FYS4150: Project 2

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Abstract

In this project we study the three-dimensional Schrödinger equation for two electrons in a harmonic oscillator potential, with and without Coulomb interaction. The equations are solved as eigenvalue problems, using the Jacobi rotation algorithm. The Jacobi rotation method was compared to the *eig_sym* solver in the linear algebra library *Armadillo*. The results found Jacobi's method to be inferior to *eig_sym* when considering computational efficiency. The source code and benchmarks can be found on GitHub: `https://github.com/Kjernlie/FYS3150/tree/master/clean/project2`.

Physical Background

The aim of this project will be to solve the three-dimensional Schrödinger equation for two electrons numerically, both in the interacting and non-interacting case. We will use the Jacobi rotation method. Since spherical symmetry is assumed, we start by considering the radial part of the Schrodinger equation for a single particle:

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

Where $V(r)=\frac{1}{2}kr^2$ is the harmonic oscillator potential. The solutions of the Schrödinger equations are the so-called wave functions, which describe the probability for a particle (or a system of particles) to be found at a specific position or with a specific momentum. A particle in a harmonic oscillator can only be at specific, quantized energy levels:

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

Where the principal quantum number $n = 0, 1, 2...$ and orbital angular momentum quantum number $l = 0, 1, 2....$ In this project we set $l = 0$, so the energy levels are dependent only of n. Energy levels are therefore non-degenerate. By performing several simplifications and subsitutions we aquire the relevant equation for our project:

$$-\frac{d^2}{d\rho^2}u(\rho) + \rho^2 u(\rho) = \lambda u(\rho) \tag{3}$$

Where the eigenvalues in our case ($l = 0$) are $\lambda = \frac{2m\alpha^2}{\hbar^2}E$; $\lambda_0 = 3$, $\lambda_1 = 7$, $\lambda_2 = 11...$, where α is a normalization constant. The lowest energy, λ_0 is called the *ground state energy*.

For two electrons, we need to add an interaction term. The Coulomb interaction accounts for the repulsive electric force between the electrons (which both have negative charge). The Schrödinger equation is now:

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

Where $r = r_1 - r_2$ is the relative coordinate between the electrons, and $R = \frac{1}{2}(r_1 + r_2)$ is the center-of-mass coordinate. The equation can be separated into one r- and one R-dependent part. Adding the repulsive Coulomb interaction $V(r) = \frac{\beta e^2}{r}$ and considering the r-dependent equation, we get:

$$\Big(-\frac{\hbar^2}{m}\frac{d^2}{dr^2} + \frac{1}{4}kr^2 + \frac{\beta e^2}{r}\Big)\psi(r) = E_r\psi(r) \tag{5}$$

This can be rewritten as:

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \omega_r^2\rho^2\phi(\rho) + \frac{m\alpha\beta e^2}{\rho\hbar^2}\psi(\rho) = \frac{m\alpha^2}{\hbar^2}E_r\psi(\rho) \tag{6}$$

Where $\omega_r = \frac{1}{4}\frac{mk}{\hbar^2}\alpha^4$. Fix the normalization constant $\alpha = \frac{\hbar^2}{m\beta e^2}$, and define the new eigenvalue $\lambda = \frac{m\alpha^2}{\hbar^2}E$, and we get the equation:

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \omega_r^2\rho^2\psi(\rho) + \frac{1}{\rho} = \lambda\psi(\rho) \tag{7}$$

Numerical Approximation

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

$$u'' = \frac{u(\rho + h) - 2u(\rho) + u(\rho - h)}{h^2} + \mathcal{O}(h^2) \tag{8}$$

So the mathematical error in this case is of the order of $\mathcal{O}(h^2)$. We set the boundary conditions:

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

$$\rho_{min} = \rho_0 = 0$$

$$\rho_{max} = \rho_N = \infty$$

The latter can't be implemented, so we use several large values for ρ_{max}.

