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

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Contents

1 Abstract

For an arbitrary potential, the Schrödinger equation quickly becomes impossible to solve analytically. Therefore, numerical methods have become extremely important in predicting the behaviour of quantum systems.

Here, energy eigenstates of the infinite well and bounded harmonic potential were found using a "shooting" method together with a numerical integration scheme. The found values correspond well (to within 5%) with the analytic solutions.

The uncertainties of x and p in both potentials were calculated at different energy states. Their product was found to increase linearly with excitation number in both cases and the uncertainty principle was shown to hold.

Finally, the bounded harmonic potential energies were shown to be approximately evenly spaced for the first 10 states, and become quadratic - as in the case of the infinite well - past that point.

2 Theoretical Background

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, the Schrödinger equation can be converted to its dimensionless form:

$$\frac{d^2\psi(\tilde{x})}{d\tilde{x}^2} + \gamma^2(\epsilon - \nu(\tilde{x})))\psi(\tilde{x}) = 0 \tag{1}$$

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

To solve Equation 1 for the infinite potential well, write: $\nu(\tilde{x}) = \begin{cases} -1, & 0 < \tilde{x} < 1 \\ \infty, & \text{else.} \end{cases}$

In the allowed $(0 < \tilde{x} < 1)$ region, Equation 1 has a simple solution of the form:

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

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

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

$$\implies \epsilon_n = \frac{4\pi^2 n^2}{\gamma^2} - 1, \quad n = 1, 2, ... \tag{3}$$

Note in particular, the energy values increase quadratically with n.

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

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

To convert the potential $V(x)$ into the dimensionless form being analysed, $\nu(\tilde{x}) = 8(\tilde{x} - 0.5)^2 - 1$, set $k = \frac{16V_0}{L^2}$. This allows us to solve for ϵ_n:

$$\epsilon_n = E_n/V_0 = (n + \frac{1}{2})\frac{\hbar}{V_0}\sqrt{\frac{k}{m}} - 1 = (n + \frac{1}{2})\frac{4\sqrt{2}}{\gamma} - 1 \tag{5}$$

Note that here E was shifted down by V_0, together with $V(x)$ and the whole system moved to the right by $L/2$. The energy values in this case are evenly spaced.

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, $\langle\tilde{x}\rangle = 0.5$.

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

$$\langle\tilde{x}^2\rangle = \int_0^1 \tilde{x}^2|\psi(\tilde{x})|^2 d\tilde{x} \tag{6}$$

To find the uncertainty $\Delta\tilde{p}$, one needs to use that the non-dimensional momentum operator is $\hat{\tilde{p}} = -i\frac{d}{dx}$. 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 $\langle\hat{\tilde{p}}\rangle = -\langle\hat{\tilde{p}}\rangle = 0$.

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:

$$\Delta\tilde{p} = \sqrt{-\int_0^1 \psi\frac{d^2\psi}{d\tilde{x}^2}d\tilde{x}}. \tag{7}$$

3   Method

To solve the Schrödinger equation numerically, the variable $\tilde{x}$ gets discretized into N values x_n, $n = 1, 2, ..., N$, 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:

$$\psi_{n+1} \approx \frac{2(1 - \frac{5}{12}l^2k_n^2)\psi_n - (1 + \frac{1}{12}l^2k_{n-1}^2)\psi_{n-1}}{1 + \frac{1}{12}l^2k_{n+1}^2} \quad \text{with } k_n^2 = \gamma^2(\epsilon - \nu(\tilde{x}_n)) \tag{8}$$

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:

$$\psi_n'' \approx \frac{\psi_{n-1} - 2\psi_n + \psi_{n+1}}{l^2} \tag{9}$$

When the value ϵ is given, a numerical integration algorithm, following (8) can generate a wavefunction, provided two initial conditions. For the purposes of this lab, the conditions were the following: $\psi(x_1) = 0, \quad \psi(x_2) = 10^{-4}$.

