Linear Boundary Values Problems

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5th of April / 2025

1 Introduction

This project aims to solve the time-independent Schrödinger equation (TISE) in one dimension, one of the most well-known eigenvalue problems in quantum mechanics. Various cases of this problem are considered, such as the harmonic oscillator and the infinite potential well. The Numerov algorithm is used to integrate the second-order differential equation, and the shooting method (in addition with bracketing and bisection) is applied to determine the corresponding eigenvalues and eigenfunctions for each case. The general form of the linear second-order equation that is of interest is the following:

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

where $\psi(x)$ = eigenfunction, $V(x)$ = potential, ϵ = eigenvalue.

In the upcoming sections, I will test a sum of different cases, like the case of a dipole consisting of two charges of opposite signs placed at a certain distance using Dirichlet, Neumann and Periodic Boundary conditions. The mesh size will be limited due to the computationally intensive nature of increasing N (mesh size). To avoid confusion with the units, I will be using arbitrary units (a.u.) and thus the TISE is re-written as:

$$-\frac{1}{2}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = \varepsilon\psi(x) \tag{2}$$

2 Multiple cases of different potentials

2.1 Particle in infinite square potential well

The aim is to determine the stationary states of the infinite square potential well. Given its infinite depth, it is necessary that the appropriate boundary conditions must be applied to ensure that the wavefunctions vanish at the edges. Specifically:

$$\psi(x = -\frac{L}{2}) = \psi(x = \frac{L}{2}) = 0 \tag{3}$$

or

$$\psi[0] = \psi[N] = 0 \tag{4}$$

The applied potential in this case, will be:

$$V(x) = \begin{cases} 0, & -0.5 \leq x \leq 0.5 \\ inf, & \text{otherwise} \end{cases}$$

For obvious reasons, infinite potential values can cause numerical instability in computations, a very small but finite value, 10^{-6}, is used instead.

Using the process described in Introduction, the four lowest energy eigenvalues found:

ϵ_n	**Value**
ϵ_1	4.9348
ϵ_2	19.7393
ϵ_3	44.4133
ϵ_4	78.9570

Table 1: The four lowest energy eigenvalues in an infinite well.

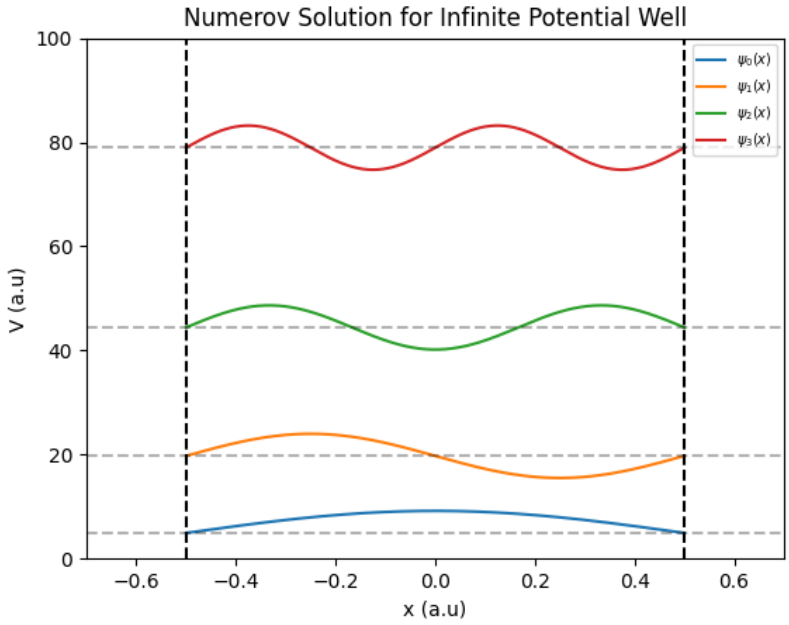

Figure 1: The four eigenfunctions, corresponding to the four lowest energy eigenvalues.

The eigenfunctions are multiplied by a coefficient, $c = 3$, to make them more visible. This scaling does not affect the physics of the problem, since the y-axis represents the potential, and eigenfunctions can be multiplied by a constant without changing their physical meaning.

The chosen length is $L = 1$ and mesh size $N = 1000$. The actul eigenvalues and eigenfunctions for this problem are given by (for $m = h = 1$):

$$\varepsilon_n = \frac{n^2}{2L^2}\pi^2 \tag{5}$$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \tag{6}$$

As clearly shown in the plots of the eigenfunctions above, and considering the boundary conditions, the eigenfunctions are zero outside the boundaries, which aligns with our physical intuition. Furthermore, the eigenvalues calculated numerically, agree with the analytical results (eq. 5 for $L = 1$).

