Numerical solution of the time-independent 1-D Schrödinger equation

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1 Aim of the computational lab

- Implement a numerical solution of the one-dimensional stationary Schrödinger equation. This uses a stepping algorithm with the "shooting" method to find the energies and eigenfunctions.

- Test the code on the infinite square well, and check accuracy by comparing with the analytic solution.

- Implement code to normalise the eigenfunctions and compute the right-hand side of the Heisenberg uncertainty relation, $\Delta p \Delta x \geq \hbar/2$. Check if it is satisfied.

- Investigate how the uncertainty product $\Delta x \Delta p$ depends on the quantum number n.

- Expand your investigation to study the eigenstates of a harmonic potential bounded by infinite walls.

2 Overview

2.1 The Schrödinger Equation

The Schrödinger equation lies at the heart of quantum mechanics. In this computational project you will numerically solve for the stationary solutions of the Schrödinger equation in one spatial dimension. The time-independent form of the Schrödinger equation is

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

where $\psi(x)$ is the wavefunction, $V(x)$ the potential energy, m the particle mass, and $\hbar$ is Planck's constant divided by 2π. For simplicity the particle will be bound by infinite wells, such that the potential $V(x = 0)$ and $V(x = L)$ is infinite.

This is an eigenvalue equation; only for certain values of E there will be a solution that satisfies the boundary conditions. Moreover, any solution $\psi(x)$ multiplied by an arbitrary constant is still a solution to this equation.

In order to avoid computations with small numbers such as $\hbar$, we non-dimensionalise the equation

$$\frac{d^2\psi(\tilde{x})}{d\tilde{x}^2} + \gamma^2 \left(\epsilon - \nu(\tilde{x})\right)\psi(\tilde{x}) = 0, \tag{2}$$

where $\nu(\tilde{x}) = V(\tilde{x})/V_0$ is a dimensionless potential energy with a range of values between -1 and $+1$. This can always be achieved by taking V_0 to be the maximum deviation from zero energy. $\epsilon = E/V_0$ is a dimensionless energy, and

$$\gamma^2 = \frac{2mL^2V_0}{\hbar^2}, \tag{3}$$

where L is the physical size of the well. γ^2 is also dimensionless and depends on the mass m of the particle, the depth V_0 of the well, and the size of the well. Note that the spatial variable is also rescaled $\tilde{x} = x/L$ and goes from 0 (left side of the wall) to $+1$ (right side of the wall).

In general the wave function is complex, but the stationary solutions of the time-independent Schrödinger equation are real.

2.2 Numerical Discretization

To solve a differential equation, such as (2), on a computer we must *discretize* the spatial coordinate $\tilde{x}$. Let us suppose we have N points over the range of integration, from $\tilde{x} = 0$ to $\tilde{x} = 1$, separated by $l = 1/(N-1)$. The function $\psi(\tilde{x})$ is then replaced by a set of N values, $\psi_n = \psi(\tilde{x}_n = nl)$, corresponding to the wavefunction at each grid point. The index n here varies from 0, the left-most point of our grid, to $N-1$, the right-most point.

Provided our grid spacing is small, the derivatives in a differential equation can be approximated by so-called finite-differences, which leads to recurrence relations that can be used to construct the solutions iteratively. For example, suppose we had a simple first-order differential equation

$$d\psi/dx + k(x)\psi = 0. \tag{4}$$

The derivative here could be approximated as

$$d\psi/dx \approx (\psi_{n+1} - \psi_n)/l. \tag{5}$$

Substituting this in gives an equation we can solve to determine ψ_{n+1} as a function of ψ_n. This recurrence could be used to construct the whole solution iteratively from left to right – we start with a value of ψ_0, use it to compute ψ_1, use that to compute ψ_2, until eventually we get to the other side of our region.

This idea can be extended to construct iterations which solve second-order differential equations, like (2). It can also be improved on to give iteration schemes with better accuracy and stability.

- Accuracy is, as you would expect, about how accurately the computed ψ_n agrees with the true solution $\psi(x)$. The simplest thing to consider is the accuracy across one step of the iteration – if ψ_n is perfect, how good is ψ_{n+1}? This can be summed up in terms of the 'order of accuracy' of the iteration – a method can be described as 'first-order accurate' if, when we advance by one step, the difference between the true solution and the approximate solution is proportional to l^2 (so the terms proportional to l agree).

- Stability is about what happens to the error introduced at one step in the next step(s). In some cases, the iteration is unstable, meaning the error grows exponentially as you iterate. It then quickly swamps the real solution you're trying to find.

