CP Activity 6

Numerical integration of the Schrödinger equation

Hand-out: 16 October 2023 **Hand-in:** 26 October 2023

6.1 The Problem

Solve for the stationary states of an electron in a ramped infinite square well.

6.2 Introduction

A basic problem in quantum mechanics is to find the stationary states ("energy levels") of a bound system, using the time-independent Schrödinger equation (TISE)

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

You will learn several methods to do this in your lectures. However, these methods are only applicable to a relatively small number of problems that can be solved analytically. In general we will need to solve the problem numerically. In this activity, we will look at the numerical integration of the differential equation.

The problem we face here is not that of the *initial value problem* of mechanics, that we dealt with earlier. We can't just start from some initial value, use numerical integration, and end up somewhere after some time. Instead, solving the TISE is a *boundary value problem*. There is an unknown quantity (E) in the differential equation, and we need to *solve* for this, subject to constraints on the boundary conditions of the wave function.

How to go about this? How do we tell if we have a correct value for E (called an eigenvalue)? We have to look at the properties of the required solution. We find that if E is an energy eigenvalue, the wave function $\psi(x)$ has the expected behaviour at the boundaries. If we choose the wrong value for E, then the wave function will not have this property.

Let us consider a specific example. Suppose that we have an electron in a ramped infinite square well with walls at $x = 0$ and $x = a$:

$$V(x) = \begin{cases} bx & \text{for } 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

Since the potential energy is infinite outside the well, the electron cannot be beyond the well's walls. Continuity of the wave function then implies that $\psi(0) = \psi(a) = 0$, exactly as in the case of the unramped infinite square well considered in lectures. However, owing to the changing potential energy in the well, this is a more interesting problem than the one done in class.

A way of finding a solution numerically then suggests itself:

1. *Assume* a value for E.
2. Start at one of the walls (e.g. the left wall at $x = 0$), setting ψ to zero there.
3. *Integrate* numerically to the other wall.
4. If the numerical solution is close (?!) to zero there, we have a correct value for E.

5. If we don't have a correct value, choose another and *try again*.

Ideally, we would use some sort of root-finding algorithm to drive this process, but we will see that it can be done by hand.

6.3 Numerical Methods

We can do the numerical integration as we have for Newton's equation, by splitting the second order ODE into coupled first order equations. But it's just as easy to use a numerical approximation to the second derivative:

$$\frac{d^2\psi(x)}{dx^2} \approx \frac{\psi(x-\Delta x) - 2\psi(x) + \psi(x+\Delta x)}{(\Delta x)^2} \tag{6.1}$$

! Where does this approximation come from? Substitute the Taylor expansion of $\psi(x \pm \Delta x)$ into the RHS of Eq. 6.1 and see.

Note that the integration is over x, using a fixed step size Δx.

Then we obtain for the TISE:

$$\psi_{i+1} = 2\psi_i - \psi_{i-1} + (\Delta x)^2\, g(E, x_i)\, \psi_i$$

where

$$g(E, x_i) = -\frac{2m}{\hbar^2}\,(E - V(x)) = -\frac{2mc^2}{\hbar^2 c^2}\,(E - V(x))$$

for $i = 1 \ldots N-1$.

Note that, to start this off, we need two values of the wave function. One is at the left wall: $\psi_0 = 0$. What about the next, ψ_1? We can take *any* value for this. The wave function is usually taken to be normalised, but this is not a consequence of the solution, but is imposed by our interpretation of the wave function. Any multiple of $\psi(x)$ is still a solution. We can take any value for ψ_1 — this simply affects the scaling of the wave function — and normalise afterwards.

6.4 Model

Use the following: $a = 3.0$ nm, $b = 0.5$ eV nm^{-1}, $mc^2 = 5.11 \times 10^5$ eV, $\hbar c = 197.3$ eV nm, where c is the speed of light. Note that these values allow you to use "natural scale" units of eV and nm for an atom-sized problem. (And you don't have to bother with laborious conversions to SI units).

6.5 Computer Solution

Given the discussion above, we can outline an algorithm for searching for the energy levels in our problem.

1. Integrate from $x = 0$ nm to $x = a = 3.0$ nm with a step size of, say, 0.01 nm and a suitable initial value of E (perhaps close to the ground state of the infinite unramped square well of the same dimensions). For the initial values choose $\psi_0 = 0$ and ψ_1 something small, say 10^{-6}. Some experimenting might be necessary. Print out the value ψ_N of the wave function at the right wall.

```
psi = np.zeros(N+1,float)
psi[0] = 0.0        # two initial conditions
```

```
psi[1] = 1.0e-6
    # integrate
    for i in range(1,N):
        ...
```

2. You can adjust the value of E in order to home in on the eigenvalue for the ground state. Find the region where ψ_N changes sign. This indicates that an eigenvalue has been stepped over. You will probably need to read in a value of E from the keyboard. This is easy:

```
...
while 1:   # loop forever while trying new values of E
    E = input( 'Enter a value for E: ' )
    ...
    # integrate
    for i in range(1,N):
        ...
    # print out last value
```

3. Normalize and then plot out the wave function. A simple approximation for an integral is given by the trapezoidal rule

$$\int_{x_0}^{x_N} f(x)\,dx \approx \Delta x \left(\frac{f_0 + f_1}{2} + \frac{f_1 + f_2}{2} + \cdots + \frac{f_{N-1} + f_N}{2} \right)$$
$$= \Delta x \left(\sum_{i=0}^{N} f_i - f_0/2 - f_N/2 \right)$$

Can you interpret this equation? ?

Using `numpy` this can be written:

```
integral = deltax*(np.sum(f[0:N]) - (f[0]+f[N])/2.0)
```

Remember that the integrand is the *square* of the wave function.

4. Now try to find the energies of the first and second excited states. How do you know you have not missed any energy levels? How are the levels spaced? !

5. Finally, calculate the expectation values of the position and momentum of the electron in the first three states. !

6.6 Python

You might like to plot out the graph for each value of E. You can keep an array of ψ values and plot them out. But you can only use the `plt.show()` command once. In order to plot "interactively", i.e. input a value, calculate, plot, enter next value,... you must use `plt.draw()` instead. Depending on the way your computer is set up, you might need to choose a suitable plotting engine.

The following code is an example:

```
import matplotlib as mpl
import matplotlib.pyplot as plt

mpl.interactive(True)
mpl.use("TkAgg")

...
while 1:
    ...
 plt.plot(x,psi)
 plt.draw()

plt.show() # at end of program, to keep window open.
```

6.7 Report

Please submit a brief report containing your results (i.e. the energy eigenvalues of the first three states of the ramped infinite square well, the expectation values, and plots of the corresponding wave functions) and the answers to all questions in the instructions. Include also a printout of your code.

The 15 marks for the report will be allocated as follows:

- Derivation of equation 6.1 - 2 marks
- Results
  - E_1, E_2 and E_3 suitably quoted - 3 marks
  - Answer to questions regarding spacing of energy levels and missing levels - 2 marks
  - ψ_1, ψ_2 and ψ_3 suitably normalised and plotted - 3 marks
  - $\langle x \rangle_{1,2,3}$ and $\langle p \rangle_{1,2,3}$ suitably quoted - 2 marks
- Code (style, comments, efficiency ...) - 3 marks