

Finite Difference of Schrodinger's Equation

of Particle in Coulomb Potential

Computational Physics

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One of the most arguably most important equation to quantum mechanics, The Schrodinger equation is used all the time in its field. For particles in subatomic level they do not adhere to the standard classical laws that were brought forth by Isaac Newton. So, from the late 1800s to mid-1900s a revolution happened in physics known as the quantum revolution. Which still happens today with new discoveries in its subfield. Today we are going to evaluate the 1-dimensional Time-Independent Schrodinger equation by taking the finite difference method of it. Essentially making it a particle in a box simulation where we can visualize the wave function for a particle. Using the finite difference method of this is useful to better understand the Schrodinger equation and how waves behave.

Erwin Schrodinger was a professor at the University of Vienna at the time of proposing the now famous equation for wave mechanics in 1926. It was said to come about from the failure of the Bohr model which could not predict energy levels of atoms with more than one electron. Looking at the equation might start make you seeing stars, however its quite simple just like the classical equation to find total energy the Schrodinger equation can be thought of that way

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x) + U(x)\psi(x) = E\psi(x)$$

$$\nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \text{Lapacian Operator}$$

$$\hbar = \frac{h}{2\pi} \quad \text{reduced Plancks Constant}$$

$$\begin{cases} \frac{\hbar^2}{2m}\nabla^2\psi(x) & \text{Kinetic Energy} \\ U(x)\psi(x) & \text{Potential Energy} \\ E\psi(x) & \text{Total Energy} \end{cases}$$

Now it does not seem so bad now! Using this equation physicist can build on it describe many different problems. Such as building models of atoms, quantum tunneling, and many more.

For our problem we are using the finite difference method, this is a numerical method that is used to solve partial differential equations that are too complex to solve analytically. This method is widely use in areas such as fluid mechanics, heat flow, and data analysis. There are three different finite difference formulas that are

$$\frac{du}{dt} = \frac{u(t_{n+1}) - u(u_n)}{\Delta t} + \Omega(\Delta t) \quad \text{Foward Euler}$$

$$\frac{du}{dt} = \frac{u(t_n) - u(u_{n+1})}{\Delta t} + \Omega(\Delta t) \quad \text{Backward Euler}$$

$$\frac{du}{dt} = \frac{u(t_{n+1}) - u(u_{n-1})}{2\Delta t} + \Omega(\Delta t^2) \quad \text{Central Difference}$$

As you can see from the formulas this method takes two points to find the interval between them with allowance of some error. By using this method on the Schrodinger equation, we can

make the popular problem of having a particle in a box which is a particle that can be defined in the interval $[a, b]$.

To begin to solve this problem we need to define a few things. For the equation since we are defining a particle in 1 dimension, we can reduce the Laplacian

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$$

Then solve for the second derivative

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} [U(x)\psi(x) + E\psi(x)]$$

We can then use the finite difference formula, the Central difference scheme for the first order derivative

$$\begin{aligned} \left. \frac{d\psi(x)}{dx} \right|_{x=x_i} &\approx \frac{\psi_{i+1} - \psi_{i-1}}{x_{i+1} - x_{i-1}} \\ &= \frac{\psi_{i+1} - \psi_{i-1}}{2\Delta} \quad \text{where } \Delta \text{ is the step size} \end{aligned}$$

Then we calculate the second order derivative to be

$$\left. \frac{d^2\psi(x)}{dx^2} \right|_{x=x_i} \approx \frac{\psi_{i+1} - 2\psi_i + \psi_{i-1}}{\Delta^2}$$

Using this method, we can then sub it into to Schrodinger equation

$$\frac{\psi_{i+1} - 2\psi_i + \psi_{i-1}}{\Delta^2} = \frac{2m}{\hbar^2} [U_i\psi_i + E\psi_i]$$

then we can solve for the total energy of the equation

$$-\frac{\hbar^2}{2m} \left(\frac{\psi_{i+1} - 2\psi_i + \psi_{i-1}}{\Delta^2} \right) + U_i \psi_i = E \psi_i$$

