

FYS3150/4150

Computational Physics

Project 2

Magnus Ulimoen
Krister Stræte Karlsen

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1 Introduction

In this project the Schrödinger's equation for two electrons in a three-dimensional harmonic oscillator well will be solved numerically. Both computational and physical aspects of the problem will be discussed throughout the report.

The program and results of this project is found in a GitHub repository available at <https://github.com/mulimoen/FYS3150CompPhy> under the /project2 folder.

2 Method

2.1 Schrödinger's equation

2.1.1 Time-independent Schrödinger's equation

From quantum mechanics we have Schrödinger's equation on the form

$$\hat{H} |\Psi\rangle = i\hbar \frac{\partial}{\partial t} |\Psi\rangle \quad (2.1)$$

If the Hamiltonian \hat{H} is independent of time this is separable, and the left side of (2.1) is taken as E , and we get the time-independent Schrödinger equation;

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (2.2)$$

For a single electron the Hamiltonian has the form

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\mathbf{r}) \quad (2.3)$$

Or if written in the function basis,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \quad (2.4)$$

2.1.2 Spherical harmonics

Writing out (2.4) in spherical coordinates we end up with the equation

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \right) + V(r, \theta, \phi) \quad (2.5)$$

If V is spherically symmetrical, the solution is separable into $\Psi = R(r)Y_l^m(\theta, \phi)$ where Y_l^m is the associated Laguerre polynomials. The part in the square brackets is an eigenfunction of Y_l^m , with eigenvalue $-l(l+1)$.

2.1.3 Radial equation

The radial part of the Schrödinger's equation now reads:

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R(r) + V(r)R(r) = ER(r) \quad (2.6)$$

The l quantum number tends to "throw" the radial part outwards, and works as a centrifugal barrier.

2.2 Harmonic oscillator

In our case $V(r)$ is the harmonic oscillator potential $V = \frac{1}{2}kr^2$ with $k = m\omega^2$.

We make the substitution $R(r) = (1/r)u(r)$ in the radial equation and obtain

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u(r) + \left(V(r) + \frac{l(l+1)}{r^2} \frac{\hbar^2}{2m} \right) u(r) = Eu(r). \quad (2.7)$$

The boundary conditions are $u(0) = 0$ and $u(\infty) = 0$ to avoid an unnormalizable wave function.

Introducing the dimensionless variable $\rho = (1/\alpha)r$ where α is a constant with dimension length we get

$$-\frac{\hbar^2}{2m\alpha^2} \frac{d^2}{d\rho^2} u(\rho) + \left(V(\rho) + \frac{l(l+1)}{\rho^2} \frac{\hbar^2}{2m\alpha^2} \right) u(\rho) = Eu(\rho). \quad (2.8)$$

In this project we will only study the situation $l = 0$. Inserting $V(\rho) = (1/2)k\alpha^2\rho^2$ we end up with

$$-\frac{\hbar^2}{2m\alpha^2} \frac{d^2}{d\rho^2} u(\rho) + \frac{k}{2}\alpha^2\rho^2 u(\rho) = Eu(\rho). \quad (2.9)$$

Multiplying with $2m\alpha^2/\hbar^2$ on both sides to obtain

$$-\frac{d^2}{d\rho^2} u(\rho) + \frac{mk}{\hbar^2}\alpha^4\rho^2 u(\rho) = \frac{2m\alpha^2}{\hbar^2} Eu(\rho). \quad (2.10)$$

The constant α can now be fixed such that

$$\frac{mk}{\hbar^2}\alpha^4 = 1, \quad (2.11)$$

and the constant is now

$$\alpha = \left(\frac{\hbar^2}{mk} \right)^{1/4} \quad (2.12)$$

Defining

$$\lambda = \frac{2m\alpha^2}{\hbar^2} E, \quad (2.13)$$

we can rewrite Schrödinger's equation as

$$-\frac{d^2}{d\rho^2} u(\rho) + \rho^2 u(\rho) = \lambda u(\rho). \quad (2.14)$$

This equation can now be discretized and solved as a linear system using for example Jacobi's algorithm for eigenvalues.

2.2.1 Eigenvalues of the harmonic oscillator

The eigenvalues of (2.6) can be found analytically, and are the energies

$$E_{nl} = \hbar\omega \left(2n + l + \frac{3}{2} \right), \quad (2.15)$$

where n and l are quantum numbers, with $n = 0, 1, 2, \dots$ and $l = 0, 1, 2, \dots$

2.2.2 Two electrons in harmonic oscillator

If two electrons are put in the same potential a repulsive Coulomb interaction will emerge between them. If we use a relative coordinate and a COM coordinate, it can be shown that Schrödinger's equation reduces to

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \omega_r^2\rho^2\psi(\rho) + \frac{1}{\rho} = \lambda\psi(\rho) \quad (2.16)$$

with ω_r reflecting the strength of the potential.

