Numerical Solution of the Time-Independent 1-D Schrödinger equation

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CONTENTS

1 ABSTRACT

In this computational lab we discretised the wavefunction for an infinite potential well and a harmonic potential, and used the *shooting method* to find the values of energy for the eigenstates of the wavefunctions. Heisenberg's uncertainty inequality is investigated for the two potentials and we can observe that the boundaries of the infinite potential well place a limit on the value of Δx. It is concluded that the accuracy of our result depended heavily on the tolerance of our algorithm. The code used has a tolerance of 10^{-8} leading to accuracy in eigenvalues of the same order.

While investigating the difference in the energy of adjacent eigenvalues of the harmonic oscillator potential that for lower eigenstates the energy difference remains constant however after the 10th eigenstate the difference increases linearly, the same as the infinite potential well. This shows that the infinite boundaries of the harmonic potential cause it to act as an infinite potential well for higher energies.

2 INTRODUCTION & THEORY

In this computational lab, we numerically solve for the stationary states of the Schrödinger equation in 1D. The time-independent Schrödinger equation is given by:

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) \tag{2.1}$$

Where $\psi(x)$ is the wavefunction, E is the energy, m is the particle's mass, $V(x)$ is the potential energy. In our case, we consider the particle in a box; $V(x = 0)$ and $v(x = L)$ in infinite where L is the length of the box. Using dimensionless quantities $v(\tilde{x}) = V(\tilde{x})/V_0$, dimensionless energy $\epsilon = E/V_0$, the rescaled spatial variable $\tilde{x} - x/L$ (goes from the left side 0 to the right side of the box +1), and $\gamma^2 = \frac{2mL^2V_0}{\hbar^2}$, where V_0 is the depth of the well, we can rewrite equation 2.1 as:

$$\frac{d^2\psi(\tilde{x})}{d\tilde{x}^2} + \gamma^2\left(\epsilon - v(\tilde{x})\right)\psi(\tilde{x}) = 0, \tag{2.2}$$

By numerically discretising the spatial coordinate $\tilde{x}$ so that we have N points over the range of integration from 0 to 1, separated by $l = 1/(N-1)$ we can approximate the wavefunction as,

$$\psi_{n+1} = \frac{2\left(1 - \frac{5}{12}l^2k_n^2\right)\psi_n - \left(1 + \frac{1}{12}l^2k_{n-1}^2\right)\psi_{n-1}}{1 + \frac{1}{12}l^2k_{n+1}^2}. \tag{2.3}$$

By specifying two neighboring points, one can obtain a third point. Where $k_n^2 = \gamma^2\left(\epsilon - v(x_n)\right)$. Picking an arbitrary value for ψ_1 we can use the above equation to build up a solution to the wave equation from left to right.

Solving the wave equation for the infinite potential well analytically and normalizing it,

$$\psi_n(\tilde{x}) = \sqrt{2}sin(n\pi\tilde{x}) \tag{2.4}$$

$$\epsilon_n = \frac{n^2\pi^2}{\gamma^2} + v \tag{2.5}$$

we can compare our numerical results and determine the accuracy of our methods.

Lastly, Heisenberg's uncertainty principle is investigated numerically. $\Delta\tilde{x}\Delta\tilde{p} \geq \frac{\hbar}{2}$. Where $\tilde{x} = x/L$ and $\tilde{p} = pL/\hbar$. The uncertainties can be calculated by, $(\Delta\tilde{x})^2 = \langle\tilde{x}^2\rangle - \langle\tilde{x}\rangle^2$ and $(\Delta\tilde{p})^2 = \langle\tilde{p}^2\rangle - \langle\tilde{p}\rangle^2$. However in this case, the Simpson's rule function from the scipy package is used to calculate the following in python.

$$\langle\bar{x}^n\rangle = \int_0^1 \bar{x}^n\psi(\bar{x})^2 d\bar{x} \qquad \Delta\bar{p} = \sqrt{\langle\bar{p^2}\rangle} = \sqrt{-\int_0^1 \psi\frac{d^2\psi}{d\bar{x}^2}d\bar{x}}$$

3 SHOOTING METHOD

One of the aims in this lab is to find the eigenstate energies. To do this for an infinite square well, we must satisfy the boundary conditions $\psi_0 = \psi(\tilde{x} = 1) = \psi_{N-1} = 0$. Starting the wavefunction at 0 is straightforward; however, to satisfy the other boundary condition, we can use the *shooting method*.