From here we can put it into matrix form to get the eigenvalues

$$-\frac{\hbar^2}{2m\Delta^2} \begin{bmatrix} -2 & 1 & 0 & \dots & \dots & 0 \\ 1 & -2 & 1 & 0 & \dots & 0 \\ 0 & 1 & \ddots & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & 1 & 0 \\ 0 & \dots & 0 & 1 & -2 & 1 \\ 0 & \dots & \dots & 0 & 1 & -2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \vdots \\ \vdots \\ \vdots \\ \psi_{i-1} \\ \psi_i \end{bmatrix} + \begin{bmatrix} U_1 & 0 & 0 & \dots & \dots & 0 \\ 0 & U_2 & 0 & 0 & \dots & 0 \\ 0 & 0 & \ddots & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & 0 & 0 \\ 0 & \dots & 0 & 0 & U_{i-1} & 0 \\ 0 & \dots & \dots & 0 & 0 & U_i \end{bmatrix} \begin{bmatrix} \psi_1 \\ \vdots \\ \vdots \\ \vdots \\ \psi_{i-1} \\ \psi_i \end{bmatrix} = E \begin{bmatrix} \psi_1 \\ \vdots \\ \vdots \\ \vdots \\ \psi_{i-1} \\ \psi_i \end{bmatrix}$$

Substitute these values

$$\left\{ \begin{array}{l} -\frac{\hbar^2}{2m\Delta^2} \begin{bmatrix} -2 & 1 & 0 & \dots & \dots & 0 \\ 1 & -2 & 1 & 0 & \dots & 0 \\ 0 & 1 & \ddots & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & 1 & 0 \\ 0 & \dots & 0 & 1 & -2 & 1 \\ 0 & \dots & \dots & 0 & 1 & -2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \vdots \\ \vdots \\ \vdots \\ \psi_{i-1} \\ \psi_i \end{bmatrix} = K\psi \text{ for kinetic energy} \\ \begin{bmatrix} U_1 & 0 & 0 & \dots & \dots & 0 \\ 0 & U_2 & 0 & 0 & \dots & 0 \\ 0 & 0 & \ddots & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & 0 & 0 \\ 0 & \dots & 0 & 0 & U_{i-1} & 0 \\ 0 & \dots & \dots & 0 & 0 & U_i \end{bmatrix} \begin{bmatrix} \psi_1 \\ \vdots \\ \vdots \\ \vdots \\ \psi_{i-1} \\ \psi_i \end{bmatrix} = U\psi \text{ for potential energy} \\ E \begin{bmatrix} \psi_1 \\ \vdots \\ \vdots \\ \vdots \\ \psi_{i-1} \\ \psi_i \end{bmatrix} = E\psi \text{ for total energy} \end{array} \right.$$

We can further reduce the formula for which the kinetic + potential is the Hamiltonian

$$K\psi + U\psi = H\psi$$

$$H\psi = E\psi$$

This is the reduced Schrodinger Equation with the Hamiltonian for which can be found in many different textbooks in quantum mechanics specifically equation 2.12, page 27 in *Introduction to Quantum Mechanics 2nd Edition by David J. Griffiths*.

Using this hand solved Schrodinger equation, we can then apply it to the problem at hand which is the atom in coulomb potential. In this problem we can replace the potential with are coulomb potential formula

$$U(x) = \frac{Ze^2}{x}$$

$$\text{where } \begin{cases} Z & \text{is the number of protons in the atom} \\ e = -1.60218 * 10^{-19} \text{ C} & \text{the charge between the proton and electron} \\ x & \text{radius} \end{cases}$$

Also, that needs to be stated is are other constants in the code

m is the mass of the electron $0.511 * 10^6 \text{ eV}/c^2$

ħ is going to be it times the speed of light $197.326972 \text{ eV} * \text{nm}$

In the code we are going to model the atom to have a Z of 1 which is like that of a Hydrogen atom. Using this we will display the ground state and some of the excited energy states, this is noted by the quantum number n. Furthermore, the length of the well is set to 70 which it can be changed to be a wide range of numbers. However, for the code the minimum well length must be a positive nonzero number, or it would cause the graph to go to infinity. The number of iterations is set to 70 due to some error detailed later but also to give it a general smoothness which would not happen at lower iteration values. Also too compare the error of the finite element analysis we can use the formula

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

Where L is the well length, n is the quantum number, and x is the position of the wave.

