

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

_____ FYS3150: COMPUTATIONAL PHYSICS _____

SEBASTIAN G. WINTHER-LARSEN
TRYGVE L. SVALHEIM
GITHUB.COM/GREGWINTHER

ABSTRACT. THIS IS NOT THE ABSTRACT FOR THIS PROJECT :) A one-dimensional version of the Poisson equation with Dirichlet boundary conditions is solved using two different algorithms. The two algorithms employed are the tridiagonal matrix algorithm and the LU decomposition method. We find that a fine-tuned version of the tridiagonal matrix algorithm is 10^5 times faster than the general LU decomposition method and 10 times as precise.

CONTENTS

1. Introduction	1
2. Theory	1
2.1. A single electron	1
2.2. Two electrons	2
2.3. Preservation of orthogonality and dot product in unitary transform	2
3. Algorithm	3
3.1. Jacobi's method	3
3.2. Implementation	4
4. Results	4
5. Summary Remarks	5
References	5
Appendix A. Laguerre Polynomials	5

1. INTRODUCTION

The aim of this study is to solve Schrödinger's equation for two electrons in a three-dimensional harmonic oscillator well with and without repulsive Coulomb interaction. The equation is reformulated to a discretized in order to be represented as a matrix eigenvalue problem that can be solved with Jacobi's method.

2. THEORY

We assume that electrons confined in a small area move in a three-dimensional harmonic oscillator potential and repel each other via the static Coulomb interaction. To simplify the problem, spherical symmetry is assumed.

2.1. A single electron. The radial part of Schrödinger's equation for a single electron reads

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

where $V(r)$ is the harmonic oscillator potential¹, $V(r) = \frac{1}{2}kr^2$ where $k = m\omega^2$, and consequently E is the energy of the harmonic oscillator in three dimensions. The angular frequency of the oscillator is given by ω and is related to the energy of the system as follows

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

However, we will consider cases with zero angular momentum only ($l = 0$). Moreover, by a somewhat lengthy substitutive exercise will culminate in a rewriting of Schrödinger's equation in 1 to a dimensionless form

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

where $u(r) = R(r)/r$ and $\rho = r/\alpha$ is a dimensionless parameter for length. The constant α is $\alpha = \sqrt{\hbar^2/mk}$ and the energy parameter (eigenvalues) are $\lambda = 2m\alpha^2 E/\hbar^2$. The three first eigenvalues will be $\lambda_0 = 3$, $\lambda_1 = 7$ and $\lambda_0 = 11$.

The second derivative in equation 3 will be approximated by the well-known central finite difference method for the second derivative,

$$(4) \quad \frac{du^2}{d\rho^2} = \frac{u(\rho+h) - 2u(\rho) + u(\rho-h)}{h^2} + \mathcal{O}(h^2)$$

where $h = (\rho_N - \rho_0)/h$ is the step size. By denoting $u(\rho_0 + ih)$ by u_i , equation 3 can be further rewritten to

$$(5) \quad -\frac{1}{h^2} u_{i-1} + \left(\frac{2}{h^2} + \rho_i^2 \right) u_i - \frac{1}{h^2} u_{i+1} = \lambda u_i$$

$$(6) \quad \mathbf{A}\mathbf{u} = \lambda\mathbf{u}$$

where the matrix in 6 is

$$(7) \quad \begin{bmatrix} \frac{1}{h^2} + \rho_i^2 & -\frac{1}{h^2} & 0 & 0 & 0 & \dots & 0 \\ -\frac{1}{h^2} & \frac{1}{h^2} + \rho_i^2 & -\frac{1}{h^2} & 0 & 0 & \dots & 0 \\ 0 & -\frac{1}{h^2} & \frac{1}{h^2} + \rho_i^2 & -\frac{1}{h^2} & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & -\frac{1}{h^2} & \frac{1}{h^2} + \rho_i^2 & -\frac{1}{h^2} \\ 0 & 0 & 0 & 0 & \dots & -\frac{1}{h^2} & \frac{1}{h^2} + \rho_i^2 \end{bmatrix}$$

¹One can in theory insert any potential into the Schrödinger equation, but in this case the harmonic oscillator potential is employed.