This method shoots out a trajectory starting from one boundary and varies the energy until the second boundary condition is satisfied. The energy value at which both boundary conditions are satisfied corresponds to the eigenstate energy.
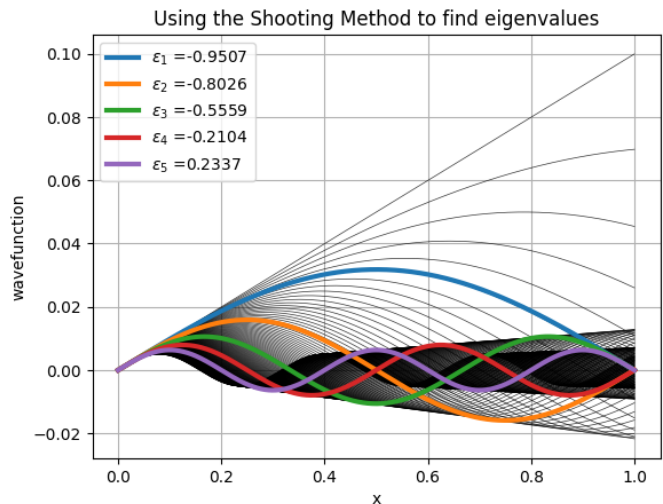
Figure 3.1 shows a sample of the first section of this lab. It can be clearly seen that the code varies the energies until the boundary condition is met and keeps going finding each energy level until five are found above an energy of -1.

Figure 3.1: Using the shooting method to find the eigenvalues for an infinite potential well.

4 METHODOLOGY

Initially we are working with a particle in a box where $v(\tilde{x}) = -1$ for $0 < \tilde{x} < 1$. The wavefunction is determined numerically using the recurring relation from equation 2.3. Next set γ^2 to 200, N to 1000. Use the shooting method to determine the eigenvalues. The sample of code uses this method to find the first eigenvalue.

```
#changing delta e when the parity of the wavefunction changes
e = -0.99 #initial guess
de = 0.01 #initial step size
while abs(de) > 1e-6: #accuracy
    psi = wave(e) #numerical wavefunction for energy e
    psi2 = wave(e+de)
    if psi[N-1]*psi2[N-1] < 0: #if it changes sign then the product of the two
values will be negative
        e = e + de
        de = -de/2
    else: #keep iterating the energy by de until a sign changes, essentially
the bisection method
        e += de
print(e)
```

Extend this code to find the next 9 eigenvalues and compare with the analytical solution and investigate the effect of the tolerance on the accuracy. The wavefunction needs to be normalised using Simpsons Rule from the *scipy* package. `simps(psi**2, dx=l` where `l=1/(N-1)`. Compare the numerically normalised wavefunction to the analytical.
The uncertainties are calculated using the final two equations given in the introduction with the simpson function. Again we compare the values we get and compare with the analytical solutions to comment on any errors.

The potential is changed to $v(x) = 8(x - 0.5)^2 - 1$, a harmonic potential. Also change γ^2 to 1000 and repeat the above procedure. This time determine the first 20 eigenvalues and compute the difference between two adjacent energy eigenstates. To investigate the relationship between the energy difference and quantum number, the two are plot on a log-log scale.

