report on project 2

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GitHub: `https://github.com/CPekaterina/project-no2`

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Introduction

Quantum dots are semiconductor nanocrystals and a very interesting research area because they have the potential to be used in a wide range of applications. There is research on using them in solar cells and LED's as well as in quantum computation. Another important field is biology and medicine where quantum dots are used as dyes for tracking molecules or cells and medical imaging. In quantum dots the electrons are bound in a small area so that there energy is quantized. In this project we solve Schrödinger's equation for two electrons in a threedimensional harmonic oscillator potential with and without a repulsive Coulomb interaction. In order to do so we formulate it as an eigenvalue problem and solve it numerically with **jacobi**'s method. We are going to see that we can manipulate the energies of the electrons by varying the strength of the potential wall which traps them in the said small area.

Reformulation of Schrödinger's equation

The radial part of Schrödinger's equation is

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

We can rewrite it for our problem as

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

where $\rho = \left(\frac{1}{\alpha}\right)r$ is a dimensionless variable, α is a constant with dimension length, and $u(r) = rR(r)$ with the boundary conditions $u(0) = 0$ and $u(\infty) = 0$. λ is defined as

$$\lambda=\frac{2m\alpha^2}{\hbar^2}E \tag{3}$$

with E beeing the energy of the harmonic oscillator in three dimensions. We approximate the second derivative with

$$u''(\rho)=\frac{u(\rho+h)-2u(\rho)+u(\rho-h)}{h^2} \tag{4}$$

where h is the step length and define $\rho_{min} = 0$ and ρ_{max} as minimum and maximum values of ρ. The step length h is then given by

$$h=\frac{\rho_{max}-\rho_{min}}{n_{step}} \tag{5}$$

Defining

$$\rho_i=\rho_{min}+ih\ i=0,1,2,...n_{step} \tag{6}$$

we can rewrite Schrödinger's equation as

$$-\frac{u_{i+1}-2u_i+u_{i-1}}{h^2}+\rho_i^2u_i=\lambda u_i \tag{7}$$

This set of equations can be written in form of a matrix eigenvalue problem.

$$\begin{pmatrix} d_1 & e_1 & 0 & 0 & \dots & 0 & 0 \\ e_1 & d_2 & e_2 & 0 & \dots & 0 & 0 \\ 0 & e_2 & d_3 & e_3 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots & d_{n_{\rm step}-2} & e_{n_{\rm step}-1} \\ 0 & \dots & \dots & \dots & \dots & e_{n_{\rm step}-1} & d_{n_{\rm step}-1} \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ \dots \\ \dots \\ \dots \\ u_{n_{\rm step}-1} \end{pmatrix} = \lambda \begin{pmatrix} u_1 \\ u_2 \\ \dots \\ \dots \\ \dots \\ u_{n_{\rm step}-1} \end{pmatrix} \tag{8}$$

We get a tridiagonal $(n_{step}-1)$ x $(n_{step}-1)$ matrix for which all non-diagonal elements are equal and given by

$$e_i = -\frac{1}{h^2} \tag{9}$$

The diagonal elements of the matrix are

$$d_i = \frac{2}{h^2} + \rho_i^2 \tag{10}$$

so the explicit form of the tridiagonal matrix is

$$\begin{pmatrix} \frac{2}{h^2}+\rho_1^2 & -\frac{1}{h^2} & 0 & 0 & \dots & 0 & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2}+\rho_2^2 & -\frac{1}{h^2} & 0 & \dots & 0 & 0 \\ 0 & -\frac{1}{h^2} & \frac{2}{h^2}+\rho_3^2 & -\frac{1}{h^2} & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots & \frac{2}{h^2}+\rho_{n_{\rm step}-2}^2 & -\frac{1}{h^2} \\ 0 & \dots & \dots & \dots & \dots & -\frac{1}{h^2} & \frac{2}{h^2}+\rho_{n_{\rm step}-1}^2 \end{pmatrix} \tag{11}$$

jacobi algorithm

To find the eigenvalues of this matrix we use the **jacobi**'s method. A real and symmetric matrix A has n eigenvalues and it exists a matrix S that is real and orthogonal such that

$$S^T A S = D \tag{12}$$

where D is the diagonal matrix with the eigenvalues on the diagonal. The general idea is now to perform similarity transformations on matrix A until it has the form of matrix D.