3.1 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 positive or negative values at the end of the interval. 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 $\psi(1) = 0$.

```
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
    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
```

# 4 Results & Discussion

4.1 Infinite well potential

The wavefunctions of the first three found eigenstates were plotted (Figure 5) and the result appears to correspond to the analytic solutions. To actually check the accuracy, the error in the first eigenstate was plotted (Figure 6) and found to be less than 0.005.

Table 1: Normalised eigenstate energies ϵ_n - infinite well

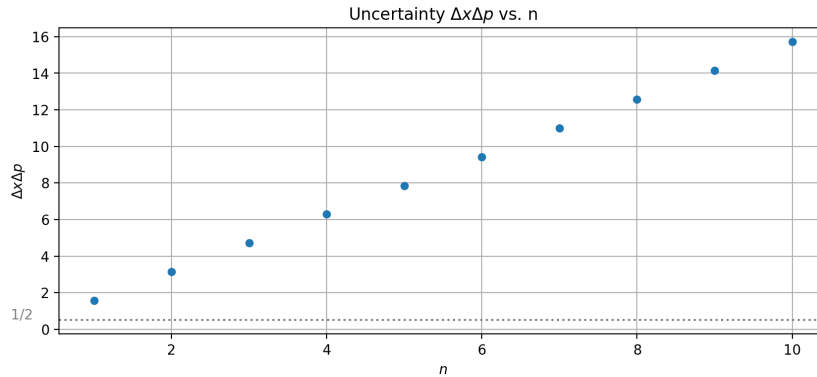| n	numerical result (`tol=1e-5`)	analytic result	absolute error
1	-0.95055	-0.95065	0.00010
2	-0.80220	-0.80260	0.00040
3	-0.55498	-0.55586	0.00088
4	-0.20884	-0.21043	0.00159
5	0.23616	0.23370	0.00247
6	0.78008	0.77652	0.00355
7	1.42290	1.41805	0.00485
8	2.16459	2.15827	0.00632
9	3.00518	2.99718	0.00800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

The obtained eigenstate energies were compared with the analytical results for a given tolerance and the errors were calculated (Table 1). The errors are relatively small, but for higher energy states increase beyond the tolerance.

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 its value affects the resulting accuracy significantly. However, Figure 1 also shows the existence of other sources of error - which have the dominant effect when tolerance is low enough.
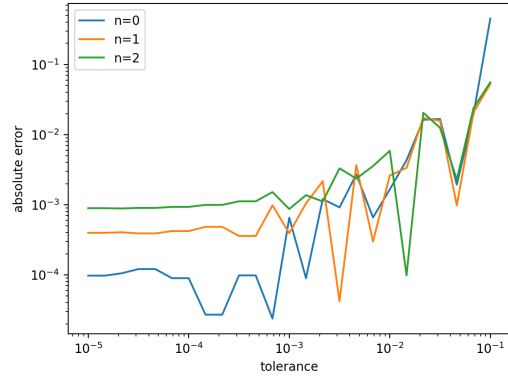
Figure 1: Absolute error in eigenstate energies vs. tolerance

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 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 (Figure 2). It is clear that the uncertainty increases linearly with energy, and the minimum value of $1/2$ is not achieved for any of the eigenstates.

Figure 2: Uncertainty relation - infinite well

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4.2   Bounded harmonic potential

Table 2: Normalised eigenstate energies ϵ_n - bounded harmonic potential

n	numerical result (`tol=1e-9`)	analytic result	absolute error
0	-0.910557280	-0.910557281	0.000000001
1	-0.731671835	-0.731671843	0.000000008
2	-0.552786242	-0.552786405	0.000000163
3	-0.373898901	-0.373900966	0.000002065
4	-0.194996989	-0.195015528	0.000018539
5	-0.016005948	-0.016130090	0.000124141
6	0.163395485	0.162755348	0.000640137
7	0.344230419	0.341640786	0.002589633
8	0.528873026	0.520526225	0.008346801
9	0.721278843	0.699411663	0.021867180

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 were 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, the results correspond well but it is clear that there are other sources of error than the set tolerance - particularly at higher energies.