Using this formula, we can compare the error by using the percent error formula,

$$\%error = \left| \frac{FDM - exact}{exact} \right| * 100$$

Which exact is the formula listed previously for a well.

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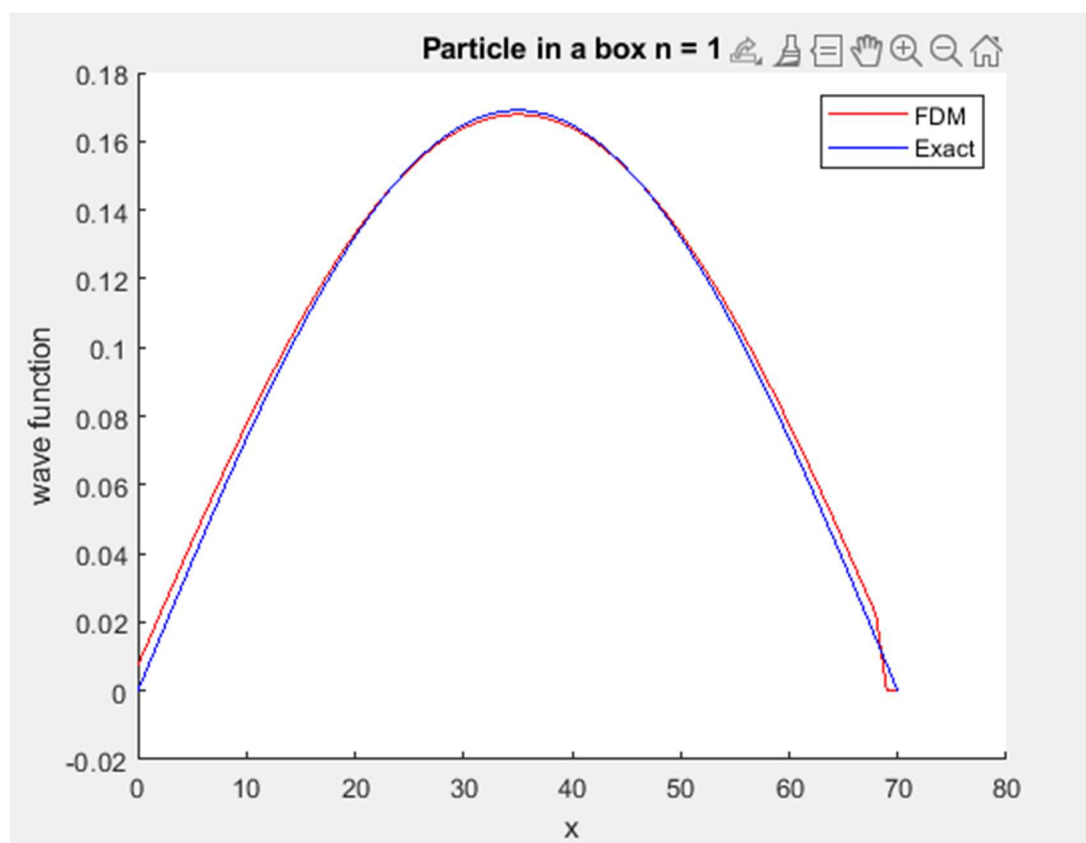
clc
%%Final Project Computational Physics
%Finite Difference Method of Schrodinger Equation
%for particle in colomb potential
opengl software
%Constants
m = 0.511*10^6; %mass of the electron in eV/c^2
e = -1.60218*10^-19;% Charge between electron and proton in C
hbar = 197.36977; %Planks Constant in eV*nm
Z = 1; % # of protons in the atom
xmin = 0.01; % min starting x value
xmax = 70.01; %max ending x value
n = 70; %the number of iterations
x = linspace(xmin, xmax, n); %creating all the value ppints of x
delta = x(2)-x(1); %the step coefficient
Columb = (-Z*(e^2)/delta);
U = eye(n,n)* Columb ; %the potential energy matrix
K = eye(n,n)*(-2); %creating the kinetic energy identity matrix
%this sets both sides of the middle diagonal to be 1
for i = 1: (n-1)
    K(i, i+1) = 1; %for the left side
    K(i+1, i) =1; %for the right side
end
H = (-1*(hbar^2)/(2*m*(delta)^2))*K + U;% the hamiltonian equation
[wave, EU] = eig(H); %computes eigenvalues and returns matrix of the hamiltonian
func = @(x , state) ((sqrt(2/(xmax-xmin)))*sin(state*pi*x/(xmax - xmin)));%wave function for potential well
fdm1 = zeros(1, n);%converting the wave to array for ground state
fdm4 = zeros(1, n);%converting the wave to array for n = 4
fdm7 = zeros(1,n);%converting the wave to array for n =7
%converts the points
for i = 1:n-2
    fdm1(i) = wave(i, 1);
    fdm4(i) = wave(i, 4);
    fdm7(i) = wave(i, 7);
end
error1 = abs(fdm1-func(x, 1))*100;% error for n =1
error4 = abs(fdm4 - func(x, 4))*100;% error for n = 4
error7 = abs(fdm7 - func(x, 7))*100;%error for n = 7
%plotting ground state
figure(1)
hold on
plot(x, fdm1, '-r','DisplayName', 'FDM');
plot(x, func(x, 1), '-b', 'DisplayName', 'Exact');
hold off
title("Particle in a box n = 1");
xlabel("x");
ylabel("wave function");

