  $\theta$  is arbitrary. The trick is to choose a value of  $\theta$  so that the largest non-diagonal element  $a_{kl}$  becomes zero. Hence we have the equation:

$$b_{kl} = (a_{kk} - a_{ll})cs + a_{kl}(c^2 - s^2) = 0 \quad (5)$$

dividing by  $c^2$  on both sides gives

$$(a_{kk} - a_{ll})t + a_{kl}(1 - t^2) = 0$$

We now define

$$\tau = -\frac{a_{kk} - a_{ll}}{2a_{kl}} \quad (6)$$

dividing by  $(-a_{kl})$  on both sides leave us with

$$t^2 + 2\tau t - 1 = 0$$

which has solutions:

$$t = -\tau \pm \sqrt{1 + \tau^2}$$

$$t = \frac{(-\tau \pm \sqrt{1 + \tau^2})(-\tau \mp \sqrt{1 + \tau^2})}{-\tau \mp \sqrt{1 + \tau^2}}$$

$$t = \frac{-1}{-\tau \mp \sqrt{1 + \tau^2}} \tag{7}$$

Since we always choose the smaller of the roots we will always have the absolute value of the denominator grater then 1! This ensures that

$$|\tan \theta| \leq 1 \Rightarrow |\theta| \leq \pi/4$$

# Algorithm

The algorithms I have used is pretty much a copy of the ones in the textbook. Basically the only difference is that I am using armadillo matrices. However I fully understand it and will try to express my understanding of it. The program is divided into three functions.

- **max\_offdiagonal:**

Simply runs through the input-matrix, finds the largest element above the diagonal. It does not search beneath because it takes advantage of the fact that  $\hat{A}$  is a symmetric matrix. It then changes the value of  $k$  and  $l$ , which represent the row and column indices of the largest non-diagonal element. At last it returns the value of the element.

- **rotate:**

First of it checks if  $A(k, l) = 0$ . If it is, then equation (5) allows us to set  $\cos \theta = 1$  and  $\sin \theta = 0$ . If  $A(k, l) \neq 0$  we have to use the relation (7), when choosing the lowest of the roots, to obtain the values of  $c$ ,  $s$  and  $\theta$ . We construct a variable  $\tau$  as in (6), then to get the smaller of the roots it checks if  $\tau$  is positive or negative. Once the angle ( $c$  and  $s$ ) are decided the function continues to doing the actual rotation by the algorithms shown on page 2. However, instead of having a second matrix  $\hat{B}$  we update the present matrix. In addition to this it also updates a matrix containing the eigenvectors of the transformed matrix. The theory is easy and I will explain it later.

- **Jacobi:**

Sets up conditions of how diagonal the final matrix has to be. In other words how large the biggest non-diagonal matrix element is allowed to be. I set this to be E-10, which is essentially zero compared to the diagonal elements values. It then runs a while loop which transforms the matrix using the *rotate-function*, then finds the largest non-diagonal element of this matrix using the *max\_offdiagonal-function*. The loop runs until the maximum value of all the non-diagonal elements of the transformed matrix is less than the condition. It also counts the number of iterations it does. This function returns the final transformed, diagonal, matrix.

I added a section that writes the values of  $\rho$  and the eigenfunctions of the three lowest energy states and their squared.

The main function of the program sets up the the amount of steps we are to consider and hence also the dimension of the matrix we start out with, the maximum value of  $\rho$ , and stores the step-length. It then constructs the matrix  $\hat{A}$ , which is the Hamiltonian of the system. I made a vector containing the values of  $\rho(i)$  and call upon its elements, instead of calculating them over and over. I did this by using *linspace*(0,  $p\_max$ ,  $n\_step + 1$ ), however I never use the first element of this vector.