Numerical Implementation

The mesh points of the calculation are

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

So the one-particle equation is approximated by:

$$-\frac{u_{i+1} - 2u_i + u_{i-1}}{h^2} + \rho_i^2 u_i = \lambda u_i \tag{9}$$

Where we have use that $V_i = \rho_i^2$ is the harmonic oscillator potential. We see that this can be written as a $(N-1) \times (N-1)$-matrix equation:

$$\begin{bmatrix} \frac{2}{h^2} + V_1 & -\frac{1}{h^2} & 0 & ... & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2} + V_2 & -\frac{1}{h^2} & ... & 0 \\ \vdots & & \ddots & & \vdots \\ 0 & ... & -\frac{1}{h^2} & \frac{2}{h^2} + V_{N-2} & -\frac{1}{h^2} \\ 0 & 0 & ... & -\frac{1}{h^2} & \frac{2}{h^2} + V_{N-1} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_{N-2} \\ u_{N-1} \end{bmatrix} = \lambda \begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_{N-2} \\ u_{N-1} \end{bmatrix}$$

This can be generalized to the two-particle interacting case by changing the potential to $\omega_r^2 \rho^2 + \frac{1}{\rho}$.

Jacobi's Rotation Method

We want to solve the eigenvalue problem for a tridiagonal matrix:

$$\begin{pmatrix} d_0 & e_0 & 0 & ... & 0 & 0 \\ e_1 & d_1 & e_1 & ... & 0 & 0 \\ 0 & e_2 & d_2 & e_2 & ... & 0 \\ \vdots & & & \ddots & & 0 \\ 0 & ... & ... & 0 & e_N & d_N \end{pmatrix} \begin{pmatrix} u_0 \\ u_1 \\ \vdots \\ u_{N-1} \\ u_N \end{pmatrix} = \lambda \begin{pmatrix} u_0 \\ u_1 \\ \vdots \\ u_{N-1} \\ u_N \end{pmatrix} \tag{10}$$

We want to use Jacobi's rotation method. We define an orthogonal matrix S to operate on our matrix A:

$$B = S^T A S \tag{11}$$

With all elements in S equal to zero, except:

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

1. Find $\max(a_{kl})$.

2. Compute the rotation parameters $t = \tan\theta$, $c = \cos\theta$, $s = \sin\theta$:

$$\tau = \cot\theta = \frac{a_{ll} - a_{kk}}{2a_{kl}} \tag{12}$$

$$t = -\tau \pm \sqrt{1 + \tau^2} \tag{13}$$

$$c = \frac{1}{\sqrt{1 + t^2}} \ , \ s = tc \tag{14}$$

3. Calculate the elements of B:

$$b_{ii} = a_{ii} \ , \ i \neq k \ i \neq l$$

$$b_{ik} = a_{ik}c - a_{il}s \ , \ i \neq k \ i \neq l$$

$$b_{il} = a_{il}c + a_{ik}s \ , \ i \neq k \ i \neq l$$

$$b_{kk} = a_{kk}c^2 - 2a_{kl}c * s + a_{ll}s^2$$

$$b_{ll} = a_{ll}c^2 + 2a_{kl}c * s + a_{kk}s^2$$

$$b_{kl} = (a_{kk} - a_{ll})c * s + a_{kl}(c^2 - s^2)$$

4. If $\max(b_{kl}) \geq \epsilon$ run the algorithm again.

Figure 1: Jacobi rotation algorithm for tridiagonal matrix

Unitary and Orthogonal Transformations

A rotation, including Jacobi's rotation matrix, is a *unitary* operation. This means that the length and orthogonality of a set of vectors is preserved. A unitary matrix U has the properties:

$$U^{-1} = U^{\dagger} \tag{15}$$

An orthogonal matrix (the corresponding real matrix) has the properties:

$$U^{T} = U^{-1} \tag{16}$$

Where $U^{\dagger}$ is for matrices in Hilbert space (complex matrices). It represents the transpose of the complex conjugate, i.e. $U^{\dagger} = (U^{*})^{T}$.