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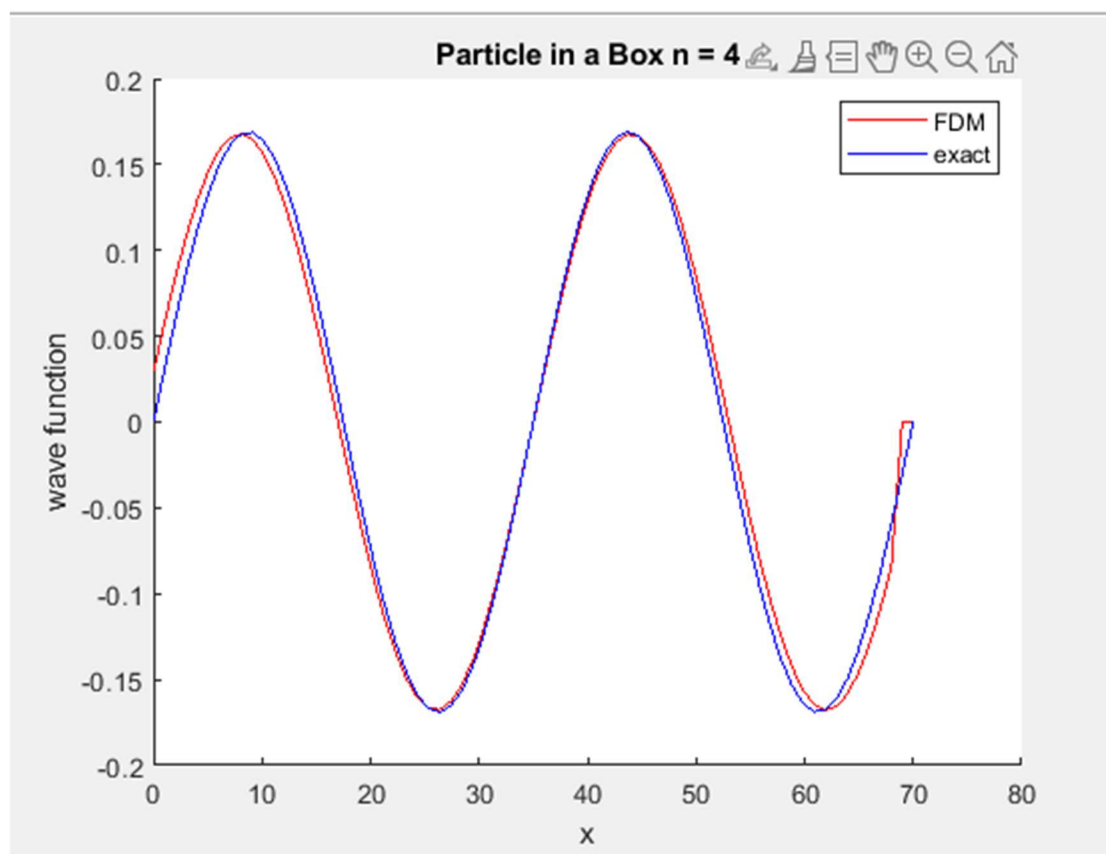
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legend;
%plotting the 6th excited state
figure(2)
hold on
plot(x, fdm7, '-r', 'DisplayName', 'FDM');
plot(x, func(x, 7), '-b', 'DisplayName', 'Exact');
hold off
title("Particle in a box n = 7");
xlabel("x");
ylabel("wave function");
legend;
%plotting 3rd excited state
figure(3)
hold on
plot(x, fdm4, '-r', 'DisplayName', 'FDM');
plot(x, func(x, 4), '-b', 'DisplayName', 'exact');
hold off
title("Particle in a Box n = 4");
xlabel("x");
ylabel("wave function");
legend;
%error plot for ground state
figure(4)
plot(x, error1);
xlabel("x");
ylabel("percent error");
title("Error For n = 1");
%error plot for 3rd excited state
figure(5)
plot(x, error4);
xlabel("x");
ylabel("percent error");
title("Error For n = 4");
%error plot for the 6th excited state
figure(6)
plot(x, error7);
xlabel("x");
ylabel("percent error");
title("Error For n = 7");