By finding the eigenvectors, or the energies, corresponding to the eigenvalues λ_i equation 5 above, one has found the wave function that describe the behavior of the electron for a particular state i . It is of interest to also state the exact, analytical wave function for the three lowest states, because the Schrödinger equation in general is only analytically solvable for a select few potentials, and the harmonic oscillator potential is amongst these. The general form of these radial wave function solutions is

$$(8) \quad R_{n,l=0}(r) = N_n e^{-\frac{m\omega}{2\hbar}r^2} \sqrt{L_n} \left(-\frac{m\omega}{2\hbar}r^2 \right)$$

where L_n refers to a particular Laguerre polynomial. More on the Laguerre polynomials can be found in appendix A. Reevaluating this function for the three lowest energy states and normalizing yields the following equations

$$(9) \quad |u_0(\rho)|^2 = \frac{4}{\sqrt{\pi}} \rho^2 e^{-\rho^2}$$

$$(10) \quad |u_1(\rho)|^2 = \frac{8}{3\sqrt{\pi}} \rho^2 \left(\frac{3}{2} - \rho^2 \right) e^{-\rho^2}$$

$$(11) \quad |u_2(\rho)|^2 = \frac{8}{15\sqrt{\pi}} \rho^2 \left(\frac{15}{4} - 5\rho^2 + \rho^4 \right) e^{-\rho^2}$$

It is only sensible to deal with the absolute squared values of the wave functions, because this is a probability density function for the position of the electron.

2.2. Two electrons. Now there are two harmonic oscillating electrons in the well. At first these are assumed to be non-interacting. The radial part of the Schrödinger equation for this situation reads

$$(12) \quad \left(-\frac{\hbar^2}{2m} \frac{d^2}{dr_1^2} - \frac{\hbar^2}{2m} \frac{d^2}{dr_2^2} + \frac{1}{2}kr_1^2 + \frac{1}{2}kr_2^2 \right) u(r_1, r_2) = E^{(2)} u(r_1, r_2)$$

We now introduce the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and the center of mass coordinate $R = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ as well as assuming separation of variables $u(r, R) = \psi(r)\phi(R)$. When the energy is given as a sum of the relative energy and center of mass energy, $E^{(2)} = E_r + E_R$ we get

$$(13) \quad \left(-\frac{\hbar^2}{m} \frac{d^2}{dr^2} + \frac{1}{4}kr^2 + \frac{\beta e^2}{r} \right) \psi(r) = E_r \psi(r)$$

when also including the repulsive Coulomb interaction, $V(r) = \beta e^2/|\mathbf{r}_1 + \mathbf{r}_2| = \beta e^2/r$. By once again introducing a dimensionless variable $\rho = r/\alpha$ with $\alpha = \hbar^2/(m\beta e^2)$. By, in addition, including the relative angular frequency $\omega_r^2 = (\frac{2\omega}{2\hbar}\alpha^2)^2$ and an energy parameter $\lambda = \frac{m\alpha^2}{\hbar^2} E_r$, we arrive at an equation comparable to 5

$$(14) \quad -\frac{d\psi(\rho)}{d\rho^2} + \left(\omega_r^2 \rho^2 + \frac{1}{\rho} \right) \psi(\rho) = \lambda \psi(\rho)$$

It is easy to see that the only difference from the situation with two electrons and a single electron is that the potential is changed from ρ^2 to $\omega_r^2 \rho^2 + 1/\rho$. In discretization, this is achieved by changing the diagonal of the matrix in 6 to $d_i = \frac{2}{\hbar^2 m \alpha^2} \omega_r^2 \rho^2 + \frac{1}{\rho_i}$.

2.3. Preservation of orthogonality and dot product in unitary transform. Consider a basis of vectors

$$(15) \quad \mathbf{v}_i = \begin{bmatrix} v_{i1} \\ \vdots \\ v_{in} \end{bmatrix}$$

We assume that the basis is orthogonal, that is

$$(16) \quad \mathbf{v}_j^T \mathbf{v}_i = \delta_{ij}.$$

It can be shown that a unitary transformation $\mathbf{w}_i = U\mathbf{v}_i$, where U is a unitary matrix such that $U^T U = I$, the dot product and orthogonality is preserved.

$$(17) \quad \begin{aligned} \mathbf{w}_i^T \mathbf{w}_j &= (U\mathbf{v}_i)^T U\mathbf{v}_j = \mathbf{v}_i^T U^T U \mathbf{v}_j = \mathbf{v}_i^T I \mathbf{v}_j \\ &\rightarrow \mathbf{w}_i^T \mathbf{w}_j = \mathbf{v}_i^T \mathbf{v}_j = \delta_{ij}, \end{aligned}$$

which means that both the dot product and orthogonality is preserved.

This proof is important to the algorithm which is described in the next section. As a result of Abel and Ruffini's theorem, regarding the impossibility of a solution to equations degree five and higher, a discretized problem as described herein is unsolvable by conventional, analytical means, and an iterative process is thus necessary.

