AA 2021/2022 Computational Methods
Lesson 12 - Schrödinger Equation

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Particle in an Infinite Square Well

Suppose that we want to solve the Schrödinger equation

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

for a particle in the following potential:

$$V(x) \;=\; \begin{cases} +\infty, & |x| > L \\ 0, & -L \leq x \leq L \end{cases} \tag{2}$$

so that the wave function $\psi(x)$ exists only inside $[-L, L]$ interval and equals zero anywhere else. Therefore, the solution of the Schrödinger equation (1) should satisfy the boundary conditions $\psi(\pm L) = 0$. Because of the symmetry of the potential, we can define two different classes of solutions, with even and odd parity. The even solutions, for which $\psi(-x) = \psi(x)$, are given by:

$$\psi_k(x) = A cos(\pi k x/2L), \;\; k = 2n - 1, n \in \mathbb{N} \tag{3}$$

The odd solutions, for which $\psi(-x) = -\psi(x)$, are given by:

$$\psi_k(x) = A sin(\pi k x/2L), \;\; k = 2n, n \in \mathbb{N} \tag{4}$$

The energy levels are defined by:

$$E_k = \frac{\hbar^2 \pi^2 k^2}{8mL^2} \tag{5}$$

Shooting Method

As in the case of harmonic oscillator, we can decompose the Schrödinger equation (1) into two coupled 1st order equations

$$\begin{cases} \frac{d}{dx}\psi(x) = \psi'(x) \\ \frac{d}{dx}\psi'(x) = -\frac{2mE}{\hbar^2}\psi(x) \end{cases} \tag{6}$$

and integrate them through the Euler-Cromer method, by introducing the space discretization Δx:

$$\begin{cases} \psi'(x + \Delta x) = \psi'(x) - \frac{2mE}{\hbar^2}\psi(x)\Delta x \\ \psi(x + \Delta x) = \psi(x) + \psi'(x + \Delta x)\Delta x \end{cases} \tag{7}$$

Hint. Since we know the solutions should be even or odd, it is sufficient to solve numerically inside the interval $[0, L]$. If required, the solution on $[-L, 0]$ can then be recovered using the evenness or oddness property.

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If we are 'shooting' the even solution, our initial conditions for the scheme (7) are:

$$\psi(0) = 1, \quad \psi'(0) = 0, \tag{8}$$

while we are choosing the odd solution by setting:

$$\psi(0) = 0, \quad \psi'(0) = 1. \tag{9}$$

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1. Implement the shooting method based on the pseudocode below. For simplicity, set $\hbar = m = 1$.

Algorithm 1 Shooting method for 1D Schrödinger equation

1: Define $L = 1$ and $dx = 0.001$. Discretize your interval $[0, L]$ with a step dx.
2: Set the starting energy $E = 0.1$, the energy increment $dE = 0.1$, and the tolerance $tol = 10^{-5}$.
3: Choose even initial conditions (8).
4: **The first 'shoot'**: Use the Euler-Cromer integration scheme (7) to evolve the solution from $x = 0$ to $x = L$. We suggest you writing a separate function `EulerCromer` for that. It should return the full solution $\psi(x)$ as a vector.
5: `psi_old` $= \psi(L)$ ▷ we will need this value later
6: **while** $|dE| \geq tol$ **do**
7:     $E = E + dE$
8:     **'shoot'**: Use the Euler-Cromer integration scheme (7) to evolve the solution from 0 to L.
9:     `psi_new` $= \psi(L)$
10:    **if** `psi_old` $\cdot$ `psi_new` < 0 **then**   ▷ check the change of the sign
11:        $dE = -0.1 \cdot dE$ ▷ recall the bisection method
12:    **end if**
13:    `psi_old` = `psi_new`
14: **end while**

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2. Run your code. As a result, you should obtain the wave function and the energy for the ground state ($k = 1$) of a particle in an infinite square well. Compare your E to the analytical value given by (5). Plot your wave function $\psi(x)$ and the analytical solution (3) on one plot. Have you managed to converge to the correct solution?

3. Now try to obtain the solutions by shooting method for $k = 2, 3, 4$. Keep in mind that for different k you will have different parities, so that you have to choose the proper initial conditions. Do your values of E_k correctly reproduce the energetic spectrum?

4. Continue your wave functions from 3) to the whole $[-L, L]$ interval and plot them. Determine the number of nodes (i.e. points where $\psi(x) = 0$) they have. Is the number of nodes correctly reproduced in each case?

5. The wave functions you have calculated are not yet normalized. Choose your favorite numerical integration method from the Lesson 4 and use it to make your wave function for the ground state normalized. Now also normalize the analytical wave function (by paper and pen). Plot together the numerical and analytical wave function (now both normalized) to compare the results.