Numerical solutions of Schrödinger's equation applied to atomic physics

Lucas Madeira [1]

Lecture 1
School on Light and Cold Atoms

IFSC UNIVERSITY OF SÃO PAULO
São Carlos Institute of Physics

March 14, 2023

[1] madeira@ifsc.usp.br

Program

- March 14 - Lecture 1 - The shooting method (1/2)
  - Strategy
  - Units
  - Numerical differentiation and integration
  - Infinite square well
- March 15 - Lecture 2 - The shooting method (2/2)
  - Code development
  - Q&A
- March 16 - Lecture 3 - Low-energy scattering (1/2)
  - Phase shifts
  - Scattering length
  - Spherical well
- March 17 - Lecture 4 - Low-energy scattering (2/2)
  - Code development
  - Q&A

Frequently asked questions

- Which programming language should I use?
- Can I attend the lectures without developing my own code?
- Are you going to grade the projects?
- Which software should I use to plot the figures?
- Can I discuss the programs with other students?

Homework

- Setup an environment to write, compile, and run your codes

Reference

- Computational Physics, N. J. Giordano and H. Nakanishi (second edition, Pearson, 2006)
- Chapter 10 - Quantum Mechanics
  - 10.1 - “Time-independent Schrödinger equation: some preliminaries”
  - 10.2 - “One dimension: shooting and matching methods”

Time-independent one-dimensional Schrödinger's equation

- Only a few problems can be solved analytically in quantum mechanics
  - Harmonic oscillator, particle in a box, hydrogen atom, ...
- Important role of perturbative and numerical methods
- This lecture: time-independent solutions for one particle in 1D
- Schrödinger's equation:

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

- Strategy: grid covering the region where we want the solution
- Discretization: $x_i = i\Delta x$, with integer i
- Objective: to determine ψ_i on the lattice points

Units

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

- Example: typical electron quantities - SI
  - $\hbar \sim 10^{-34}$ Js
  - Electron mass $\sim 10^{-30}$ kg
  - $E, V(x) \sim 1$ eV $\sim 10^{-19}$ J
  - $x \sim \AA = 10^{-10}$ m
- We do not want to work with such small numbers
- "$\hbar = m = 1$":

$$-\frac{1}{2}\frac{d^2\bar{\psi}(\bar{x})}{d\bar{x}^2} + \bar{V}(\bar{x})\bar{\psi}(\bar{x}) = \bar{E}\bar{\psi}(\bar{x})$$

- After the simulation is done, we want to recover the desired units

Units

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

- Let us choose a length scale ℓ
  - $\bar{x} = x/\ell$
- ψ has units! In 1D:

$$\int_{-\infty}^{+\infty} dx\, |\psi(x)|^2 = 1$$

- ψ has units of [length]$^{-1/2}$
  - $\bar{\psi}(\bar{x}) = \psi(x)/\ell^{-1/2}$

Units

- The second derivative: $\frac{d^2}{dx^2} = \frac{1}{\ell^2}\frac{d^2}{d\bar{x}^2}$
- Schrödinger's equation:

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

- $\epsilon = \frac{\hbar^2}{m\ell^2}$ has energy units
- $\bar{V} = V/\epsilon$ and $\bar{E} = E/\epsilon$

$$\boxed{-\frac{1}{2}\frac{d^2\bar{\psi}(\bar{x})}{d\bar{x}^2} + \bar{V}(\bar{x})\bar{\psi}(\bar{x}) = \bar{E}\bar{\psi}(\bar{x})}$$

- The exact same equation as "$\hbar = m = 1$", but now we know how to recover the units:
    - $\bar{x} = x/\ell$
    - $\bar{\psi}(\bar{x}) = \psi(x)/\ell^{-1/2}$
    - $\bar{E} = E/\epsilon = m\ell^2 E/\hbar^2$

Infinite square well

- Our goal is to obtain the eigenstates and eigenvalues numerically
- First, let us obtain the analytical solution

$$V(x) = \begin{cases} 0, & \text{if } -L \leqslant x \leqslant L, \\ \infty, & \text{otherwise.} \end{cases}$$

- If $x \geqslant L$ or $x \leqslant -L$: the wave function vanishes
- In the region $-L \leqslant x \leqslant L$ we want to solve:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