Eq. (2) is of the form

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi(x) = 0. \tag{6}$$

An accurate, stable iteration to integrate equations of this form is derived in the Appendix. It is :

$$\psi_{n+1} = \frac{2\left(1 - \frac{5}{12}l^2 k_n^2\right)\psi_n - \left(1 + \frac{1}{12}l^2 k_{n-1}^2\right)\psi_{n-1}}{1 + \frac{1}{12}l^2 k_{n+1}^2}. \tag{7}$$

By specifying two neighbouring points, one can obtain the third point. For the Schrödinger equation

$$k_n^2 = \gamma^2\left(\epsilon - \nu(x_n)\right). \tag{8}$$

Eq. 7 can be used to solve the Schrödinger equation by stepping the solution from left ($x = 0$) to right. Since we have an infinite well, we know that the wave function ψ vanishes at the left-hand boundary, $\psi_0 = \psi(\tilde{x} = 0) = 0$. To solve Eq. 7 for ψ_2 we will need also ψ_1 - what value should we take? This is arbitrary, because $\psi(\tilde{x})$ can always be rescaled by any constant. (This property will be needed later, when we normalise the wave function such that $\int_0^1 |\psi(\tilde{x})|^2 d\tilde{x} = 1$). So we pick an arbitrary value for ψ_1, and use Eq. 7 to get ψ_2. Then we use Eq. 7 again to get ψ_3, and so on, repeatedly applying it to build up the solution from left to the right.

2.3 Shooting Method

What about the boundary condition at the right-hand side? Because we have infinite walls, we want $\psi_{N-1} = \psi(\tilde{x} = 1) = 0$. Remember though that the problem is to find the eigenenergies, i.e. the values of E or ϵ, for which the solutions fit both the boundary conditions. The approach, then, is to try iterating from left-to-right for some value of E or ϵ. This will give us a solution which will fit the left-hand boundary condition but will not, in general, fit the right-hand one. However, what we can do then is to vary E or ϵ, until we find those special values for which it does. This 'shooting method' is one way (there are others) of solving boundary-value problems like this – one 'shoots out' trajectories starting from one boundary, and adjusts the parameters – in our case the eigenvalue – until they hit the desired point on the other.

3 General remarks

You will use Python to write the program. It is recommended that you use the Spyder development environment and the following packages:

```
import numpy as np
import matplotlib.pyplot as plt
import math
from scipy.integrate import simps
```

This will give you `arrays`, maths functions like `sqrt` and plotting capabilities. Later we will use `simps` (Simpson's rule) from `scipy` for numerical integration. It is a good programming practice not to hardcode any relevant parameters into the code. As parameters appear usually more than once in the code, their numerical value should be defined as a variable in the main program. e.g.

```
N=1000
psi=np.zeros(N)
```

If you need to change `N`, you just have to change it in one place. It also makes the code easier to read.

You should modularise the code by using functions that are called from a main program, e.g.

```
def function(parameter1,parameter2):
    result=(parameter1+parameter2)**2
    return result
```

4 Tasks

1. Solve the *non-dimensional* Schrödinger equation (2) analytically for the infinite square well where $\nu(\tilde{x}) = -1$ for $0 < \tilde{x} < 1$ and find an expression for the **non-dimensional** energy eigenvalues in terms of γ^2. Also, find the normalised wave functions (in non-dimensional units).

2. You will now find the wave function ψ numerically in the infinite square well for a given non-dimensional trial energy ϵ. Note that $\epsilon \geq -1$ by definition.

   - Define an array `psi` in which you store the wave function. Use `N=1000` points.

   - The physical parameters that describe the particle and the well are subsumed in γ^2 (Eq. 3). Set $\gamma^2 = 200$.

   - We will use the same constant potential $V(x) = -V_0$ for $0 < x < L$ as in (1.). In non-dimensional units this is just $\nu(\tilde{x}) = -1$ for $0 < \tilde{x} < 1$. Define an array `potential` that stores this potential using the same number of points `N`.

   - You can compute k^2 (Eq. 8) from the potential and your trial energy.

   - In order to obtain `psi` from Eqs. 7 and 8 we also need two starting values: `psi[0]=0` by definition and `psi[1]=1e-4`. The last value is arbitrary and only sets the initial slope. You can now evaluate `psi[2]` using eq. 7 and 8. After that you can obtain `psi[3]` from `psi[1]` and `psi[2]`, and so on. Now integrate `psi` up to `psi[N-1]` (right boundary). Do this for a few ϵ's close to the ground energy you obtained in task 1 and plot `psi`. You should see that for trial energies that are different from the energy eigenstates in task 1 `psi[N-1]` will not vanish which is required by the boundary conditions.

