

Fys3150, Project 2

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Abstract

In this project I have solved the schroedinger equation for one and two electrons by using the jacobi method. I found that using a big enough distance between the electrons is imperative for getting the right results, and that the strength of the potential has a big impact on the shape and probability of the wavefunction.

Link to github: <https://github.com/kristtuv/FYS3150/tree/master/Project2>

Introduction

The aim of this project is to solve Schroedinger's equation for two electrons in a three-dimensional harmonic oscillator well with and without a repulsive Coulomb interaction.

I will solve this equation by reformulating it in a discretized form as an eigenvalue equation to be solved with Jacobi's method.

Theory

Schroedinger equation for one electron

We are first interested in the solution of the radial part of Schroedinger's equation for one electron. This equation reads

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R(r) + V(r)R(r) = ER(r).$$

In our case $V(r)$ is the harmonic oscillator potential $(1/2)kr^2$ with $k = m\omega^2$ and E is the energy of the harmonic oscillator in three dimensions. The oscillator frequency is ω and the energies are

$$E_{nl} = \hbar\omega \left(2n + l + \frac{3}{2} \right),$$

with $n = 0, 1, 2, \dots$ and $l = 0, 1, 2, \dots$.

Since we have made a transformation to spherical coordinates it means that $r \in [0, \infty)$. The quantum number l is the orbital momentum of the electron. Then we substitute $R(r) = (1/r)u(r)$ and obtain

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u(r) + \left(V(r) + \frac{l(l+1)}{r^2} \frac{\hbar^2}{2m} \right) u(r) = Eu(r).$$

The boundary conditions are $u(0) = 0$ and $u(\infty) = 0$.

We introduce a dimensionless variable $\rho = (1/\alpha)r$ where α is a constant with dimension length and get

$$-\frac{\hbar^2}{2m\alpha^2} \frac{d^2}{d\rho^2} u(\rho) + \left(V(\rho) + \frac{l(l+1)}{\rho^2} \frac{\hbar^2}{2m\alpha^2} \right) u(\rho) = Eu(\rho).$$

In this case we will set $l = 0$. Inserting $V(\rho) = (1/2)k\alpha^2\rho^2$ we end up with

$$-\frac{\hbar^2}{2m\alpha^2} \frac{d^2}{d\rho^2} u(\rho) + \frac{k}{2}\alpha^2\rho^2 u(\rho) = Eu(\rho).$$

We multiply thereafter with $2m\alpha^2/\hbar^2$ on both sides and obtain

$$-\frac{d^2}{d\rho^2} u(\rho) + \frac{mk}{\hbar^2}\alpha^4\rho^2 u(\rho) = \frac{2m\alpha^2}{\hbar^2} Eu(\rho).$$

The constant α can now be fixed so that

$$\frac{mk}{\hbar^2}\alpha^4 = 1,$$

or

$$\alpha = \left(\frac{\hbar^2}{mk} \right)^{1/4}.$$

Defining

$$\lambda = \frac{2m\alpha^2}{\hbar^2} E,$$

we can rewrite Schroedinger's equation as

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

This is the first equation to solve numerically. In three dimensions the eigenvalues for $l = 0$ are $\lambda_0 = 3, \lambda_1 = 7, \lambda_2 = 11, \dots$.

We use the standard expression for the second derivative of a function u

$$u'' = \frac{u(\rho + h) - 2u(\rho) + u(\rho - h)}{h^2} + O(h^2), \quad (1)$$

where h is our step. Next we define minimum and maximum values for the variable ρ , $\rho_{\min} = 0$ and ρ_{\max} , respectively. It is important to check the results for the energies against different values ρ_{\max} , since we cannot set $\rho_{\max} = \infty$ and we need to make sure the entire wavefunction is contained within the interval $\rho_{\max} - \rho_{\min}$.

With a given number of mesh points, N , we define the step length h as, with $\rho_{\min} = \rho_0$ and $\rho_{\max} = \rho_N$,

$$h = \frac{\rho_N - \rho_0}{N}.$$

The value of ρ at a point i is then

$$\rho_i = \rho_0 + ih \quad i = 1, 2, \dots, N.$$

We can rewrite the Schroedinger equation for a value ρ_i as

$$-\frac{u(\rho_i + h) - 2u(\rho_i) + u(\rho_i - h)}{h^2} + \rho_i^2 u(\rho_i) = \lambda u(\rho_i),$$

or in a more compact way

$$-\frac{u_{i+1} - 2u_i + u_{i-1}}{h^2} + \rho_i^2 u_i = -\frac{u_{i+1} - 2u_i + u_{i-1}}{h^2} + V_i u_i = \lambda u_i,$$

where $V_i = \rho_i^2$ is the harmonic oscillator potential.