2.3 Discretization

Using a standard center approximation for the second derivative: u

$$u'' = \frac{u(\rho+h) - 2u(\rho) + u(\rho-h)}{h^2} + O(h^2), \quad (2.17)$$

where h is our step length.

For a finite value of ρ_{\max} , we can define

$$h = \frac{\rho_{\max} - \rho_{\min}}{n_{\text{step}}}. \quad (2.18)$$

and

$$\rho_i = \rho_{\min} + ih, \quad i = 0, 1, 2, \dots, n_{\text{step}} \quad (2.19)$$

Then rewrite the Schrödinger equation for ρ_i as

$$-\frac{u(\rho_i+h) - 2u(\rho_i) + u(\rho_i-h)}{h^2} + \rho_i^2 u(\rho_i) = \lambda u(\rho_i) \quad (2.20)$$

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

Defining

$$d_i = \frac{2}{h^2} + V_i, \quad e_i = -\frac{1}{h^2}. \quad (2.21)$$

the Schrödinger equation takes the following form

$$d_i u_i + e_{i-1} u_{i-1} + e_{i+1} u_{i+1} = \lambda u_i, \quad (2.22)$$

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

$$\begin{pmatrix} d_1 & e_1 & 0 & 0 & \dots & 0 & 0 \\ e_1 & d_2 & e_2 & 0 & \dots & 0 & 0 \\ 0 & e_2 & d_3 & e_3 & 0 & \dots & 0 \\ \dots & \dots & \dots & \ddots & \ddots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots & d_{n_{\text{step}}-2} & e_{n_{\text{step}}-1} \\ 0 & \dots & \dots & \dots & \dots & e_{n_{\text{step}}-1} & d_{n_{\text{step}}-1} \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ \dots \\ \dots \\ u_{n_{\text{step}}-1} \end{pmatrix} = \lambda \begin{pmatrix} u_1 \\ u_2 \\ \dots \\ \dots \\ u_{n_{\text{step}}-1} \end{pmatrix} \quad (2.23)$$

Some care has to be taken when the limits are selected. Our approach has linear spacing between points, and an upper limit of ρ must be chosen. Care has to be taken to make sure the solution does not depend upon this selection.

We will now move on to see how we can solve this eigenvalue problem using Jacobi's algorithm.

2.4 Jacobi's eigenvalue algorithm

To obtain the eigenvalues of our matrix we are going to apply similarity transformations so that

$$S_N^T S_{N-1}^T \dots S_1^T A S_1 \dots S_{N-1} S_N = D$$

using an orthogonal transformation matrix on the form:

$$\begin{pmatrix} 1 & 0 & \dots & \dots & 0 \\ 0 & 1 & 0 & \dots & 0 \\ \vdots & 0 & \cos(\theta) & \dots & \sin(\theta) \\ \vdots & \dots & \dots & \ddots & \dots \\ 0 & \dots & -\sin(\theta) & \dots & \cos(\theta) \end{pmatrix}$$

To make this process effective we hunt down the largest non-diagonal element, say a_{kl} , and choose the angle of rotation, θ , so that the kl -element of the transformed matrix becomes zero. That means solving

$$(a_{kk} - a_{ll})\cos(\theta)\sin(\theta) + a_{kl}(\cos^2(\theta) - \sin^2(\theta)) = 0$$

Defining the quantities $\tan \theta = t = s/c$, with $s = \sin \theta$ and $c = \cos \theta$ and

$$\cot 2\theta = \tau = \frac{a_{ll} - a_{kk}}{2a_{kl}}. \quad (2.24)$$

We can then define the angle θ so that the non-diagonal matrix elements of the transformed matrix become non-zero and we obtain the quadratic equation (using $\cot 2\theta = 1/2(\cot \theta - \tan \theta)$)

$$t^2 + 2\tau t - 1 = 0, \quad (2.25)$$

resulting in

$$t = -\tau \pm \sqrt{1 + \tau^2}, \quad (2.26)$$

Here a clever choice of roots must be made. For for a well trained computational physicist this equation should be a red warning sign of loss of numerical precision. To avoid subtraction of to almost equal numbers the following choice should be made:

$$\begin{aligned} t &= -\tau + \sqrt{1 + \tau^2}, & 0 \geq \tau \\ t &= -\tau - \sqrt{1 + \tau^2}, & \tau < 0 \end{aligned}$$

From the equations above we obtain the following relation for c and t

$$c = \frac{1}{\sqrt{1 + t^2}}. \quad (2.27)$$

Knowing that $t \in [0, 1]$ we put restrictions such that $c \in [\frac{1}{\sqrt{2}}, 1]$ which focres θ to be in the interval $[-\frac{\pi}{4}, \frac{\pi}{4}]$.