3. Next we will implement the numerical method to find the energies and eigenstates of the infinite square well (for $\gamma^2 = 200$ as before). While

the ψ you computed in task 2 satisfies the Schrödinger equation, it only satisfies the boundary conditions for certain values of the energy ϵ. To find them, you should implement the following algorithm to find the value of ϵ which solves $\psi[N-1] = 0$. Before you try to code it, you should sketch out how it works using a pencil and paper.

> Start with a trial energy ϵ below the eigenstate. Then compute `psi` for $\epsilon + \Delta\epsilon$, where $\Delta\epsilon$ is a suitably chosen energy increment (it should be smaller than the difference between any two adjacent energy eigenvalues). Be careful that you update the k^2 array (Eq. 8) every time you change ϵ ! Compute `psi[N-1]` for ϵ and $\epsilon + \Delta\epsilon$. If the sign of `psi[N-1]` has changed, then let $\Delta\epsilon = -\Delta\epsilon/2$. You can use a conditional `while` loop to iterate until $\Delta\epsilon$ is smaller than the desired accuracy.

4. Use this method to compute the first 10 energy eigenvalues and compare with the analytic solution from task 1. How accurate are the energy eigenvalues ? Do they get more and more accurate for smaller $\Delta\epsilon$?

5. We still need to normalise the eigenfunctions `psi`. To do this, we need to multiply `psi` with a suitable constant such that $\int_0^1 |\psi|^2 d\tilde{x} = 1$. We use Simpson's rule from the `scipy` package to numerically evaluate the integral: `simps(psi**2,dx=l)`, where `l=1.0/(N-1)` is the step size (difference between adjacent $\tilde{x}_n$). Compare your normalised `psi` with the analytic solution.

6. We can now compute the uncertainty relation $\Delta x \Delta p \gtrsim \hbar/2$. In non-dimensional units $\tilde{x} = x/L$ and $\tilde{p} = pL/\hbar$ this becomes

$$\Delta\tilde{x}\Delta\tilde{p} \gtrsim 1/2. \tag{9}$$

In general $\Delta\tilde{x} = \sqrt{\langle \tilde{x}^2 \rangle - \langle \tilde{x} \rangle^2}$ and likewise, $\Delta\tilde{p} = \sqrt{\langle \tilde{p}^2 \rangle - \langle \tilde{p} \rangle^2}$.

To evaluate $\Delta\tilde{x}$ we need to compute the first two moments of $|\psi(\tilde{x})|^2$. Since ψ is real, $|\psi|^2 = \psi^2$, therefore

$$\langle \tilde{x^n} \rangle = \int_0^1 \tilde{x}^n \psi(\tilde{x})^2 d\tilde{x}. \tag{10}$$

It is crucial that ψ is normalised here. For symmetric potentials like the infinite square well, what is the value of $\langle \tilde{x} \rangle$?

To evaluate $\Delta\tilde{p}$ we need to use the momentum operator $\hat{p} = -i\hbar\frac{d}{dx}$ (in 1D). In non-dimensional units this reduces to $\hat{\tilde{p}} = -i\frac{d}{d\tilde{x}}$. The expectation value of $\tilde{p}$ is just $\langle \tilde{p} \rangle = \langle \psi^*|\hat{\tilde{p}}|\psi \rangle = -i\int_0^1 \psi \frac{d\psi}{d\tilde{x}} d\tilde{x}$. In stationary states, where ψ is real, $\langle \tilde{p} \rangle = 0$ (can you prove that?).

Likewise, $\langle \tilde{p}^2 \rangle = \langle \psi^*|\hat{\tilde{p}}^2|\psi \rangle = -\int_0^1 \psi \frac{d^2\psi}{d\tilde{x}^2} d\tilde{x}$. Therefore, $\Delta\tilde{p}$ reduces to

$$\Delta\tilde{p} = \sqrt{\langle \tilde{p}^2 \rangle} = \sqrt{-\int_0^1 \psi \frac{d^2\psi}{d\tilde{x}^2} d\tilde{x}}. \tag{11}$$

To compute $\langle \tilde{p}^2 \rangle$ we need to numerically evaluate the second derivative of `psi`. This is easily done using a finite difference scheme (see Appendix, Eq. 17 for derivation):

$$\psi_n'' \approx \frac{\psi_{n-1} - 2\psi_n + \psi_{n+1}}{l^2} \tag{12}$$

This is a 3-point formula, therefore you will not be able to compute the second derivative for `psi[0]` and `psi[N-1]`. Since the wave function vanishes at the boundaries the product $\psi \frac{d^2 \psi}{d\tilde{x}^2}$ also vanishes at the boundaries, so this is not a problem when you evaluate $\langle \tilde{p}^2 \rangle$. (Alternatively, you may calculate $\frac{d^2 \psi}{d\tilde{x}^2}$ from the Schrödinger equation (Eq. 2) instead of using the finite difference scheme).