We define first the diagonal matrix element

$$d_i = \frac{2}{h^2} + V_i,$$

and the non-diagonal matrix element

$$e_i = -\frac{1}{h^2}.$$

In this case the non-diagonal matrix elements are given by a mere constant. *All non-diagonal matrix elements are equal.* With these definitions the Schroedinger equation takes the following form

$$d_i u_i + e_{i-1} u_{i-1} + e_{i+1} u_{i+1} = \lambda u_i,$$

where u_i is unknown. We can write the latter equation as a matrix eigenvalue problem

$$\begin{bmatrix} d_0 & e_0 & 0 & 0 & \dots & 0 & 0 \\ e_1 & d_1 & e_1 & 0 & \dots & 0 & 0 \\ 0 & e_2 & d_2 & e_2 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots e_{N-1} & d_{N-1} & e_{N-1} \\ 0 & \dots & \dots & \dots & \dots & e_N & d_N \end{bmatrix} \begin{bmatrix} u_0 \\ u_1 \\ \dots \\ \dots \\ \dots \\ \dots \\ u_N \end{bmatrix} = \lambda \begin{bmatrix} u_0 \\ u_1 \\ \dots \\ \dots \\ \dots \\ \dots \\ u_N \end{bmatrix}. \quad (2)$$

Since the values of u at the two endpoints are known via the boundary conditions, we can skip the rows and columns that involve these values. Inserting the values for d_i and e_i we have the following matrix

$$\begin{bmatrix} \frac{2}{h^2} + V_1 & -\frac{1}{h^2} & 0 & 0 & \dots & 0 & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2} + V_2 & -\frac{1}{h^2} & 0 & \dots & 0 & 0 \\ 0 & -\frac{1}{h^2} & \frac{2}{h^2} + V_3 & -\frac{1}{h^2} & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & -\frac{1}{h^2} & \frac{2}{h^2} + V_{N-2} & -\frac{1}{h^2} \\ 0 & \dots & \dots & \dots & \dots & -\frac{1}{h^2} & \frac{2}{h^2} + V_{N-1} \end{bmatrix} \quad (3)$$

Schroedinger equation for two electrons

We will now study two electrons in a harmonic oscillator well which also interact via a repulsive Coulomb interaction. Let us start with the single-electron equation written as

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u(r) + \frac{1}{2} k r^2 u(r) = E^{(1)} u(r),$$

where $E^{(1)}$ stands for the energy with one electron only. For two electrons with no repulsive Coulomb interaction, we have the following Schroedinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr_1^2}-\frac{\hbar^2}{2m}\frac{d^2}{dr_2^2}+\frac{1}{2}kr_1^2+\frac{1}{2}kr_2^2\right)u(r_1,r_2)=E^{(2)}u(r_1,r_2).$$

Note that we deal with a two-electron wave function $u(r_1, r_2)$ and two-electron energy $E^{(2)}$.

With no interaction this can be written out as the product of two single-electron wave functions, that is we have a solution on closed form.

We introduce the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and the center-of-mass coordinate $\mathbf{R} = 1/2(\mathbf{r}_1 + \mathbf{r}_2)$. With these new coordinates, the radial Schroedinger equation reads

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

The equations for r and R can be separated via the ansatz for the wave function $u(r, R) = \psi(r)\phi(R)$ and the energy is given by the sum of the relative energy E_r and the center-of-mass energy E_R , that is

$$E^{(2)} = E_r + E_R.$$

We add then the repulsive Coulomb interaction between two electrons, namely a term

$$V(r_1, r_2) = \frac{\beta e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{\beta e^2}{r},$$

with $\beta e^2 = 1.44 \text{ eVnm}$.