- We define $k \equiv \sqrt{2mE/\hbar^2}$

$$\psi'' = -k^2\psi \qquad \rightarrow \qquad \psi(x) = A\sin(kx) + B\cos(kx)$$

Infinite square well

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

- Boundary conditions: $\psi(L) = \psi(-L) = 0$

$$\begin{aligned} \psi(L) &= A\sin(kL) + B\cos(kL) = 0 \\ \psi(-L) &= A\sin(-kL) + B\cos(-kL) = -A\sin(kL) + B\cos(kL) = 0 \end{aligned}$$

- Taking the sum of the equations: $2B\cos(kL) = 0$

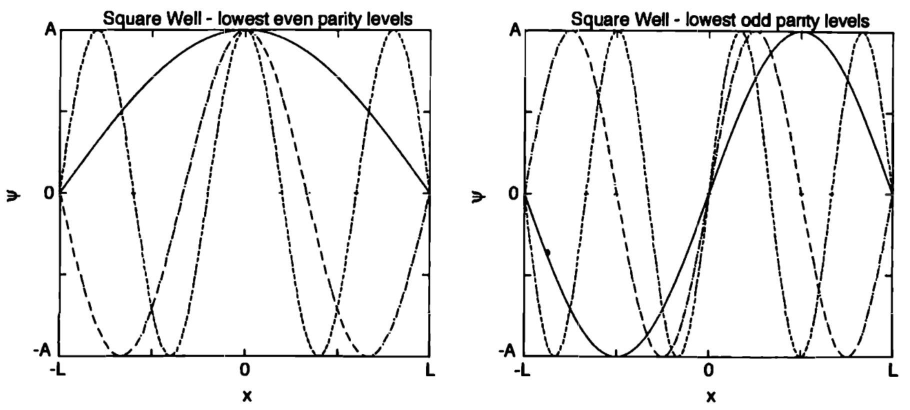
- Case (i): $B = 0$, $A \neq 0$ for a non-trivial solution

$$\sin(k_- L) = 0 \;\rightarrow\; k_- = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \cdots \;\rightarrow\; k_- = \frac{n\pi}{L} \text{ with } n = 1, 2, 3, \cdots$$

- Case (ii): $A = 0$ and $\cos(k_+ L) = 0$:

$$\cos(k_+ L) = 0 \rightarrow k_+ = \frac{\pi}{2L}, \frac{3\pi}{2L}, \frac{5\pi}{2L}, \cdots \rightarrow k_+ = \frac{(2n-1)\pi}{2L} \text{with } n = 1, 2, 3, \cdots$$

Infinite square well



Infinite square well

- The eigenenergies are:

$$E_- = \frac{\hbar^2}{2mL^2}(n\pi)^2 \qquad \text{and} \qquad E_+ = \frac{\hbar^2}{8mL^2}((2n-1)\pi)^2.$$

- Dimensionless quantities:
  - $\bar{x} = x/L \rightarrow$ the well is located at $-1 \leqslant \bar{x} \leqslant 1$
  - $\bar{E} = EmL^2/\hbar^2$

$$\bar{E}_- = \frac{(n\pi)^2}{2} \qquad \text{and} \qquad \bar{E}_+ = \frac{((2n-1)\pi)^2}{8}$$

- Parity: the $\cos(kx)$ solutions are even [$\cos(-kx) = \cos(kx)$], while the $\sin(kx)$ solutions are odd [$\sin(-kx) = -\sin(kx)$]
- How to solve this problem numerically?

Numerical derivative

- Taylor series:
$$f(x+h) = f(x) + hf'(x) + \frac{h^2}{2} f''(x) + \frac{h^3}{6} f'''(x) + \cdots$$
- Numerical derivative:
$$f'(x) \approx \frac{f(x+h) - f(x)}{h}$$
- Taylor series:
$$f(x-h) = f(x) - hf'(x) + \frac{h^2}{2} f''(x) - \frac{h^3}{6} f'''(x) + \cdots$$
- Numerical derivative:
$$f'(x) \approx \frac{f(x) - f(x-h)}{h}$$