You can now test the uncertainty relation (eq.9) using eqs.10,11 and 12. Plot $\Delta\tilde{x}\Delta\tilde{p}$ for the first 10 eigenstates. You may also derive the analytic solution to compare with.

7. Change the potential from the infinite square well to a harmonic potential bounded by infinite walls,

$$\nu(\tilde{x}) = 8(x - 0.5)^2 - 1 \tag{13}$$

for $0 < \tilde{x} < 1$. Also, change the value of γ^2 from 200 to 1000. Compute the first 10 energy eigenstates and corresponding uncertainty relations. What will happen to the eigenstates at higher energies?

8. Compute the energy difference between two adjacent eigenstates for the harmonic potential and plot it for the first 20 states on a log-log scale. Comment on the result.

5 Appendix I

5.1 Discretization of Schrodinger equation

The method we use applies to equations of the form:

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi(x) = 0, \tag{14}$$

of which the stationary Schrödinger equation is one example. In principle this could be solved via a 4th order Runge-Kutta. However, one can take advantage of the particular structure of the equation, which involves no first derivative and is linear in ψ, to derive another method.

The Taylor expansion of $\psi(x + l)$ gives

$$\psi(x + l) = \psi(x) + l\psi'(x) + \frac{l^2}{2}\psi^{(2)}(x) + \frac{l^3}{6}\psi^{(3)}(x) + \frac{l^4}{24}\psi^{(4)}(x) + \dots \tag{15}$$

Adding this to the series expansion of $\psi(x - l)$ all the odd powers of l vanish:

$$\psi(x + l) + \psi(x - l) = 2\psi(x) + l^2\psi^{(2)}(x) + \frac{l^4}{12}\psi^{(4)}(x) + O(l^6) \tag{16}$$

Solving for the second derivative we obtain

$$\psi^{(2)}(x) = \frac{\psi(x + l) + \psi(x - l) - 2\psi(x)}{l^2} - \frac{l^2}{12}\psi^{(4)}(x) + O(l^4) \tag{17}$$

In order to evaluate the 4th order derivative that appears on the RHS, we apply $1 + (l^2/12)d^2/dx^2$ to eqn.14:

$$\psi^{(2)}(x) + \frac{l^2}{12}\psi^{(4)}(x) + k^2(x)\psi(x) + \frac{l^2}{12}\frac{d^2}{dx^2}[k^2(x)\psi(x)] = 0 \tag{18}$$

Substituting $\psi^{(2)}(x) + \frac{l^2}{12}\psi^{(4)}(x)$ form eqn. 18 into eqn. 17 we obtain

$$\psi(x+l) + \psi(x-l) - 2\psi(x) + l^2k^2(x)\psi(x) + \frac{l^4}{12}\frac{d^2}{dx^2}[k^2(x)\psi(x)] + O(l^6) = 0 \tag{19}$$

By applying the centred difference twice we can evaluate the last term:

$$\frac{d^2}{dx^2}[k^2(x)\psi(x)] \approx \frac{k^2(x+l)\psi(x+l) + k^2(x-l)\psi(x-l) - 2k^2(x)\psi(x)}{l^2} \tag{20}$$

Combining eqns. 19 and 20 and solving for $\psi(x + h)$ we get

$$\psi(x + l) = \frac{2\left(1 - \frac{5}{12}l^2k^2(x)\right)\psi(x) - \left(1 + \frac{1}{12}l^2k^2(x - l)\right)\psi(x - l)}{1 + \frac{1}{12}l^2k^2(x + l)} \tag{21}$$

We rewrite the above expression by setting $x = x_n \equiv x_0 + nl$ and $k_n \equiv k(x_n)$. Then we obtain

$$\psi_{n+1} = \frac{2\left(1 - \frac{5}{12}l^2k_n^2\right)\psi_n - \left(1 + \frac{1}{12}l^2k_{n-1}^2\right)\psi_{n-1}}{1 + \frac{1}{12}l^2k_{n+1}^2}. \tag{22}$$

As can be seen from the derivation, the local error (at each integration step) is $O(l^6)$, so this is a fourth-order method. However, the error accumulates over many steps, so that the global error (in the final value after integrating over all the steps) is $O(l^4)$.