$$S_N^T ... S_2^T S_1^T A S_1 S_2 .... S_N = D \tag{13}$$

We call matrix B a similarity transformation of matrix A when

$$B = S^T A S \qquad S^T S = S^{-1} S = I \tag{14}$$

is fulfilled. Matrix B than has the same eigenvalues as matrix A, but generally different eigenvectors. **jacobi**'s method uses a transformation matrix S of the form

$$S = \begin{pmatrix} 1 & 0 & ... & 0 & 0 & ... & 0 & 0 \\ 0 & 1 & ... & 0 & 0 & ... & 0 & 0 \\ ... & ... & ... & ... & ... & ... & ... & ... \\ 0 & 0 & ... & \cos\theta & 0 & ... & 0 & \sin\theta \\ 0 & 0 & ... & 0 & 1 & ... & 0 & 0 \\ ... & ... & ... & ... & ... & ... & ... & ... \\ 0 & 0 & ... & 0 & 0 & ... & 1 & 0 \\ 0 & 0 & ... & -\sin\theta & ... & ... & 0 & \cos\theta \end{pmatrix} \tag{15}$$

with $S^T = S^{-1}$ what is a rotation matrix that performs a plane rotation around the angle θ. If we now do the similarity transformation

$$B = S^T A S \tag{16}$$

the matrix elements of B are given by

$$\begin{aligned} b_{ii} &= a_{ii}, i \neq k, i \neq l \\ b_{ik} &= a_{ik}\cos\theta - a_{il}\sin\theta, i \neq k, i \neq l \\ b_{il} &= a_{il}\cos\theta + a_{ik}\sin\theta, i \neq k, i \neq l \\ b_{kk} &= a_{kk}\cos\theta^2 - 2a_{kl}\cos\theta\sin\theta + a_{ll}\sin\theta^2 \\ b_{ll} &= a_{ll}\cos\theta^2 + 2a_{kl}\cos\theta\sin\theta + a_{kk}\sin\theta^2 \\ b_{kl} &= (a_{kk} - a_{ll})\cos\theta\sin\theta + a_{kl}(\cos\theta^2 - \sin\theta^2) \end{aligned} \tag{17}$$

The idea is now to perform similarity transformations on the original matrix A until all non-diagonal elements are smaller than a chosen tolerance ϵ. The first step in each iteration is to search for the largest non-diagonal matrix element. Because our matrix is symmetric we only look at the lower triangular. If the largest non-diagonal matrix element is bigger than the chosen tolerance ϵ we choose the angle θ in matrix S so that this element is ?zero/smaller? after the similarity transformation. We define $\tan\theta = t = \frac{s}{c}$ with $s = \sin\theta$,$c = \cos\theta$ and

$$\tau = \frac{a_{ll} - a_{kk}}{2a_{kl}} \tag{18}$$

what results in the equation

$$t = -\tau \pm \sqrt{1 + \tau^2} \tag{19}$$

To see which of the two roots we should take we look at the equation

$$|t| = \left|-\tau \pm \sqrt{1 + \tau^2}\right| \tag{20}$$

and consider the three cases $\tau = 0$, $\tau > 0$ and $\tau < 0$. For $\tau = 0$ we get

$$|t| = |\pm 1| = 1 \tag{21}$$

For $\tau > 0$ the absolute value of t is smaller for the solution with plus.

$$|t| = \left|-\tau + \sqrt{1 + \tau^2}\right| \tag{22}$$

Now we look at $\tau \to \infty$:

$$\lim_{\tau\to\infty} |t| = \lim_{\tau\to\infty} \left|-\tau + \sqrt{1 + \tau^2}\right| = 0 \tag{23}$$

For $\tau < 0$ the absolute value of t is smaller for the solution with minus.

$$|t| = \left|-\tau - \sqrt{1 + \tau^2}\right| \tag{24}$$

So now we look at $\tau \to -\infty$:

$$\lim_{\tau\to-\infty} |t| = \lim_{\tau\to-\infty} \left|-\tau - \sqrt{1 + \tau^2}\right| = 0 \tag{25}$$

Table 1: Number N of similarity transformations performed in the **jacobi** algorithm with respect to the dimensionality n of the matrix. The ratio N/n^2 suggests a behaviour that can be written as $N(n) \approx a \cdot n^2$ with a ranging in the order of 10^0. More about the behaviour of a in figure 1.

n	N	$a = N/n^2$
10	94	0.94
25	811	1.29
50	3542	1.42
100	14900	1.49
500	386898	1.55
1000	$> 10^6$	-

We have seen that for $\tau = 0$ the absolute value of t is one and if we increase or decrease τ it approaches zero. The absolute value of $\tan\theta$ is smaller or equal one for $|\theta| \leq \frac{\pi}{4}$. So if we choose t to be the smaller of the roots $|\theta| \leq \frac{\pi}{4}$ what is minimizing the difference between the matrices A and B. This can be seen if we look at the given equation

$$||\mathbf{B} - \mathbf{A}||_F^2 = 4(1-c) \sum_{i=1, i\neq k,l}^{n} (a_{ik}^2 + a_{il}^2) + \frac{2a_{kl}^2}{c^2} \tag{26}$$