Adding this term, the r -dependent Schroedinger equation becomes

$$\left(-\frac{\hbar^2}{m}\frac{d^2}{dr^2}+\frac{1}{4}kr^2+\frac{\beta e^2}{r}\right)\psi(r)=E_r\psi(r).$$

This equation is similar to the one we had previously in (b) and we introduce again a dimensionless variable $\rho = r/\alpha$. Repeating the same steps as above, we arrive at

$$-\frac{d^2}{d\rho^2}\psi(\rho)+\frac{1}{4}\frac{mk}{\hbar^2}\alpha^4\rho^2\psi(\rho)+\frac{m\alpha\beta e^2}{\rho\hbar^2}\psi(\rho)=\frac{m\alpha^2}{\hbar^2}E_r\psi(\rho).$$

We want to manipulate this equation further to make it as similar to that in (a) as possible. We define a new 'frequency'

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

and fix the constant α by requiring

$$\frac{m\alpha\beta e^2}{\hbar^2} = 1$$

or

$$\alpha = \frac{\hbar^2}{m\beta e^2}.$$

Defining

$$\lambda = \frac{m\alpha^2}{\hbar^2} E,$$

we can rewrite Schroedinger's equation as

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

We treat ω_r as a parameter which reflects the strength of the oscillator potential.

Here we will study the cases $\omega_r = 0.01$, $\omega_r = 0.5$, $\omega_r = 1$, and $\omega_r = 5$ for the ground state only, that is $l = 0$

Properties of the transformed vectors

Next we will prove that a unitary transformation preserves the orthogonality and dot product of the obtained vectors. This is important because in the Jacobi method we will perform a series of unitary transformations, and we need to know that our new vectors will keep these properties.

To see this consider first a basis of vectors \mathbf{v}_i ,

$$\mathbf{v}_i = \begin{bmatrix} v_{i1} \\ \vdots \\ \vdots \\ v_{in} \end{bmatrix}$$

We assume that the basis is orthogonal, that is

$$\mathbf{v}_j^T \mathbf{v}_i = \delta_{ij}.$$

Now, we do a unitary transformation:

$$w_i = A v_i$$

Where \mathbf{A} is a unitary matrix.

We take the dot product of the transformation:

$$\mathbf{w}_i \cdot \mathbf{w}_j = \mathbf{A}\mathbf{v}_i \cdot \mathbf{A}\mathbf{v}_j = (\mathbf{A}\mathbf{v}_i)^T \mathbf{A}\mathbf{v}_j = \mathbf{v}_i^T \underbrace{\mathbf{A}^T \mathbf{A}}_{\mathbb{I}} \mathbf{v}_j = \mathbf{v}_i^T \mathbf{v}_j = \mathbf{v}_i \cdot \mathbf{v}_j = \delta_{ij}$$

As we can see the dot product and the orthogonality is preserved.

Methods

The Jacobi Method

Consider an ($n \times n$) orthogonal transformation matrix

$$\begin{pmatrix} 1 & 0 & \dots & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & \dots & \dots & 0 & 0 & 0 & 0 \\ \dots & \dots & \dots & \dots & 0 & \dots & \dots & \dots \\ 0 & 0 & \dots & \cos \theta & 0 & \dots & 0 & \sin \theta \\ 0 & 0 & \dots & 0 & 1 & 0 & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & 0 & \dots \\ 0 & 0 & \dots & 0 & 0 & \dots & 1 & \dots \\ 0 & 0 & \dots & -\sin \theta & \dots & \dots & 0 & \cos \theta \end{pmatrix}$$

with the property $\mathbf{S}^T = \mathbf{S}^{-1}$. It performs a plane rotation around an angle θ in the Euclidean n -dimensional space. It means that the matrix elements that differ from zero are given by

$$s_{kk} = s_{ll} = \cos \theta, s_{kl} = -s_{lk} = -\sin \theta, s_{ii} = -s_{ii} = 1 \quad i \neq k \quad i \neq l$$

A similarity transformation

$$\mathbf{B} = \mathbf{S}^T \mathbf{A} \mathbf{S}$$

results in

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

The angle θ is arbitrary. The recipe is to choose θ so that all non-diagonal matrix elements b_{kl} become zero.

The main idea is to perform a number of iterations until the norm of the off-diagonal matrix elements of a matrix become zero, or as close to zero as possible. When all the off-diagonal elements have become zero, we find our eigenvalues on the diagonal of the new matrix.