3. ALGORITHM

3.1. Jacobi's method. First, consider a simple two-dimensional, symmetric matrix

$$(18) \quad A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}$$

where, because the matrix is symmetric, $a_{12} = a_{21}$. Second, consider an orthogonal rotation matrix

$$(19) \quad R = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix}$$

which when multiplied with some vector \mathbf{v} , rotates the vector by an angle θ . Now, we simplify the notation a bit by substituting the trigonometric functions $c = \cos \theta$ and $s = \sin \theta$. We can now write the similarity transform as

$$(20) \quad R^{-1} A R = \begin{bmatrix} a_{11}c^2 + 2a_{12}cs + a_{22}s^2 & (a_{22} - a_{11})cs + a_{12}(c^2 - s^2) \\ (a_{22} - a_{11})cs + a_{12}(c^2 - s^2) & a_{11}s^2 - 2a_{12}s + a_{22}c^2 \end{bmatrix}$$

Notice that this matrix is symmetric as well. We want to rotate in such a manner that the offdiagonal elements of the new matrix are zero. Hence we need to solve $(a_{22} - a_{11})cs + a_{12}(c^2 - s^2) = 0$, which gives

$$(21) \quad \tau = \cot 2\theta = \frac{a_{11} - a_{22}}{2a_{12}}$$

Now we can express all the trigonometric functions in terms of τ . Setting $t = \tan \theta$, $c = \cos \theta = 1/\sqrt{t^2 + 1}$ and $s = ct$. This yields $\cot 2\theta = 1/2(\cot \theta - \tan \theta) = 1/2(2^{-1} - t)$, all boiling down the quadratic equation

$$(22) \quad t^2 - 2\tau t - 1 = 0$$

which has two roots. Of these two roots we pick the smallest in order to ensure maximum numerical stability. To put it another way, we rotate a tiny angle rather than a large one at each iteration.

The eigenvalues can now be expressed in terms of t . The diagonalized matrix will look like this

$$(23) \quad R^{-1} A R = \begin{bmatrix} a_{11} & 0 \\ 0 & a_{22} \end{bmatrix}$$

Solving the characteristic equation provides the eigenvalues, while an inverse rotation of the identity matrix supplies the eigenvectors².

²Bear in mind that the eigenvectors and the eigenvalues will in this particular study represent the wave function and the corresponding energy levels respectively.

The algorithm for the 2×2 -case can easily be extended to a general case by using a $n \times n$ -matrix instead. Such a matrix is called the Givens rotation matrix and looks like this

$$(24) \quad G(i, j, \theta) = \begin{bmatrix} 1 & \dots & 0 & \dots & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & & \vdots & & \vdots \\ 0 & \dots & c & \dots & -s & \dots & 0 \\ \vdots & & \vdots & \ddots & \vdots & & \vdots \\ 0 & \dots & s & \dots & c & \dots & 0 \\ \vdots & & \vdots & & \vdots & \ddots & \vdots \\ 0 & \dots & 0 & \dots & 0 & \dots & 1 \end{bmatrix}$$

where $c = \cos \theta$ and $s = \sin \theta$.

Performing the corresponding transform as the one above for a particular $i = k$ and $j = l$ yields the following set of equations

$$(25) \quad \begin{aligned} a'_{hk} &= a'_{kh} = ca_{hk} - sa_{hl} \\ a'_{hl} &= a'_{lh} = ca_{hl} - sa_{hk} \\ a'_{kl} &= a'_{lk} = (c^2 - s^2)a_{kl} + sc(a_{kk} - a_{ll}) = 0 \\ a'_{kk} &= c^2 a'_{kk} + s^2 a_{ll} - 2sca_{kl} \\ a'_{ll} &= s^2 a'_{kk} + c^2 a_{ll} + 2sca_{kl} \end{aligned}$$

