Project 2 - FYS3150*

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In this project we solve the Schrodinger equation for two electrons in a 3D harmonic oscillator potential. We solve with and without electron repulsion, and compare the results. To accomplish this we apply a general method of discretizing the domain and reducing the problem to an eigenvalue equation. We thereafter apply Jacobi's rotation algorithm to obtain the eigenvalues of the matrix. We also apply the principles of unit testing by testing the algorithm for some simple problems with known solutions.

I. INTRODUCTION

In this project we aim to solve the Schrodinger equation for two electrons in a 3D harmonic oscillator potential. We will be solving with and without the repulsive Coulomb potential, and comparing the results. For the case of no repulsion we have an analytical expression for the energies, and this will be useful in determining the accuracy of our results. Assume spherical symmetry.

II. THEORY AND METHODS

A. The radial equation

We begin by studying the radial part of Schrodingers' equation for a single electron in a harmonic oscillator potential [1].

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

The potential $V(r)=\frac{1}{2}kr^2$ is the harmonic oscillator potential with $k=m\omega^2$ and E is the energy of the electron. ω is the oscillator frequency and the allowed energies are

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

Where the quantum number $n=0,1,2..$ is the energy quantum number and $l=0,1,2...$ is the orbital momentum quantum number. Introducing $R(r)=(1/r)u(r)$ our equation can be rewritten in terms of the second derivative d^2/dr^2:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u(r)+(V(r)+\frac{l(l+1)}{r^2}-\frac{\hbar^2}{2m})u(r)=Eu(r) \quad (3)$$

We introduce a dimensionless variable $\rho=(1/\alpha)r$ where alpha is a constant of dimension length and obtain

$$-\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{d\rho^2}u(\rho)+(V(\rho)+\frac{l(l+1)}{\rho^2}\frac{\hbar^2}{2m\alpha^2})u(\rho)=Eu(\rho) \quad (4)$$

In this project we will be interested in the case $l=0$. Now since we are working in spherical coordinates, $r\in[0,\infty)$. Since we require $R(r)$ to go to zero at the boundaries, when we make the substituion $R(r)=(1/r)u(r)=(1/r)u(\alpha\rho)$ we obtain the boundary conditions for $u(\rho)$: $u(0)=u(\infty)=0$.

We insert $V(\rho)=\frac{1}{2}k\alpha^2\rho^2$ and obtain

$$-\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{d\rho^2}u(\rho)+\frac{1}{2}k\alpha^2\rho^2u(\rho)=Eu(\rho) \quad (5)$$

To obtain a simpler expression we multiply by $2m\alpha^2\rho^2/\hbar^2$ and fix α such that

$$\frac{mk}{\hbar^2}\alpha^4=1 \quad (6)$$

and define

$$\lambda=\frac{2m\alpha^2}{\hbar^2}E \quad (7)$$

so we can rewrite our equation as

$$-\frac{d^2}{d\rho^2}u(\rho)+\rho^2u(\rho)=\lambda u(\rho) \quad (8)$$

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To solve this equation we discretize the domain and define minimum and maximum values for ρ, $\rho_{min} = \rho_0 = 0$ and ρ_{max}. ρ_{max} cannot be chosen to be ∞ so we must take care to set it sufficiently large in order to obtain the correct solution. With N mesh points let

$$h = \frac{\rho_{max} - \rho_0}{N} \tag{9}$$

and we obtain a discrete set of values for ρ,

$$\rho_i = \rho_0 + ih \qquad i = 0, 1, 2..., N \tag{10}$$

Replacing the second order derivative by the 2nd order central difference we can write our equation as

$$-\frac{u_{i+1} + u_{i-1} - 2u_i}{h^2} + \rho_i^2 u_i = \lambda u_i \tag{11}$$

Where $u_i = u(\rho_i)$ is the discretized version of our function. We let $V_i = \rho_i^2$ and rewrite this as a matrix equation

$$\boldsymbol{Au} = \lambda \boldsymbol{u} \tag{12}$$

Since the endpoints are known we let A be a matrix of dimension $(n-2)\cdot(n-2)$ and u a vector of dimension (n-2).