5 RESULTS

For the infinite potential well where $v(\tilde{x}) = -1$ everywhere in the well, figures 5.1 show the shooting method obtaining solutions for the energy when the wavefunction satisfies the boundary conditions. Then normalising it we can see the figure to the right where all the waves have equal amplitudes which makes sense for an infinite potential well. We can compare to the analytical solutions using equations 2.4 and 2.5.
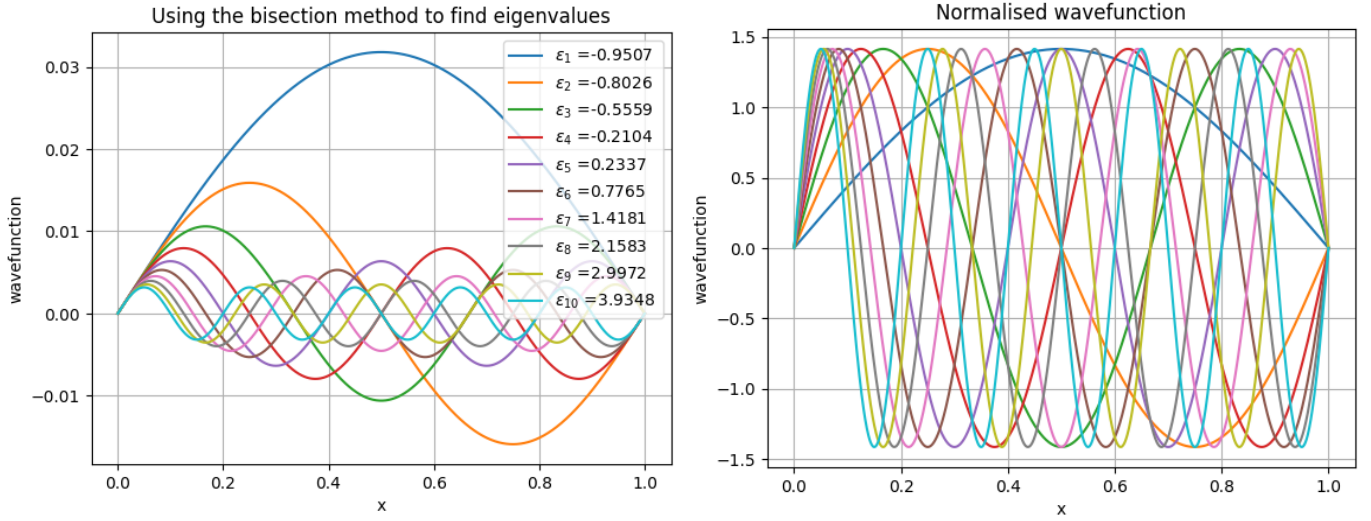

Figure 5.1: The shooting method is used to obtain the first ten eigenstate energies (left) and then the wavefunction is normalised and plot again (right)

Changing to the harmonic potential and following the same procedure as done for the infinite square well yields figures 5.2. As the energy increases the frequency increases accordingly. This follows the analytical solution $\epsilon_n = \hbar\omega(n + 1/2)$ which tells us that as the frequency increases, so does the energy.
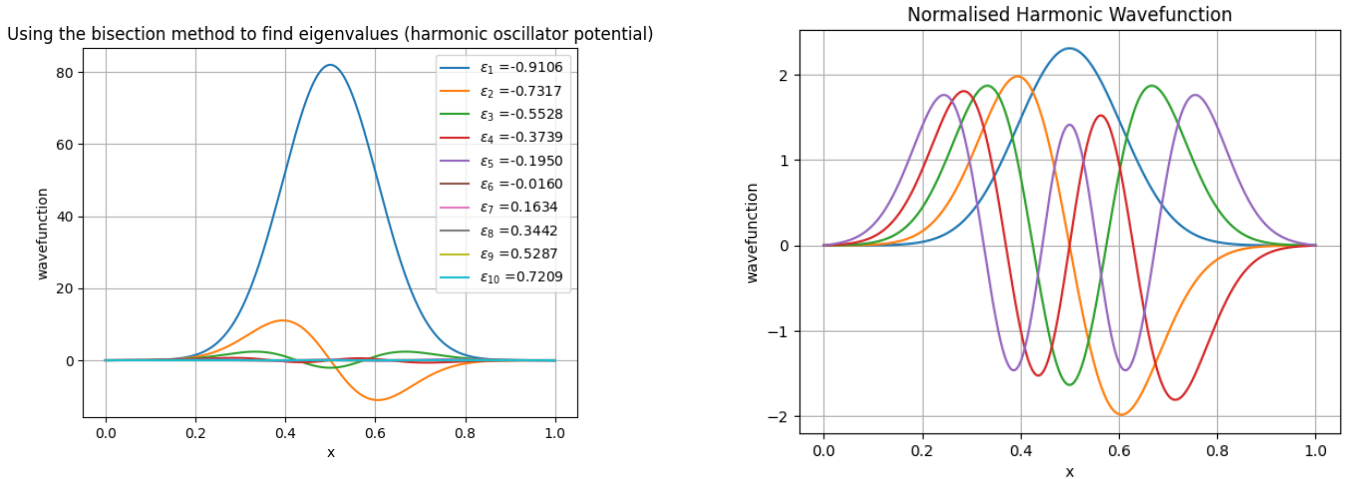

Figure 5.2: The same method is repeated to find the eigenstate energies of the harmonic oscillator potential. The first 5 normalised eigenfunctions are plot on the right.

