

Experiment 2.4: One-Dimensional Schrödinger Equation

Introduction

At the core of quantum mechanics lays the dualism between particles and waves, by which a particle – e.g. an electron – will display particle or wave behaviour according to the characteristics of the system (e.g. its typical lengths) and the quantities we want to measure. The Schrödinger Equation is the fundamental equation in quantum mechanics, and its solutions provide us with the wave description of particles, their time evolution when interacting among each other or with external potentials and their corresponding energies.

In this experiment we will consider the time-independent Schrödinger Equation – a second order differential equation – for a single particle in one dimension, in an external confining potential given by a square well. The modulus squared of the solution to this equation – the wave function – will give the probability that the particle is found at certain point x in space in an experimental measurement.

This time-independent Schrödinger Equation may be written as

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x) \quad (1)$$

where $\psi(x)$ is the quantum mechanical wave function, m the mass of the particle and E its energy. If we use the dimensionless units $\hbar^2/2m = 1$ this can be simplified as

$$\frac{d^2\psi(x)}{dx^2} + [E - V(x)] \psi(x) = 0 \quad (2)$$

and the boundary conditions for a bound state are given by $\psi(x \rightarrow \pm\infty) = 0$.

In general the wave function must satisfy several continuity constraints if moving between two regions (I and II) of different potential at the point $x = a$:

$$\psi_I(a) = \psi_{II}(a) \quad (3)$$

and as long as the potential is not infinite

$$\left. \frac{d\psi_I(x)}{dx} \right|_{x=a} = \left. \frac{d\psi_{II}(x)}{dx} \right|_{x=a} \quad (4)$$

but if the potential is infinite then Eq.4 is replaced by

$$\psi_I(a) = 0 \quad (5)$$

One familiar example of this is the particle in the 1D infinite square well of width L , which is given by

$$V(x) = \begin{cases} 0 & |x| < L/2 \\ \infty & \text{otherwise} \end{cases} \quad (6)$$

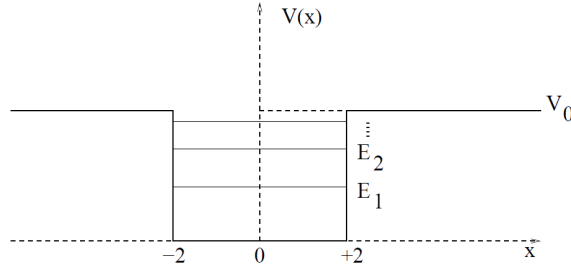


Figure 1: Confining potential $V(x)$

which has as its solutions the eigenenergies

$$E_n = \frac{n^2 \pi^2}{L^2} \quad (7)$$

and corresponding eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi(x - L/2)}{L}\right). \quad (8)$$

Solving the Schrödinger Equation

In this experiment we shall use the 2nd-order coupled Runge-Kutta method, as developed in experiment 2.3 (The Duffing Oscillator) to integrate the Schrödinger equation. Hence, just as with the Duffing Oscillator, we need to rewrite a 2nd-order differential equation as two coupled 1st-order differential equations. However, unlike the case of the Duffing Oscillator, we do not know all the terms in the equation we wish to integrate – in particular, we need to know a value for E to insert into Eq. 2 – and for a bound state, this needs to be an exact eigenenergy. Hence in general we need to solve the equation many times as we search for the correct value of E , for example by using the *shooting method*.

The shooting method

This method finds the solutions to a differential equation when the value of a parameter as well as the solution to the differential equation must be found at the same time. In the case of Eq. 2, this parameter is the energy E and for bound state solutions, these will only be allowed for specific, discrete values of E , i.e. $E_1, E_2, E_3 \dots$. The main idea is that Eq. 2 will be solved many times by varying the value of E and only the values which will satisfy the boundary conditions and provide continuous solutions are acceptable. A specific example of $V(x)$ – a square well of width $L = 4$ and depth V_0 – is sketched in figure 1.