$(1-c)$ at the beginning of the equation becomes zero when $\cos\theta = 1$ and than the total first part of the equation is zero. Also the second part of the equation reaches its minimum value for $\cos\theta = 1$. For $|\theta| \leq \frac{\pi}{4}$ the value of $\cos\theta$ is between 1 and ≈ 0.7 so the difference between the matrices A and B we get is near the minimum. This means that the non-diagonal matrix elements of A are nearly zero, what is what we want to achieve. After calculating t we obtain c and s with

$$c = \frac{1}{\sqrt{1+t^2}} \tag{27}$$

and

$$s = tc \tag{28}$$

and perform the similarity transformation. After that we search again for the largest non-diagonal matrix element and continue to perform similarity transformations until all non-diagonal matrix elements are smaller than the chosen tolerance ϵ. We can than simply read the eigenvalues from the diagonal of the matrix.

Estimation of the execution time

To estimate the number N of similarity transformations performed we assume that the algorithm needs roughly $O(n^2)$ of the latter simply because each transformation sets a non-diagonal element to zero. The algorithm converges as shown above but in general we still may obtain up to $n-2$ new non-zero, non-diagonal matrix elements after every transformation. Therefore this assumption has to be verified numerically. Up to this point we have not yet considered the dependence of the convergence rate on the precision ϵ of the search for the maximal non-diagonal element.
In the following discussion we set $\epsilon = 10^{-12}$ and $\rho_{max} = 5$ and vary the dimensionality of the

matrix in order to estimate the program's behaviour with respect to n.
In table 1 the number of similarity transformations is listed against the dimensionality n of the matrix for some significant numbers. The range of n is limited upwards due to the growth of the execution time, which goes with n^3. For $n = 1000$ more than a million transformations are required and because each transformation takes $O(n)$ time the running time of the program falls outside of tolerance for greater n.
From this table we conclude that the assumption made in the beginning is correct if we add a parameter a to the function

$$N(n) = a \cdot n^2 \tag{29}$$

Let us now have a closer look at this parameter and assume a dependence on n, thus leading to

$$N(n) = a(n) \cdot n^2 \tag{30}$$

If we now plot a against n we can approximate its behaviour to a exponential decay function as shown in figure 1. We note that in this model a approaches the saturation limit for n of the order of 10^2 so that we can lean back and perform the algorithm for greater n knowing that a should not change significantly. But, however, more computational power is needed to verify this theory.

Dependency on the choice of ρ_{max}

To find out how the accuracy of the computed eigenvalues depends on the choice of ρ_{max} we computed the lowest three eigenvalues for $n = 50, 100$ and 200 steps and different values of ρ_{max}. For every ρ_{max} and each of the three eigenvalues we calculated the difference between the exact solution and the computed result and added them to the total error. In figure 2 the total error depending on the value of ρ_{max} is shown for $n = 50, 100$ and 200.
For small ρ_{max} the computed eigenvalues have nothing in common with the exact solutions and small changes of ρ_{max} lead to big changes of the computed eigenvalues. The reason is that when we make ρ_{max} too small we set our wave functions zero at a point where the exact solutions are not even close to zero. The result is that our computed wave functions look very different than the exact solutions and due to that we also get completely different eigenvalues. If we increase ρ_{max} the total error gets rapidly smaller, until it reaches a minimum for ρ_{max} between 4 and 5.
The exact solutions of the wave functions are now essentially zero and the error we make through setting $u(\rho_{max}) = 0$ is very small. If we increase ρ_{max} further the total error increases slowly again, because with increasing ρ_{max} we also increase the step length (if the number of steps is constant). From $\rho_{max} = 50$ the total error increases quite fast for $n = 50$ because the step length becomes too large. Also for $n = 100$ the total error increases faster from the point where ρ_{max} is equal to the number of steps but not as fast as for $n = 50$ because the step length is increasing slower with increasing ρ_{max}.

Comparison with function tqli

To compare the results of our **jacobi** algorithm with the function **tqli** in the file **lib.cpp** we computed the lowest three eigenvalues for $\rho_{max} = 5$ and $n = 50, 100, 200, 400$. The results are shown in table 2 The eigenvalues computed with **jacobi** and **tqli** are nearly equal. The

Table 2: The lowest three eigenvalues for $\rho_{max} = 5$ and different numbers of steps with **jacobi** and **tqli** algorithm

N	ev1 **jacobi**	ev1 **tqli**	ev2 **jacobi**	ev2 **tqli**	ev3 **jacobi**	ev3 **tqli**
50	2.99687	2.99687	6.98434	6.98434	10.9619	10.9619
100	2.99922	2.99923	6.99609	6.99610	10.9907	10.9907
200	2.9998	2.9998	6.99904	6.99903	10.9978	10.9978
400	2.99995	2.99994	6.99976	6.99978	10.9996	10.9999

Table 3: Comparison between the results λ_0 for the ground state gained with the **jacobi**-algorithm and M. Taut's closed form results λ_T from 1993 for various ω_r. n_{step} is chosen 200 throughout, stable results are given for the chosen ρ_{max}. The order of the ω_r is kept from the original paper.

