Eigenfunctions in Quantum Mechanics

We solve the stationary Schrödinger equation in one-space dimension

Objectives

To study slightly more complicated eigenfunction problems than the ones coming from solving the heat equation.

Introduction

The stationary Schrödinger equation for a particle moving in one space dimension is

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

where $\psi(x)$ is the probability density of finding the particle at the position x, V is the potential function that creates the force felt by the particle, $\hbar$ is the Planck constant divided by 2π, m is the particle mass, and E is the energy of particle.

The equation above is part of an **eigenfunction problem**, where $\hbar$, m and $V(x)$ are given, and one looks for the **eigenfunctions** ψ and the **eigenvalues** E. We said that the equation above is *part of* an eigenfunction problem, because to have an eigenfunction problem we still need to provide boundary conditions. These boundary conditions depend, among other things, on the particular type of the potential function V. We study two cases:

- A free particle in a one-dimensional **infinite well** of size $a > 0$. In this case the potential is

  $$V(x) = \begin{cases} \infty & \text{for} \quad x \leqslant 0, \\ 0 & \text{for} \quad 0 < x < a, \\ \infty & \text{for} \quad x \geqslant a, \end{cases}$$

  In this case the eigenfunction problem is similar to the eigenfunction problem in the heat equation.

- A free particle in a **semi-infinite well** of size $a > 0$. In this case the potential is

  $$V(x) = \begin{cases} \infty & \text{for} \quad x \leqslant 0, \\ -V_0 & \text{for} \quad 0 < x < a, \\ 0 & \text{for} \quad x \geqslant a, \end{cases}$$

  where V_0 is a positive constant. In this case the eigenfunction problem is quite different from the eigenfunction problem in the heat equation.

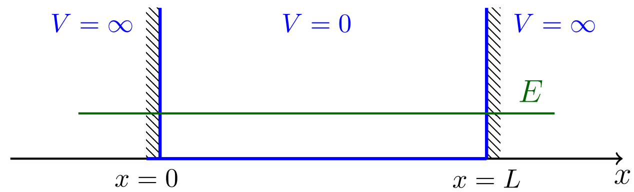
Particle in an Infinite Well

A one dimensional infinite square well is a system where one quantum particle, for example an electron, can move freely inside a finite region, but it can never leave that region. Such a system is described by the eigenfunctions, ψ, and eigenvalues, E, of the Schrödinger equation (1). The potential vanishes inside the box, which means that the particle can move freely inside the box. The potential becomes infinite at the border of the box, which means that particle can never leave the box. This also means that the particle wave function must vanish at the border of the box.

We put all these conditions together into the following boundary value problem.

$$-\frac{\hbar^2}{2m}\,\psi''(x) = E\,\psi(x),$$

$$\psi(0) = 0, \qquad \psi(L) = 0.$$



Question 1:

(1a) *(20 points)* Find all the eigenvalues and eigenfunctions in the problem above.

The Graph of the Eigenfunctions of the Infinite Well

The answer to Question 1 is that the energy E of the quantum particle cannot be any real number. Instead, the energy must be one of the (discrete) allowed values. People say that the energy of the particle is quantized. A quantum particle cannot have an arbitrary velocity inside the box, instead it must have a velocity compatible with one of the allowed energies. This behavior of the quantum particle is in direct opposition with our intuition, which is based on the behavior of classical particles. A classical particle can move inside a box with any velocity, that is, it can have any energy. This is not the case for a quantum particle.

In the interactive graph below we consider the case $a = 3$, $c_2 = 4$, and we plot the function

$$y_\alpha(x) = 4\sin\Big(\frac{\alpha\pi x}{3}\Big)$$

for $\alpha \in [0, 20]$. The inside of the box is shaded in green, the outside in red.

Eigenfunctions for the Infinite Well

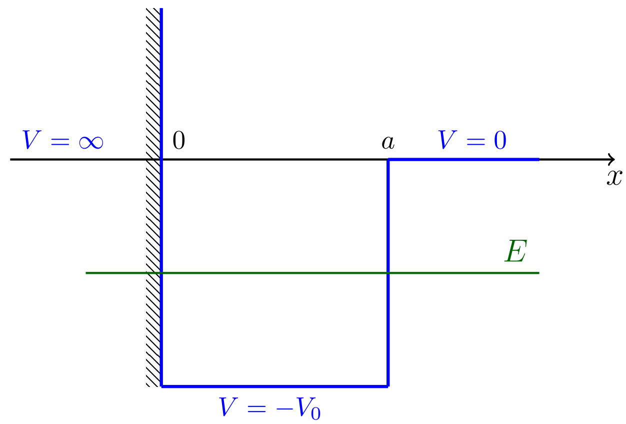
(1b) *(10 points)* In the interactive graph above vary the parameter α and use the graph of the function y_α to re-obtain the eigenvalues and eigenfunctions found in part **(1a)**.

Particle in a Semi-Infinite Well

We now describe the behavior of a quantum particle inside a box that has an infinite wall on one side but only a finite wall on the other. The quantum particle is again described by the eigenvalues and eigenfunctions of the Schrödinger equation (1).