In this case, since the boundary conditions are set at the edges of the box, we will solve Eq. 2 from starting from both the left ($\psi_L(x; E)$) and (independently) from the right ($\psi_R(x; E)$) using the 2nd-order coupled Runge-Kutta method. The correct energies E will be those for which the solutions and their derivatives match at the centre $x = 0$. This is described in Fig. 2, with the notation $z_1(x) = \psi(x)$ and $z_2(x) = d\psi/dx$. The boundary conditions on the wavefunction are $z_{1L}(x \rightarrow -\infty) = 0$ and $z_{1R}(x \rightarrow \infty) = 0$ but this is not enough to solve a 2nd-order differential equation – we also need boundary conditions on the derivative of the wavefunction.

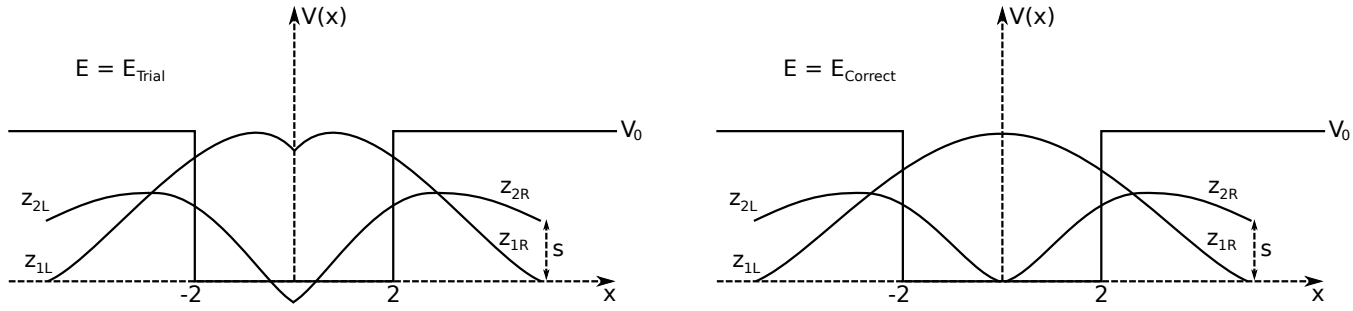


Figure 2: Shooting Method in action. The left-hand figure shows what happens if the trial energy is not right - the left and right solutions for z_1 and z_2 do not match in the centre. The right-hand figure shows what happens when the value of the trial energy is correct - we now have continuity in z_1 and z_2 in all parts of the well, including the matching in the centre.

For this particular potential, the wavefunction must be symmetric and so we choose a symmetric constraint on the derivatives: $z_{2L}(x \rightarrow -\infty) = s$ and $z_{2R}(x \rightarrow \infty) = -s$. The value of s is arbitrary – it just sets the scale of the unnormalized wavefunction – and so you may set $s = 1$ (but if your box is very large, you may want to reduce the value of s to stabilize your solution).

Since any linear combination of eigenfunctions (e.g. $\alpha\psi_1 + \beta\psi_2$) is a solution of the Schrödinger Equation, we can combine the matching conditions $z_{1L}(0) = z_{1R}(0)$ and $z_{2L}(0) = z_{2R}(0)$ into a single condition

$$\frac{z_{2L}(0)}{z_{1L}(0)} = \frac{z_{2R}(0)}{z_{1R}(0)} \quad (9)$$

$$= \frac{1}{\psi(0)} \frac{d\psi}{dx} \bigg|_{x=0} \quad (10)$$

which is known as the Derivative of the Log of the Solution (DLS). Hence we see that the values of the DLS for the left and right solutions must match at the centre. By plotting the DLS versus the parameter E it is then possible to find the solutions to Eq. 9 and to our problem.

Objectives

- to solve computationally an eigenvalue problem using the shooting method
- to compare the numerical solution with an exact limiting case.
- to analyse computationally how the behaviour of the solutions $\psi(x)$ and the energies E change as $V(x)$ is varied

Experiment

The relative amount of time you should spend on each section is shown as [X%].