Choosing the smaller t makes c the larger and minimizes

$$\|\mathbf{B} - \mathbf{A}\|_F^2 = 4(1 - c) \sum_{i=1, i \neq k, l}^n (a_{ik}^2 + a_{il}^2) + \frac{2a_{kl}^2}{c^2}. \quad (2.28)$$

2.4.1 Implementation

The Jacobi algorithm takes the form

Algorithm I

Find the largest element, a_{kl} , in A

Compute τ :

$$\tau = \frac{a_{ll} - a_{kk}}{2a_{kl}}$$

Compute t according to:

$$\begin{aligned} t &= -\tau + \sqrt{1 + \tau^2}, & 0 \geq \tau \\ t &= -\tau - \sqrt{1 + \tau^2}, & \tau < 0 \end{aligned}$$

Set

$$c = \frac{1}{\sqrt{1 + t^2}}, \quad s = ct$$

Compute the new matrix elements:

$$\begin{aligned} b_{kl} &= a_{kl}, & k, l \neq i, j \\ b_{ik} &= b_{ki} = ca_{ik} - sa_{jk}, & k \neq i, j \\ b_{jk} &= b_{kj} = sa_{ik} + ca_{jk}, & k \neq i, j \\ b_{ij} &= b_{ji} = (c^2 - s^2)a_{ij} + cs(a_{ii} - a_{jj}) \\ b_{ii} &= c^2a_{ii} - 2csa_{ij} + s^2a_{jj} \\ b_{jj} &= s^2a_{ii} + 2csa_{ij} + c^2a_{jj} \end{aligned}$$

2.4.2 Eigenvectors

From the similarity transformation we have

$$y = Sx \tag{2.29}$$

Multiplying by $S^{-1} = S^\top$ from the left

$$x = S^\top y \tag{2.30}$$

By considering multiple similarity transformations we obtain the recurrence relation

$$S_{(i)}^\top = S_i^\top S_{(i-1)}^\top \tag{2.31}$$

And finally

$$x = S_N^\top y \tag{2.32}$$

With y as the identity vector

Algorithm II

When each similarity transformation is completed, the new matrix

$$\tilde{S}^{n+1} = S^\top \tilde{S}^n$$

is computed and saved. An effective way of computing this if the factors c, s, l and k from algorithm I are known, dropping the transpose symbol;

$$\begin{aligned}\tilde{S}_{ij}^{n+1} &= \tilde{S}^n \quad \text{for } i \neq k, l \\ \tilde{S}_{kj}^{n+1} &= c\tilde{S}_{kj}^n - s\tilde{S}_{lj}^n \\ \tilde{S}_{lj}^{n+1} &= s\tilde{S}_{kj}^n - c\tilde{S}_{lj}^n\end{aligned}$$

To find the eigenvector belonging to an eigenvalue, its index i is found and the eigenvector is given by

$$x_j = \tilde{S}_{ji}^N$$

3 Results and reflection

3.0.3 Similarity transformations and matrix dimensionality

Doing numerical experiments, simply counting the similarity transformations needed in *Jacobi's algorithm*, we tried to extract a general behavior.

Table 1: Number of similarity transformations needed in Jacobi's algorithm and matrix dimensionality

Matrix dimension	No. similarity transformations
25	950
50	3945
75	9037
100	16377
150	36903
200	66079

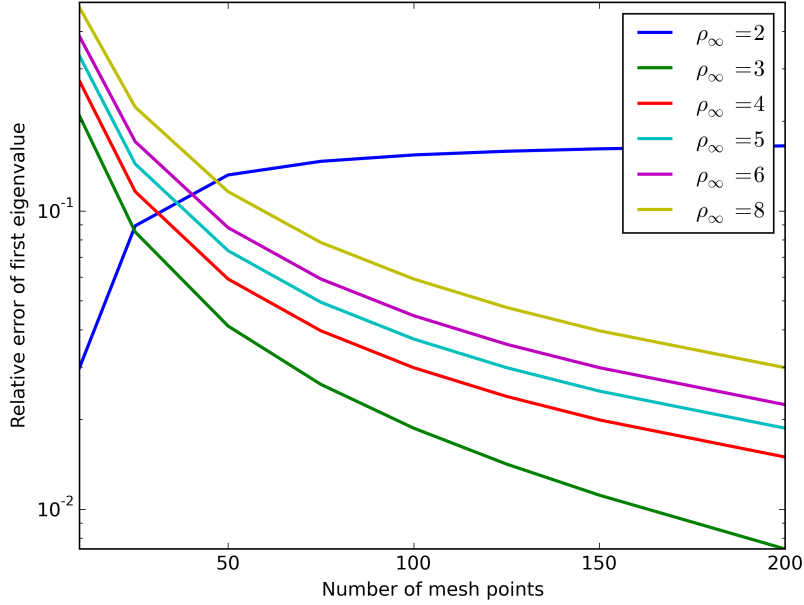


Figure 1: Relative error in the first energy level for different N and ρ_∞

3.1 Single electron in harmonic oscillator

A single electron in the harmonic oscillator potential has been explored using the above algorithms. Analytical solutions have been found, and it is therefore possible to compare these cases.