In this case we choose the potential function $V(x)$ as follows

$$V(x) = \begin{cases} \infty & \text{for} \quad x \leqslant 0, \\ -V_0 & \text{for} \quad 0 < x < a, \\ 0 & \text{for} \quad x \geqslant a. \end{cases}$$



Potential functions $V(x)$ that differ by a constant describe the same physics. In this case we chose the potential so that inside the box it takes a negative value, $V(x) = -V_0$, for $0 < x < a$, instead of zero. The solution formulas for the eigenfunctions look a bit nicer with this choice of the additive constant in the potential function.

We want to study particles mostly confined inside this box $0 < x < a$. That's why we consider only the case where the particle energy is $E \leqslant 0$, equivalently $E = -|E|$. The boundary value problem satisfied by the quantum particle in this potential is

$$-\frac{\hbar^2}{2m}\,\psi''(x) + V(x)\,\psi(x) = E\,\psi(x), \quad E < 0,$$

$$\psi(0) = 0, \quad \lim_{x\to\infty} \psi(x) = 0.$$

The formula for the solution ψ in the region $0 < x < a$ is different form the formula in the region $x > a$. So it is convenient to split ψ and the whole problem into two regions, $0 < x < a$ and $x > a$. One finds the general solution ψ on each region and then imposes the boundary conditions on each region. The final step is to match the two solutions at $x = a$. The matching conditions are

$$\psi_{0<x<a}(a) = \psi_{x>0}(a), \qquad \psi'_{0<x<a}(a) = \psi'_{x>0}(a).$$

It is from these matching conditions that the energy of the quantum particle E gets quantized. We now solve this eigenfunction problem, splitting the calculation in several parts.

Question 2:

(2a) *(20 points)* Split the solution function ψ as follows,

$$\psi(x) = \begin{cases} \psi_1(x) & \text{for} \quad 0 \leqslant x \leqslant a, \\ \psi_2(x) & \text{for} \quad \quad x \geqslant a, \end{cases}$$

Show that if you split the Schrödinger differential equation in the same way you can write it as

$$\psi_1'' = -k^2\,\psi_1, \qquad 0 \leqslant x \leqslant a,$$
$$\psi_2'' = \kappa^2\,\psi_2, \qquad\qquad x \geqslant a,$$

where k and κ are appropriate positive constants given in terms of m, $\hbar$, V_0, and $|E|$. Find the formulas for $k > 0$ and $\kappa > 0$ in terms of the mass m, Planck constant $\hbar$, potential $V_0 > 0$, and energy $|E| > 0$. Also find one the boundary condition for ψ_1 and one boundary condition for ψ_2, obtained from the boundary conditions on ψ at $x = 0$ and at $x \to \infty$.

(2b) *(20 points)* The second part of the problem is to find all the solutions, ψ_1 and ψ_2, of their respective boundary value problems. Write these functions in terms of k and κ. Recall to use the boundary conditions for ψ_1 and for ψ_2 found in the previous part.

Note: So far there should be no condition on the possible values of the energy E.

(2c) *(20 points)* In the previous part you should have found that ψ_1 is proportional to a sine function; let's call the proportionality factor c. Also in the previous part you should have found that ψ_2 is proportional to an exponential; let's call the proportionality factor d. The third part of the problem is to match the functions ψ_1 and ψ_2 found in (2b) at $x = 0$. Impose the matching conditions

$$\psi_1(a) = \psi_2(a), \qquad \psi_1'(a) = \psi_2'(a).$$

From these equations find a relation between k and κ and between the scaling factor for ψ_1, which we called it c, and the scaling factor for ψ_2, which we called it d, of the form

$$\frac{k}{\kappa} = -f(ka), \qquad d = c\, g(k, \kappa)\, e^{\kappa a},$$

Find the functions $f(ka)$ and $g(k, \kappa)$. These functions do not depend on c or d.

Note: The first equation above implies that the energy E of the system cannot take arbitrary values, instead, the energy is quantized. Indeed, from question (2c) we know that E is related to k and κ. From this relation one gets

$$k^2 + \kappa^2 = \frac{2mV_0}{\hbar^2},$$

which is a circle on the $k\kappa$-plane. The intersection of this circle with the curve given by

$$\frac{k}{\kappa} = -f(ka)$$

determines the allowed values of the energy E.

The Graph of the Eigenfunctions of the Semi-Infinite Well

In the interactive graph below we choose an arbitrary value for the potential $V_0 = 10$, the particle mass $m = 1$, and the box size $a = 3$. We then plot the function $\psi(x)$. We leave the energy $E \in [-10, 0]$ as a free parameter. As in the previous interactive graph, the inside of the box is shaded in green, the outside in red.

Eigenfunctions for the Semi-Infinite Well

Since the energy E is a real number, the function displayed in the graph is not an eigenfunction of the Schrödinger equation above. This function becomes an eigenfunction for very specific values of the energy, which then become eigenvalues. Move the slider for the energy in the interactive graph, and see if you can find the energy values for which the function becomes an eigenfunction.

(3) *(10 points)* How many eigenvalues, E, are in the range displayed in the interactive graph and what are they values?