Project 2 - FYS3150[*]

Andreas G. Lefdalsnes
Student: University of Oslo, Department of Physics
email-address: andregl@student.matnat.uio.no

Tellef Storebakken
Student: University of Oslo, Department of Physics
email-address: tellefs@student.matnat.uio.no

(Dated: October 5, 2016)

In this project we solve the Schrodinger equation for two electrons in a 3-dimensional harmonic oscillator potential. We solve with and without electron repulsion, and compare the results. We find that varying the factor ω_R, which reflects the strength of the oscillator potential, has a larger effect on the wavefunction than introducing the Coulomb repulsion. And we find that for a relatively small ω_R the Coulomb repulsion dominates the wavefunction.
To accomplish this we apply a general method of discretizing the domain and reducing the problem to an eigenvalue equation. We thereafter apply Jacobi's rotation algorithm to obtain the eigenvalues of the matrix. This is a robust way of solving the eigenvalue-problem, but it is highly ineffective compared to the Armadillo-library functions, which take advantage of the sparsity of our matrix. We also apply the principles of unit testing by testing the algorithm for some simple problems with known solutions.

I. INTRODUCTION

In this project we aim to solve the Schrodinger equation for two electrons in a 3D harmonic oscillator potential, with and without the repulsive Coulomb potential. For the case of no repulsion we have an analytical expression for the energies, and thus the eigenvalues of the Hamiltonian, and this will be useful in determining the accuracy of our results. Electrons confined to small areas form an exciting field of research, expected to have many applications to computing, material research and medicine.

We will be solving the radial part of Schrodinger's equation, assuming a spherically symmetric potential, from which the full wavefunction can be obtained by tacking on the solutions to the angular equation. We will also be examining the efficiency of Jacobi's rotation method in solving the eigenvalue equation. Jacobi's rotation method is known to be an inefficient method for most eigenvalue problems. It has however gained popularity in recent years for it's relatively simple implementation, which makes it a good candidate for parallellization.

[*] Computational Physics, autumn 2016, University of Oslo

II. THEORY AND METHODS

A. The radial equation

We begin by studying the radial part of Schrodingers' equation for a single electron in a harmonic oscillator potential [1].

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

The potential $V(r)=\frac{1}{2}kr^2$ is the harmonic oscillator potential with $k=m\omega^2$ and E is the energy of the electron. ω is the oscillator frequency and the allowed energies are

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

Where the quantum number $n=0,1,2..$ is the energy quantum number and $l=0,1,2...$ is the orbital momentum quantum number. Introducing $R(r)=(1/r)u(r)$ our equation can be rewritten in terms of the second derivative d^2/dr^2:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u(r)+\left(V(r)+\frac{l(l+1)}{r^2}-\frac{\hbar^2}{2m}\right)u(r)=Eu(r) \quad (3)$$

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

$$-\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{d\rho^2}u(\rho)+\left(V(\rho)+\frac{l(l+1)}{\rho^2}\frac{\hbar^2}{2m\alpha^2}\right)u(\rho)=Eu(\rho) \quad (4)$$

In this project we will be interested in the case $l = 0$. Now since we are working in spherical coordinates, $r \in [0, \infty)$. Since we require $R(r)$ to go to zero at the boundaries, when we make the substitution $R(r) = (1/r)u(r) = (1/r)u(\alpha\rho)$ we obtain the boundary conditions for $u(\rho)$: $u(0) = u(\infty) = 0$.

We insert $V(\rho) = \frac{1}{2}k\alpha^2\rho^2$ and obtain

$$-\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{d\rho^2}u(\rho) + \frac{1}{2}k\alpha^2\rho^2u(\rho) = Eu(\rho) \tag{5}$$

To obtain a simpler expression we multiply by $2m\alpha^2\rho^2/\hbar^2$ and fix α such that

$$\frac{mk}{\hbar^2}\alpha^4 = 1 \tag{6}$$

and define

$$\lambda = \frac{2m\alpha^2}{\hbar^2}E \tag{7}$$

so we can rewrite our equation as

$$-\frac{d^2}{d\rho^2}u(\rho) + \rho^2u(\rho) = \lambda u(\rho) \tag{8}$$

To solve this equation we discretize the domain and define minimum and maximum values for ρ, $\rho_{min} = \rho_0 = 0$ and ρ_{max}. ρ_{max} cannot be chosen to be ∞ so we must take care to set it sufficiently large in order to obtain the correct solution. With N mesh points let

