Quantum mechanics

Schrödinger equation

Recall that in quantum mechanics, particles can be represented as probability waves. But how do we mathematically quantify these waves?

For a single 1-dimensional particle whose state is not evolving over time, the wavefunction $\psi(x)$, the square of which gives the probability of a particle being at some location x (see the "Probability" section for details on this), is calculated by the following second-order ODE:

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

This is the Schrödinger equation.

The constant $\hbar$ is a constant called Planck's constant, and m is the mass.

E is the energy of the particle, and V is a function which represents the distribution of potential energy in which the particle is found.

Particle in a box

How do we define a box, then? The simplest approach is to define a region where $V = 0$ inside the box, and $V = \infty$ outside the box. So inside the box, the equation simplifies to

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

If we rearrange the terms, it begins to look very similar to an equation you've seen before:

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

Boundary conditions

We know the equation we need to solve, but we need to impose certain restrictions on our result in order for it to be physically possible.

In regions where $V = \infty$, the particle cannot exist. Hence, at the edges of the box, $x = 0$ and $x = L$, we require that $\psi(0) = 0$, and $\psi(L) = 0$.

We can also set $\psi' = 1$ at the boundary.

However, as we solve the equations, we start at $x = 0$ and move to $x = L$, so cannot set $\psi(L) = 0$.

How, then, do we ensure the boundary conditions at L?

We have one more parameter to work with: E, the energy of the particle. Hence, we want to find an E so that the solution ψ we obtain has a value of $\psi(L) = 0$.

The easiest way to do this is to iterate over values of E until we find one that gives us a sufficiently good value of ψ. You can put your code for solving the Schrödinger equation in a for loop that tries different values of E; some example pseudocode is in the appendix, although there are other ways to approach this problem. (For example, you can use a while loop, instead; consult your instructor for more information on this if you wish.)

If you need help writing nested loops, (i.e. loops inside loops,) consult a counsellor or your instructor.

Higher energy levels

There are several values of E for which ψ is a valid solution; in fact, there are infinitely many. Higher values of E represent particles with more energy (i.e. particles which, on average, tend to move faster). However, these values of energy are *quantized*; only certain discrete values of E are valid, and a particle cannot have values of E between these values.

Probability

In order to get the probability of a particle being between two points x_1 and x_2, we need to integrate the wavefunction:

$$P(x_1, x_2) = \int_{x_1}^{x_2} |\psi(x)|^2 dx$$

This gives us an additional condition to impose: the probability of the particle being inside the box ($x_1 = 0, x_2 = L$) has to be equal to 1. (A probability greater than 1 would imply a more than 100% chance of the particle being in the box, which is impossible. A probability of less than 1 would imply that there's a chance of the particle not being in the box at all, which is also impossible for this scenario.)

We impose this condition as

$$\int_0^L |\psi(x)|^2 dx = 1$$

When calculating your result, you may need to scale it by some constant value in order for this condition to hold. If you're stuck on how to do this, consult your instructor or your counsellor.

Your task

Starting from the starter code, solve the Schrödinger equation for the particle in a box, and find the lowest value of E which gives a valid solution. What shape does the wavefunction have? What does this mean? Try finding higher values of E which also give valid solutions.

Think about how you'll explain this result to your peers.

Possible intermediate steps

1. Write pseudocode describe your approach to solving the problem
2. Create a loop to solve the Schrödinger equation given some energy E
3. Enclose this loop in another loop to iterate through different possible values of E until you find a valid solution
4. Scale your wavefunction with a constant factor so that $\int_0^L |\psi(x)|^2 dx = 1$
5. Plot the wavefunction $\psi(x)$, and the probability distribution $\int |\psi(x)|^2 dx$

Theoretical solution

The particle-in-a-box with $V = 0$ inside and $V = \infty$ outside has an exact solution, given by

$$\psi_n(x) = A\sin(n\pi x/L)$$
$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

where A is the scaling factor to ensure that the integral is 1. If you like, you can use this theoretical value to check your solution.

If you have time: bonus task

Solve the Schrödinger equation for a differently-shaped box; i.e. one with a nonzero V(x).

Some possibilities:

$V(x) = k$	for some constant value k
$V(x) = \frac{1}{2}mx^2$	quantum harmonic oscillator
$V(x) = x$	

Appendix

Pseudocode:

```
dE = 0.01
E_vals = np.arange(0,7,dE)
threshold = 0.1

for E in E_vals:
    [solve the equation for that value of E]
    if psi[-1] < threshold:
        print(E)
        break
```