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

Ruaidhrí Campion JS Theoretical Physics 19333850

 $1^{\rm st}$ November 2021

Contents

1	Introduction	1				
2	Method	2				
3	Results					
4	Conclusions					
5	Appendix5.1Infinite Square Well Potential Plots5.2Harmonic Potential Plots	7 7 10				

1 INTRODUCTION

This laboratory focuses on solving solutions to the time-independent Schrödinger equation

$$E\,\psi(x) = -\frac{\hbar^2}{2m}\,\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x)$$
(1)

or, using non-dimensional quantities $\tilde{x} = \frac{x}{L}$, $\gamma^2 = \frac{2mL^2 V_0}{\hbar^2}$, $\epsilon = \frac{E}{V_0}$, and $\nu(\tilde{x}) = \frac{V(\tilde{x})}{V_0}$,

$$\frac{d^2\psi(\tilde{x})}{d\tilde{x}^2} + \gamma^2 \left(\epsilon - \nu(\tilde{x})\right)\psi(\tilde{x}) = 0.$$
⁽²⁾

For an infinite square well potential, ν is constant for $0 < \tilde{x} < 1$. By considering an ansatz $\psi_n(\tilde{x}) = c \sin(n \pi \tilde{x})$ corresponding to ϵ_n (since $\psi(0) = \psi(1) = 0$), from (2) and the fact that ψ is normalised, the analytic solutions are derived as

$$(2) \implies 0 = -c n^2 \pi^2 \sin(n \pi \tilde{x}) + \gamma^2 (\epsilon_n - \nu) c \sin(n \pi \tilde{x}) \qquad 1 = \int_0^1 c^2 \sin^2(n \pi \tilde{x}) d\tilde{x}$$
$$\epsilon_n = \frac{n^2 \pi^2}{\gamma^2} + \nu, \qquad \psi_n(\tilde{x}) = \sqrt{2} \sin(n \pi \tilde{x}). \qquad (3)$$

The Numerov algorithm can be used to numerically find ψ , as

$$\psi_{n+1} = \frac{2\left(1 - \frac{5}{12}l^2k_n^2\right)\psi_n - \left(1 + \frac{1}{12}l^2k_{n-1}^2\right)\psi_{n-1}}{1 + \frac{1}{12}l^2k_{n+1}^2},\tag{4}$$

where l is the separation between points and, for the Schrödinger equation,

$$k_n^2 = \gamma^2 \left(\epsilon - \nu(x_n)\right). \tag{5}$$

In this laboratory, the Numerov algorithm is used to find ψ for a given number of points N, the potential energy $\nu(\tilde{x})$, the first two points ψ_0 and ψ_1 , and a trial energy ϵ , where $\psi_n = \psi(\tilde{x}_n) = \psi(\frac{n}{N})$. Using the shooting method, ϵ is varied until a non-normalised ψ is found meeting the boundary conditions, which is then normalised using $\int_0^1 |\psi(\tilde{x})|^2 dx = 1$. Finally, Heisenberg's uncertainty principle $\Delta \tilde{x} \Delta \tilde{p} \gtrsim \frac{1}{2}$ is verified, using the expressions

$$\Delta \tilde{x} = \sqrt{\langle \tilde{x}^2 \rangle - \langle \tilde{x} \rangle^2}, \qquad \qquad \Delta \tilde{p} = \sqrt{\langle \tilde{p}^2 \rangle - \langle \tilde{p} \rangle^2}. \tag{6}$$

In this laboratory only real ψ and symmetric potentials about $\tilde{x} = \frac{1}{2}$ are considered, and so $\langle \tilde{x} \rangle = \frac{1}{2}$ and $\langle \tilde{p} \rangle = -i \int_0^1 \psi \frac{d\psi}{d\tilde{x}} d\tilde{x} = 0$. The remaining terms in (6) are given by

$$\left\langle \tilde{x}^2 \right\rangle = \int_0^1 \tilde{x}^2 \,\psi(\tilde{x})^2 \,d\tilde{x}, \qquad \left\langle \tilde{p}^2 \right\rangle = -\int_0^1 \psi(\tilde{x}) \,\frac{d^2 \psi(\tilde{x})}{d\tilde{x}^2} \,d\tilde{x}. \tag{7}$$

To numerically calculate the second derivative in (7), a finite difference scheme is used:

$$\psi_n'' \approx \frac{\psi_{n-1} - 2\psi_n + \psi_{n+1}}{l^2}.$$
 (8)

From (3), (7) reduces to¹

for a square well potential. Combining this leads to, for an infinite square well potential,¹

$$\Delta \tilde{x} \,\Delta \tilde{p} = \frac{1}{2} \sqrt{\frac{n^2 \,\pi^2}{3}} - 2. \tag{10}$$

¹Computed using Mathematica (Wolfram Research, Inc., Mathematica, Version 12.3.1, Champaign, IL (2021).)

