

Numerical Solutions of the Time-Independent 1D Schrodinger Equation

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Abstract

The Schrodinger equation was solved both analytically and numerically for the potentials of a infinite square well, harmonic and the Hydrogen atom. The numerical and analytical solutions agreed up to an error of 10^{-7} . The dependence of the uncertainty product $\Delta x \Delta p$ on the quantum number n was investigated and the Heisenberg Uncertainty Relation HUR was satisfied.

Background

The Schrodinger equation is differential equation (DE) analogous to Newton's second law. Given Initial Conditions (IC) it describes the path a system takes over time. The most general version of Schrodinger's equation is

$$i\hbar \frac{d}{dt}|\psi\rangle = \hat{H}|\psi\rangle \quad (1)$$

where \hat{H} is the Hamiltonian operator and ψ is the wavefunction satisfying $\langle\psi|\psi\rangle = 1$. Here we consider the special cases of a steady state Schrodinger equation (SSSE) (no time dependence) and a partical in an infinite box (bounded by infinite potentials).

The SSSE is given by

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

where E is the energy, m is mass and V is the potential.

In the infinite square well the potential satisfies

$$V(x) = \begin{cases} V_0 & \text{if } 0 < x < L \\ \infty & \text{otherwise} \end{cases} \quad (3)$$

We have a harmonic potential given by

$$V(x) = \begin{cases} 8(x - 0.5)^2 - 1 & \text{if } 0 < x < L \\ \infty & \text{otherwise.} \end{cases} \quad (4)$$

The potential of a Hydrogen atom is given by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad (5)$$

where e is the charge of an electron ?? Griffiths [1].

We have the dimensionless TISE given by

$$\frac{d^2\psi(\tilde{x})}{d\tilde{x}^2} + \gamma^2(\epsilon - \nu(\tilde{x}))\psi(\tilde{x}) = 0 \quad (6)$$

Introduction

Numerical Discetization

We solve the DE equation 6 using discretized spacial coordinates \tilde{x} with N points in $\tilde{x} \in [0, 1]$. We can use

$$\psi_{n+1} = \frac{2(1 - \frac{5}{12}l^2k_n^2)\psi_n - (1 + \frac{1}{12}l^2k_{n-1}^2)\psi_{n-1}}{1 + \frac{1}{12}l^2k_{n+1}^2} \quad (7)$$

to solve using B.C. for ψ_{n-1} and taking an arbitrary ψ_n we find ψ_{n+1} and iterate.

Shooting Method

We can find eigenenergies which satisfy the left ψ_L

BC but these may not also satisfy ψ_R . We can try guessing (or shooting) trajectories from ψ_L and adjusting our parameters until both ψ_L and ψ_R B.C. are satisfied.

Method

Firstly, we compute the solutions to the TISE analytically using the anzats $\psi = Ae^{ax} + Be^{-bx}$. Then we numerical discretization to store ψ in an array for $N = 1000$ and $\gamma^2 = 200$. Define a potential array e.g. set $V(\tilde{x}) = -1 \forall 0 < x < 1$. We can approximate a derivative $d\psi/dx \approx \frac{\psi_{n+1} - \psi_n}{l}$ this is iterated, and could be modified to improve error and stability. In our case from using a finite difference scheme

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

we have $O(l^4)$.

```
def wave_function(epsilon):
    psi = np.zeros(N)
    k_squared = gamma_squared * (epsilon - potential)
    psi[0] = 0
    psi[1] = 1e-4

    for i in range(1, N - 1):
        psi[i + 1] = ((1 + (l/12) * dx**2 * k_squared[i]) * psi[i] -
                    (1 + (l/12) * dx**2 * k_squared[i-1]) * psi[i-1]) / \
                    (1 + (l/12) * dx**2 * k_squared[i+1]))

    return psi
```

Figure 1: Function which gives discrete values of ψ in an array (essentially a translation of 7 into code).

```
# function to find the eigenvalue using the shooting method
def find_eigenvalue(initial_epsilon, delta_epsilon):
    epsilon = initial_epsilon
    psi = wave_function(epsilon)
    psi_last = psi[-1]

    while abs(delta_epsilon) > accuracy:
        epsilon_new = epsilon + delta_epsilon
        psi_new = wave_function(epsilon_new)
        psi_last_new = psi_new[-1]

        if psi_last * psi_last_new < 0:
            delta_epsilon = -delta_epsilon / 2

        epsilon = epsilon_new
        psi_last = psi_last_new

    #psi = wave_function(epsilon)
    return epsilon, psi_new
```

Figure 2: Function to find energy-eigenvalues in a infinite square well.

We have $\psi(\epsilon)$ for a given an initial ϵ we add a small $\Delta\epsilon$ and multiply them. If there is a change of sign we change the change the sign and half $\Delta\epsilon$. This is done until we are within the desired accuracy.