3.2. Implementation. HER SKAL DET NOE OM HVORDAN KODEN SER UT e.l.

4. RESULTS

STORT SETT BARE KOMMENTARER TIL FIGURENE

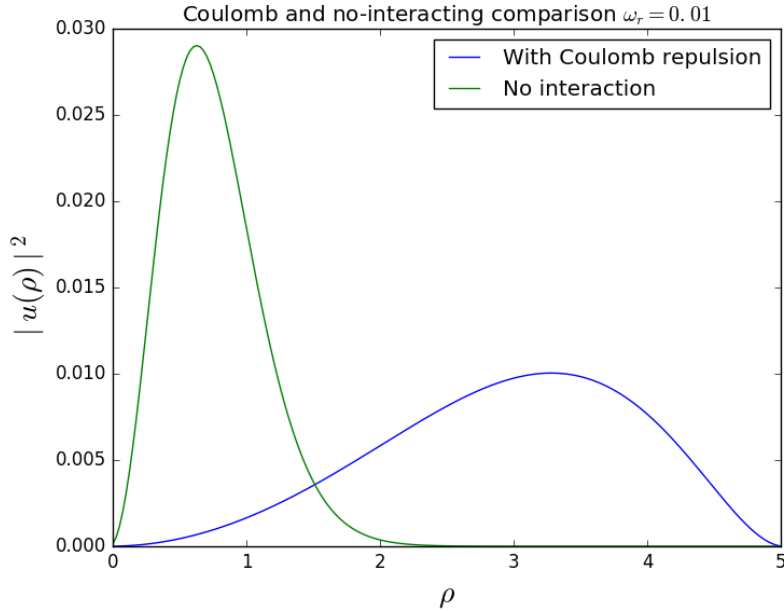


FIGURE 1. Plot showing the difference between the ground state with and without Coulomb repulsion.

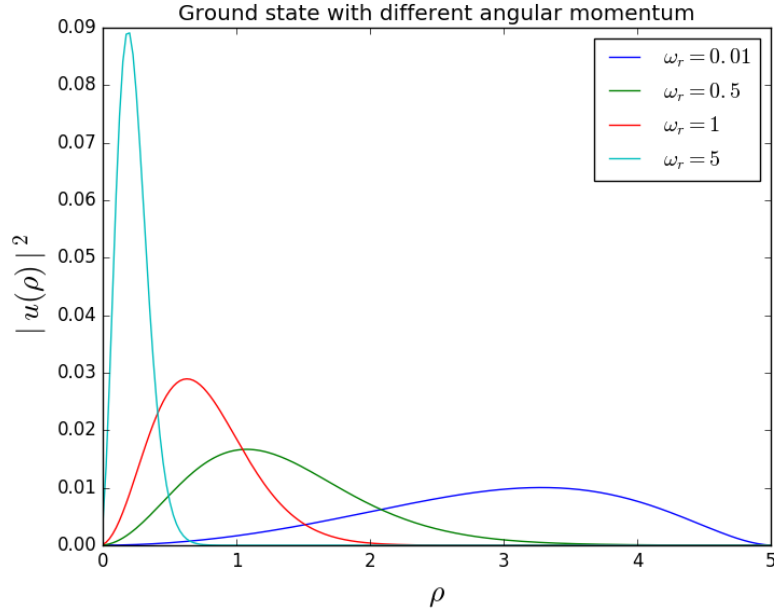


FIGURE 2. Plot of the ground state with Coulomb repulsion and varying angular momentum

5. SUMMARY REMARKS

KONKLUSJON OG OPPSUMMERING

REFERENCES

- [1] Hiorth-Jensen, M., *Project 2, Computational Physics I FYS3150/FYS4150*, University of Oslo, 2016.
- [2] Abel, N.H., Memoire sur le équations algébriques, ou l'on démontre l'impossibilité de la résolution de l'équation générale de cinquième degré, In Sylow, L. and Lie, S., *Æuvres Complètes de Niels Henrik Abel*, 2nd ed., Grøndahl & Søn, pp. 28-33, 1881.

APPENDIX A. LAGUERRE POLYNOMIALS

Generally, the name Laguerre polynomials is used for solutions to

$$(26) \quad x \frac{d^2 y}{dx^2} + (\alpha + 1 - x) \frac{dy}{dx} + ny = 0.$$

These polynomials, usually denoted, L_0 , L_1 , L_2 etc are a polynomial sequence which may be defined by the Rodriguez formula

$$(27) \quad L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} (e^{-x} x^n) = \frac{1}{n!} \left(\frac{d}{dx} - 1 \right) x^n$$

The first few Laguerre polynomials are shown in table 1.

TABLE 1. The first few Laguerre polynomials

n	$L_n(x)$
0	1
1	$-x + 1$
2	$\frac{1}{2}(x^2 - 4x + 2)$
3	$\frac{1}{6}(-x^3 + 9x^2 - 18x + 6)$
4	$\frac{1}{24}(x^4 - 16x^3 + 72x^2 - 96x + 24)$
5	$\frac{1}{120}(-x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120)$
6	$\frac{1}{720}(x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720)$