This time, in plotting the uncertainty, 20 of the first eigenstate energies were used. Again, as in the previous case, the uncertainty increases linearly with energy, however this time reaching the minimum value of $1/2$ at $n = 0$ - showing that the lowest state of the harmonic oscillator is the minimum uncertainty packet.
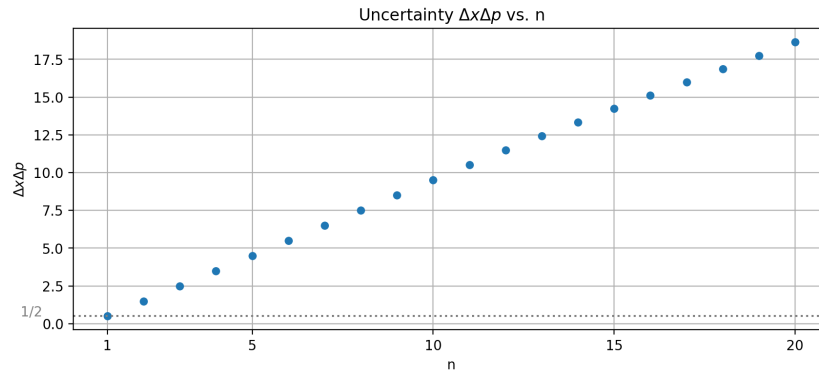
Figure 3: Uncertainty relation - bounded harmonic potential

Plots of the generated eigenstates (Figure 7) show that the bounded harmonic approximation is accurate at lower energies but breaks down at higher ones. There, the system effectively starts behaving like an infinite square well - the solutions appear to have roots at $x = 0$ and $x = 1$, instead of identically converging to 0.

Another way of clearly observing the limitations of this approach is to look at differences between consecutive eigenstate energies calculated by the algorithm: 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, indicating quadratically spaced energies, as predicted by that type of potential.
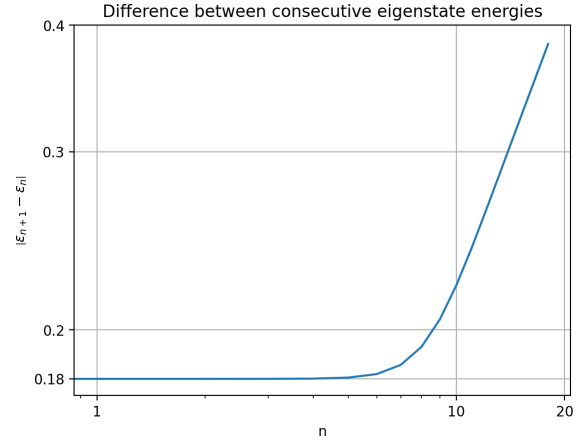
Figure 4: Differences between consecutive energies - bounded harmonic

5 Conclusion

It is clear that numerical methods of solving the Schrödinger equation are indispensable in many cases. They were shown to produce accurate solutions as well as being able to find eigenvalues of the energy operator.

The computed eigenstate energies were shown to become more accurate with smaller values of tolerance, up to a certain limit. Below that limit, other sources of error were shown to be dominant, especially for higher energies.

The uncertainties in x and p were found to increase linearly with the excitation number n both in the case of the infinite well and the bounded harmonic potential. However, only the lowest energy state in the harmonic potential obtained the minimum possible value corresponding to $\hbar/2$.

The limitations of approximating the harmonic potential by its bounded counterpart were found to become more prominent at higher energies. There, the system appeared to behave as if the potential was an infinite well - the eigenstate energies began to be spaced quadratically in n, instead of linearly as would be the case in the quantum harmonic oscillator.
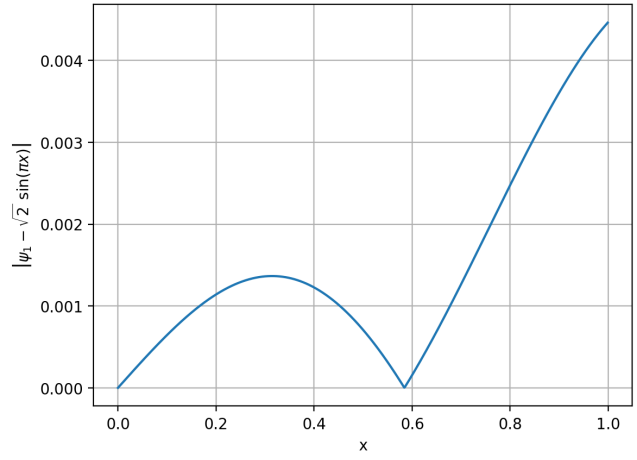
References