ρ_{max}	ω_r	λ_0	λ_T [1]
10	0.25000	1.2500	1.2500
20	0.05000	0.3500	0.3500
30	0.01826	0.1644	0.1644
10	0.19000	1.7106	1.7102
50	0.00867	0.0954	0.0954
30	0.04048	0.4454	0.4452

greatest difference between them is of the order 10^{-4}. You can also see that for both algorithms the computed eigenvalues get closer to the exact solution with increasing number of steps. The difference between the execution times of **tqli** and **jacobi** for $\rho_{max} = 5$ and different numbers of steps is shown in figure 3. For small numbers of steps both algorithms need nearly the same time but already for $n = 200$ **tqli** is twice as fast as the **jacobi** algorithm. For $n = 400$ it is more than three times as fast as **jacobi**. **jacobi** also provides the accuracy of four leading digits for $n \approx 275$ and larger.

Eigenvalues

In the next step we looked at the behaviour of two electrons in a harmonic oscillator potential instead of only one. The corresponding Schrödinger's equation for non-interacting electrons

Table 4: Eigenvalues λ_0 for the ground state for different strengths ω_r of the oscillator potential. The corresponding ρ_{max} guarantees the stability of the algorithm. The number of steps is $n_{step} = 300$ throughout.

ρ_{max}	ω_r	λ_0
50	0.01	0.1058
15	0.5	2.2299
5	1	4.0578
5	5	17.4464

then is

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr_1^2}-\frac{\hbar^2}{2m}\frac{d^2}{dr_2^2}+\frac{1}{2}kr_1^2+\frac{1}{2}kr_2^2\right)u(r_1,r_2)=E^{(2)}u(r_1,r_2). \tag{31}$$

These two equations can be solved with a product-ansatz. Introducing the relative coordinate r and the center of mass coordinate R we substitute:

$$\left(-\frac{\hbar^2}{m}\frac{d^2}{dr^2}-\frac{\hbar^2}{4m}\frac{d^2}{dR^2}+\frac{1}{4}kr^2+kR^2\right)u(r,R)=E^{(2)}u(r,R). \tag{32}$$

We omit the center of mass motion and focus on the relative motion. Then we add a repulsive Coulomb potential to the latter and obtain

$$\left(-\frac{\hbar^2}{m}\frac{d^2}{dr^2}+\frac{1}{4}kr^2+\frac{\beta e^2}{r}\right)\psi(r)=E_r\psi(r). \tag{33}$$

with $\beta e^2 = 1.44\text{eVnm}$. We again introduce the dimensionless coordinate ρ and after a few substitutions we end up with an equation similar to the one dealing with only one electron except for the potential now being $V=\omega_r^2\rho^2+\frac{1}{\rho}$:

$$-\frac{d^2}{d\rho^2}\psi(\rho)+\omega_r^2\rho^2\psi(\rho)+\frac{1}{\rho}\psi(\rho)=\lambda\psi(\rho). \tag{34}$$

Thus we can reuse the **jacobi**-algorithm we developed for the one-electron problem by simply replacing the potential. ω_r represents the strength of the oscillator potential and the following analysis deals with its values ranging between $\omega_r = 0.01$ and $\omega_r = 5$.
First of all repeating the procedure for finding the eigenvalues of the discretized Schrödinger's equation in (34) we find that the stability of the algorithm is dependent on the choice of ω_r. The weaker the potential wall is the larger ρ_{max} has to be set to guarantee reasonable results. The reason for this becomes obvious in the next part of the report when the plots of the probability distribution provide an overview. Some significant results however can be found in table 4.
The results for the eigenvalues show a linear dependency on the value of ω_r that can be clearly seen from the plot of λ_0 over ρ. That means that the energy of the ground state is linearly dependent on the strength of the potential wall. The weaker the potential wall, the lower the ground state energy is going to be. However the reader may be warned not to make any too fast conclusions on the ground state energy of free electrons from this. Nonetheless the linearity can be seen as a useful proxy for the eigenvalues.

We also reproduced some of the analytic results for the eigenvalues that Mr M.Taut (see [1]) found for the given problem in 1993. Table 3 shows that our results verify once more the outcome of his calculations. Also these values validate the assumption of a linear dependency of the energy on ω_r for they yield a very similar slope which is not shown in this report.