Assume we have an orthogonal basis for the n-dimensional space v_i, where $v_j^T v_i = \delta_{ij}$:

$$\mathbf{v}_i = \begin{bmatrix} v_{i1} \\ \cdots \\ \cdots \\ v_{in} \end{bmatrix} \ , \ U\mathbf{v}_i = \mathbf{w}_i$$

Under orthogonal transformations, both the dot product and orthogonality of vectors is conserved:

$$\mathbf{w}_i^T \mathbf{w}_j = (U\mathbf{v}_i)^T (U\mathbf{v}_j) = \mathbf{v}_i^T U^T U \mathbf{v}_j = \mathbf{v}_i^T U^{-1} U \mathbf{v}_j = \mathbf{v}_i^T \mathbf{v}_j = \delta_{ij}$$

Unit Tests

The program and results for the unit tests can be found in the GitHub repository given in the abstract in *benchmarks.txt*. Here we will also present some benchmarks of our program.

Jacobi Rotation

We check the ability of our implemented Jacobi method to find eigenvalues on the matrix A, for which we aso find the eigenvalues analytically:

$$A = \begin{pmatrix} 1 & 2 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \ , \ \det(A - \lambda \mathbb{1}) = \begin{vmatrix} 1-\lambda & 2 & 0 \\ 2 & 1-\lambda & 0 \\ 0 & 0 & 1-\lambda \end{vmatrix}$$

$$\det(A - \lambda \not{1}) = (1-\lambda)^3 - 2 \cdot 2(1-\lambda) = (1-\lambda)[(1-\lambda)^2 - 4]$$

$$= (1-\lambda)[\lambda^2 - 2\lambda - 3] \rightarrow \lambda = -1 \cap \lambda = 3$$

$$\rightarrow (\lambda - 1)(\lambda + 1)(\lambda - 3)$$

Which gives us $\lambda_1 = -1$, $\lambda_2 = 1$ and $\lambda_3 = 3$.

Largest Non-Diagonal Element

We will test our function for finding the largest non-diagonal element on the following matrix

$$\begin{pmatrix} 1 & 4 & 1 & 1 \\ 3 & 1 & 6 & 1 \\ 1 & -5 & 1 & 5 \\ 1 & -4 & 3 & 1 \end{pmatrix}$$

where the largest non-diagonal element is 6.

Results

One Electron in a Harmonic Oscillator Well

To find the best values of ρ_{max} and the mesh size N we run our algorithm several times for different values of ρ_{max} and N. We know that the exact eigenvalues are $\lambda = 3, 7, 11, \ldots$. In Tab. 1 we can can see that $\rho_{max} = 5$ yields the best accuracy for the eigenvalues. Tab. 2 shows that for $\rho_{max} = 5$ accuracy is improved as the mesh size N is increased. For $N = 300$ we have four leading digits in the two lowest eigenvalues and three leading digits for the third eigenvalue. To get 4 leading digits in all of the three lowest eigenvalues we would have to increase the mesh size, but because of the long run time we have not done this here.

In Tab. 3 we have listed the execution times of the Jacobi method and Armadillo's solver *eig_sym* [2]. *eig_sym* is faster than Jacobi's method for all mesh sizes, and that the execution time of Jacobi's method rapidly increases for increasing mesh sizes, N. Thus, when using Jacobi's method on our system of equations, doing computations on large mesh sizes will be unfeasible

N	ρ_{max}	λ_1	λ_2	λ_3
200	2	3.52958	11.1685	23.5259
200	4	2.99991	7.00276	11.0772
200	5	2.99981	6.99904	10.9978
200	6	2.99972	6.99861	10.9966
200	8	2.9995	6.99752	10.994
200	10	2.99923	6.99613	10.9906

Table 1: The three lowest eigenvalues of our system are calculated using Jacobi's method. $N = 200$ is used while the value of ρ_{max} is varied.