$$h = \frac{\rho_{max} - \rho_0}{N} \tag{9}$$

and we obtain a discrete set of values for ρ,

$$\rho_i = \rho_0 + ih \qquad i = 0, 1, 2..., N \tag{10}$$

Replacing the second order derivative by the 2nd order central difference we can write our equation as

$$-\frac{u_{i+1} + u_{i-1} - 2u_i}{h^2} + \rho_i^2u_i = \lambda u_i \tag{11}$$

Where $u_i = u(\rho_i)$ is the discretized version of our function. We let $V_i = \rho_i^2$ and rewrite this as a matrix equation

$$\boldsymbol{Au} = \lambda\boldsymbol{u} \tag{12}$$

Since the endpoints are known we let A be a matrix of dimension $(n-2)\cdot(n-2)$ and u a vector of dimension (n-2).

$$\boldsymbol{Au} = \begin{pmatrix} \frac{2}{\hbar^2} + V_1 & -\frac{1}{\hbar^2} & 0 & \cdots & \cdots & 0 \\ -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_2 & -\frac{1}{\hbar^2} & 0 & \cdots & \cdots \\ 0 & -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_3 & -\frac{1}{\hbar^2} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & \cdots & -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_{N-3} & -\frac{1}{\hbar^2} \\ 0 & \cdots & \cdots & \cdots & -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_{N-2} \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ \\ u_{N-2} \end{pmatrix} = \lambda \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ \\ u_{N-2} \end{pmatrix} \tag{13}$$

where $u_0 = u_{N-1} = 0$.

B. Coulomb Interaction

For two electrons with no Coulomb interaction in a harmonic oscillator potential the Schrodinger equation can be written as

$$(-\frac{\hbar^2}{2m}\frac{d^2}{dr_1^2} - \frac{\hbar^2}{2m}\frac{d^2}{dr_2^2} + \frac{1}{2}kr_12 + kr_2^2)u(r_1, r_2) = Eu(r_1, r_2) \tag{14}$$

With no interaction the two-electron wavefunction $u(r_1, r_2)$ can be written as a product of two single-electron wavefunction. Introducing the relative coordinate $\boldsymbol{r} = \boldsymbol{r_1} - \boldsymbol{r_2}$ and the center of mass coordinate $\boldsymbol{R} = \frac{1}{2}(\boldsymbol{r_1} + \boldsymbol{r_2})$ the radial equation becomes

$$(-\frac{\hbar^2}{m}\frac{d^2}{dr^2} - \frac{\hbar^2}{4m}\frac{d^2}{dR2} + \frac{1}{4}kr^2 + kR^2)u(r, R) = Eu(r, R) \tag{15}$$

The solution can be separated as $u(r, R) = \psi(r)\phi(R)$ and the energy is a sum of the relative energy E_r and center-of-mass energy E_R

$$E = E_r + E_R \tag{16}$$

adding the repulsive Coulomb interaction

$$V(r_1, r_2) = \frac{\beta e^2}{|\boldsymbol{r_1} - \boldsymbol{r_2}|} = \frac{\beta e^2}{r} \tag{17}$$

where $\beta e^2 = 1.44$ eVnm. The relative motion Schrodinger equation becomes

$$(-\frac{\hbar^2}{m}\frac{d^2}{dr^2} + \frac{1}{4}kr^2 + \frac{\beta e^2}{r})\psi(r) = E\psi(r) \tag{18}$$

introducing $\rho = r/\alpha$, defining a new frequency

$$\omega_r^2 = \frac{1}{4}\frac{mk}{\hbar^2}\alpha^4 \tag{19}$$

fixing α

$$\alpha\frac{m\beta e^2}{\hbar^2} = 1 \tag{20}$$

and defining

$$\lambda = \frac{m\alpha^2}{\hbar^2}E \tag{21}$$

and we obtain Schrodinger's equation

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \omega_r^2\rho^2\psi(\rho) + \frac{1}{\rho} = \lambda\psi(\rho) \tag{22}$$

which using the methods described in the previous section can be solved numerically as an eigenvalue problem.