$$\boldsymbol{Au} = \begin{pmatrix} \frac{2}{\hbar^2} + V_1 & -\frac{1}{\hbar^2} & 0 & \cdots & \cdots & 0 \\ -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_2 & -\frac{1}{\hbar^2} & 0 & \cdots & \cdots \\ 0 & -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_3 & -\frac{1}{\hbar^2} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & \cdots & -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_{N-3} & -\frac{1}{\hbar^2} \\ 0 & \cdots & \cdots & \cdots & -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_{N-2} \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ \\ u_{N-2} \end{pmatrix} = \lambda \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ \\ u_{N-2} \end{pmatrix} \tag{13}$$

where $u_0 = u_{N-1} = 0$.

B. Coulomb Interaction

For two electrons with no Coulomb interaction in a harmonic oscillator potential the Schroedinger equation can be written as

$$(-\frac{\hbar^2}{2m}\frac{d^2}{dr_1^2} - \frac{\hbar^2}{2m}\frac{d^2}{dr_2^2} + \frac{1}{2}kr_1 2 + kr_2^2)u(r_1, r_2) = Eu(r_1, r_2) \tag{14}$$

With no interaction the two-electron wavefunction $u(r_1, r_2)$ can be written as a product of two single-electron wavefunction. Introducing the relative coordinate $\boldsymbol{r} = \boldsymbol{r_1} - \boldsymbol{r_2}$ and the center of mass coordinate $\boldsymbol{R} = \frac{1}{2}(\boldsymbol{r_1} + \boldsymbol{r_2})$ the radial equation becomes

$$(-\frac{\hbar^2}{m}\frac{d^2}{dr^2} - \frac{\hbar^2}{4m}\frac{d^2}{dR2} + \frac{1}{4}kr^2 + kR^2)u(r, R) = Eu(r, R) \tag{15}$$

the solution can be separated as $u(r, R) = \psi(r)\phi(R)$ and the energy is a sum of the relative energy E_r and center-of-mass energy E_R

$$E = E_r + E_R \tag{16}$$

adding the repulsive Coulomb interaction

$$V(r_1, r_2) = \frac{\beta e^2}{|\boldsymbol{r_1} - \boldsymbol{r_2}|} = \frac{\beta e^2}{r} \tag{17}$$

where $\beta e^2 = 1.44$ eVnm. The relative motion Schroedinger equation becomes

$$(-\frac{\hbar^2}{m}\frac{d^2}{dr^2} + \frac{1}{4}kr^2 + \frac{\beta e^2}{r})\psi(r) = E\psi(r) \tag{18}$$

introducing $\rho = r/\alpha$, defining a new frequency

$$\omega_r^2 = \frac{1}{4}\frac{mk}{\hbar^2}\alpha^4 \tag{19}$$

fixing α

$$\alpha\frac{m\beta e^2}{\hbar^2} = 1 \tag{20}$$

and defining

$$\lambda = \frac{m\alpha^2}{\hbar^2}E \tag{21}$$

and we obtain Schroedinger's equation

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \omega_r^2\rho^2\psi(\rho) + \frac{1}{\rho} = \lambda\psi(\rho) \tag{22}$$

which using the methods described in the previous section can be solved numerically as an eigenvalue problem.

C. Jacobi's rotation method

For a real symmetric $n \cdot n$ matrix $\boldsymbol{A}$, we have n eigenvalues λ_i and there exists a real orthogonal matrix $\boldsymbol{S}$ such that

$$\boldsymbol{S^T A S} = diag(\lambda_1, \lambda_2, ..., \lambda_n) \tag{23}$$

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[1] All theory in this project adapted from FYS3150 Project 2 (Fall 2016) $< link >$.