Table 5.1	Square well potential			Harmonic potential
n	Numerical ϵ_n	Analytic ϵ_n	Absolute error	Numerical ϵ_n
1	-0.950651989	-0.950651978	1.10×10^{-8}	-0.91055728
2	-0.802607918	-0.802607912	5.81×10^{-9}	-0.73167185
3	-0.555867805	-0.555867802	3.53×10^{-9}	-0.55278625
4	-0.210431652	-0.210431648	4.16×10^{-9}	-0.37389898
5	0.233700542	0.233700550	7.69×10^{-9}	-0.19499763
6	0.776528778	0.776528792	1.41×10^{-8}	-0.01600986
7	1.418053074	1.418053078	4.38×10^{-9}	0.16337725
8	2.158273392	2.158273408	1.66×10^{-8}	0.34416523
9	2.997189770	2.997189782	1.27×10^{-8}	0.52869154
10	3.934802170	3.934802201	3.07×10^{-8}	0.72087549

Table 5.1: Comparison of the Eigenstate Energy Values

Figure 5.3: Uncertainty in position for infinite square well.

Table 5.1 above allows us to investigate the accuracy of the shooting method. Our algorithm to implement the shooting method has a tolerance of 1e-8 which is easily reflected in the absolute error. The error scales linearly with the tolerance. Figure 5.4 shows just how accurate this numerical method is where there is almost negligible inaccuracy with this tolerance.

Next we numerically solved for the uncertainties in table 5.2. To see how each uncertainty depends on energy each respective uncertainty is plot vs the quantum number. Figure 5.5 shows that Δx initially increases rapidly but eventually plateaus for large values of n. As n increases, the wavefunction oscillates more rapidly

Figure 5.4: Numerical (blue) vs Analytical (red)

while remaining confined within the "box," leading to the continual increase in Δp shown in figure 5.6. As a result, Δx approaches a minimum value to satisfy the uncertainty principle.
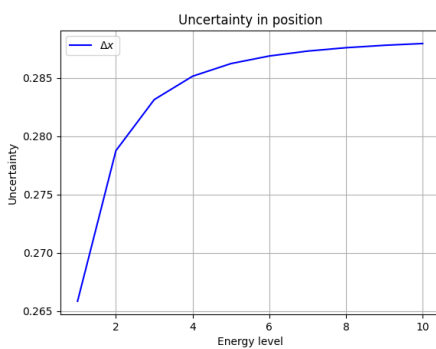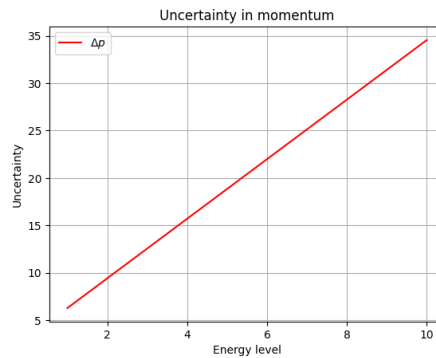