C. Jacobi's rotation method

For a real symmetric $n \cdot n$ matrix $\boldsymbol{A}$, we have n eigenvalues λ_i and there exists a real orthogonal matrix $\boldsymbol{S}$ such that [2]

$$\boldsymbol{S^T A S} = diag(\lambda_1, \lambda_2, ..., \lambda_n) \tag{23}$$

In general a similarity transform

$$\boldsymbol{B = S^T A S} \qquad\qquad \boldsymbol{S^T S = I} \tag{24}$$

will have the same eigenvalues as $\boldsymbol{A}$, but different eigenvectors. If we have an orthogonal basis v_i such that

$$\boldsymbol{v_j^T v_i = \delta_{ij}} \tag{25}$$

a unitary transformation $\boldsymbol{U^T U = I}$ will preserve the orthogonality of the basis vectors, such that if $w_i = Uv_i$

$$\boldsymbol{w_j^T w_i = (Uv_j)^T(Uv_i) = v_j^T U^T U v_i = \delta_{ij}} \tag{26}$$

The idea of Jacobi's method is to perform a series of similarity transformations such that we receive a diagonal matrix $\boldsymbol{D}$ with the eigenvalues of $\boldsymbol{A}$ on the diagonal.

Consider a $N \times N$ matrix

$$S = \begin{pmatrix} 1 & 0 & \cdots & 0 & 0\cdots & 0 & 0 \\ 0 & 1 & \cdots & 0 & 0\cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & 0 & \cdots \\ 0 & 0 & \cdots & \cos(\theta) & 0\cdots & 0 & \sin(\theta) \\ 0 & 0 & \cdots & 0 & 1\cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & 0 & \cdots \\ 0 & 0 & \cdots & 0 & 0\cdots & 1 & 0 \\ 0 & 0 & \cdots & -\sin(\theta) & 0\cdots & 0 & \cos(\theta) \end{pmatrix} \tag{27}$$

with $\boldsymbol{S^T = S^{-1}}$. It performs a plane rotation around an angle θ in n-dimensional space. We apply a similarity transformation $\boldsymbol{S^T A S}$ to our matrix $\boldsymbol{A}$ such that the largest non-diagonal elements $a_{kl} = a_{lk}$ become zero. For a real symmetric matrix we thus reduce the norm of the offdiagonal elements

$$\text{off}(\boldsymbol{A}) = \sqrt{\sum_{i=1}^{n}\sum_{j=1,j\neq i}^{n} a_{ij}^2} \tag{28}$$

and after a sufficient number of iterations we are guaranteed a matrix

$$\boldsymbol{S_N^T S_{N-1}^T....S_1^T A S_1....S_{N-1} S_N = diag(\lambda_1, ..., \lambda_N)} \tag{29}$$

Numerically it is sufficient that the largest non-diagonal element is smaller than some tolerance ϵ

$$max(a_{ij}^2) \leq \epsilon \tag{30}$$

Convergence is guaranteed with the Jacobi method, however the number of floating point operations is quite large, typically $\mathcal{O}(12n^3 - 20n^2)$ operations in order to zero out non-diagonal elements.

D. Unit testing

In order to test the accuracy of our methods we can introduce some simple unit tests. For example we could check that our implementation of Jacobi's method for a simple symmetric matrix with known eigenvalues produces the exact results. For our problem the 3 lowest eigenvalues are known in the case of no interaction, and it is easy to test for example if our algorithm produces the lowest eigenvalue to some precision.
In addition, the solutions to the Schrodinger equation form an orthogonal basis. In the previous subsection we show that an orthogonal transformation preserves orthogonality, so we test our algorithm by checking to see if the resulting eigenvectors are orthogonal.
Finally, we test our function to find the maximum off-diagonal value of a matrix by testing it on a simple 3x3 symmetric matrix.

III. RESULTS AND DISCUSSION

A. No interaction

First we checked how many mesh points N we needed. We ran the program for equation (11) where we knew the lowest eigenvalue λ and wanted the difference $|\lambda_{theory} - \lambda_{num}|$ to be less than 10^{-4}, or 4 leading digits. The lowest eigenvalue should have been $\lambda_{theory} = 3$ and we found that we needed roughly $N = 200$ mesh points to obtain this precision.
We also checked how many similarity transformations were needed before all the non-diagonal elements were essentially zero. In the program we checked this by adding a counter which checked how many times we rotated matrix elements. We found that with $N = 200$ mesh points, we needed approximately 66600 transformations. Our tolerance when doing this was that the diagonal elements had to be smaller than $tol = 10^{-8}$.

Now that we found our right mesh point precision, we timed our algorithm and compared it to the $C{+}{+}$ library Armadillo. In Table (1) the times are included.