1 Results for the eigenfunctions

The program we developed not only computes the eigenvalues but also provides the corresponding eigenvectors v_i. These contain discretized values ψ_i of the wave-function that

go with each step ρ_i. However these vectors have to be normalized first. Discretizing the normalization condition leads to the following expression:

$$\int_{\rho_{min}}^{\rho_{max}} |\psi(\rho)|^2 \, \mathrm{d}\rho = 1 \quad \rightarrow \quad \underbrace{h \sum_{i=0}^{n_{step}} |v_i|^2}_{=1} = 1 \tag{35}$$

We choose the initial eigenvector matrix to be 1 and keep updating it by multiplying with the rotation matrices we obtain from the **jacobi** algorithm. Therefore the norm of the eigenvectors is equal 1 at any time. The normalizing factor k for the probability distribution then is $k = \frac{1}{h}$.
Figures (4) to (9) visualize the probability distributions with and without a repulsive Coulomb potential for the given problem in the ground and first two excited states. We choose ω_r to be 0.5, 1 and 5 in this case. From these plots one can clearly see the following:

1. The weaker the strength of the oscillator potential is the wider the distribution of the electrons is going to be. This goes along with a decrease of th energy of the state as seen in the previous discussion.

2. The probability to find an electron in the outer area inside the potential wall is higher than in the center and increases with heightened state of excitement. Here an analogy to the classical harmonic oscillator can be drawn where the probability to meet a mass point is higher at larger deflections.

3. The distribution is slightly wider when the repulsive Coulomb force is considered which is first of all logical in a classical view since a repulsive force tends to increase the distances.

4. The increment of the state leads to an increment of the number of nodes. Taking this as a rule we can deduce from a given probability distribution what state the system is in in that case.

Comments

With the **jacobi** algorithm we have found a general diagonalization method that we can use in order to find solutions to eigenvalue problems. The latter are widespread in physics and therefore this algorithm is a good basis that can be tuned to specific needs depending on the problem such that in some cases the $O(n^3)$ execution time can even be reduced.

To put it in a nutshell we developed an algorithm that yields reasonable and fairly precise results for the wave functions of one or two electrons in a harmonic oscillator potential for $l = 0$ and omitted center of mass movement. The latter can be included in further analysis because the center of mass motion can be computed separately also using the **jacobi** method and then combined with the relative movement over a product ansatz. The eigenvalues can be simply added then.

References

[1] 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.

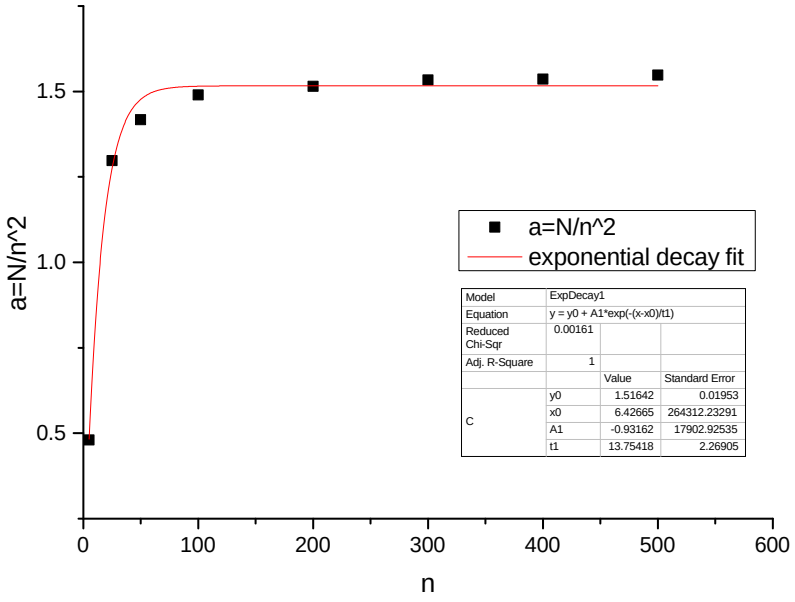

Figure 1: The behaviour of the parameter a in the $N(n)$ function that describes the number of similarity operations on the matrix can be approximated with an exponential function as shown in this figure.

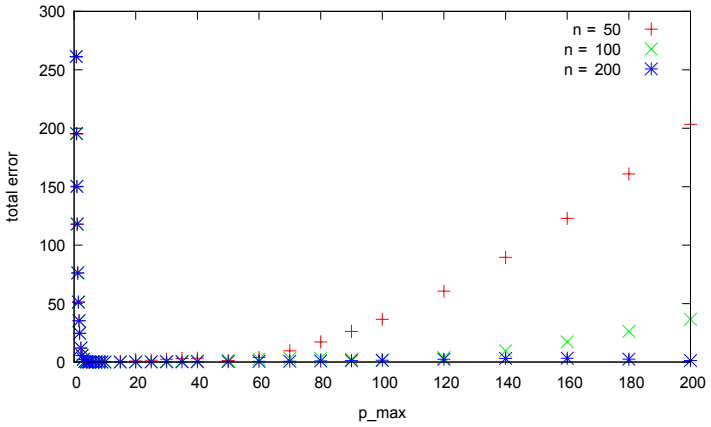

Figure 2: The total error of the three lowest computed eigenvalues for different ρ_{max} and $n = 50, 100, 200$