The hamiltonian of the system was constructed from the Schrödinger's equations given in the text (different for the two systems). However they both shared the same general form:

$$\hat{A} = \begin{pmatrix} \frac{2}{h^2} + V_1 & -\frac{1}{h^2} & 0 & 0 & \dots & 0 & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2} + V_2 & -\frac{1}{h^2} & 0 & \dots & 0 & 0 \\ 0 & -\frac{1}{h^2} & \frac{2}{h^2} + V_3 & -\frac{1}{h^2} & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots & \frac{2}{h^2} + V_{n\_step-2} & -\frac{1}{h^2} \\ 0 & \dots & \dots & \dots & \dots & -\frac{1}{h^2} & \frac{2}{h^2} + V_{n\_step-1} \end{pmatrix} \quad (8)$$

Where for the single-electron system  $V_i = \rho_i^2$  and for the two-electron system  $V_i = \omega_r^2 \rho_i^2 + \rho_i^{-1}$ . In the script I only constructed the two up-most diagonals and used armadillos function *symmatu*( $A$ ) to mirror the top one beneath the main diagonal. In the *Jacobi-function* we construct an eigenvector-matrix,  $R$ , with the same dimensions. These are defined to be the eigenvectors of  $\hat{A}$ . This eigenvector-matrix is constructed such that all the eigenvectors are orthonormal. When we at last end up with the eigenvector-matrix

$$\hat{R}_N = \hat{S}_N^T \dots \hat{S}_1^T \hat{R}_0$$

This is still orthonormal! And therefore we do not need to include a normalization algorithm in the script.

# Results

## Singe-electron system

First of I checked if the code I had written would actually return correct eigenvalues of a symmetric, real matrix. In order to do this I made such a matrix and ran the code. I then made the same matrix in *matlab* and used the function *eig()* to get the eigenvalues. I was pleased to see that they were equal.

In the first part of the project we considered only a single particle in a three-dimensional oscillator well. This system has well known energy values  $\lambda = 3, 7, 11, \dots$ . These are the lowest of the energystates. I ran my code several times with different dimensions ( $n\_step$ ) and logged the number of iterations.

n_step	50	100	150	200	250	300	350
Iterations	4.3e3	1.7e4	4.0e4	7.1e4	1.1e5	1.6e5	2.2e5

Tabell 1: Iterations vs dimension of the matrix

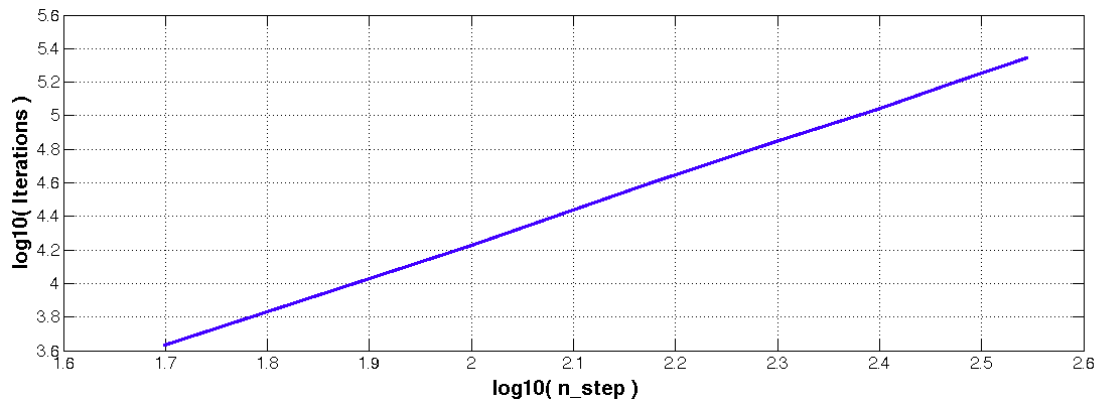


Figure 1: Iterations vs dimensionality of the matrix.

As we can see, there seems to be a relation (at least in this region) between the number of iterations and the dimensionality of the matrix.

