
Experiment: Numerical solution of the time-independent 1-D Schrödinger equation

Dominik Kuczynski (student id: 21367544)

Sep-Oct 2023, Monday AM

1 Abstract

2 Introduction

3 Theoretical Background

The time-independent form of the Schrödinger equation is:

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

Now, in considering a system contained within a finite region of space, say from $x = 0$ to $x = L$, and with a given potential and particle mass, it is useful to transform Equation 1 into a dimensionless form:

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

$$\iff \psi''(\tilde{x}) + k^2(\tilde{x})\psi(\tilde{x}) = 0$$

where $\tilde{x} = x/L$, $\epsilon = E/V_0$, $\nu(\tilde{x}) = V(\tilde{x})/V_0$, $\gamma^2 = \frac{2mL^2V_0}{\hbar^2}$.

To solve Equation 2 for the infinite potential well, write:

$$V(\tilde{x}) = \begin{cases} -V_0, & 0 < \tilde{x} < 1 \\ \infty, & \text{else} \end{cases} \implies \nu(\tilde{x}) = \begin{cases} -1, & 0 < \tilde{x} < 1 \\ \infty, & \text{else} \end{cases}$$

In the allowed ($0 < \tilde{x} < 1$) region, Equation 2 becomes:

$$\psi''(\tilde{x}) = -\omega^2\psi \quad (3)$$

where $\omega^2 = \gamma^2(\epsilon + 1)$. The solution is of the form:

$$\psi(\tilde{x}) = c_1 e^{i\gamma\sqrt{\epsilon+1}x} + c_2 e^{-i\gamma\sqrt{\epsilon+1}x} \quad (4)$$

The disallowed region imposes additional conditions that $\psi(\tilde{x}) = 0$ for $\tilde{x} \leq 0$ or $\tilde{x} \geq 1$. These as well as normalisation allow for the solving of c_1 and c_2 , as well as restrict the values of ω . The final solution becomes:

$$\psi(\tilde{x}) = \sqrt{2} \sin(\gamma \sqrt{\epsilon + 1} \tilde{x}), \quad \gamma \sqrt{\epsilon + 1} = 2\pi n, \quad n = 1, 2, \dots \quad (5)$$

$$\implies \epsilon = \frac{4\pi^2 n^2}{\gamma^2} - 1, \quad n = 1, 2, \dots \quad (6)$$

To solve for the harmonic potential, first consider the dimensionful solution when $V(x) = \frac{1}{2}kx^2[1]$:

$$E_n = (n + \frac{1}{2})\hbar\omega, \quad \psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}, \quad n = 0, 1, 2, \dots \quad (7)$$

where $\xi = \sqrt{\frac{m\omega}{\hbar}}x$.

To convert this into the dimensionless form similar to one being analysed, write $V(x) = \frac{1}{2}k(x-L/2)^2 - V_0 = \frac{1}{2}kL^2(\tilde{x} - 0.5)^2 - V_0$. Since $\nu(\tilde{x}) = V(\tilde{x})/V_0 = 8(\tilde{x} - 0.5)^2 - 1$:

$$k = \frac{16V_0}{L^2} \quad (8)$$

This allows us to solve for ϵ_n :

$$\epsilon_n = E_n/V_0 = (n + \frac{1}{2}) \frac{\hbar}{V_0} \sqrt{\frac{k}{m}} - 1 = (n + \frac{1}{2}) \frac{\hbar}{V_0} \sqrt{\frac{16V_0}{L^2 m}} - 1 = (n + \frac{1}{2}) \frac{4\sqrt{2}}{\gamma} - 1 \quad (9)$$

Note that here E was shifted down by V_0 , together with $V(x)$.

3.1 Uncertainty relation

To calculate $\Delta\tilde{x} = \sqrt{\langle\tilde{x}^2\rangle - \langle\tilde{x}\rangle^2}$, it is useful to note that for symmetric potentials, the particle is as likely to be "on the left" as it is "on the right" of the axis of symmetry, meaning $\langle\tilde{x}\rangle$ is precisely the position of that axis. In the cases examined here, $\langle x \rangle = 0.5$.