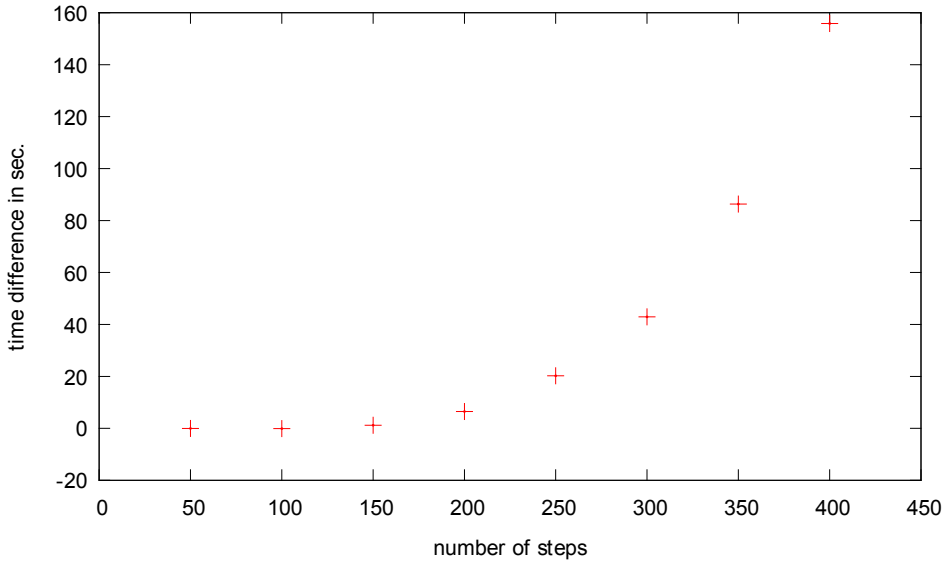

Figure 3: The difference between the execution times of **jacobi** and **tqli** for $\rho_{max} = 5$ and different numbers of steps

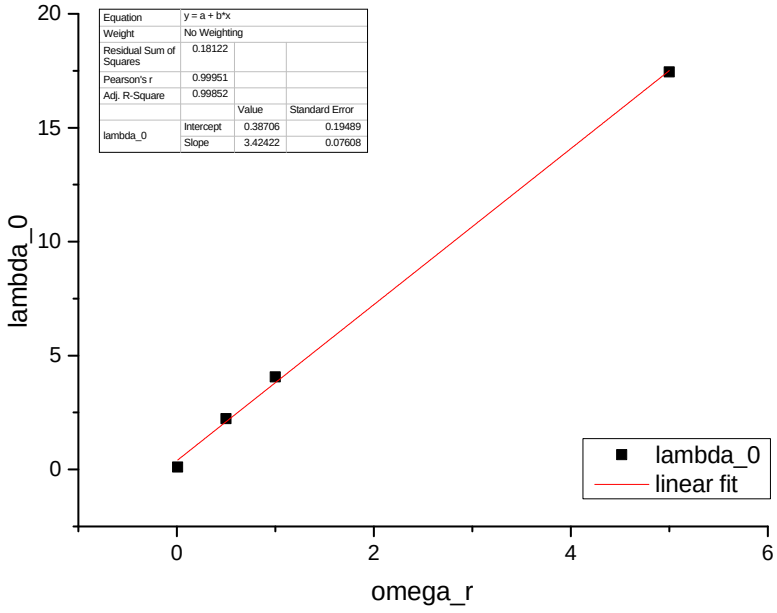

Figure 4: The ground state eigenvalues as a function of the strength of the oscillator potential