[1] David J. Griffiths. *Introduction to Quantum Mechanics*. Cambridge University Press; 3rd edition, 2018.
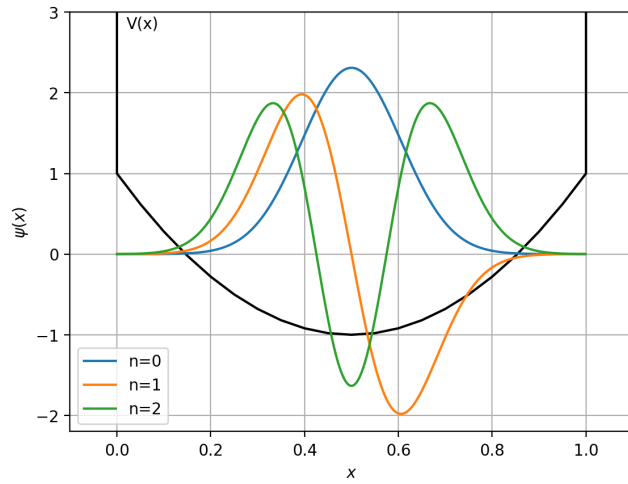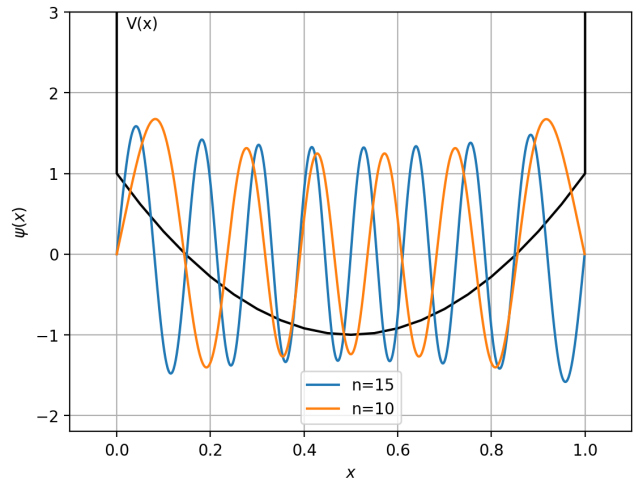
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6 Appendix
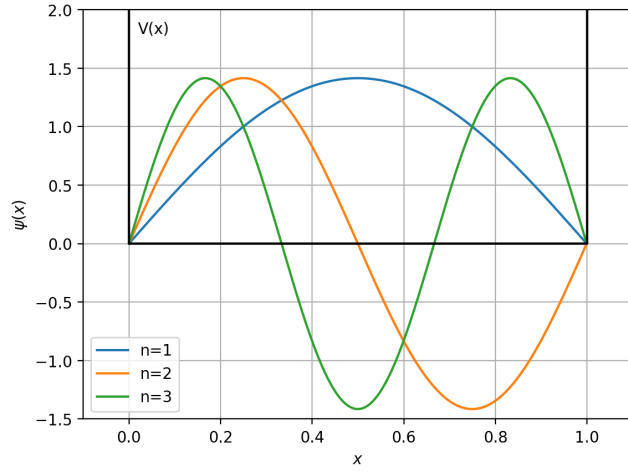
Figure 5: First three generated eigenstates of the infinite well potential

Figure 6: Absolute error between the generated and analytic solution

(a) Low energy states

(b) High energy states

Figure 7: Example eigenstates of the bounded harmonic potential