3.1.1 Energies

The three lowest energies are analytically known. Comparing these values with the one numerically computed gives plots 1, 2 and 3. If a higher N is chosen, the absolute error tends to decrease.

This is however not the case for all selections of ρ_∞ . If this limit is chosen too low the energies will not be as accurate, since the wave function can not unfold itself. An example of this is for the lowest energy level, figure 1, where the error for $\rho_\infty = 2$ does not tend to zero.

For larger energies this lower limit must be selected larger, as the wave function tends outwards. For the third lowest eigenvalue, 3 one must choose a higher ρ_∞ to compensate for this.

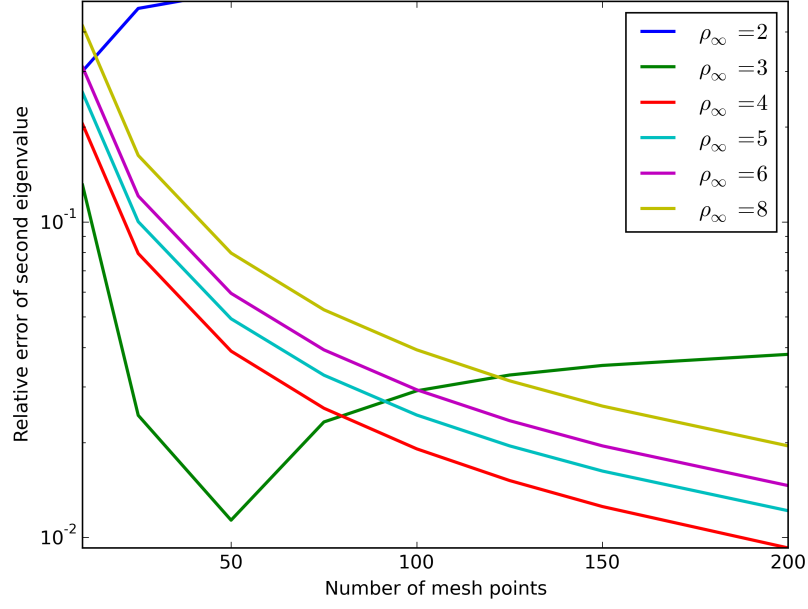


Figure 2: Relative error in the second energy level for different N , and ρ_∞

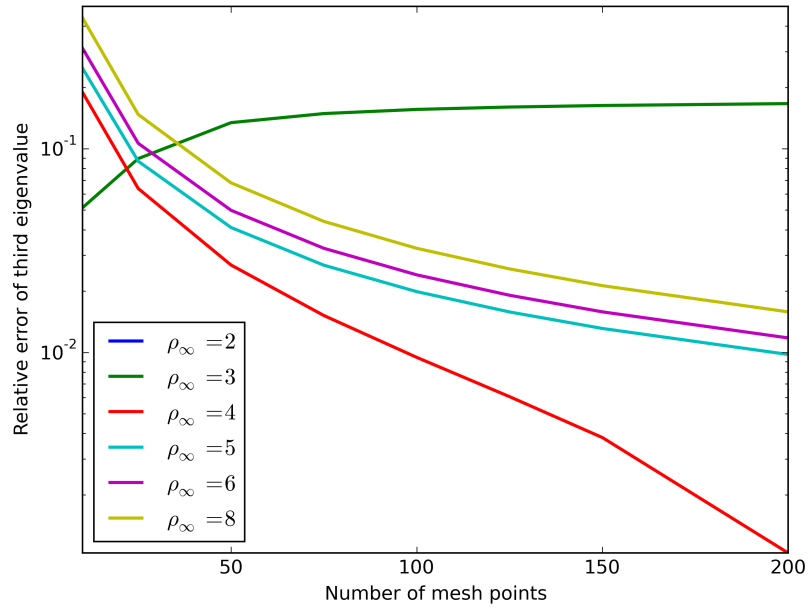


Figure 3: Relative error in the third energy level for different N , and ρ_∞

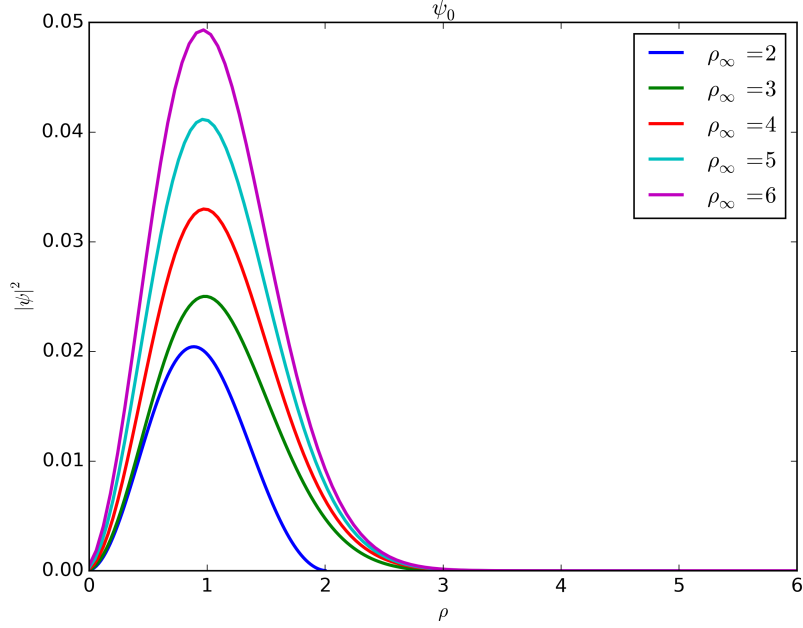


Figure 4: Wave function for different values of ρ_∞ for the eigenvector associated with the lowest energy