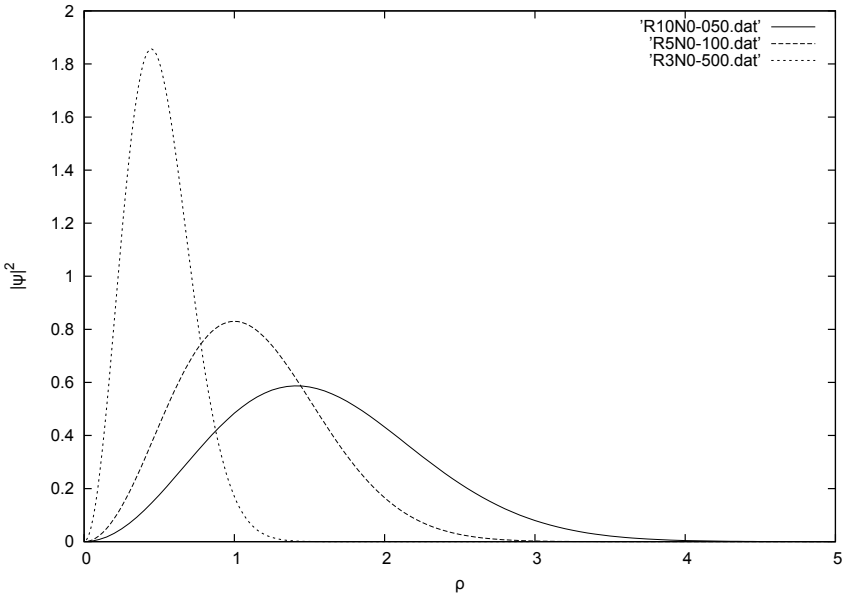

Figure 5: ground state, no Coulomb repulsion

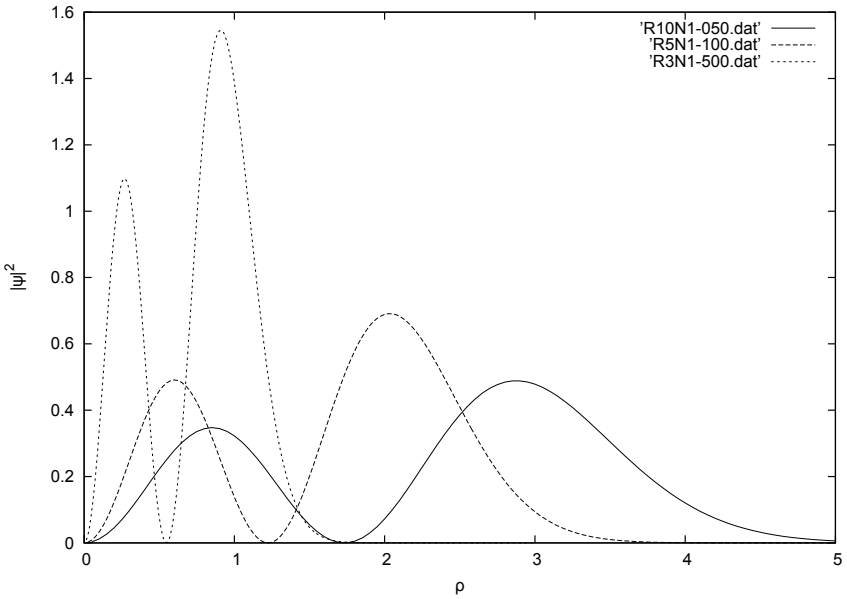

Figure 6: first excited state, no Coulomb repulsion

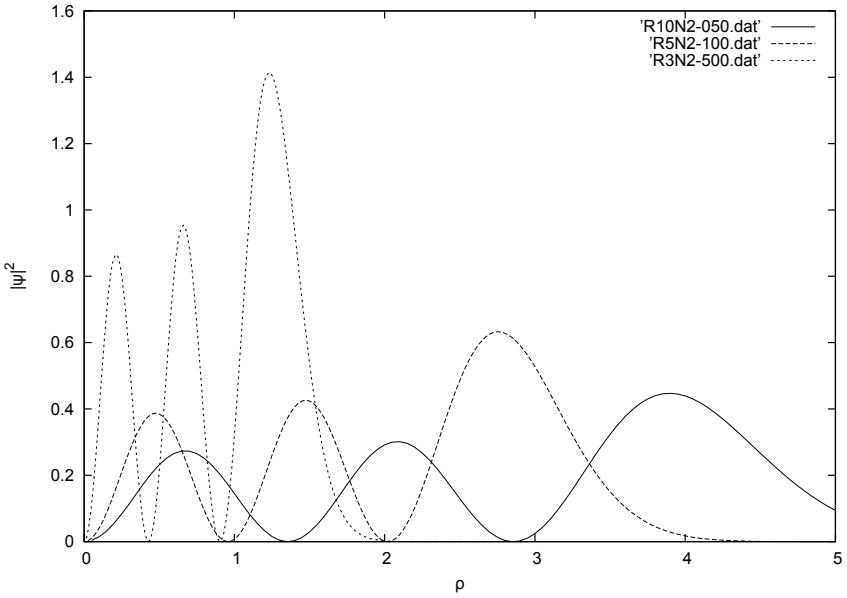

Figure 7: second excited state, no Coulomb repulsion

