FYS4150: Project 2

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Abstract

The three-dimensional Schrödinger equation is solved for two electrons in a harmonic oscillator potential, with and without Coulomb interaction. The equations are solved as eigenvalue problems, using the Jacobi rotation algorithm.

Introduction

The aim of this project was to solve the three-dimensional Schrödinger equation for two electrons, both in the interacting and non-interacting case. Since spherical symmetry is assumed, we start by considering the radial part of the Schrodinger equation for a single particle:

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

Where $V(r)=\frac{1}{2}kr^2$ is the harmonic oscillator potential. The solutions of the Schrödinger equations are the so-called wave functions, which describe the probability for a particle (or a system of particles) to be found at a specific position or with a specific momentum. A particle in a harmonic oscillator can only be at specific, quantized energy levels:

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

Where the principal quantum number $n=0,1,2...$ and orbital angular momentum quantum number $l=0,1,2....$ In this project we set $l=0$, so the energy levels are dependent only of n. Energy levels are therefore non-degenerate. By performing several simplifications and subsitutions we aquire the relevant equation for our project:

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

Where the eigenvalues in our case ($l = 0$) are $\lambda = \frac{2m\alpha^2}{\hbar^2}E$, $\lambda_0 = 3$, $\lambda_1 = 7$, $\lambda_2 = 11...$, where α is a normalization constant. The lowest energy, λ_0 is called the *ground state energy*.

For two electrons, we need to add an interaction term. The Coulomb interaction accounts for the repulsive electric force between the electrons (which both have negative charge). The Schrödinger equation is now:

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

Where $r = r_1 - r_2$ is the relative coordinate between the electrons, and $R = \frac{1}{2}(r_1 + r_2)$ is the center-of-mass coordinate. The equation can be separated into one r- and one R-dependent part. Adding the repulsive Coulomb interaction $V(r) = \frac{\beta e^2}{r}$ and considering the r-dependent equation, we get:

$$\Big(-\frac{\hbar^2}{m}\frac{d^2}{dr^2} + \frac{1}{4}kr^2 + \frac{\beta e^2}{r}\Big)\psi(r) = E_r\psi(r) \tag{5}$$

This can be rewritten as:

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \omega_r^2\rho^2\phi(\rho) + \frac{m\alpha\beta e^2}{\rho\hbar^2}\psi(\rho) = \frac{m\alpha^2}{\hbar^2}E_r\psi(\rho) \tag{6}$$

Where $\omega_r = \frac{1}{4}\frac{mk}{\hbar^2}\alpha^4$. Fix the normalization constant $\alpha = \frac{\hbar^2}{m\beta e^2}$, and define the new eigenvalue $\lambda = \frac{m\alpha^2}{\hbar^2}E$, and we get the equation:

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

Numerical approximation

We use the standard expression for the second derivative of a function:

$$u'' = \frac{u(\rho + h) - 2u(\rho) + u(\rho - h)}{h^2} + \mathcal{O}(h^2) \tag{8}$$

So the mathematical error in this case is of the order of $\mathcal{O}(h^2)$. We set the boundary conditions:

$$h = \frac{\rho_N - \rho_0}{N}$$

$$\rho_{min} = \rho_0 = 0$$

$$\rho_{max} = \rho_N = \infty$$

The latter can't be implemented, so we use several large values for ρ_{max}.

Numerical implementation

The mesh points of the calculation are

$$\rho_i = \rho_0 + ih \ , \ i = 1, 2, ..., N$$

So our expression becomes:

$$-\frac{u_{i+1} - 2u_i + u_{i-1}}{h^2} + \rho_i^2 u_i = \lambda u_i \tag{9}$$

Where we have use that $V_i = \rho_i^2$ is the harmonic oscillator potential. We see that this can be written as a $(N-1) \times (N-1)$-matrix equation:

$$\begin{bmatrix} \frac{2}{h^2} + V_1 & -\frac{1}{h^2} & 0 & ... & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2} + V_2 & -\frac{1}{h^2} & ... & 0 \\ \vdots & & \ddots & & \vdots \\ 0 & ... & -\frac{1}{h^2} & \frac{2}{h^2} + V_{N-2} & -\frac{1}{h^2} \\ 0 & 0 & ... & -\frac{1}{h^2} & \frac{2}{h^2} + V_{N-1} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_{N-2} \\ u_{N-1} \end{bmatrix} = \lambda \begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_{N-2} \\ u_{N-1} \end{bmatrix}$$

Unitary and orthogonal transformations (a)

A unitary matrix U has the properties:

$$U^{-1} = U^\dagger \tag{10}$$

An orthogonal matrix (the corresponding real matrix) has the properties:

$$U^T = U^{-1} \tag{11}$$

Where $U^\dagger$ is for matrices in Hilbert space (complex matrices). It represents the transpose of the complex conjugate, i.e. $U^\dagger = (U^*)^T$.