3.1.2 Wave function

The wave function is found by squaring the eigenvectors found for the Hamiltonian. The three lowest wave functions have been selected and plotted for different values of ρ_∞ , 4, 5, 6 and different values of N , 7, 8 and 9.

When N is increased the solutions tends to decrease and get smoother. This decrease is due to a better approximation of the integral for larger N , as the granularity causes the wave function to not be normalized appropriately.

The different values of ρ_∞ gives different eigenvectors. If it is chosen to low, the wave function will have a cutoff, and some of the true behaviour may be lost. On the other hand will choosing this limit to high ensure a worse approximation, since we do not sample the most critical points.

3.2 Two electrons

For a selection of ω_r with $N = 100$ and $\rho_\infty = 6$ we obtain the plots 11, 12 and 13 for the three lowest eigenvalues and associated eigenvectors.

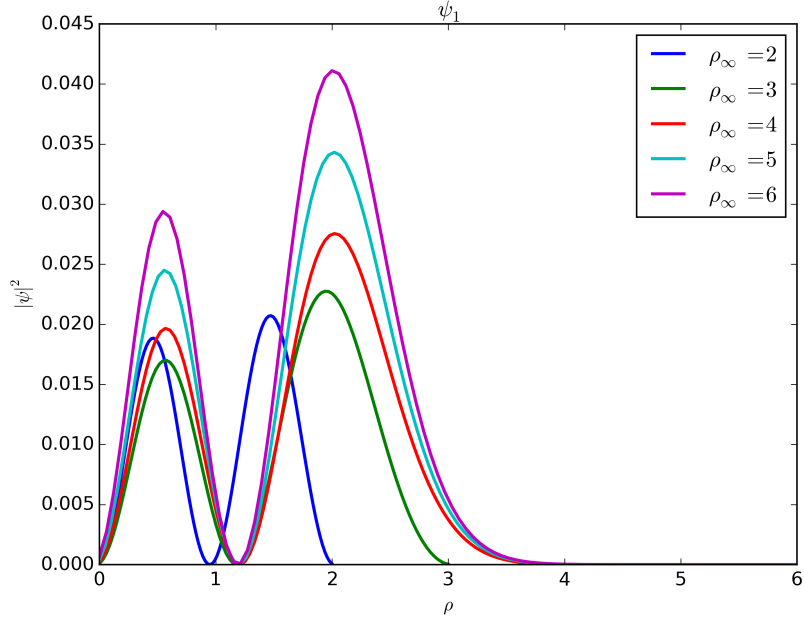


Figure 5: Wave function for different values of ρ_∞ for the eigenvector associated with the second lowest energy