Algorithm

- Choose a tolerance ϵ , making it a small number, typically 10^{-8} or smaller.
- Setup a while-test that continues until all off-diagonal elements are smaller than ϵ
- Find maximum value of the off-diagonal elements.
- Compute the similarity transformation (rotation of the matrix) until the maximum value is smaller than ϵ

Results

I ran my program for one electron for $\rho_{max} = \{1, 2, 3, 4, 5, 6, 7, 10, 15\}$ and $N = \{50, 100, 150, 200, 250, 300\}$

For the three lowest eigenvalues I got the closest results to the true eigenvalues, 3, 7 and 11, for $\rho_{max} = 5$ and ofcourse $N = 300$

λ_1	2.99991
λ_1	6.99957
λ_1	6.99957

The drawback was that for such a big NxN matrix I had to do 150798 iterations to make all the off diagonal elements zero.

For $\rho_{max} = 5$ and $N = 200$ the precision was still good, and the program only did 66828 iterations.

λ_1	2.99981
λ_1	6.99904
λ_1	10.9978

Because of the big difference in iterations from the 200x200 matrix to the 300x300 matrix, it is interesting to see how the Iterations goes as a function of the matrix size N. Using Python's polyfit-function, we get the result:

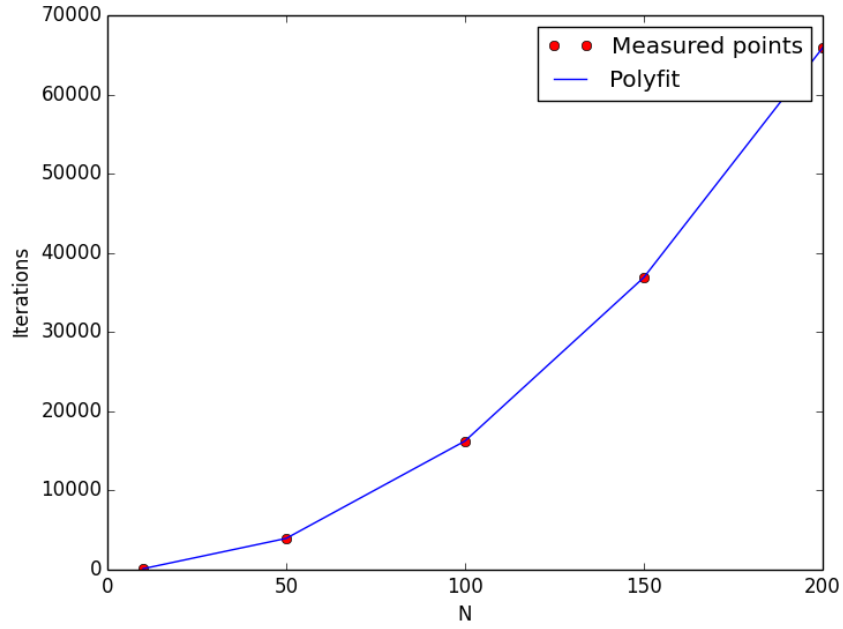
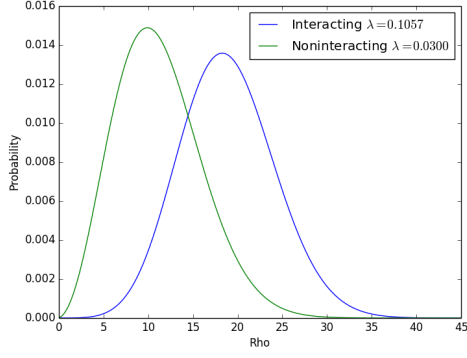
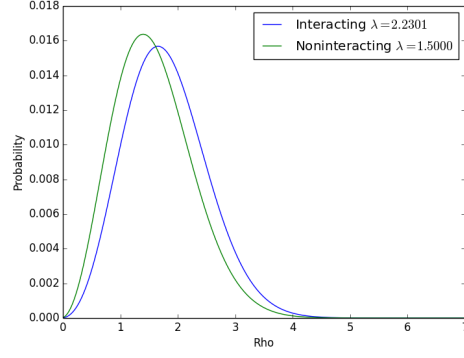


Figure 1: Plot of the measured points and the result from the polyfit function. As we see the number of iterations goes as a second degree polynomial $1.6703N^2 - 4.5714N + 5.8511$