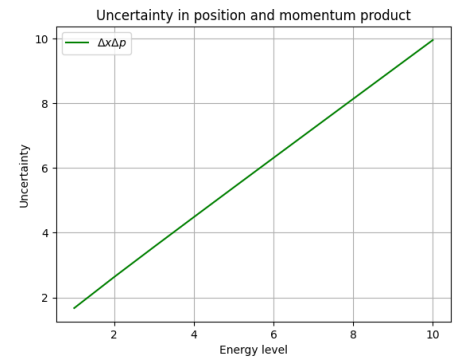Figure 5.5: Δx

Figure 5.6: Δp

Figure 5.7: $\Delta x \Delta p$

Table 5.2 compares the analytical uncertainty (doing the same calculation as the numerical but replacing the wavefunction with the one we determined analytically) for the infinite potential well with our numerical value. This numerical method is accurate to order 1e-11 and increases as the energy and the quantum number increases. Our method is clearly accurate for the square well potential however all we can say about the harmonic potential is that Heisenberg's uncertainty inequality is satisfied for the first 5 eigenstates.
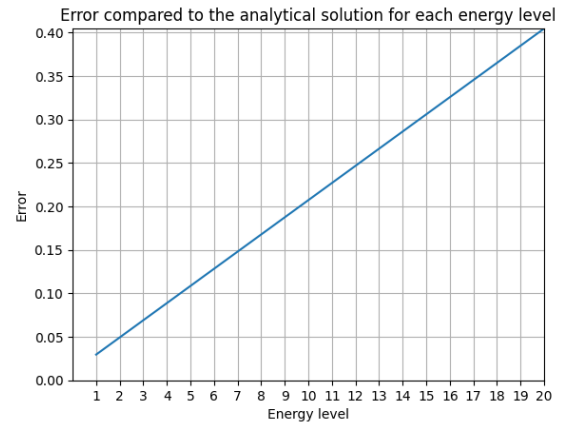
	Square well potential			Harmonic potential
n	Numerical $\Delta\tilde{x}\Delta\tilde{p}$	Analytic $\Delta\tilde{x}\Delta\tilde{p}$	Absolute Error	Harmonic $\Delta\tilde{x}\Delta\tilde{p}$
1	0.56786	0.567862	3.57×10^{-11}	0.54637369
2	1.6703	1.67029	2.47×10^{-10}	0.55665879
3	2.6272	2.6272	8.79×10^{-10}	3.91571376
4	3.558	3.55802	2.28×10^{-9}	5.17577527
5	4.479	4.47903	5.00×10^{-9}	4.08826840
6	5.3953	5.39526	9.84×10^{-9}	-
7	6.3088	6.30879	1.79×10^{-8}	-
8	7.2207	7.22066	3.06×10^{-8}	-
9	8.1314	8.13141	4.98×10^{-8}	-
10	9.0414	9.04139	7.80×10^{-8}	-

Table 5.2: Comparison of the Uncertainty Relation Values with algorithm tolerance of 10^{-8}

Figure 5.8 is a plot of the difference between adjacent eigenstate energies vs quantum number on a log-log scale. For the first 8 or so eigenstates there is a constant energy difference. Then the plot starts to incline and after 10 or so eigenstates there is a constant increase in energy difference. Looking back on figure 5.3 we can recognise this constant increase in energy difference as the potential acting as an infinite potential well as n approaches infinity. This can be expected for a harmonic potential bound by infinite potential walls, at higher energies the eigenstates start to feel the influence of the boundaries of the system.
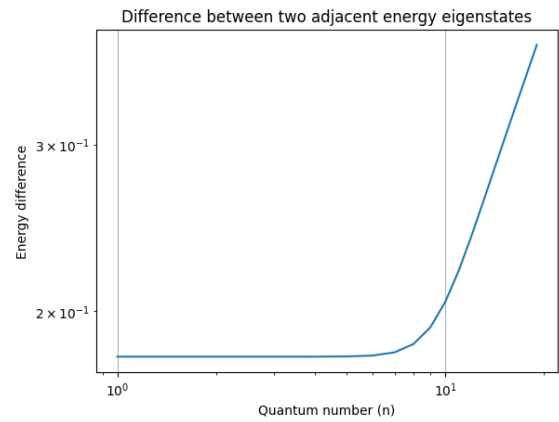

Figure 5.8: Difference in adjacent eigenstate energies up to n = 20

6 CONCLUSION

In this lab we used an iterative relation to discretise the wavefunction and employed the shooting method to find the eigenstate energies. This proved to be very effective, with accuracies of order 10^{-8} and 10^{-9} for the infinite potential well. However it is clear that the tolerance of our algorithm will scale the error linearly. Hence for a small enough tolerance the shooting method is extremely accurate.

Heisenberg's uncertainty inequality was then investigated for the square well potential and the harmonic potential. Table 5.2 shows that all uncertainties satisfy the inequality and the numerical method is accurate to an order of 10^{-11} for n=1 and error increases as n increases. Plot 5.5 shows that Δx plateaus, which is due to the particle being confined in an infinite potential well. As energy is increases Δp increases linearly however due to the potential being restricted by infinite boundaries Δx must plateau and hence the uncertainty principle is satisfied.

Finally, we investigated the difference in energy between adjacent eigenvalues for the quantum harmonic oscillator. It was concluded that the different remains constant for lower energy eigenstates ($1 \leq n \leq 8$) however the difference starts to increase and for $n \geq 10$ is linearly increasing. Meaning that for a harmonic potential bound by infinite potential walls feels the influences of the boundaries for higher energies and begins to act as an infinite potential well for $n \geq 10$.

However something to note about the accuracy of the experiment is the machine epsilon of our computers, which is the smallest difference between two floating-point numbers that a computer can distinguish (approximately 2.2×10^{-16}). This machine epsilon would effect the accuracy of our results if we set our tolerance to anything below it. For example if the tolerance is set to 1e-20 the shooting method may not converge correctly since it may lose precision due to rounding errors. Hence tolerances below 1e-16 would no longer improve our accuracy, plus honestly the code would take a long long time to run, and time is a precious commodity us Theoretical Physicists don't have a lot of.