The second moment of \tilde{x} can be calculated using

$$\langle\tilde{x}^2\rangle = \int_0^1 \tilde{x}^2 |\psi(\tilde{x})|^2 d\tilde{x} \quad (10)$$

To find the uncertainty $\Delta\tilde{p}$, one needs to use that the non-dimensional momentum operator is $\hat{\tilde{p}} = -i\frac{d}{d\tilde{x}}$. Then, $\langle\tilde{p}\rangle = \langle\psi^*|\hat{\tilde{p}}|\psi\rangle = -i\int_0^1 \psi \frac{d\psi}{d\tilde{x}} d\tilde{x}$ for real ψ . But since $\psi(0) = \psi(1) = 0$, integration by parts of the above yields that $\langle\hat{\tilde{p}}\rangle = 0$.

Similarly, $\langle\tilde{p}^2\rangle = \langle\psi^*|\hat{\tilde{p}}^2|\psi\rangle = -\int_0^1 \psi \frac{d^2\psi}{d\tilde{x}^2} d\tilde{x}$ and therefore:

$$\Delta\tilde{p} = \sqrt{-\int_0^1 \psi \frac{d^2\psi}{d\tilde{x}^2} d\tilde{x}}. \quad (11)$$

4 Method

To solve the Schrödinger equation numerically, the variable \tilde{x} gets discretized into N values x_n , $n = 1, 2, \dots, N$, between 0 and 1. Then, the value of ψ at a given point x_{n+1} can be approximated using the values of ψ and ν at two previous points:

$$\psi_{n+1} \approx \frac{2(1 - \frac{5}{12}l^2k_n^2)\psi_n - (1 + \frac{1}{12}l^2k_{n-1}^2)\psi_{n-1}}{1 + \frac{1}{12}l^2k_{n+1}^2} \quad (12)$$

$$\text{with } k_n^2 = \gamma^2(\epsilon - \nu(\tilde{x}_n)) \quad (13)$$

This allows for the numerical integration of $\psi(\tilde{x})$ from 0 to 1, given its values at the two initial points x_1 and x_2 .

To obtain ψ 's second derivative at a given point, the finite difference scheme was used. Denoting by l the separation of discrete points x_n :

$$\psi_n'' \approx \frac{\psi_{n-1} - 2\psi_n + \psi_{n+1}}{l^2} \quad (14)$$

When the value ϵ is given, a numerical integration algorithm, following (13) can generate a wavefunction, provided two initial conditions. For the purposes of this lab, the conditions were the following:

$$\psi(x_1) = 0, \quad \psi(x_2) = 10^{-4}$$

x_0 and x_1 correspond to the first and second sampling points of the numerical algorithm and the value $\psi(x_1)$ is chosen to be arbitrarily non zero.

4.1 Shooting method for finding energy eigenstates

Since the energy spectrum of the infinite well potential is discrete, only specific values of energy will produce normalizable (physical) wavefunctions. The method used for finding these values makes use of the fact that non-eigenstate energies will produce wavefunctions blowing up to large positive or large negative values at the end of the interval, due to the exponential nature of the Schrödinger equation. However, since the final result is continuous in ϵ , between two energies producing ψ blowing up with opposite signs, there must be one for which $\psi(1) = 0$.

Therefore, the final method changes the value of examined ϵ by smaller and smaller corrections to find the energy at which $\psi(1)$ goes from negative to positive or vice versa, not unlike the bisection method for finding roots of functions. The stopping condition is that the corrections become smaller than a desired tolerance.

```
def shoot(energy, v, tol=5e-4, de=5e-3):
```

```

# initialize e to a starting value
e = energy

# variable for storing psi(1) of the previous iteration ,
# used for determining whether the sign has changed
prevLastPsi = 0

while(abs(de) > tol):
    psi = integratePsi(e, v)
    psi = normalize(psi)

    # if the sign of psi(1) has changed, move to in between
    # the last two energies
    if psi[-1] * prevLastPsi < 0:
        de = -de/2

    prevLastPsi = psi[-1]
    e += de

return e

```

5 Results & Discussion

5.1 Infinite well potential

The wavefunctions of the first three found eigenstates were plotted to obtain the following:

This result appears to correspond to the analytic solutions. To actually check the accuracy, the error in the first eigenstate was plotted and found to be less than 0.005.