N	ρ_{max}	λ_1	λ_2	λ_3
100	5	2.99923	6.99617	10.9908
200	5	2.99981	6.99904	10.9978
300	5	2.99991	6.99957	10.9991

Table 2: The three lowest eigenvalues of our system are calculated using Jacobi's method. $\rho_{max} = 5$ is used while the value of N is varied.

for all practical applications. The reason for the Jacobi methods large execution times is that it is a general algorithm with a slow convergence rate. The Jacobi algorithm requires typically $12N^3 - 20N^3$ operations in order to make all the non-diagonal elements zero. Although the Jacobi algorithm performs badly compared to algorithms based on tridiagonalization, it is still used because it easily can be parallelized [1]. For readers with a further interest in parallelization of Jacobi's algortihm, we recommend reading *Performance of the block Jacobi method for the symmetric eigenvalue problem on a modern massively parallel computer* [3].

N	Jacobi's method (s)	Armadillo (eig_sym) (s)
100	6.1353	0.009229
200	120.424	0.054138
300	670.29	0.168261

Table 3: The execution time for Jacobi's method and Armadillo's solver *eig_sym* with varying mesh sizes, N. $\rho_{max} = 5$ is used.

In Fig. 2 the three lowest eigenstates have been plotted. Here we used

the $\rho_{max} = 5$ that we found to yield the best accuracy in Tab. 1, and a mesh size, $N = 200$. We found a larger mesh size to be unfeasible to run. Also, $N = 200$ gives satisfying results for our purposes.

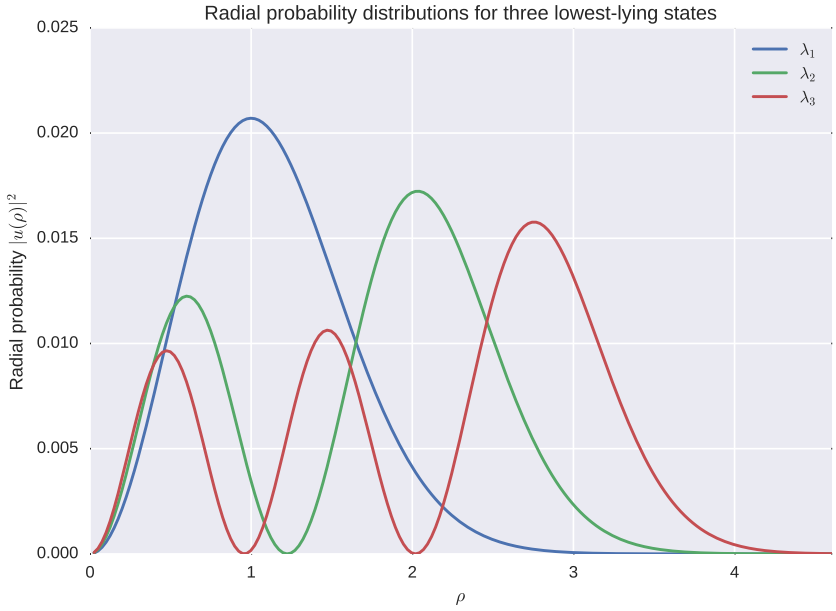

Figure 2: Radial probability distributions for three lowest-lying states for one electron in a harmonic oscillator well. The Jacobi method is used with $\rho_{max} = 5.0$ and $N = 200$.

Two Electrons in a Harmonic Oscillator Well

In the figures 3,4,5 and 6 the radial probability distributions for the three lowest-lying eigenstates are presented with and without Coulomb interaction between the electrons, for four different values of the oscillator-frequencies, ω_r. The oscillator-frequency ω_r represents the strength of the oscillator potential, so the size of ω_r controls how broad the wave function looks like, since the particles will be confined in the potential. For a larger ω_r, we will get a less broad wave function. This is backed up by our computations, since we clearly see the same relationships on our figures. For instance the functions given $\omega_r = 0.01$ are the broadest by far, and the functions given $\omega_r = 5.0$ are the thinnest. Furthermore, we have to update ρ_{max}

appropriately, or else the wave-functions will be "bounded" by the rho_max and inaccurate [1].