1. *Basic shooting method and infinite square well ground state* [40%]:

- (a) Write a simple program to implement the shooting method. You will need to scan over different values of the trial energy E and test the DLS to see if you have found an eigenenergy. To do this you will need to reuse the Runge-Kutta module you created for the Duffing Oscillator experiment. When you are writing code to test a new algorithm you need to think from the outset about how you can be sure it is coded correctly, so in this case you should test against the infinite square well results as given above, with a well of width $L = 4$ and depth $V_0 \rightarrow \infty$. You will need to choose your own trial energy value and initial boundary conditions, and use a sufficiently large (but finite) value for V_0 . See how accurately you can find the value of the lowest bound energy E_1 and corresponding wavefunction $\psi_1(x)$ as you integrate the Schrödinger Equation over a box of width $l \geq L$, imposing the boundary conditions at its borders. The precision of your solution will depend on the size l of this box and on the step size h you use to integrate the equation using the Runge-Kutta method. You should normalize your solution so that the integral of $|\psi_1(x)|^2$ is equal to 1. Plot a graph of $\psi_1(x)$ and the derivative of the logarithm of the solution (DLS) you have used to find the correct E_1 . Clearly record the complete set of final parameter values chosen. N.B. Whenever you use a discretization approximation (such as the Runge-Kutta method) it is always important to check for convergence (e.g. if the step size h is appropriate for the precision required by the problem).

2. *Excited states of infinite square well* [20%]:

- (a) Can you find the next two bound solutions E_2 and E_3 for this system? You will need to vary both the trial energy and the initial boundary conditions and plot the corresponding DLS. How does the accuracy w.r.t. the analytical solution vary as you go to higher excited states?
- (b) Can you now extend your program to automatically test the value of the DLS at the matching point and adjust the trial energy E up or down as appropriate until the corresponding eigenenergy E_n is found to any desired precision?

3. *Finite square well* [40%]:

- (a) Once you are confident that your program is correct, you can now study with confidence a system for which you do not know the analytical values. One such potential is the finite well, given by a square well of width $L = 4$ and depth V_0 (see Fig. 1). If V_0 is large but finite, the eigenenergies should be very similar to the infinite well but the eigenfunctions should now show some tunnelling into the classically forbidden region and hence you shall have to be careful in testing how large you need to make l . Study how E_1 and $\psi_1(x)$ change as V_0 is reduced from an initially large value. Plot your results for E_1 versus V_0 and the wavefunctions

$\psi_1(x)$ for some representative values of V_0 . Separately normalise each solution so that all the wavefunctions are comparable and can be plotted in a single figure.

- (b) How low can you make V_0 and still have E_1 reasonably approximated by the limiting exact case solution (e.g. when the fractional error in the energy $|E_{1,num} - E_{1,exact}|/E_{1,exact}$ is no more than 5%)? How low can you make V_0 such that E_2 and E_3 can be approximated by the limiting exact solutions, e.g. with a fractional error in the energy of the order of a few percent? Plot the DLS used to support your answers and the comparison between the exact and the numerical wavefunctions.

Coding Hints

It is always a very good idea to plan out your program before you start. Make sure you understand the physics and what you are required to do, both for the first part and successive steps – this might change how you design your program, and give you ideas about what code you can re-use from previous experiments, and what code you might create that could usefully be reused in the future. Think too about how you can test your code in stages ...

- Flow chart
 - This is a useful way of planning out the steps in your program. See <http://en.wikipedia.org/wiki/Flowchart> for a simple description of the symbols to use. The University has a subscription to “lucidchart” as part of its Google Apps package which you can use to generate elegant flow charts.
- Runge-Kutta module
 - For this task you should reuse your Runge-Kutta module from the Duffing Oscillator experiment. It would be very useful if it contained a routine for solving a single 1st order differential equation using RK2, and a pair of coupled first order equations as used before. All of these routines should work with generic input functions f_1 and f_2 . You should also think about what other data should be stored in this module, e.g. the step size, etc. to make it reasonably complete and self-contained.
- Other modules
 - What other modules would be helpful in writing this program, and might be reusable in the future? One obvious one is something to hold basic constants, such as your precision definitions, values of pi, etc.
 - What about something for the wavefunction, e.g. a subroutine to normalize an input wavefunction? What is the best way to store a wavefunction? How can you plot it?
- Compiler flags
 - Finally, don't forget to use appropriate compiler flags as before.