Numerical derivative

- Taylor series:

$$f(x+h) = f(x) + hf'(x) + \frac{h^2}{2}f''(x) + \frac{h^3}{6}f'''(x) + \cdots$$

$$f(x-h) = f(x) - hf'(x) + \frac{h^2}{2}f''(x) - \frac{h^3}{6}f'''(x) + \cdots$$

- Their difference:

$$f(x+h) - f(x-h) = 2hf'(x) + \frac{h^3}{3}f'''(x) + \cdots$$

$$\boxed{f'(x) \approx \frac{f(x+h) - f(x-h)}{2h}}$$

Second numerical derivative

- Taylor series:

$$f(x+h) = f(x) + hf'(x) + \frac{h^2}{2}f''(x) + \frac{h^3}{6}f'''(x) + \cdots$$

$$f(x-h) = f(x) - hf'(x) + \frac{h^2}{2}f''(x) - \frac{h^3}{6}f'''(x) + \cdots$$

- Their sum:

$$f(x+h) + f(x-h) = 2f(x) + h^2 f''(x) + \cdots$$

$$\boxed{f''(x) \approx \frac{f(x+h) - 2f(x) + f(x-h)}{h^2}}$$

Time-independent one-dimensional Schrödinger's equation

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

- Discretization:

$$-\frac{\hbar^2}{2m}\left[\frac{\psi_{i+1} - 2\psi_i + \psi_{i-1}}{(\Delta x)^2}\right] + V(x_i)\psi_i = E\psi_i$$

- Rearranging:

$$\boxed{\psi_{i+1} = 2\psi_i - \psi_{i-1} - \frac{2m(\Delta x)^2}{\hbar^2}\left[E - V(x_i)\right]\psi_i}$$

- If we know two consecutive values of the wave function (ψ_i and ψ_{i-1}), then we can compute the next (ψ_{i+1})
- We can also move in the other direction

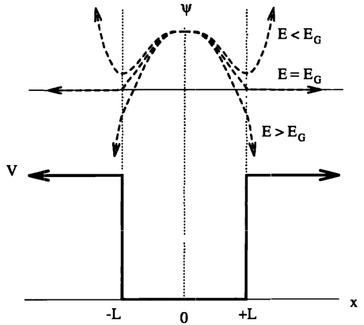
Parity

- We need two consecutive values of the wave function to start our algorithm
- We will deal with the normalization afterwards
- Parity
- Even: $\cos(-kx) = \cos(kx)$
  - $\psi(0) =$[constant] and $\psi'(0) = 0$
  - We can take: $\psi_0 = 1$ and $\psi_1 = 1$
- Odd: $\sin(-kx) = -\sin(kx)$
  - $\psi(0) = 0$ and $\psi'(0) =$[constant]
  - We can take: $\psi_0 = 0$ and $\psi_1 = \Delta x$

The shooting method

$$\boxed{\psi_{i+1} = 2\psi_i - \psi_{i-1} - \frac{2m(\Delta x)^2}{\hbar^2}\left[E - V(x_i)\right]\psi_i}$$

- We need some value E to use our algorithm
- But we want to determine E!
- *Shooting* method: shoot a cannon to hit a specific target
- We start with a guess for E
- We look at the solutions for $x < -L$ and $x > L$
- We want a solution such that: $\psi(x < -L) = \psi(x > L) = 0$

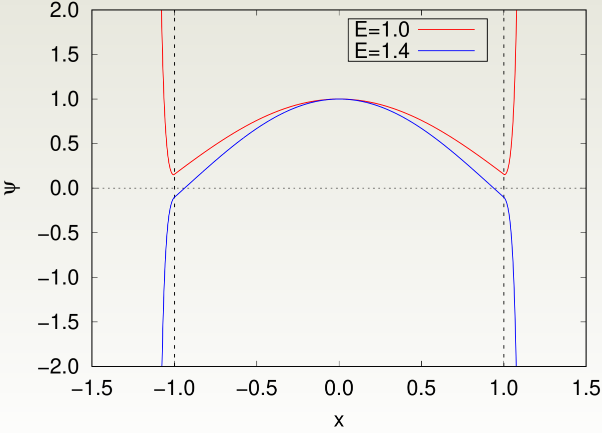


Shooting method

- Input: number of points N or their spacing Δx; initial guess for E; energy increment ΔE
- Set ψ_0 and ψ_1 according to the desired parity
- Initialize `last_div`
- Main loop
  - Use E, ψ_0, and ψ_1 to compute all $\{\psi_i\}$
  - $\psi_{i+1} = 2\psi_i - \psi_{i-1} - 2(\Delta x)^2 \left[E - V(x_i)\right] \psi_i$
  - Is ψ diverging to $+\infty$ or $-\infty$? Compare with the sign of `last_div`
    - If they have opposite signs, then $\Delta E = -\Delta E/2$
  - Update the energy guess: $E = E + \Delta E$
  - Update the value of `last_div` with $+$ or $-$
  - If ΔE is small enough, then E is acceptable and you found the desired solution. Exit the loop.
  - Repeat the process.