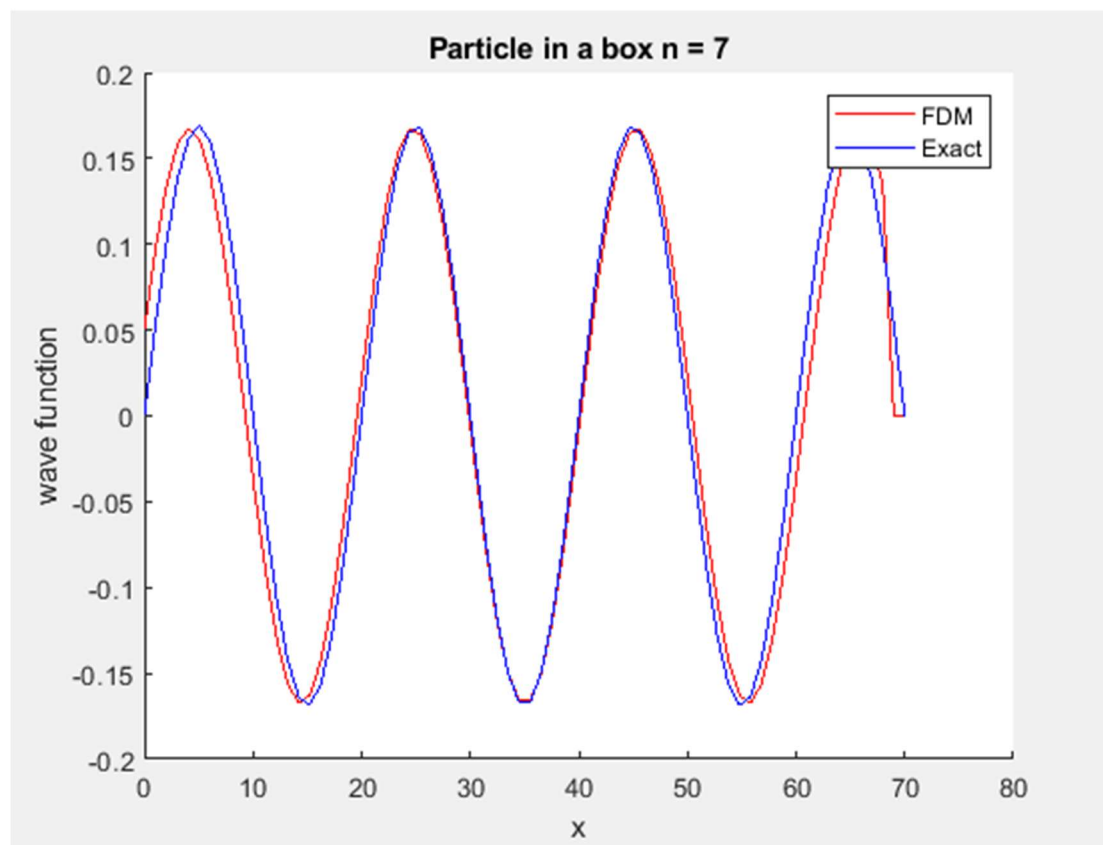
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