2 Method

- 1. $N \equiv N = 1000$, $l \equiv l = 1./(N 1.)$, and $\tilde{x} \equiv x = np.linspace(0., 1., N)$ were defined as instructed, and the system was initialised for a square well potential $(\gamma^2 \equiv \text{gamma2} = 200., \nu(\tilde{x}) \equiv \text{potential} = np.full(N, -1.)).$
- 2. Functions analytic with parameter n and Numerov with parameters psi, n and k2 were defined to return the analytic wavefunction ψ as given in (3) and ψ_{n+1} as given in (4) respectively, where $\psi(\tilde{x}) \equiv \text{psi}$, $n \equiv n$, and $k^2 \equiv k2$.
- 3. A function was defined as follows to find the non-normalised wavefunction for a given energy:

```
def non_normalised(epsilon):
    psi = np.zeros(N)
    psi[0], psi[1] = 0., 10. ** -4.
    k2 = gamma2 * (epsilon - potential)
    for n in range(2, N:)
        psi[n] = Numerov(psi, n, k2)
    return psi
```

- 4. A few non-normalised wave functions were plotted for various ϵ near the analytically calculated energy for n = 1 from (3).
- 5. A function was defined as follows to return $\psi''(\tilde{x})$ as given in (8):

```
def der2(psi):
    array = np.zeros(N)
    for i in range(1, N-1):
        array[i] = (
            psi[i-1] - 2. * psi[i] + psi[i+1]
            ) / (l ** 2.)
    return array
```

6. A function was defined as follows to return an eigenstate energy and corresponding nonnormalised wavefunction given a starting trial energy and energy increment:

```
def shoot(trial_epsilon, delta, tolerance):
    shooting_epsilon, last_psi = trial_epsilon, []
    psi1, psi2 = non_normalised(shooting_epsilon), \
        non_normalised(shooting_epsilon + delta)
    last_psi.extend([psi1[-1], psi2[-1]])
    while delta ** 2. > tolerance ** 2.:
        if last_psi[-1] * last_psi[-2] < 0.:
            delta *= -1./2.
        elif last_psi[-1] == 0.:
            break
        shooting_epsilon += delta
        psi = non_normalised(shooting_epsilon)
        last_psi.append(psi[-1])
    return psi, shooting_epsilon, delta</pre>
```

- 7. For a given trial ϵ , the first energy eigenvalue and corresponding non-normalised wavefunction were found using the above function. The wavefunction was normalised by scaling by a factor of the integral of its absolute value squared (calculated using scipy.integrate.simps), and plotted. The uncertainties (6) were found by calculating the expressions (7) by using scipy.integrate.simps and der2, and their product was plotted. Finally, the trial ϵ and increment were updated for the next case. This was placed in a for loop over 10 iterations.
- 8. Step 7 was repeated for a harmonic potential (gamma2 = 200., potential = 8.
 * (x 0.5) ** 2. 1.), and the difference between the first 20 adjacent energy eigenvalues was plotted by continuing the loop for another 10 iterations.

3 Results

For the square well potential of $\nu(\tilde{x}) = -1$, the ground energy is $\epsilon_1 = \frac{1^2 \pi^2}{200} - 1 \approx -0.9506519779946$. The following wavefunctions were plotted for ϵ close to ϵ_1 .



Figure 1: Graph of various wavefunctions for $\epsilon = -0.94, -0.96, -0.95, \epsilon_1$

As can be seen in Figure 1, the wavefunction ψ is very sensitive to the given energy of the system; even a slight variance from an energy eigenvalue will result in a ψ not meeting the boundary conditions.

For the square well potential, the calculated wavefunctions and their difference from the analytic wavefunction were plotted. For the harmonic potential, the calculated wavefunctions were plotted. Below are a few of the wavefunction plots (all plots can be found in the appendix):



Figure 2: Plots of ψ for the square well potential for n = 1, 5, 10 and their corresponding difference from the analytic solution $\psi_n(\tilde{x}) = \sqrt{2} \sin(n \pi \tilde{x})$.



Figure 3: Plots of ψ for the harmonic potential for n = 1, 5, 10.

From Figure 2 it can easily be seen that the numerical solutions of the wavefunctions are very close to the analytic solutions, suggesting that the numerical method of calculating the wavefunction is accurate. Since the same method is used to calculate the wavefunction for the harmonic potential, it can be deduced that the calculated wavefunctions for the harmonic potential also have a very low error from the true solution.