The obtained eigenstate energies were compared with the analytical results for a given tolerance and the errors were calculated (Table 1).

To further investigate how the tolerance value affects the accuracy, the errors of the first three energies were plotted for different tolerances:

It is clear that the tolerance value affects the resulting accuracy significantly. However, the above figure also shows the existence of other sources of error - which have the dominant effect when tolerance is low enough.

It seems most likely that the main source of these errors would be the accuracy of the numerical integration. This is consistent with the observed relation where higher energies, corresponding to

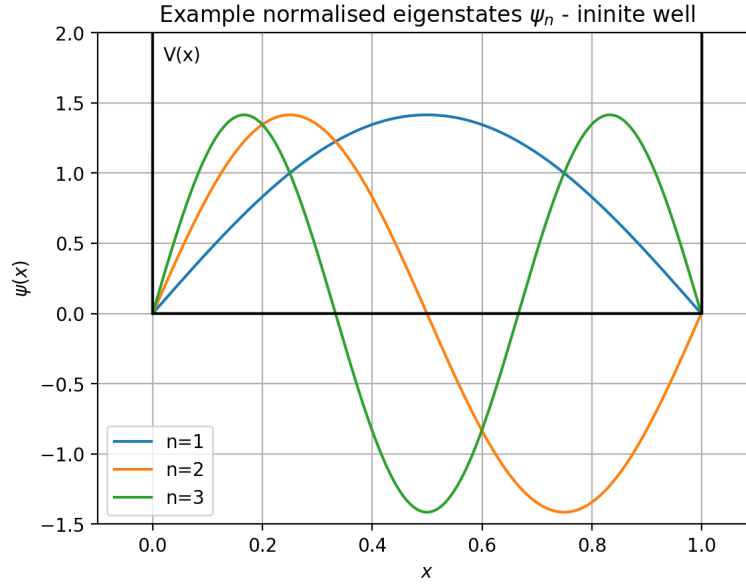


Figure 1: First three generated eigenstates of the infinite well potential

Table 1: Normalised eigenstate energies ϵ_n - infinite well

n	numerical result (tol=1e-5)	analytic result	absolute error
1	-0.95055	-0.95065	0.00010
2	-0.80220	-0.80260	0.00040
3	-0.55498	-0.55586	0.00088
4	-0.20884	-0.21043	0.00159
5	0.23616	0.23370	0.00247
6	0.78008	0.77652	0.00355
7	1.42290	1.41805	0.00485
8	2.16459	2.15827	0.00632
9	3.00518	2.99718	0.00800
10	3.94469	3.93480	0.00989

more rapidly oscillating and thus more error-prone wavefunctions, have larger errors.

The uncertainty relation for the infinite well potential was checked by plotting $\Delta x \Delta p$ at the calculated eigenstate energies ϵ_n :

5.2 Bounded harmonic potential

For $\nu(x) = 8(x - 0.5)^2 - 1$, the first three calculated eigenstates were the following:

The calculated eigenstate energies were, again, compared to the analytical solutions. However, since there is no analytic solution for the harmonic potential bounded by infinite walls, the solutions of the unbounded harmonic potential was used to compare. The discussion of this approximation can be found in the later part of this section.

Again, like in the case of the infinite well, it is clear that there are other sources of error than the set