The program printed out its three lowest calculated energy levels/eigenvalues as I registered the number of iterations. In order to have the correct values with four leading digits I had to have more then 280 steps. I used  $\rho_{max} = 5$  in order to have the entire wavefunction within the interval. In order to know if my interval included the entire function or if it was way to large, I plotted it beforehand.

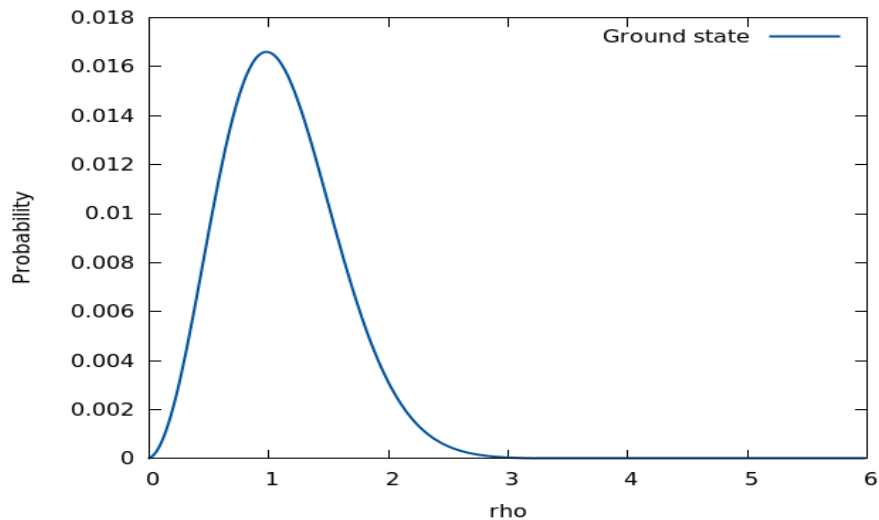


Figure 2: Probability function of the ground state of the single-electron system.

The wavefunction is good and dead at  $\rho_{max} = 5$  and in the major part of the interval the function has non-zero values. If the  $\rho_{max}$  would have been too large, the step length would have become larger as well, and my estimate of the function in the region where the function actually is non-zero would have been less precise. This is also a waste of efforts, as we are only interested in the function where it has non-zero values.

## Two-electron system

Later on we studied the two-electron system. The only difference in the code is the potential from which we build the Hamiltonian. The physical interpretation of the value  $\rho$  is now not proportional to distance from the origin, but to the distance between the two electrons. The new potential is

$$V_i = \omega_r^2 \rho_i^2 + \frac{1}{\rho_i} \quad (9)$$

where the last term is due to the repulsive force. The constant  $\omega_r$  is a ‘frequency’ and reflects the strength of the oscillator potential, or how steep the well is if you like. If we increase its value the energy levels increases. I checked for three values of  $\omega_r$ .

$\omega_r$	0.5	1	5
$\lambda$	1.5	3	15

Tabell 2: Eigenvalues  $\lambda$  of the ground state corresponding to different values of the oscillator frequency  $\omega_r$ , without repulsion.

These results surprised me at first. Yes, we see that the eigenvalue increases with  $\omega_r$ , but also that there is a proportionality between them. We have the relation:

$$\lambda = 3\omega_r$$

The reason they are proportional comes from the quantum mechanical relation for the energy

$$E_n = \hbar\omega(n + 1/2)$$

Ground state is at  $n = 0$ . The reason we get exactly a factor of 3, must have something to do with the way we define  $\omega_r$ .