2.2 Particle in finite square potential well

This case is similar to the infinite square potential well. The main difference now is the potential outside of the edges (outside of $x = -\frac{L}{2}$ and $x = \frac{L}{2}$) which is finite. Specifically, the potential outside is no longer infinite; instead, we assign it a constant value. I chose $V = 10$ and $L = 2$, and so:

$$V(x) = \begin{cases} 10, & -1 \leq x \leq 1 \\ 0, & \text{otherwise} \end{cases}$$

Following the process used on the subsection 2.1, I found the following eigenvalues:

ϵ_n	**Value**
ϵ_0	0.8192
ϵ_1	3.2252
ϵ_2	6.9731

Table 2: The three lowest energy eigenvalues in a finite well.

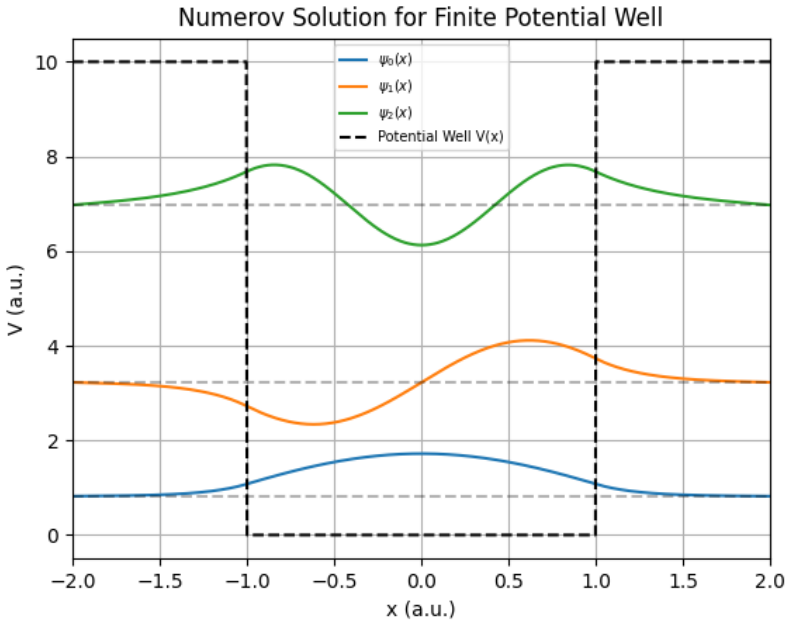

Figure 2: The three eigenfunctions, corresponding to the three lowest energy eigenvalues.

The results are satisfactory! Compared to the case of the infinite square well, the eigenfunctions here extend to the classically forbidden regions, where they fall off exponentially. This behavior agrees with the analytical solution and our theory of Quantum Mechanics.

2.3 Simplified and qualitative model of covalent bonding (Double Well)

This is another famous and well-studied case in Physics. The double finite potential well mimics the effective potential experienced by an electron in a diatomic molecule, such as the H_2 molecule ("mimics" because the actual potential is slightly different, closer to the second case we saw in class). The aim here is, following the same logic of the finite well with a few tweaks, to solve the particle in a finite square well problem to qualitatively model the bonding in the single ionized Hydrogen molecule.

As specified in the exercise, the distance between the two centers is $d = 2.26$ Bohr radii, and the ground state should have an energy of -0.5 Hartree. With these values, the depth of each well turns out to be approximately 0.87. For this depth, the eigenvalues and eigenfunctions we obtain are:

$$V(x) = \begin{cases} 0.87, & -2.13 \leq x \leq 0.13 \cup 0.13 \leq x \leq 2.13 \\ 0, & \text{otherwise} \end{cases}$$

ϵ_n	**Value**
ϵ_0	-0.6581
ϵ_1	-0.3211

Table 3: The first two eigenvalues of a double finite potential well.