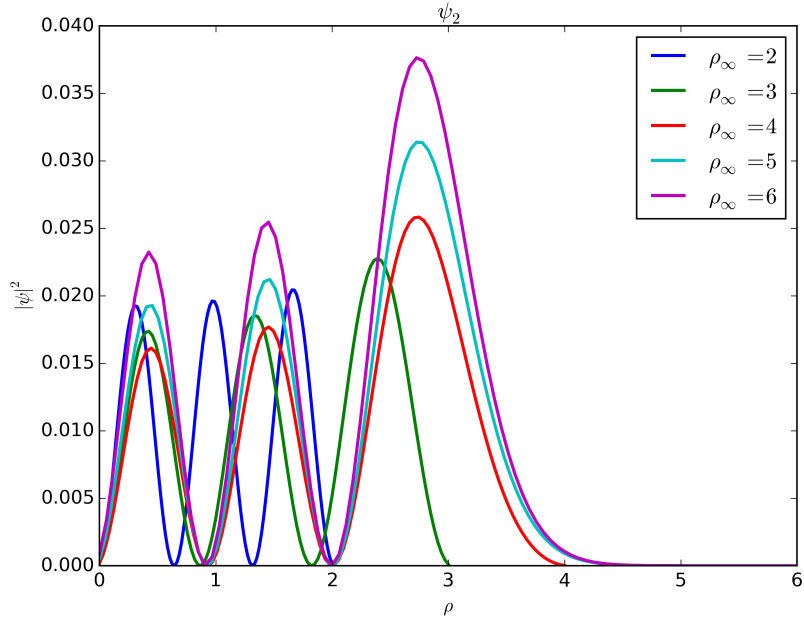


Figure 6: Wave function for different values of ρ_∞ for the eigenvector associated with the third lowest energy

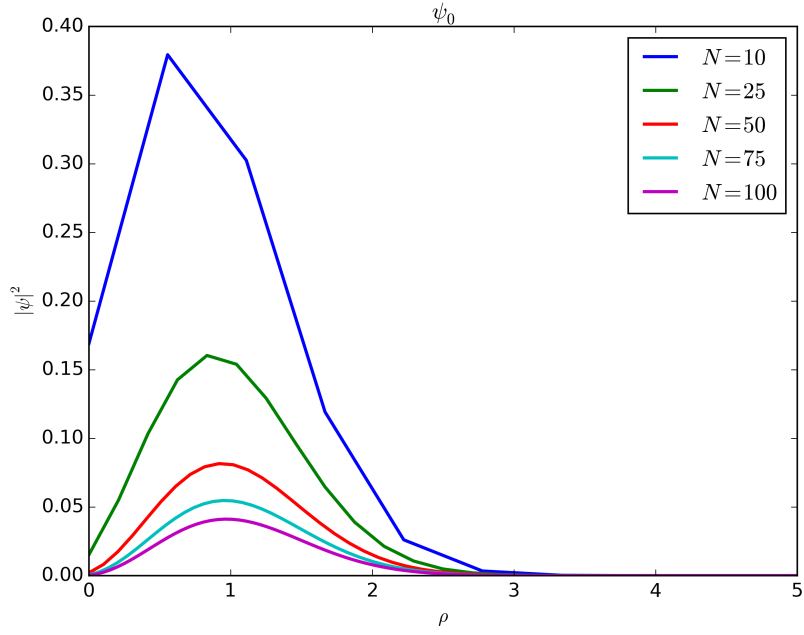


Figure 7: Wave function for different values of N for the eigenvector associated with the lowest energy

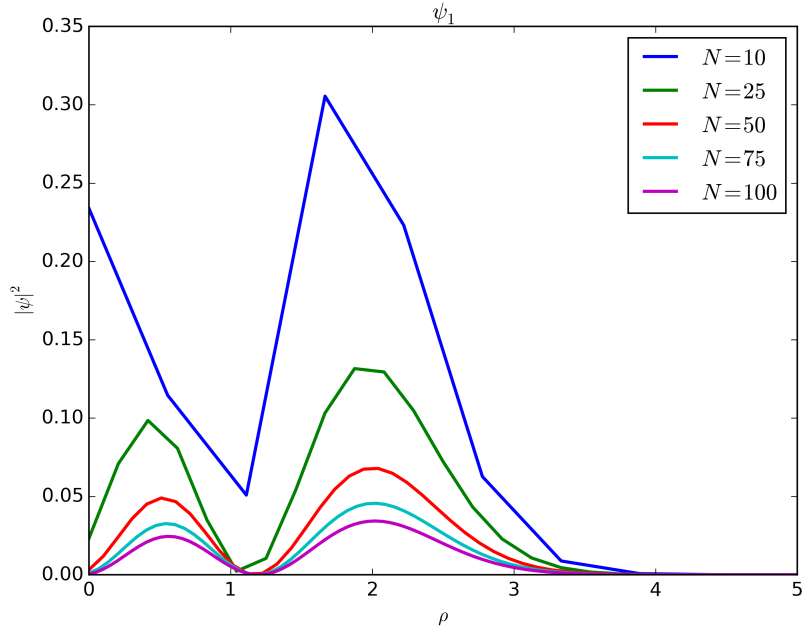


Figure 8: Wave function for different values of N for the eigenvector associated with the second lowest energy