For specific values of the oscillator frequency,  $\omega_r$ , there are analytical solutions. This is great because that means I have something to compare my results to in order to check if my code is returning reasonable results! In the article, M. Taut defined the energies differently than we did, but it is simply a factor of two different. The relation is  $\epsilon' = E/2$ . The oscillator frequencies that had analytical results were different from the ones asked about in the exercise, however I simply used the same code as in part C to calculate the energy myself. The oscillator frequencies were  $\omega_r = 1/4, 1/20, \dots$ . As we already have seen, the probability curve will stretch out wide for small values of  $\omega_r$ . How far? Well that's not as intuitive. I got a tip from Anders on how to at least guess. The idea was to let all the energy be potential,  $\rho = \rho_{max}$ , and then solve for  $\rho_{max}$ . However it wasn't very accurate because of the fact that the electrons can tunnel. I tried to set  $\rho_{max}$  to 10 for  $\omega_r = 1/4$  and 18 for  $\omega_r = 1/20$ . This turned out to be a good values. Beneath is a plot of the probability-function,  $|\psi(\rho)|^2$ .

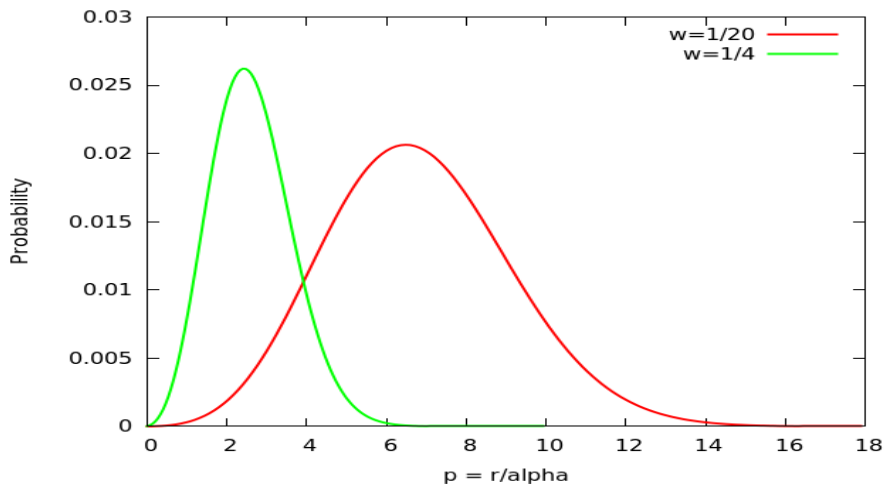


Figure 3: Probability-functions,  $|\psi(\rho)|^2$  vs  $\rho$ , for my calculation of the ground states with  $\omega_r = 1/4$  and  $\omega_r = 1/20$ .

Again, the reason I plotted this is to show that the area of the function which I am addressing actually has non-zero values in the major part of the interval. I chose  $\rho_{max} = 10$  for the largest of the frequencies and  $\rho_{max} = 18$  for the smallest. My program returned  $E/2 = 0.625$  and  $E/2 = 0.175$  respectively which was exactly what I was hoping for, as this is the analytical result shown in the article. This benchmarks my code as functioning, which means that I must have done something right! I found this as a sufficient test and therefore did not care to do the same procedure for more of the frequencies. This was ment as a test, and it is not to be found directly in my script. In order to reproduce these results: In PART C of my script, change  $w[0] = 1./4$ ,  $p_{max} = 8$  and edit the name of the output file to whatever. The values of  $\rho$  and  $|\psi(\rho)|^2$  are then stored in column 1 and 5 respectfully. Same procedure for  $\omega_r = 1/20$  but with  $w[0] = 1./20$  and  $p_{max} = 18$ .

I then continued to show how the probability function for two electrons as functions of the relative coordinate  $r$  and different values of  $\omega_r$ . I did this by plotting the square of the wave functions/eigenvectors. I had to simply guess the values of  $\rho_{max}$ .