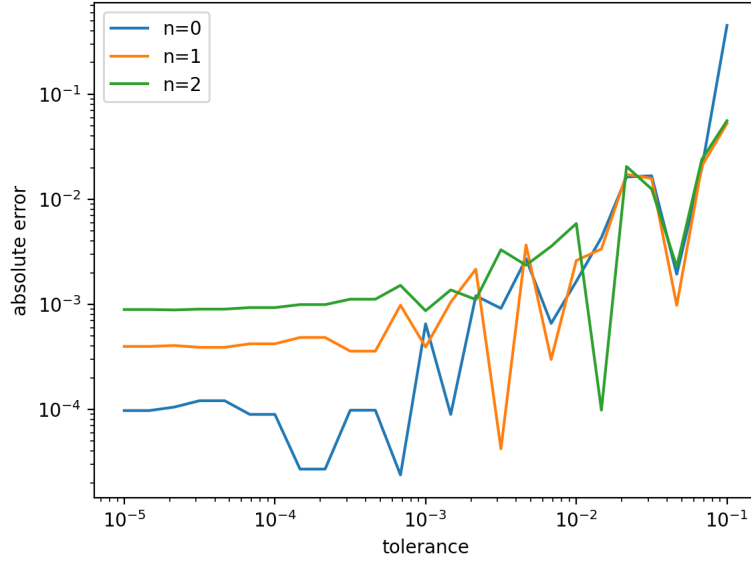


Figure 3: Absolute error between numerical and analytic values of the first three eigenstate energies - for different values of tolerance

Table 2: Normalised eigenstate energies ϵ_n - bounded harmonic potential

n	numerical result (tol=1e-9)	analytic result	absolute error
1	-0.910557280	-0.910557281	0.000000001
2	-0.731671835	-0.731671843	0.000000008
3	-0.552786242	-0.552786405	0.000000163
4	-0.373898901	-0.373900966	0.000002065
5	-0.194996989	-0.195015528	0.000018539
6	-0.016005948	-0.016130090	0.000124141
7	0.163395485	0.162755348	0.000640137
8	0.344230419	0.341640786	0.002589633
9	0.528873026	0.520526225	0.008346801
10	0.721278843	0.699411663	0.021867180

tolerance - particularly at higher energies.

The uncertainty relation was plotted next:

This time, 20 of the first eigenstate energies were used.

To see the discrepancy with the analytic solution of the unbounded harmonic potential, it is particularly useful to look at higher energy eigenstates. That is because at high enough energies, the system effectively starts behaving like an infinite square well.

One way to observe this is to plot a few examples of high-energy generated eigenstates:

It is clear that their behaviour is more like that of the infinite well eigenstates, as they appear to have roots at $x = 0$ and $x = 1$, instead of identically converging to 0.

Another way of clearly observing the discrepancy, is to look at differences between consecutive eigenstate energies calculated by the algorithm:

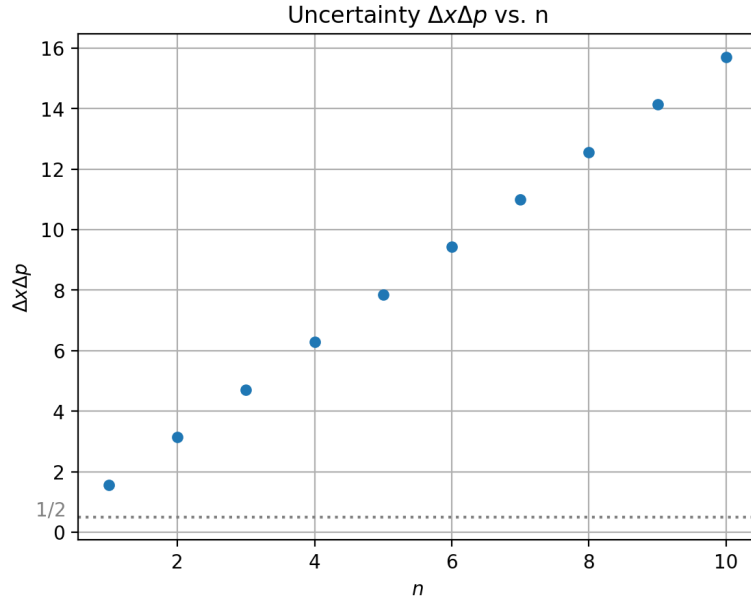


Figure 4: Uncertainty relation - infinite well

For low values of n , the energies are evenly spaced - in accordance with the harmonic potential. However, for n higher than around 10 the plot shifts into the infinite well region - and produces a line with the slope of 2, as predicted by that type of potential.