Results

Solving the SSEE analytically using the typical bound state anzats of $\psi(x) = Ae^{iax} + Be^{-ibx}$, applying B.C. ($\psi(0) = \psi(L) = 0$) and *normalising* we get $\psi(x) = \sqrt{2}\sin(n\pi\tilde{x})$, with $n \in N$. Given $k_n^2 = \gamma^2(\epsilon_n + 1)$ and $k_n = n\pi$, we have the quantisation condition

$$\epsilon_n = \frac{\pi^2 n^2}{\gamma^2} - 1. \quad (9)$$

So $\epsilon_n > -1$. This procedure was repeated for the harmonic and Hydrogen potential to give

$$\epsilon_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (10)$$

and

$$\epsilon_n = - \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \right] \frac{1}{n^2} \quad (11)$$

with m_e the mass of an electron and $n \in N^+$. The energy eigenvalues were solved numerically and can be seen in *figure 3* and *figure 5*.

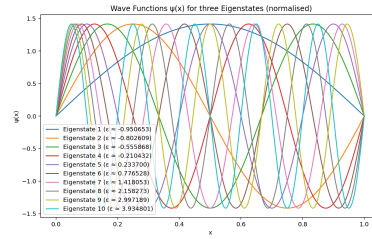


Figure 3: Plot of wavefunctions of a infinite square well $\psi(x)$ for the first ten Eigenstates. Both ψ_L and ψ_R B.C. are satisfied. Wavefunctions ψ_i oscillate from being even to odd (wrt the center of the well). Clearly the ground state ψ_1 is even. The peaks represent the most likely positions to find a particle.

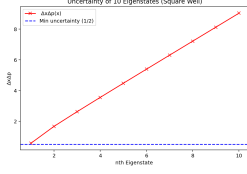


Figure 4: Plot of the uncertainty of the nth Eigenstate up to the 10th (natural units). We have the blue line being the min at $\frac{\hbar}{2}$ (SI).

Harmonic Potential

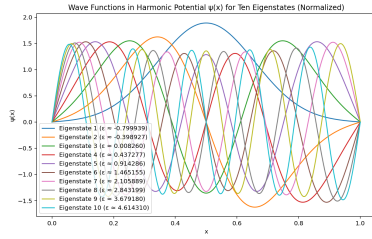


Figure 5: Plot of wavefunctions of a harmonic potential $\psi(x)$ for the first ten Eigenstates

In this case, the BC are satisfied again. We also see as expected the ground state has a gaussian shape.

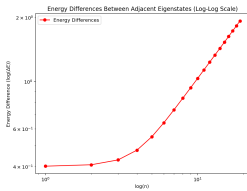


Figure 6: Log-log Plot of Energy Differences ($\Delta E = \hbar\omega$ for adjacent eigenstates in harmonic potential). We see that for large Energies there's a resemblance of the square well. Since $E \gg V(x)$ implies $\Delta E \approx \text{constant} \Rightarrow k \approx \text{constant}$. Giving our resemblance (physically kinetic energy is dominating so potential appears flat like in the infinite square well case.)

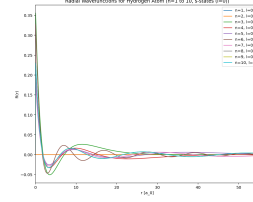


Figure 7: Plot of Wavefunctions in the Hydrogen atom for S states. Here r is radial distance in Bohr radii and $R(r)$ is dimensionless.

For the hydrogen atom 11 tells us that as $n \rightarrow \infty$, $E \rightarrow 0$. This separates the bound and scattering states.

Conclusions

The SSSE was analytically solved in a infinite square well and it was also solved numerically on python. The numerical calculation agreed with the analytical solution up to an accuracy of 10^{-7} . This uncertainty is unavoidable as for small tolerances we have floating point errors. The wavefunctions with these energies satisfied the HUR. This procedure was repeated for a harmonic and Hydrogen's potential also satisfying BC and the HUR.

References

- [1] David J. Griffiths. *Introduction to Quantum Mechanics*. 2nd. Upper Saddle River, NJ: Pearson Prentice Hall, 2005, p. 143.

Appendices

Equations

The standard normalisation condition is given by

$$\int_0^1 |\psi(\tilde{x})|^2 d\tilde{x} = 1 \quad (12)$$

In discussing the HUR we need to calculate the Uncertainty of momentum and position. This is given by

$$\Delta A = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}. \quad (13)$$

In the case of stationary states we have $\langle p \rangle = 0$. With the average given by

$$\langle A \rangle = \int_0^1 A |\psi(A)|^2 d\tilde{x} \quad (14)$$

Figures

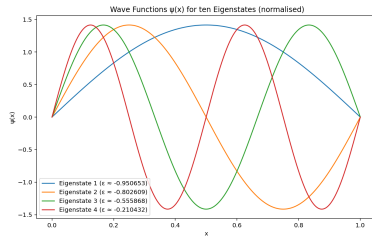


Figure 8: Plot of First 4 wavefunctions for Infinite Square well.

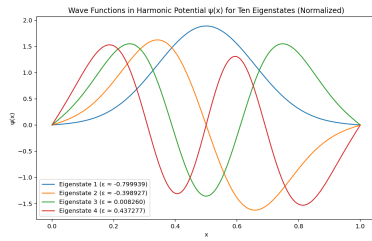


Figure 9: Plot of First 4 wavefunctions for Harmonic Potential.