TABLE (I) Time comparison

Method	**Time [s]**
Jacobi algorithm	13.73
Armadillo	0.02

From Table (1) we can see that the method we have used for finding the eigenvalues is very inefficient compared to the method Armadillo is using. The problem with Jacobi's method is that applying the rotation will often add elements to the matrix which were previously zero. Relative to our matrix dimension $N = 200$, we required over 60 000 iterations to zero out non-diagonal elements.

We have then used the armadillo-function $eig\_sym(A)$ which also solves for a symmetric matrix A just like we have done in our Jacobi-method. The main difference is likely while we assume the whole matrix is filled with elements, eig_sym takes advantage of the fact that we have a sparse matrix (we have a tridiagonal matrix where the rest of the elements are zeros).

B. Coulomb interaction

In this project we were interested in the ground state energies. For the Coulomb repulsion this corresponds to the eigenvector which has the lowest eigenvalue.

We compare the ground-state energies for the case where the electrons are interacting and where they are not interacting, for different values of ω_R (see figures 1). We can see that for low values of ω_R the interacting case gives a wider wave-function (figure a). For higher ω_R the interacting and the non-interacting case get closer (figure b and c), but when ω_R increases they start to differ again. We can see that for $\omega_R = 5$ (figure d) the non-interacting case gets a narrower wave-function. This means that for higher ω_R's it will be easier to locate the electrons i.e. the probability to find them is higher in a smaller area.

These results mean that the ω_R factor has a higher significance for the wave-function than the Coulomb-interaction $1/\rho$ (see Equation (22)). We can see this from Figure (3) where $\omega_R = 1$. This is the case where the wave-functions are most similar compared to the other plots (figure (1), (2), and (4)), and in this case the Coulomb repulsion has a fairly small effect on the wave function.

IV. CONCLUSION

In this project we have studied solutions to the Schrodinger equation in a 3D oscillator potential by solving the eigenvalue problem numerically. We have written an implementation of Jacobi's rotation method for our matrix, and found it to be highly inefficient for the problem we are considering, namely the tridiagonal eigenvalue problem. We find that we would be better served exploiting the sparsity of our matrix as in the armadillo eigenvalue solvers. We also find our method to severely limit the possible accuracy of the solution, as we cannot have a large number of mesh points.

In addition, in solving, we find that the significance of the Coulomb repulsion between the two electrons greatly depends on the strength of the harmonic oscillator potential. And we also find that increasing it by a large factor (ω_R large) will give us highly localized electrons despite the electron repulsion.

V. APPENDIX

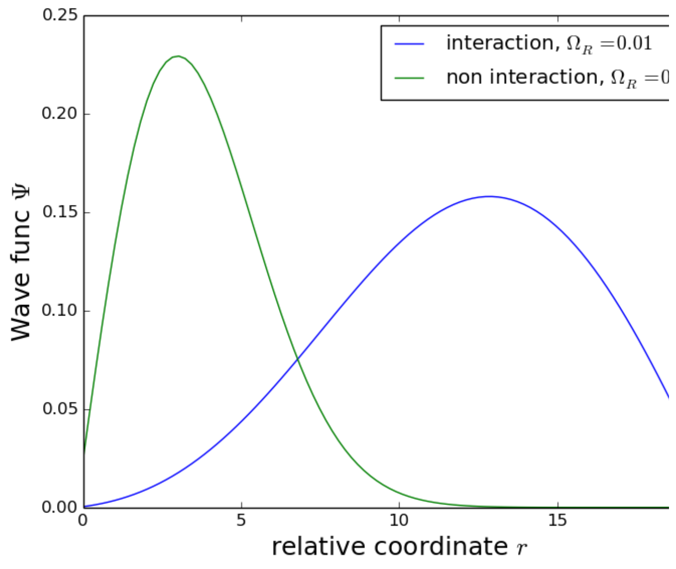
All code used is available at: link
In this section I list the main parts of code used:

main.cpp: Main program used for running the various algorithms and writing to file the results.