The effect of the Coulomb interaction force also becomes apparent in figures 3,4,5 and 6. With the interaction force the electrons will repel each other and we will see a widening of the radial probability distributions.

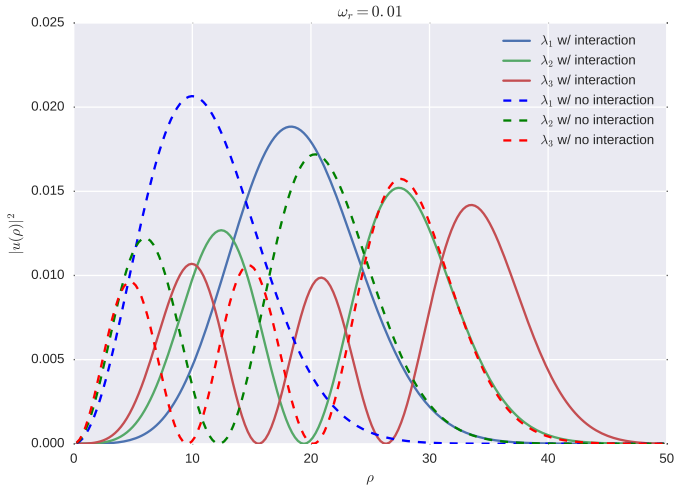

Figure 3: Radial probability distributions for the three lowest-lying states with and without Coulomb interaction, for two electrons in a harmonic oscillator well. The Jacobi method is used with $\rho_{max} = 50$, $N = 200$ and $\omega_r = 0.01$.

In Tab. 4 the numerically estimated values for the lowest eigen-states is compared to the analytical solutions, found for two specific potential strengths, $\omega_r = 0.25$ and $\omega_r = 0.05$. The analytic numbers are obtained from Taut's article *Two electrons in an external oscillator potential: Particular analytical solutions of a Coulomb correlation problem.* [4]. The computed relative error are acceptably small for our purposes. A smaller error could be obtained by using a larger mesh size, with the downside of a larger execution time.

Discussion

In this project we have studied the the behaviour of two electrons in a harmonic oscillator well. The physical problem was reformulated as discrete

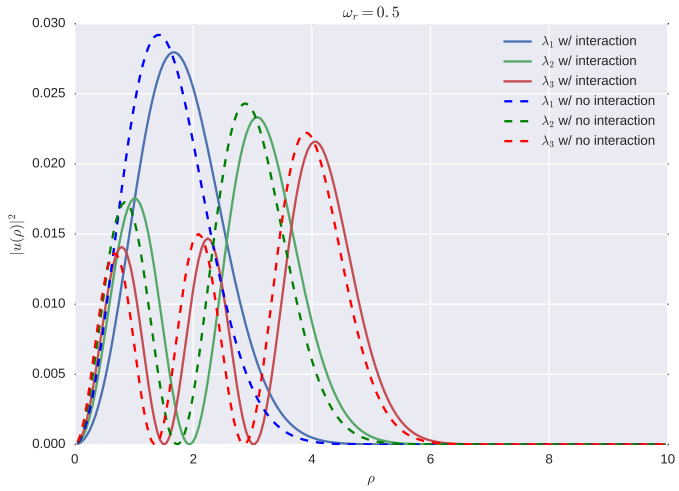

Figure 4: Radial probability distributions for the three lowest-lying states with and without Coulomb interaction, for two electrons in a harmonic oscillator well. The Jacobi method is used with $\rho_{max} = 10$, $N = 200$ and $\omega_r = 0.5$.

eigensystem and solved using Jacobi's method for diagonalizing symmetric matrices. We analyzed the results for different oscillator frequencies, and we found that or results coincided with our initial beliefs.

We found the Jacobi method to be unfeasible slow on large matrices and an interesting idea for future work would be to try to implement specialized algortihm for out tridiagonal system, and see if we could improve the accuracy and execution time.

References

[1] Morten Hjorth-Jensen. Computational physics. *Lecture notes*, 2015.