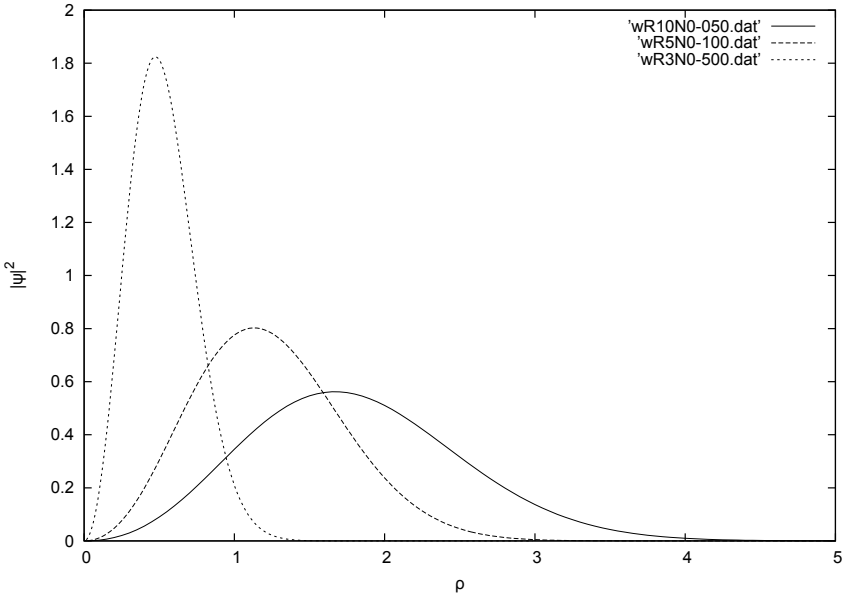

Figure 8: ground state with Coulomb repulsion

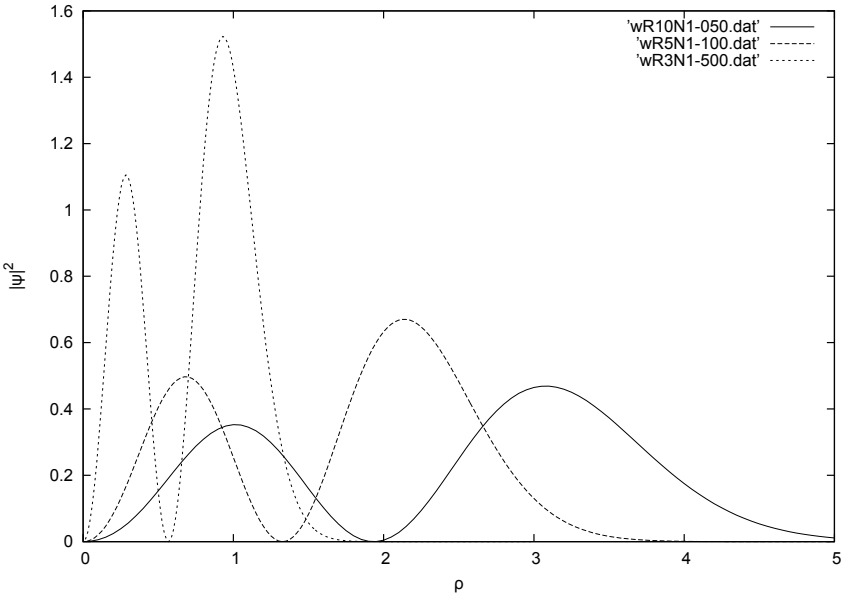

Figure 9: first excited state with Coulomb repulsion

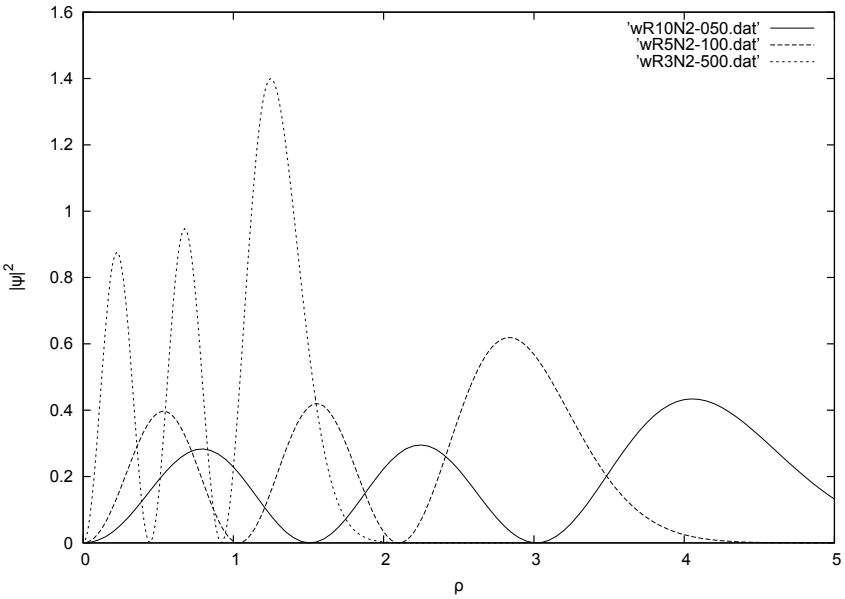

Figure 10: second excited state with Coulomb repulsion