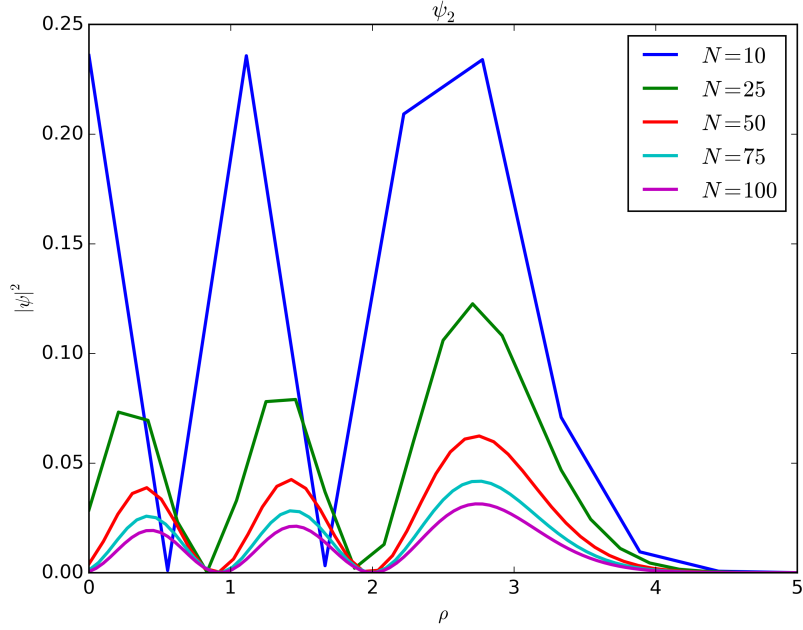


Figure 9: Wave function for different values of N for the eigenvector associated with the third lowest energy

It is clear that the strength of the harmonic oscillator determines the spread of the distribution. If the well is weak the wave function will spread past the normal limits from the single electron case. For the case ω_r approaching zero, it is not bound and one expects the electrons to separate, which is visible in figure 11 and have a binding energy that approaches zero.

For stronger bindings the binding energies increases, and the wave function concentrates closer to the centrum of the potential.

3.3 Hydrogen

My making some small modifications the program can be used for any potential. If supplied with the Coulomb interaction with a sufficiently strong interaction we achieve the bound states. An example is shown in figure 10.

4 Concluding remarks

Solving the Schrödinger equation with the help of matrices gives sufficiently good energy eigenvalues as long as care is taken to assure that the boundaries