[2] Conrad Sanderson. Armadillo: An open source c++ linear algebra library for fast prototyping and computationally intensive experiments. 2010.

[3] Yuusuke Takahashi, Yuusuke Hirohita, and Yusaku Yamamoto. Performance of the block jacobi method for the symmetric eigenvalue problem

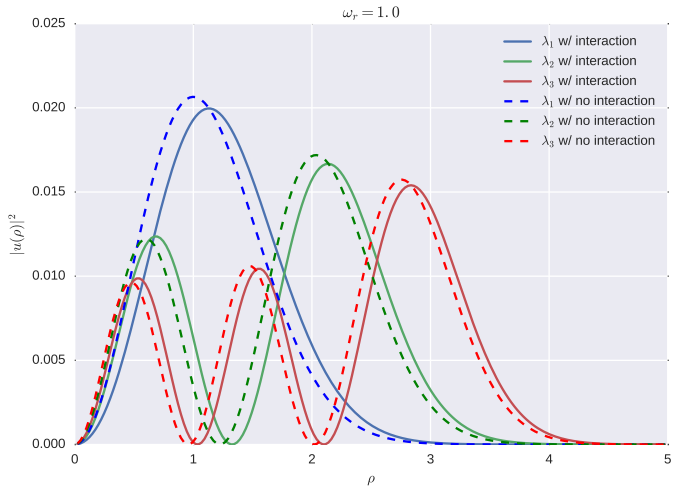

Figure 5: Radial probability distributions for the three lowest-lying states with and without Coulomb interaction, for two electrons in a harmonic oscillator well. The Jacobi method is used with $\rho_{max} = 5$, $N = 200$ and $\omega_r = 1.0$.

on a modern massively parallel computer. In *Proceedings of the Conference Algoritmy*, pages 151–160, 2015.

[4] M. Taut. Two electrons in an external oscillator potential: Particular analytic solutions of a coulomb correlation problem. *Phys. Rev. A*, 48:3561–3566, Nov 1993.

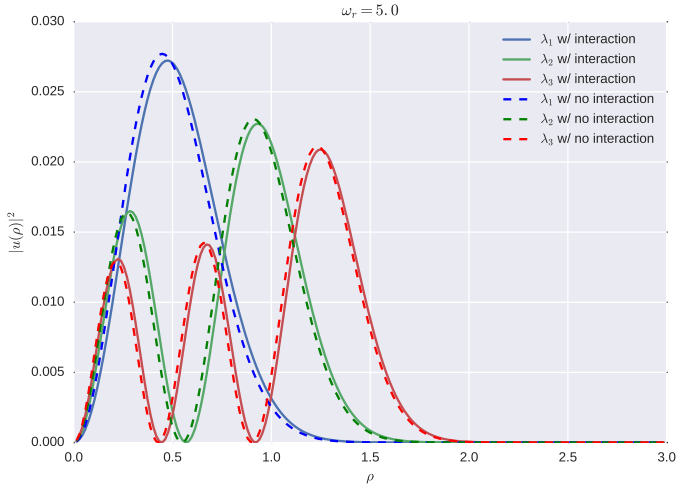

Figure 6: Radial probability distributions for the three lowest-lying states with and without Coulomb interaction, for two electrons in a harmonic oscillator well. The Jacobi method is used with $\rho_{max} = 3$, $N = 200$ and $\omega_r = 5.0$.

ω_r	Jacobi's method	Analytical	Relative Error
0.25	1.24995	1.25000	$4.0000 * 10^{-5}$
0.05	0.349985	0.35000	$4.2857 * 10^{-5}$

Table 4: The lowest eigen-state for the two particle system found using Jacobi's method is compared to the exact value found by Taut [4] for $\omega_r = 0.25$ and $\omega_r = 0.05$. For the Jacobi method $N = 200$, and $\rho_{max} = 10$ and $\rho_{max} = 30$ is used for $\omega_r = 0.25$ and $\omega_r = 0.05$, respectively.