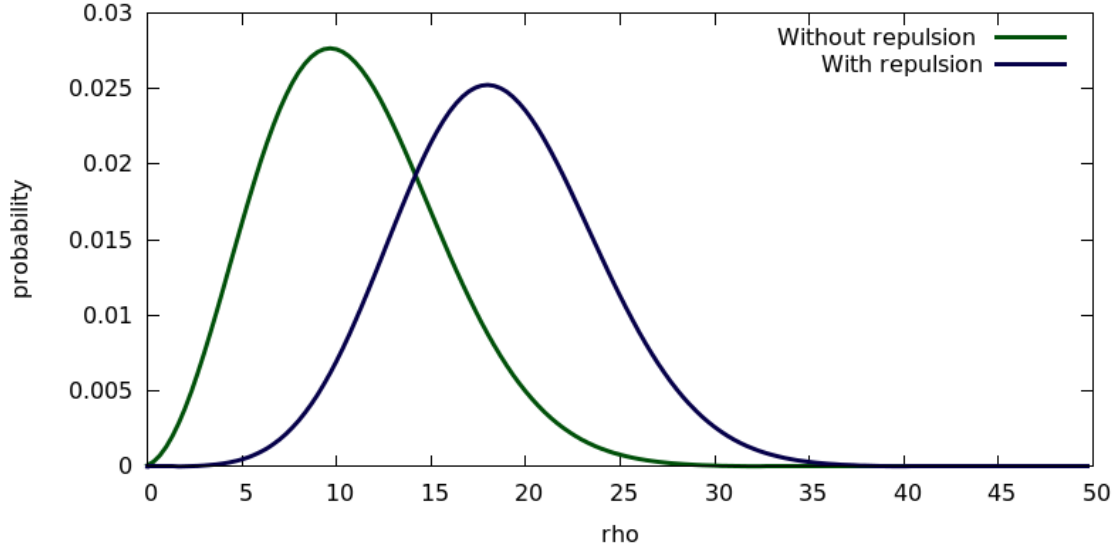


Figure 4: Probability function for the ground state as a function of relative distance, both with and without repulsion.  $\omega_r = 0.01$

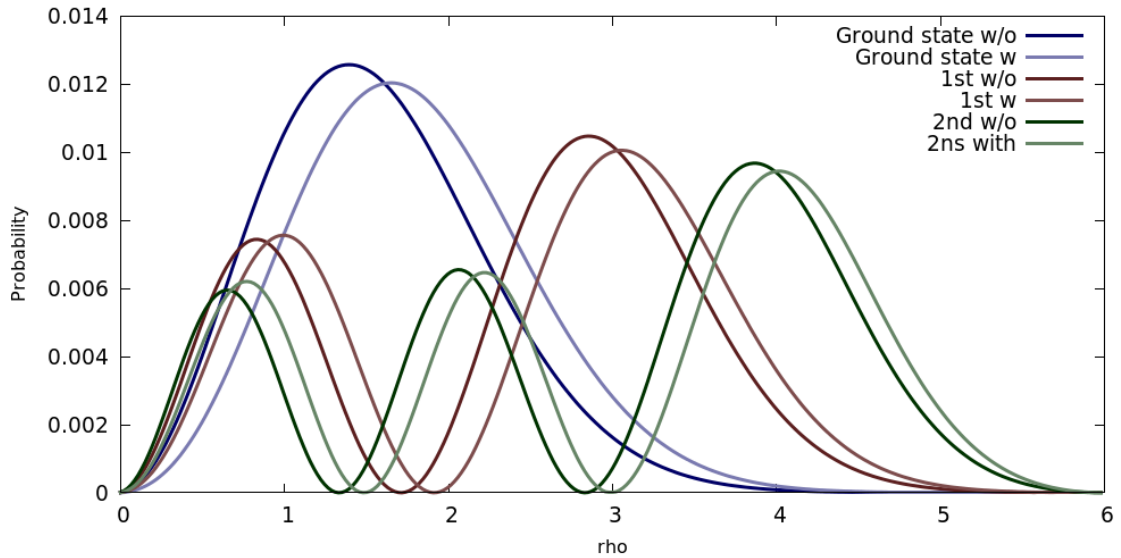


Figure 5: Probability function for the three lowest energy states as function of relative distance, both with and without repulsion.  $\omega_r = 0.5$