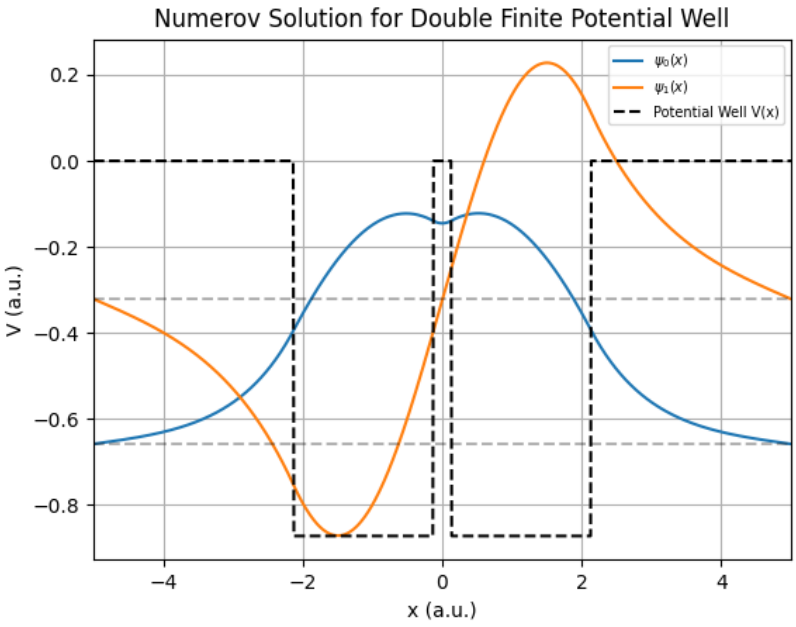

Figure 3: The two eigenfunctions of the double finite potential well.

Once again, the eigenfunctions extend into the classically forbidden regions, where they fall off exponentially, as expected, since this is similar to the case of a finite well. What would be interesting to examine here is how the total energy of the system depends on the distance between the two wells.

As the distance increases from $d = 2.26$ Bohr radii to $d = 5$, I numerically found that both the ground state and first excited state energies approach -0.5, which is close to the expected value for a single finite well.

Specifically:

ϵ_n	**Value**
ϵ_0	-0.5014
ϵ_1	-0.4784

Table 4: The first two eigenvalues for 5 Bohr radii.

These results support the theory we know so far. As the distance between the two potential wells increases, the potential barrier grows, making tunneling more difficult. The wave function becomes increasingly localized in each well, and the system can be approximated as two separate wells with distinct energy levels, as their interaction weakens.

2.4 The Quantum Harmonic Oscillator

Another well-known case, typically covered in every course related to quantum mechanics.

ϵ_n	**Value**
ϵ_0	0.5000
ϵ_1	1.4999
ϵ_2	2.4997
ϵ_3	3.4995
ϵ_4	4.5005

Table 5: The five lowest eigenvalues of the quantum harmonic oscillator.

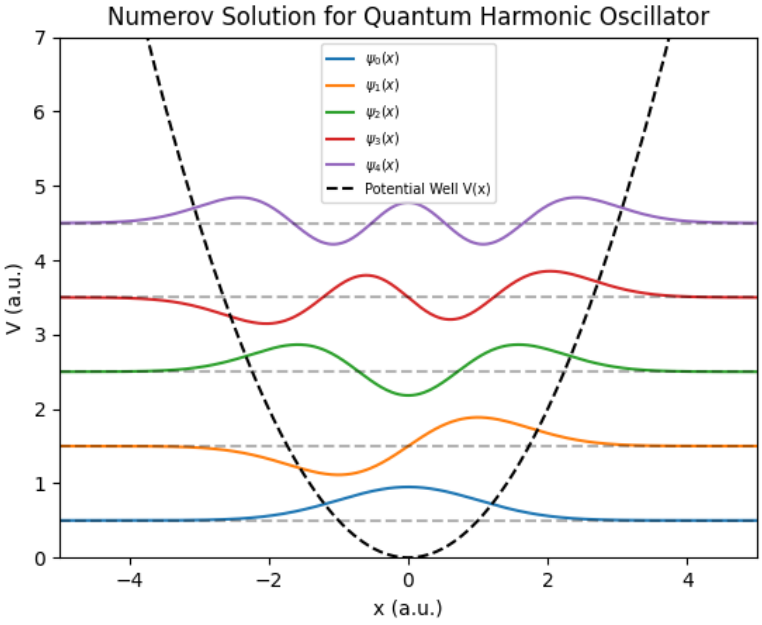

Figure 4: The (first 5) eigenfunctions of the Harmonic oscillator.

The eigenvalues should be the same as those obtained by analytically solving the equation:

$$\epsilon_n = n + \frac{1}{2} \tag{7}$$

And indeed, the numerical results match the values we would obtain analytically!

2.5 The radial Schrodinger equation

Let's step away from the typical Schrödinger equation in Cartesian coordinates and instead focus on solving the radial Schrödinger equation. Our goal is to integrate the one-electron radial Schrödinger equation:

$$-u''(r) + \left(\frac{l(l+1)}{r^2} - \frac{2Z}{r} \right) u(r) = \varepsilon u(r) \tag{8}$$

with the following boundary conditions:

$$u(0) = u(\infty) = 0$$

Before solving this problem numerically, two issues must be addressed:

- The point $r = 0$ cannot be explicitly included in our calculations because the central potential becomes infinite at this location.
- Forward integration is unstable in this scenario.