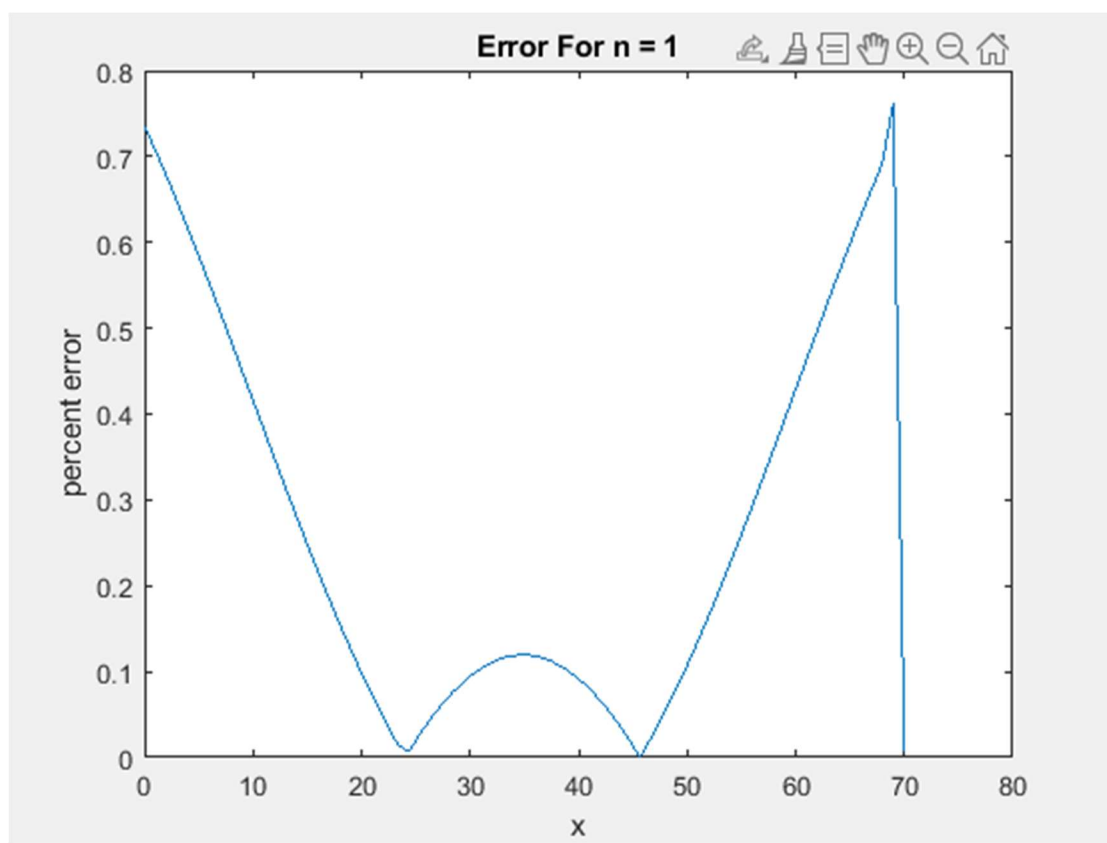
The Ground State