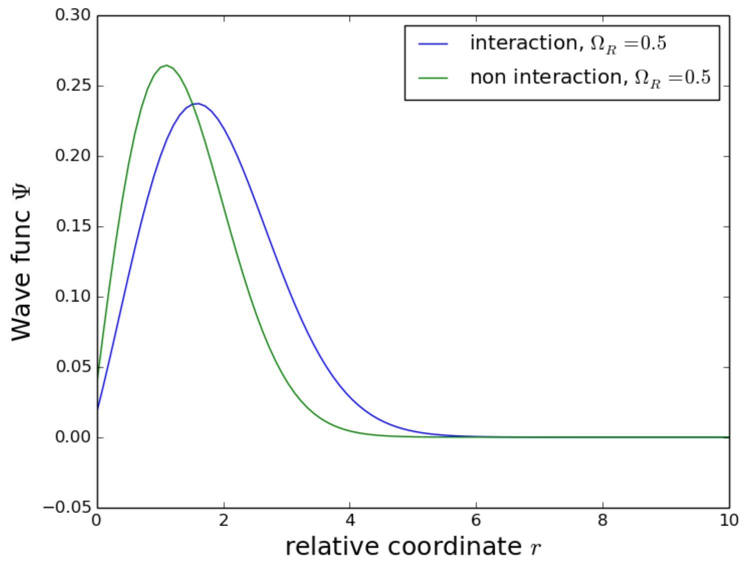
functions.cpp: As a test of header file functionality I moved some of the operations to the functions file and called upon them in the main file.

plot.py: Program for plotting the text file output from main.cpp

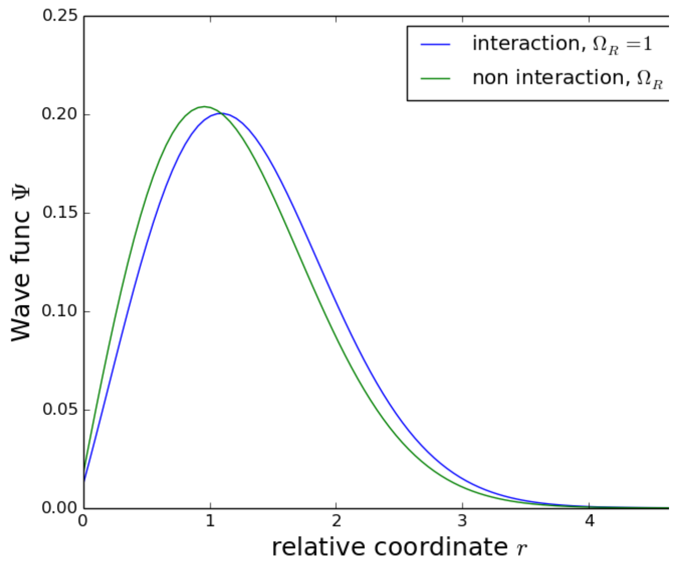
plot_eps.py: Program for plotting the max error



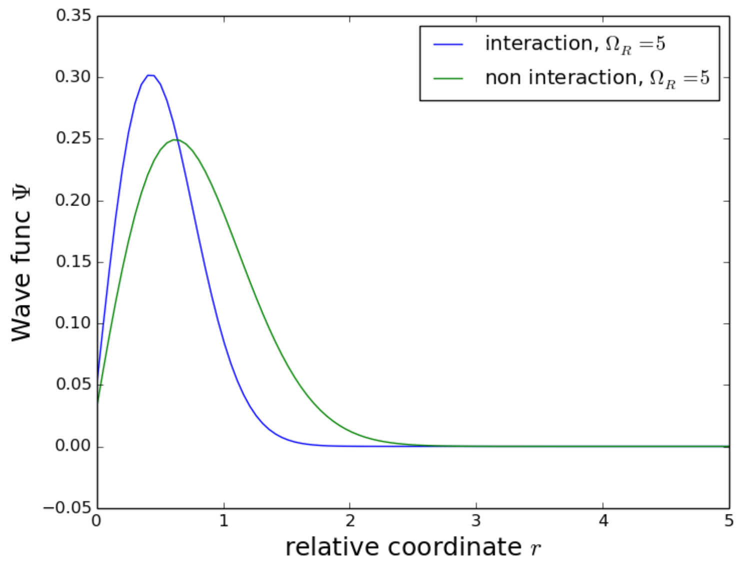
(a) Wavefunction for $\omega_r = 0.01$



(b) Wavefunction for $\omega_r = 0.5$



(c) Wavefunction for $\omega_r = 1$



(d) Wavefunction for $\omega_r = 5$

FIG. (1) Two-electron wavefunction for various values of ω_R

[1] All theory in this project adapted from FYS3150 Project 2 (Fall 2016) $< link >$.

[2] See M.H. Jensen, Computational Physics: Lecture Notes Fall 2015, ch. 7.3, available at $< link2 >$.