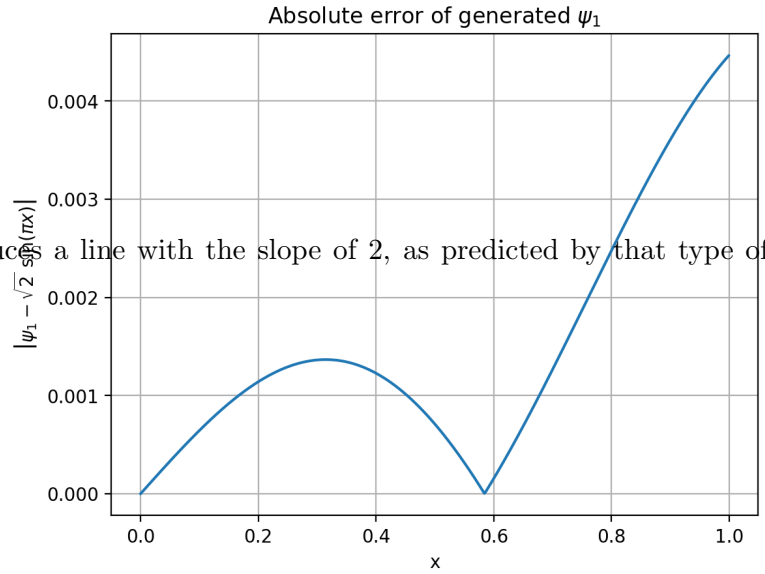


Figure 2: Absolute error between the generated and analytic solution

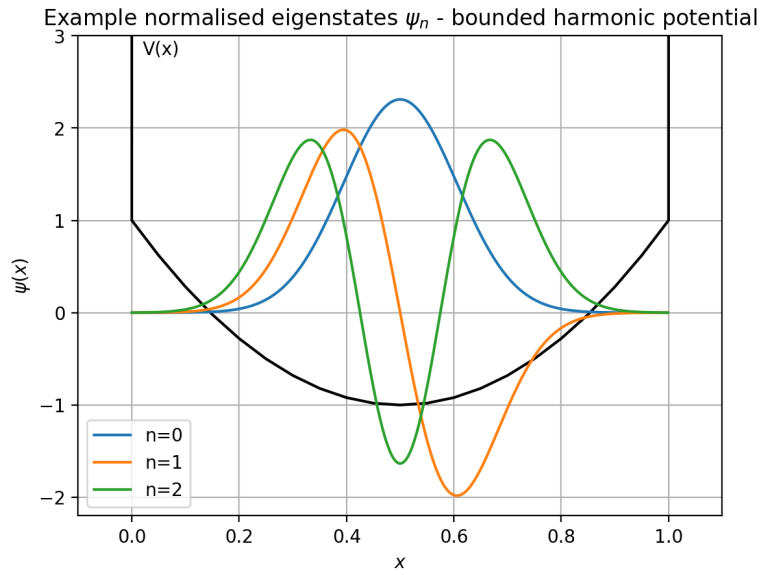


Figure 5: First three generated eigenstates of the bounded harmonic potential

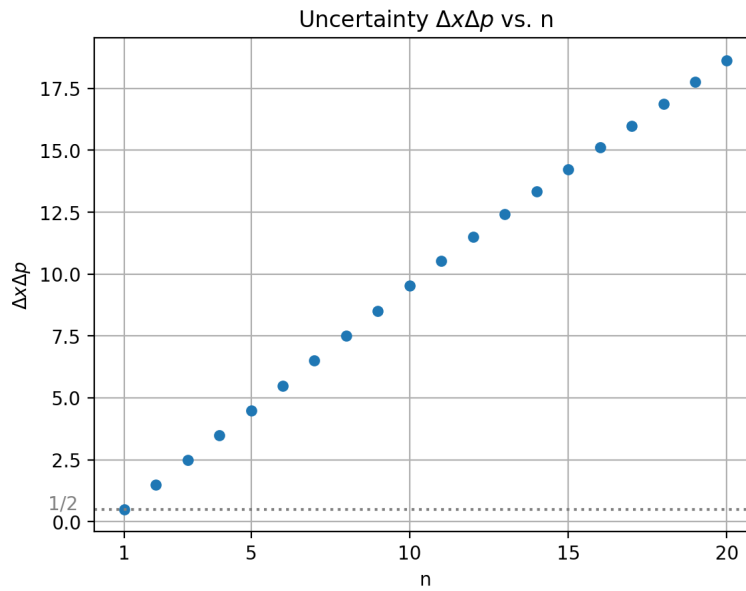


Figure 6: Uncertainty relation - bounded harmonic potential

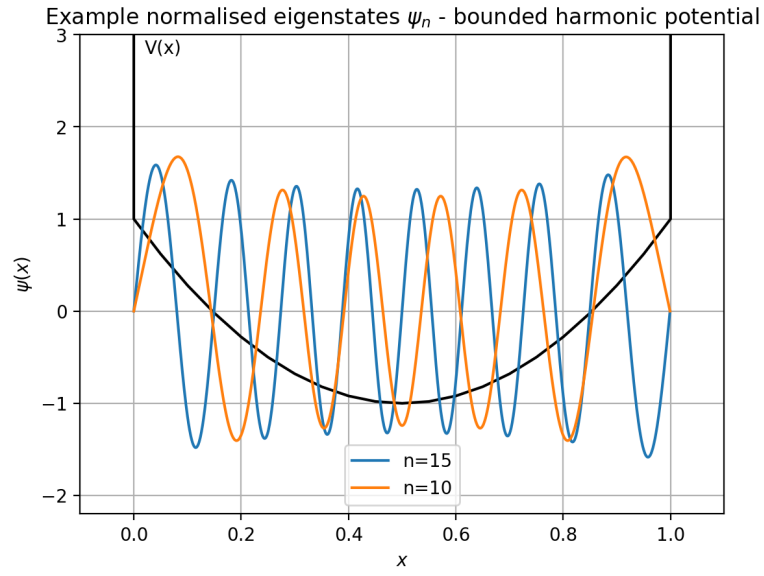


Figure 7: Example high-energy eigenstates of the bounded harmonic potential

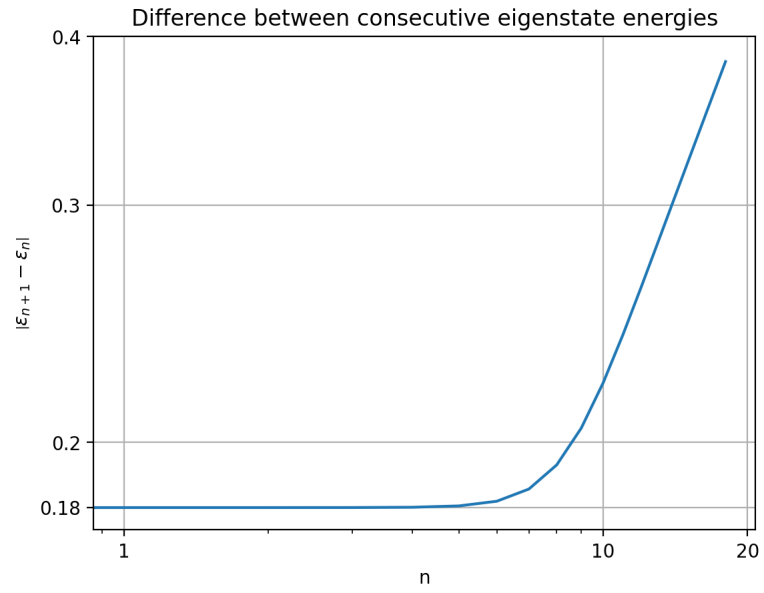


Figure 8: Differences between consecutive energies (log-log) - bounded harmonic potential

6 Conclusion

7 Appendix

List of Figures

1	First three generated eigenstates of the infinite well potential	5
2	Absolute error between the generated and analytic solution	5
3	Absolute error between numerical and analytic values of the first three eigenstate energies - for different values of tolerance	6
4	Uncertainty relation - infinite well	7
5	First three generated eigenstates of the bounded harmonic potential	8
6	Uncertainty relation - bounded harmonic potential	8
7	Example high-energy eigenstates of the bounded harmonic potential	9
8	Differences between consecutive energies (log-log) - bounded harmonic potential	9

Bibliography

References

- [1] David J. Griffiths. *Introduction to Quantum Mechanics*. Cambridge University Press; 3rd edition, 2018.