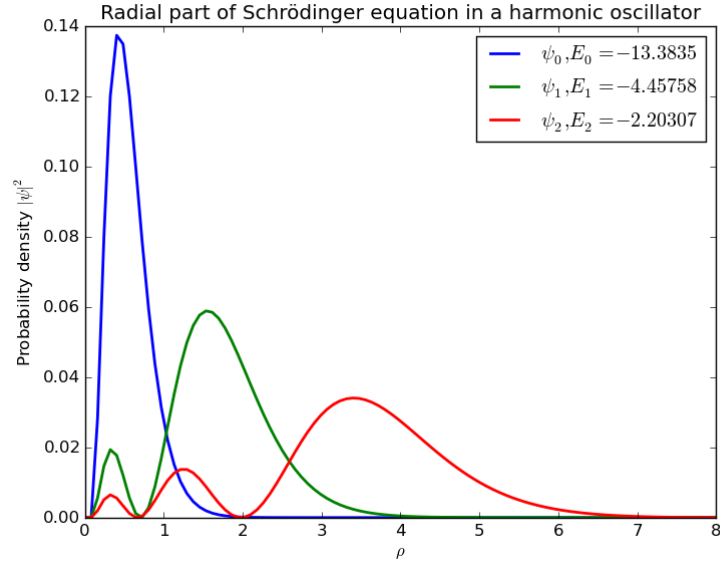


Figure 10: Electron around hydrogen atom. Title in picture is incorrect

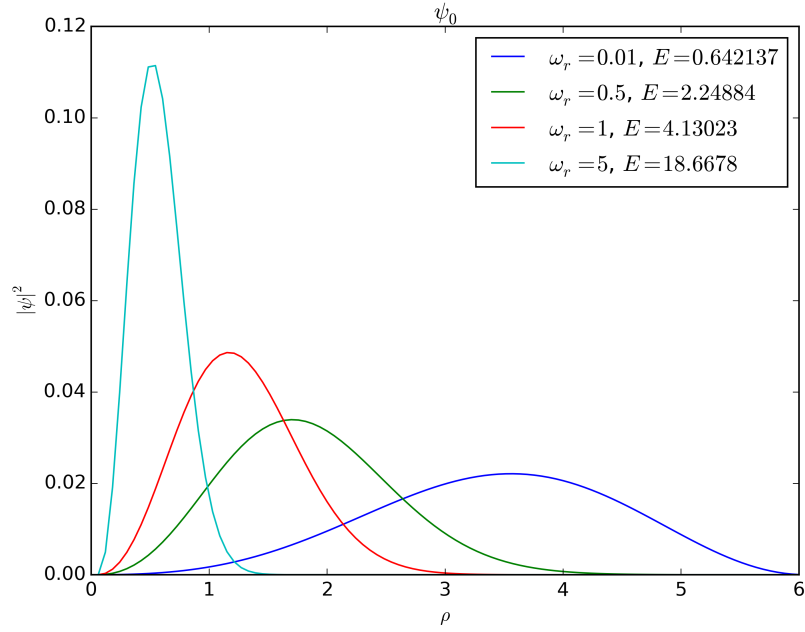


Figure 11: Wave function with lowest energy eigenvalue for different values of ω_r

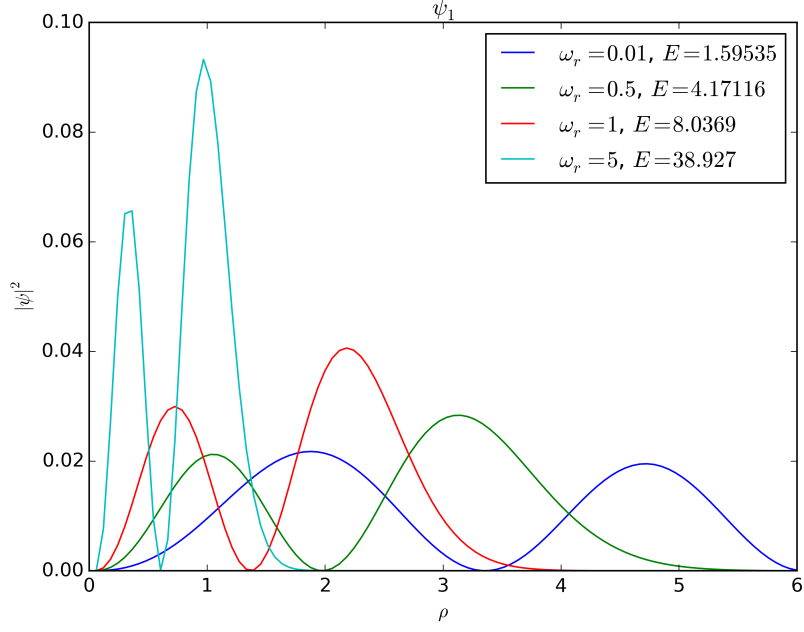


Figure 12: Wave function with second lowest energy eigenvalue for different values of ω_r

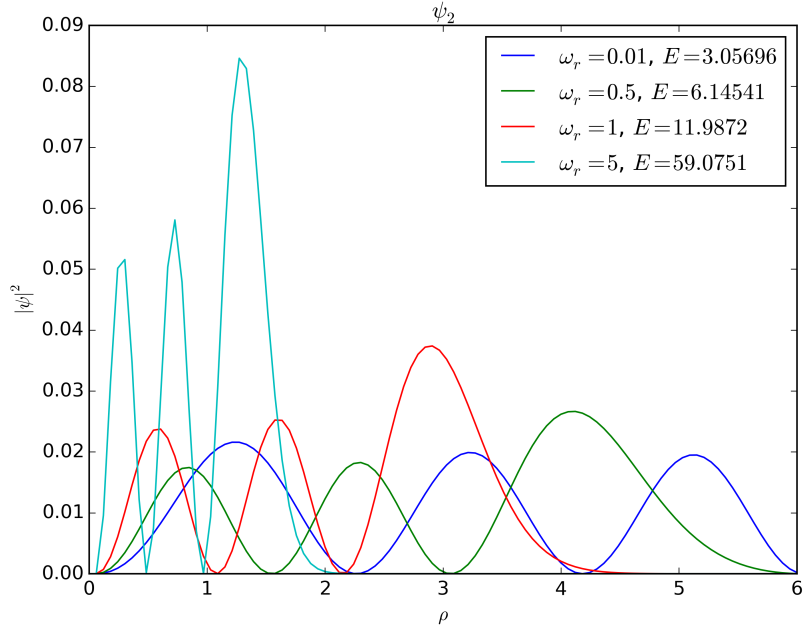


Figure 13: Wave function with third lowest energy eigenvalue for different values of ω_r

give stable solutions.

The Jacobi method is not scalable for larger N , as it requires over 15000 rotations for the 100×100 case. Other methods should be investigated to solve larger systems with less calculations.