A tolerance of 10^{-15} was chosen when calculating the energy eigenvalues for both potentials. Below is a table of the calculated energy eigenvalues for the square well potential and their error from the analytic solution, as well as the calculated energy eigenvalues for the harmonic potential.

	Square well potential			Harmonic potential
n	Numerical ϵ_n	Analytic $\epsilon_n = \frac{n^2 \pi^2}{\gamma^2} + \nu$	Absolute error	Numerical ϵ_n
1	-0.9506519779956	-0.9506519779946	1.0×10^{-12}	-0.9105572807000
2	-0.8026079119802	-0.8026079119782	2.0×10^{-12}	-0.7316718350245
3	-0.5558678019646	-0.555867801951	1.4×10^{-11}	-0.552786248607
4	-0.2104316479947	-0.2104316479129	8.2×10^{-11}	-0.3738989764372
5	0.2337005498219	0.2337005501362	3.1×10^{-10}	-0.1949976254832
6	0.7765287912572	0.7765287921961	9.4×10^{-10}	-0.01600986370961
7	1.4180530759	1.418053078267	2.4×10^{-9}	0.163377251123
8	2.158273403077	2.158273408349	5.3×10^{-9}	0.3441652390179
9	2.997189771754	2.997189782441	1.1×10^{-8}	0.5286915490383
10	3.934802180435	3.934802200545	2.0×10^{-8}	0.7208755106902

Figure 4: The calculated and analytic eigenstate energies and corresponding errors for $n = 1, \ldots, 10$.

Similarly, since the error in the calculated energy eigenvalues is very small for the square well potential, and the same method was used to find the eigenstate energies for the harmonic potential, it can immediately be concluded that all calculated energy eigenvalues have a high degree of accuracy.

The uncertainties $\Delta \tilde{x}$ and $\Delta \tilde{p}$ were calculated from (6) and (7), and their products were plotted (and compared to the analytic solution given by (10) for the square well potential).



Figure 5: Plots of the products of the uncertainties $\Delta \tilde{x}$ and $\Delta \tilde{p}$ against *n*, and their calculated values compared to the analytic values for the square well potential.

The numerically calculated uncertainty products for the square well potential have a very small error, similar to the calculated wavefunctions and energy eigenvalues for the same potential. There is, however, one uncertainty product for the harmonic potential that does not seem to satisfy the uncertainty relation. This is due to the computational method inadvertently using approximations and, if it is assumed that the error in this computed value is greater than 2.8×10^{-6} (which is reasonable given the calculated errors for the square well potential), then the uncertainty relation is verified.

The following graphs of the difference in adjacent energy eigenvalues for both potentials were plotted (using log-log axes):



Figure 6: Plots of the difference in adjacent eigenstate energies for $1 \le n \le 39$ for the harmonic potential, and $1 \le n \le 17$ for the square well potential.

From inspection of these graphs, it can be seen that after approximately 10 energy levels, the slope of the harmonic potential energy differences is the same as that of the infinite square well potential energy differences. This is as expected as, for a harmonic potential bounded by infinite walls, after a certain energy level the potential bounds mimic those of an infinite square well, and so the factor by which energy eigenvalues differ will be the same.

4 CONCLUSIONS

As was shown in this computational laboratory, the shooting method employed to find the eigenstate of the system for certain energy levels is effective, and returns wavefunctions and energy levels to a very high degree of accuracy. This was shown by comparing the calculated eigenfunctions, eigenenergies and uncertainty products with the analytical values for an infinite square well potential, and comparing the calculated difference in energy eigenvalues for a harmonic potential to that of an infinite square well potential. For the first ten energy states of the infinite square well, the largest errors were approximately 2×10^{-7} for the eigenfunction, 2×10^{-8} for the eigenenergy, and 3.7×10^{-4} for the uncertainty product.

It was also shown that the Numerov algorithm is effective at calculating the wavefunction given the energy of the system and the first two points of the wavefunction. If a larger N was used for the Numerov algorithm, the calculations of the wavefunctions would have undoubtedly been more accurate. In turn, however, the required time to find the wavefunctions would increase. The accuracy at which the wavefunctions were calculated with N = 1000 was sufficient for this laboratory.

5 APPENDIX

All code and figures used in this laboratory can be found here: https://github.com/campioru/JS_Lab_1



5.1 INFINITE SQUARE WELL POTENTIAL PLOTS



Plot of difference between analytic and numerical ψ for n = 4





Plot of difference between analytic and numerical ψ for n = 6









Plot of difference between analytic and numerical ψ for n = 8







9

5.2 HARMONIC POTENTIAL PLOTS