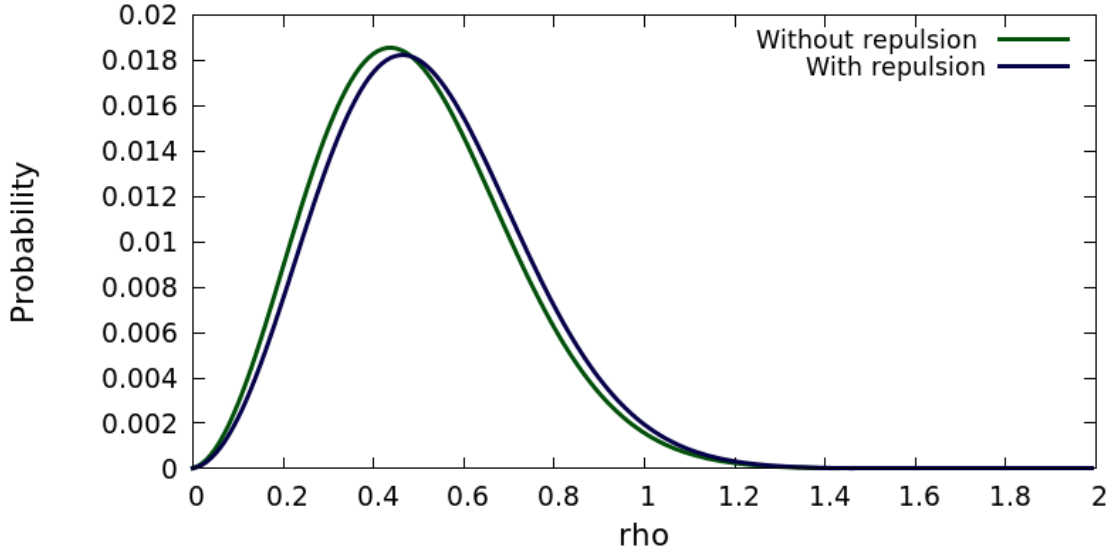


Figure 6: Probability function for the ground state as a function of relative distance, both with and without repulsion.  $\omega_r = 5$

From these plots we can see that as  $\omega_r$  increases, there is a narrower interval of possible distances the electrons can have, and the possible values become smaller. This is easy to understand, because when oscillator frequency increases, the well becomes steeper, and the electrons are forced to be closer together. We also notice that when considering the repulsion, the electrons are farther apart than without this effect. This is also intuitive, because they repel each other and thus there should be a lower probability of finding them close together and a higher probability of finding them farther apart, than without the repelling effect. This goes for all states, as illustrated in figure 5.

The last thing I read from this is the fact that the repelling effect plays a greater role when  $\omega_r$  is small than when it is large. This made me think. Because, when the electrons are in a well, with large  $\omega_r$ , then they are closer together than if  $\omega_r$  is small. The repulsion is thus stronger in this well. However it does not effect the probability function as much! I guess the reason for this can be shown from the formula for the potential, (9). If  $\omega_r$  is small, then the term due to repulsion will contribute much to the sum of the two terms. However, if  $\omega_r$  is large, the first term will be large, and whatever contribution the last term has to the total potential energy, it will be smaller in comparison.

## Comments & reflections.

Working with this project I did not think about its relevance to quantum dots at all, and I can't say I understand them a lot more. Then again I only googled 'quantum dots' for 10 minutes. The similarities I recon though, is that as the well became tighter/steeper, the energy levels increased. As for the quantum dots, smaller dots (confining the electrons to a smaller space) give higher energy in the conductive band. And larger dots have a lower energy conductive band. This is a hot topic for example in the manufacturing of various displays, because the quantum dots can have energy states such that as the electrons fall back to the valence band, they emit light with a specific energy/wavelength.

## Github repository

<https://github.com/filiph1/FYS3150.git>