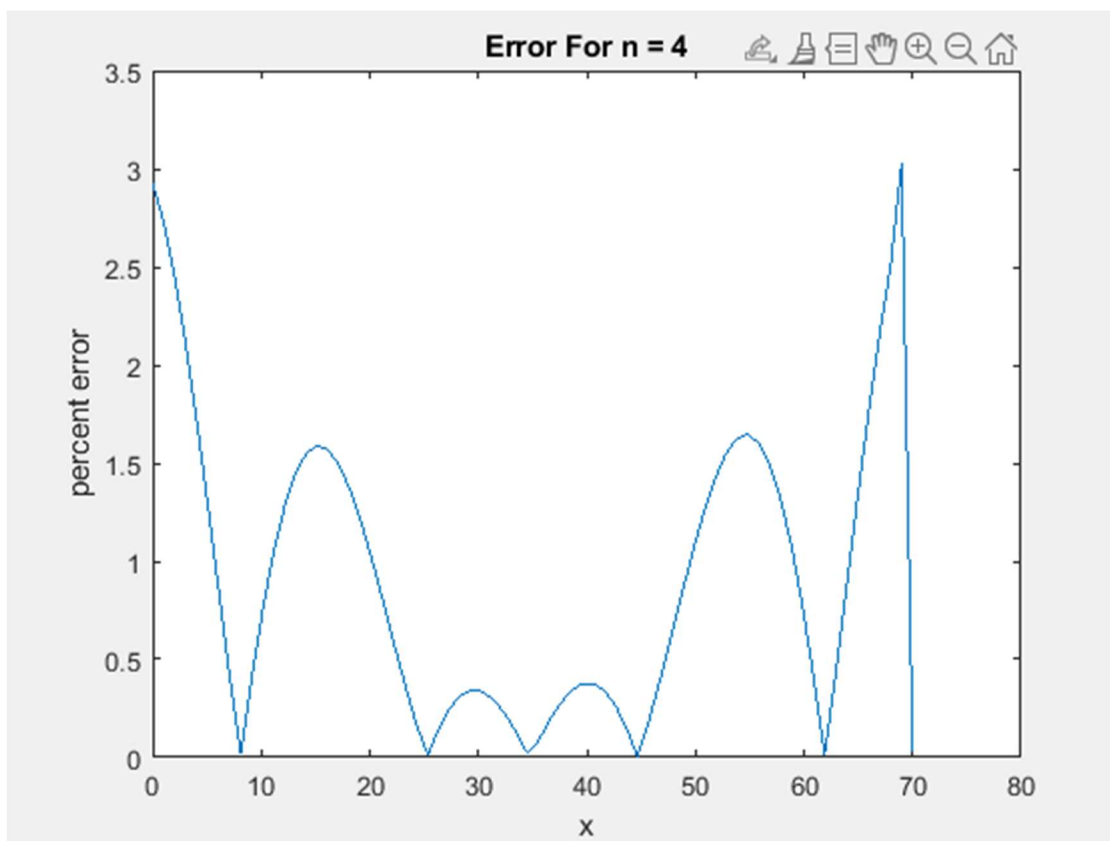
3rd Excited State



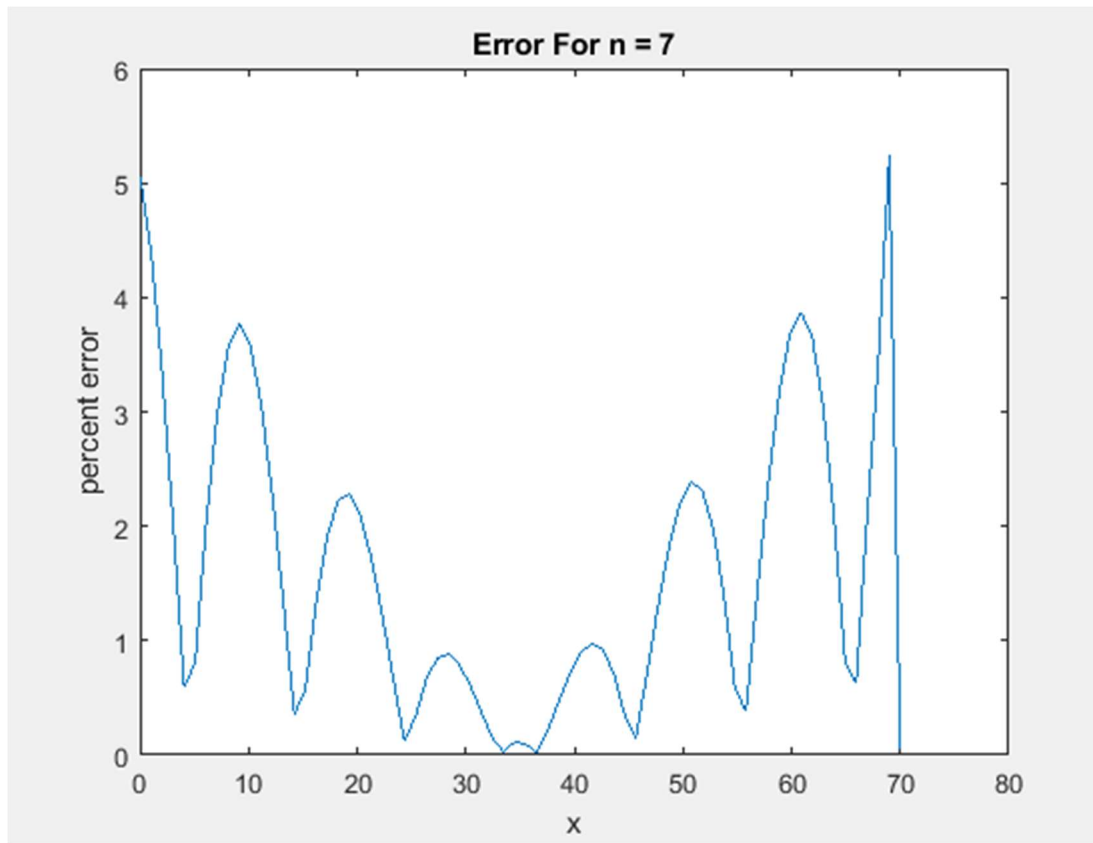
6th Excited State



The Ground State Error



3rd Excited State Error



6th Excited State

From running the code, we can see the wave functions displayed in the graphs. The error is good being mostly under 5% except on the tail end of the function. One explanation for the error is that when doing the FDM there is some truncation error that comes with the formula. Furthermore, when running the code and making tweaks to it there are some interesting findings. Once you hit 420 iterations it causes the ground state to flip. Also, I had to convert the wave function to be able to compare with the exact wave function because one being in a column array form while the other was in a row form. One more interesting note is that the 3rd and 6th excited states had its lowest error at the wave crests while the ground state had lower error just before and after the wave crest.

References

https://www.researchgate.net/publication/332241721_The_Schrodinger_equation_A_History/link/5ca86aa44585157bd3254721/download

<https://www3.nd.edu/~johnson/Class01F/chap2a.pdf>

<https://www.mpiwg-berlin.mpg.de/sites/default/files/Preprints/P437.pdf>

<https://www.sciencedirect.com/science/article/pii/S0377042796001562>

<https://www.sciencedirect.com/science/article/pii/S2405844020309063>