Assume we have an orthogonal basis for the n-dimensional space v_i, where $v_j^T v_i = \delta_{ij}$:

$$\mathbf{v}_i = \begin{bmatrix} v_{i1} \\ ... \\ ... \\ v_{in} \end{bmatrix} \ , U\mathbf{v}_i = \mathbf{w}_i$$

Under orthogonal transformations, both the dot product and orthogonality of vectors is conserved:

$$\mathbf{w}_i^T \mathbf{w}_j = (U\mathbf{v}_i)^T (U\mathbf{v}_j) = \mathbf{v}_i^T U^T U \mathbf{v}_j = \mathbf{v}_i^T U^{-1} U \mathbf{v}_j = \mathbf{v}_i^T \mathbf{v}_j = \delta_{ij}$$

Jacobi's rotation method (b)

We want to solve the eigenvalue problem for a tridiagonal matrix:

$$\begin{pmatrix} d_0 & e_0 & 0 & ... & 0 & 0 \\ e_1 & d_1 & e_1 & ... & 0 & 0 \\ 0 & e_2 & d_2 & e_2 & ... & 0 \\ \vdots & & & \ddots & & 0 \\ 0 & ... & ... & 0 & e_N & d_N \end{pmatrix} \begin{pmatrix} u_0 \\ u_1 \\ \vdots \\ u_{N-1} \\ u_N \end{pmatrix} = \lambda \begin{pmatrix} u_0 \\ u_1 \\ \vdots \\ u_{N-1} \\ u_N \end{pmatrix} \tag{12}$$

We want to use Jacobi's rotation method. We define an orthogonal matrix S to operate on our matrix A:

$$B = S^T A S \tag{13}$$

With all elements in S equal to zero, except:

$$s_{kk} = s_{ll} = \cos\theta \ , \ s_{kl} = -s_{lk} = s\sin\theta \ , \ s_{ii} = 1 \ ; \ i \neq k \ i \neq l$$

Benchmarks

Jacobi rotation

Check the Jacobi function, which finds eigenvalues of a matrix, on the matrix A:

$$A = \begin{pmatrix} 1 & 2 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \ , \ \det(A - \lambda \mathbb{1}) = \begin{vmatrix} 1-\lambda & 2 & 0 \\ 2 & 1-\lambda & 0 \\ 0 & 0 & 1-\lambda \end{vmatrix}$$

$$\det(A - \lambda \mathbb{1}) = (1-\lambda)^3 - 2 \cdot 2(1-\lambda) = (1-\lambda)[(1-\lambda)^2 - 4]$$

1. Find $\max(a_{kl})$.

2. Compute the rotation parameters $t = \tan\theta$, $c = \cos\theta$, $s = \sin\theta$:

$$\tau = \cot\theta = \frac{a_{ll} - a_{kk}}{2a_{kl}} \quad (14)$$

$$t = -\tau \pm \sqrt{1 + \tau^2} \quad (15)$$

$$c = \frac{1}{\sqrt{1 + t^2}} \ , \ s = tc \quad (16)$$

3. Calculate the elements of B:

$$b_{ii} = a_{ii} \ , \ i \neq k \ i \neq l$$

$$b_{ik} = a_{ik}c - a_{il}s \ , \ i \neq k \ i \neq l$$

$$b_{il} = a_{il}c + a_{ik}s \ , \ i \neq k \ i \neq l$$

$$b_{kk} = a_{kk}c^2 - 2a_{kl}c * s + a_{ll}s^2$$

$$b_{ll} = a_{ll}c^2 + 2a_{kl}c * s + a_{kk}s^2$$

$$b_{kl} = (a_{kk} - a_{ll})c * s + a_{kl}(c^2 - s^2)$$

4. If $\max(b_{kl}) \geq \epsilon$ run the algorithm again.

Figure 1: Jacobi rotation algorithm for tridiagonal matrix

$$= (1 - \lambda)[\lambda^2 - 2\lambda - 3] \rightarrow \lambda = 1 \cap \lambda = 2$$

$$\rightarrow (\lambda - 1)(\lambda - 1)(\lambda - 2)$$

Results