To overcome these challenges, backward integration must be used, terminating at a very small value(I used 10^{-6}). Additionally, an approximation near the origin is required to satisfy the boundary condition $u(r = 0) = 0$. By expanding $u(r)$ in a Taylor series around r_0 and applying the finite difference method to compute its first derivative:

$$u(r = 0) \approx u[0] - \frac{u[1] - u[0]}{h} r_0$$

Having incorporated this changes in my code and repeating for the last time the same process as before I get the following eigenvalues:

ϵ_n	**Value**
ϵ_0	-1.9999
ϵ_1	-0.5000
ϵ_3	-0.2222
ϵ_4	-0.1222

Table 6: The three lowest energy eigenvalues in a finite well.

And plotting their corresponding eigenfunctions:

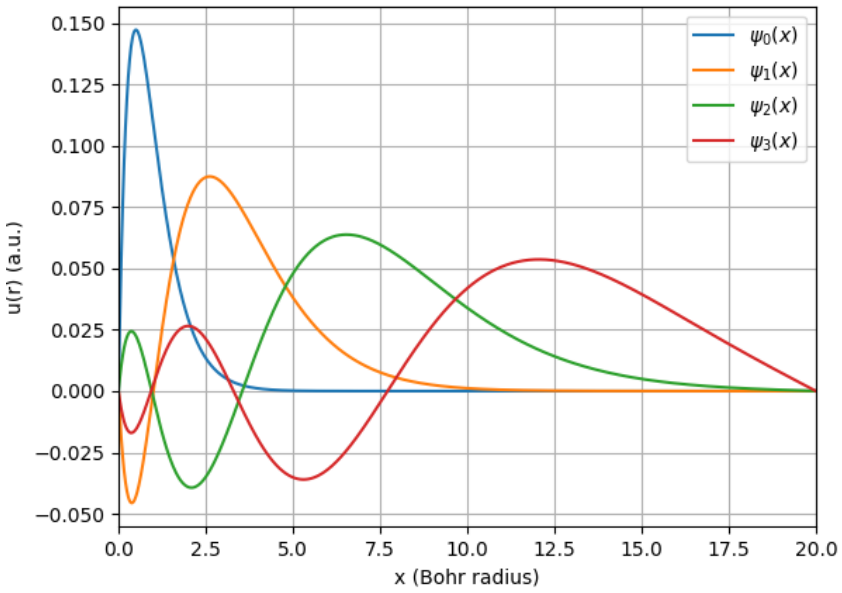

Figure 5: Eigenfunctions corresponding to the three lowest eigenvalues of Eq. 8.

The eigenvalues align well with the expected theoretical values. Specifically, the eigenvalues of the first, second, and third excited states are given by $\epsilon_1 = \epsilon/4$, $\epsilon_2 = \epsilon/9$, and $\epsilon_3 = \epsilon/16$, accordingly, which is consistent with the results observed here.

2.6 Discretization of 1D Schrödinger equation

To solve the problems mentioned above, the Numerov algorithm was used. This time, to try something different, the 1D Schrödinger equation was solved by discretizing it, basically turning the continuous equation into something that can be solved computationally.

The idea is simple: we start with eq. 2 and then break up the continuous space (x) into discrete points. Specifically:

$$x_i = ih \tag{9}$$

Then using an approximation for the derivative:

$$\frac{d^2}{dx^2} y_i \approx \frac{y_{i-1} - 2y_i + y_{i+1}}{h^2} \tag{10}$$

Ultimately, this leads to the usual matrix equation:

$$H\vec{\psi} = E\vec{\psi} \tag{11}$$

In this equation, H is our tri-diagonal matrix, so eq. 11 becomes an eigenvalue problem. By solving it using scipy.sparse.linalg.eigsh() from the SciPy library, I was able to compute the first 3 eigenvalues for the finite well and the first 5 for the harmonic oscillator. The results are as follows:

E	Numerov	Discretization	Percentage Error %
ε_0	0.8192	0.8185	0.085
ε_1	3.2252	3.2170	0.254
ε_2	6.9731	6.9530	0.289

Table 7: Comparison between Numerov and Discretization methods (Finite Well)

E	Numerov	Discretization	Percentage Error %
ε_0	0.5000	0.5000	0.000
ε_1	1.5000	1.4999	0.006
ε_2	2.5000	2.4997	0.012
ε_3	3.4999	3.4995	0.011
ε_4	4.4999	4.5005	0.013

Table 8: Comparison between Numerov and Discretization methods (Harmonic Oscillator)

As it can be seen, the percentage error is less than 1 %, meaning both methods provide high accuracy. At least for 1D problems, where things are relatively simple, it does not matter that much which method you use. However, I am certain that for higher-dimensional problems, the SciPy library (sparse) will be more efficient.