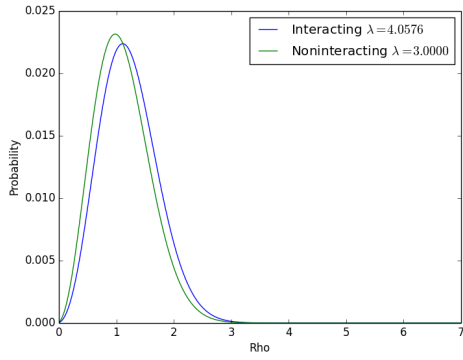
Ploting results



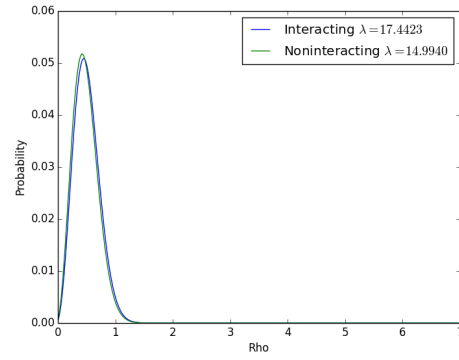
(a) $\omega = 0.01$



(b) $\omega = 0.5$



(c) $\omega = 1$



(d) $\omega = 5$

Figure 2: The interacting and non-interacting probabilitydistributions between two electrons.

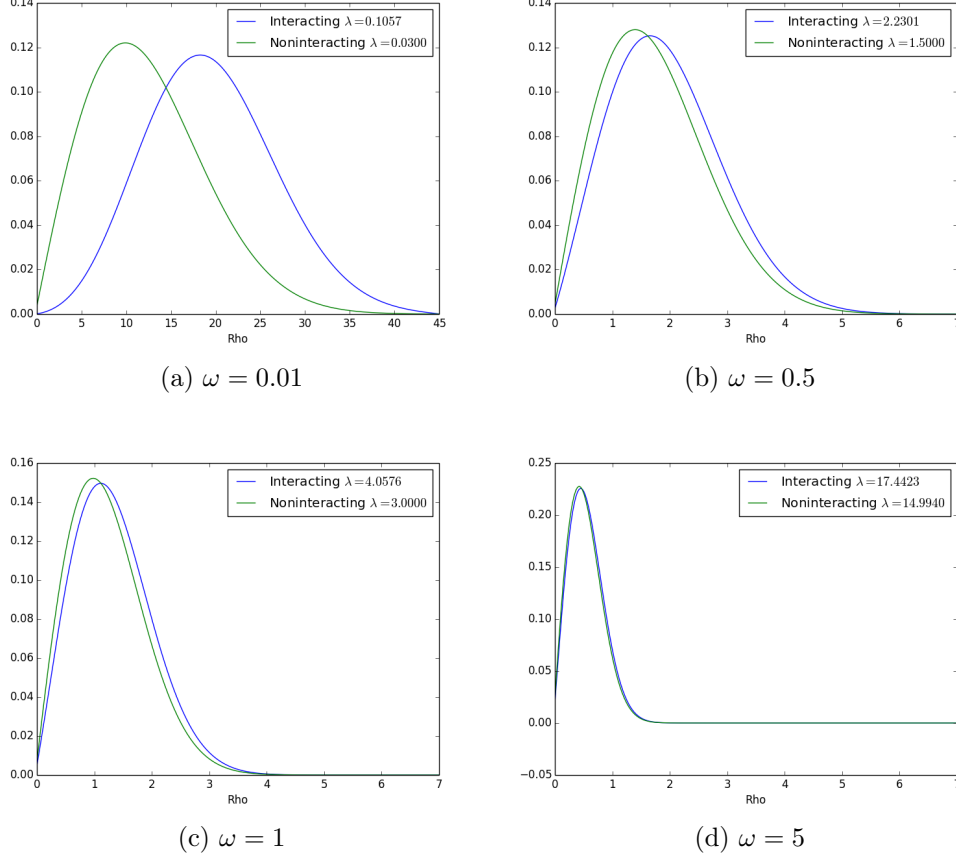


Figure 3: The interacting and non-interacting wavefunctions between two electrons.

As we can see in the plots, the distance between the electrons increases drastically when ω is small. For $\omega = 0.01$, ρ_{max} had to be increased to a minimum of 40 to contain the wavefunction. Increasing ω corresponds to increasing the part of the potential that is not repulsive, and we can see from the plot of $\omega = 5$ that the interacting and non-interacting case are almost equal.

Conclusion

The Jacobi method works very well as long as we do not work with very big matrices, because the number of iterations goes as a second degree function of the size of the matrix.

Using a suitable ρ_{max} is important. If it is too small, it will not contain the

entire wavefunction and the result for our energies will be wrong.
We have also seen that the strength of the potential in the wavefunction have a big impact on the probability of the relative distance between the electrons.