The shooting method

- $E_G = \pi^2/8 \approx 1.234$
- $V(x)$ for $x > L$ or $x < -L$: I used $V = 1000$ so we can see the effect in the figure

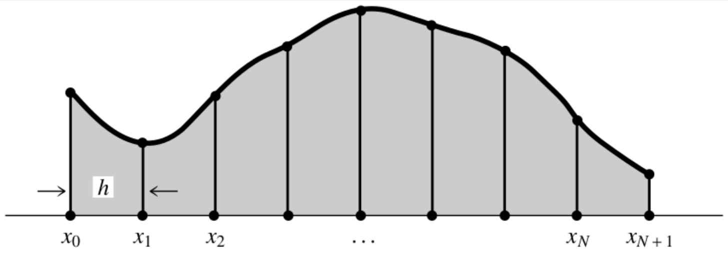


Numerical integration

- We have the desired solution, but it still needs to be normalized according to:

$$\int_{-\infty}^{\infty} dx \, |\psi(x)|^2 = 1$$

- The $f(x_i) \equiv f_i$ are known



Numerical integration

- Trapezoidal rule:

$$\int_{x_1}^{x_2} f(x)dx = h\left[\frac{1}{2}f_1 + \frac{1}{2}f_2\right] + \mathcal{O}(h^3 f'')$$

- Applying it $N-1$ times, for the intervals: $(x_1, x_2), (x_2, x_3), \cdots, (x_{N-1}, x_N)$

$$\int_{x_1}^{x_N} f(x)dx = h\left[\frac{1}{2}f_1 + f_2 + f_3 + \cdots + f_{N-1} + \frac{1}{2}f_N\right] + \mathcal{O}\left(\frac{(x_N - x_1)^3 f''}{N^2}\right)$$

Numerical integration

- Quadratic interpolation between the points
- Simpson's rule:

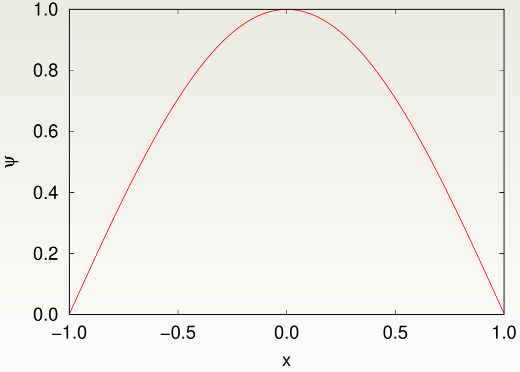
$$\int_{x_1}^{x_3} f(x)dx = h\left[\frac{1}{3}f_1 + \frac{4}{3}f_2 + \frac{1}{3}f_3\right] + \mathcal{O}\left(h^5 f^{(4)}\right)$$

- Using it repeatedly:

$$\int_{x_1}^{x_N} f(x)dx = h\left[\frac{1}{3}f_1 + \frac{4}{3}f_2 + \frac{2}{3}f_3 + \frac{4}{3}f_4 + \cdots + \frac{2}{3}f_{N-2} + \frac{4}{3}f_{N-1} + \frac{1}{3}f_N\right]$$
$$+ \mathcal{O}\left(\frac{(x_N - x_1)^5 f^{(4)}}{N^4}\right)$$

The shooting method

- $\Delta x = 10^{-3}$; tolerance for ΔE of 10^{-3}
- $V(x)$ for $x > L$ or $x < -L$: I used $V = 10^6$
- $E_G = \pi^2/8 \approx 1.234$; I obtained E =1.231
- Normalized ground state (be careful: do not forget to throw away ψ outside the well!)



Project

Using the shooting method, write a program that finds the solutions to Schrödinger's equation for the infinite square well. Your program should receive as input the parity of the desired solution.

- Find the ground state energy and wave function.
  - Investigate the precision of the result by varying the parameters of your program.
  - Let $\psi_{\rm A}$ be the analytical and $\psi_{\rm Num}$ be the numerical solution. Plot $|\psi_{\rm Num} - \psi_{\rm A}| \times x$. Do they agree?
- Find the first four eigenenergies and compare them with the analytical results. What is the relative error?

Extra

1) Pick your favorite quantum mechanics textbook and compare the analytical solutions for the infinite and finite square well potentials. What changes would you make to consider this other potential in your code?
2) What are examples of other potentials that can be solved with this method? How about some potentials that *cannot*? Why?