

FYS4150 Project 2:

Schrödinger's equation for two electrons in a 3-dimensional harmonic oscillator well

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Abstract

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Github: <https://github.com/mariahammerstrom/Project2>

1 Introduction

The aim of this project is to solve Schrödinger's equation for two electrons in a three-dimensional harmonic oscillator well with and without a repulsive Coulomb interaction. We are first interested in the solution of the radial part of Schrödinger's equation for *one* electron. This equation reads

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

In our case $V(r)$ is the harmonic oscillator potential $(1/2)kr^2$ with $k = m\omega^2$ and E is the energy of the harmonic oscillator in three dimensions. The quantum number l is the orbital momentum of the electron. The oscillator frequency is ω and the energies are

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

with $n = 0, 1, 2, \dots$ and $l = 0, 1, 2, \dots$. In this project we use $l = 0$.

We will solve Eq. (1) by reformulating it in a discretized form as an eigenvalue equation to be solved with Jacobi's method.

After some substitutions and introducing the dimensionless variable $\rho = (1/\alpha)r$ where α is of dimension length, we can rewrite Eq. (1) as

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

This is the first equation to solve numerically. In three dimensions the eigenvalues for $l = 0$ are $\lambda_0 = 3, \lambda_1 = 7, \lambda_2 = 11, \dots$

We use the by now standard expression for the second derivative of a function u

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

where h is our step length. For a given number of steps n_{step} , the step length is defined as

$$h = \frac{\rho_{\text{max}} - \rho_{\text{min}}}{n_{\text{step}}}. \quad (1)$$

Next we define minimum and maximum values for the variable ρ , $\rho_{\text{min}} = 0$ and ρ_{max} , respectively. Define an arbitrary value of ρ as

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

Now we can write the Schrödinger equation in a compact way

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

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

Define first the diagonal matrix element

$$d_i = \frac{2}{h^2} + V_i, \quad (3)$$

and the non-diagonal matrix element (which is a mere constant, and are all equal)

$$e_i = -\frac{1}{h^2}. \quad (4)$$

With these definitions the Schrödinger equation takes the following form

$$d_i u_i + e_{i-1} u_{i-1} + e_{i+1} u_{i+1} = \lambda u_i, \quad (5)$$

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

$$\begin{pmatrix} d_1 & e_1 & 0 & 0 & \dots & 0 & 0 \\ e_1 & d_2 & e_2 & 0 & \dots & 0 & 0 \\ 0 & e_2 & d_3 & e_3 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots & d_{n_{\text{step}}-2} & e_{n_{\text{step}}-1} \\ 0 & \dots & \dots & \dots & \dots & e_{n_{\text{step}}-1} & d_{n_{\text{step}}-1} \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ \dots \\ \dots \\ \dots \\ u_{n_{\text{step}}-1} \end{pmatrix} = \lambda \begin{pmatrix} u_1 \\ u_2 \\ \dots \\ \dots \\ \dots \\ u_{n_{\text{step}}-1} \end{pmatrix} \quad (6)$$

Secondly, we will consider the Schrödinger equation for *two* electrons by studying two electrons in a harmonic oscillator well which also interact via a repulsive Coulomb interaction.

We start by writing the single-electron equation as

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u(r) + \frac{1}{2} k r^2 u(r) = E^{(1)} u(r),$$

where $E^{(1)}$ stands for the energy with one electron only. For two electrons with *no* repulsive Coulomb interaction, we have the following Schrödinger equation:

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

After a series of substitutions, this can be written as

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

In this case the potential is:

$$V_i = \omega_r^2 \rho^2 + 1/\rho \quad (8)$$

where we will study the cases where the oscillator frequency ω_r is $\omega_r = 0.01$, $\omega_r = 0.5$, $\omega_r = 1$ and $\omega_r = 5$ for the ground state only, that is, the lowest-lying state.

2 Methods

2.1 Jacobi's method

In this project we will use Jacobi's method to find the eigenvalues, which consists of doing a number of similarity transformations

$$\mathbf{S}^T \mathbf{A} \mathbf{S} = \mathbf{B}$$

where \mathbf{A} is the matrix in our given problem, and \mathbf{S} is an $(n \times n)$ orthogonal transformation matrix

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

The recipe is to choose θ so that all non-diagonal matrix elements b_{kl} become zero.

The **algorithm** can be described as follows:

- Choose a tolerance ϵ , typically 10^{-8} or smaller.
- Find matrix element a_{kl} with the largest value and its indices k and l .
- Check that $\max(a_{kl}^2) > \epsilon$ for the off-diagonal matrix elements.
- Compute τ , $\sin \theta$, $\cos \theta$, $\tan \theta$.
- Compute the similarity transformations for this set of values for (k, l) , which will create a new matrix, $\mathbf{B} = \mathbf{S}(k, l, \theta)^T \mathbf{A} \mathbf{S}(k, l, \theta)$.
- Continue to follow these steps until $\max(a_{kl}^2) > \epsilon$ is no longer the case.

3 Results

3.1 Harmonic oscillator

In the case of the harmonic oscillator there is an analytical solution to what the lowest eigenvalues should be. For $l = 0$ these are $\lambda_0 = 3$, $\lambda_1 = 7$, $\lambda_2 = 11, \dots$. Solving this numerically will not lead to the exact values, but we can get very close to this. We have computed the eigenvalues using our algorithm as described in the previous section, as well as using the Armadillo package.

In order to get the lowest three eigenvalues with four leading digits, we need at least $n_{\text{step}} = 30$. Then the lowest three eigenvalues are: $\lambda_0 = 2.965$, $\lambda_1 = 6.821$ and $\lambda_2 = 10.56$ using $\rho_{\text{max}} = 10.0$.

The eigenvalues will depend on our choice for ρ_{max} . By testing we find that a lower ρ_{max} makes the eigenvalues is more precise for $\rho_{\text{max}} = 4.0$, but gets worse for lower values, making the eigenvalues larger than they should be. For values higher than 10.0 the eigenvalues also are bad, becoming too small.

The number of similarity transformation needed for the non-diagonal matrix elements to become zero depends on the dimensionality of the matrix. An upper limit to the allowed number of similarity transformations is in the range $12n^3 - 20n^3$. We have set the limit to $50n^3$ to be on the safe side. When running the code, the number of transformations is counted. For different dimensionalities we find (for $\rho_{\text{max}} = 4.0$):

n	No. of iterations	No. of iterations / n	Time (s)
5	28	5.6	0
10	42	4.2	0
20	676	33.8	0
50	4378	87.56	0
100	17789	177.89	1
200	72044	360.22	20

where the time is for our algorithm. Using Armadillo resulted in 0 seconds for all of the above n -values.

Estimate the number of transformations and extract a behavior as function of the dimensionality of the matrix ... ??

Why choose t to be the smaller of the roots ...?

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3.2 Harmonic oscillator with Coulomb interactions

For specific oscillator frequencies there is an analytical answer to Eq. (7), described in the article by M. Taut, Phys. Rev. A 48, 3561 - 3566 (1993).

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Plot of wave function for two electrons as a function of relative coordinates r and different values of ω_r : ...

3.3 Unit tests

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4 Conclusions

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5 List of codes

The codes developed for this project are:

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