# 2.2 Schrödinger's Equation

Part IB Quantum Mechanics is useful but not essential. (All required background material can be found in the project itself and/or the references.)

## 1 Introduction

Consider a single particle of mass m and energy  $\epsilon$ , in a (real) one-dimensional potential v(x). Then Schrödinger's time-independent wave equation is

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + v(x)\right]\psi(x) = \epsilon\,\psi(x) \tag{1}$$

where  $2\pi\hbar$  is Planck's constant, The state of the system is represented by a (complex) timedependent wavefunction  $\psi(x)e^{-i\epsilon t/\hbar}$ .

Let  $\epsilon_1$  be the unit of energy so that  $E = \epsilon/\epsilon_1$  is the dimensionless total energy. Define also a dimensionless co-ordinate  $X = x\sqrt{2m\epsilon_1}/\hbar$ . Then the equation simplifies as

$$\left[-\frac{d^2}{dX^2} + V(X)\right]Y(X) = EY(X)$$
<sup>(2)</sup>

where  $V(X) = v(x)/\epsilon_1$  is the dimensionless potential energy, and  $Y(X) = \psi(x)$  is the stationary wave function.

This project is about *bound states*, in which the particle is localised near X = 0. In bound states, Y(X) tends to zero as  $|X| \to \infty$ , sufficiently fast that the wave function is normalisable, that is,

$$\int_{-\infty}^{\infty} |Y(X)|^2 dX < \infty.$$

Another feature of bound states is that the real and imaginary parts of Y decay monotonically for sufficiently large positive or negative X. Such solutions to Eq. (2) only exist for certain values of E, which are the 'eigenvalues'.

The aim of this project is to determine a few of these eigenvalues, and their corresponding eigenfunctions Y(X), numerically. This will be achieved using 'forward shooting', which involves finding values of E, Y(0) and Y'(0) by trial-and-error, such that the solution of (2) behaves appropriately as  $|X| \to \infty$ .

### 2 Harmonic oscillator

Consider the harmonic oscillator potential

$$V(X) = X^2. aga{3}$$

#### 2.1 Theory

For this potential, information about the solutions to Eq. (2) can be found in textbooks about quantum mechanics, for example Refs. [1,2,3]. We summarise the relevant information for this project. The general solution to Eq. (2) is

$$Y(X) = \left[ c_{\rm e} f_{\rm e}(X) + c_{\rm o} f_{\rm o}(X) \right] \exp\left(-X^2/2\right)$$

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where  $f_e$  is an even function [that is,  $f_e(X) = f_e(-X)$ ] and  $f_o$  is an odd function  $[f_o(X) = -f_o(-X)]$ . The constants  $c_e, c_o$  depend on the values chosen for Y(0) and Y'(0). The most important properties of  $f_e$  and  $f_o$  are

- Normalisable solutions exist if and only if E is an odd positive integer. Otherwise, all solutions diverge as  $|X| \to \infty$ .
- If (E-1)/2 is an even integer then any normalisable solution must be even  $(c_0 = 0)$ . Similarly, if (E-1)/2 is odd then any normalisable solutions must be odd  $(c_e = 0)$ .
- The functions  $f_e$  and  $f_o$  that appear in the normalisable solutions are called Hermite polynomials. For E = 1, 3, 5, the relevant Hermite polynomials are 1, X, and  $1 2X^2$ .
- In general, one has

$$f_{\rm e}(X) = \sum_{n=0}^{\infty} a_n X^{2n}, \qquad f_{\rm o}(X) = \sum_{n=0}^{\infty} b_n X^{2n+1},$$

where  $a_0 = 1$ ,  $b_0 = 1$ , and the remaining coefficients satisfy recurrence relations

$$a_{n+1} = \frac{4n+1-E}{(2n+2)(2n+1)} a_n$$
,  $b_{n+1} = \frac{4n+3-E}{(2n+3)(2n+2)} b_n$ .

The first three points above can all be derived by using the last point. (If E is an odd positive integer then one sees from the recurrence relations that either  $f_e$  or  $f_o$  will be a polynomial.)

#### 2.2 Computation

In this part of the project, we restrict our attention to odd solutions by taking

$$Y(0) = 0$$
 and  $Y'(0) = 1$ . (4)

(Setting Y'(0) = 1 does not lose any generality.)

**Programming Task:** Write a program to solve Schrödinger's equation (2) with the potential (3) by numerical integration, starting from the initial conditions (4). The program should find and (optionally) plot the solution Y(X) for a given value of E and a range of integration  $X \in [0, X_{\text{max}}]$ , where you will decide on appropriate values for  $X_{\text{max}}$ . You may use one of the built-in MATLAB solvers, *e.g.* ode45 for which you can control the relative and absolute tolerances with odeset('RelTol', rtol, 'AbsTol', atol), inserting sensible values for rtol and atol. Alternatively, you might use the fixed-steplength Runge-Kutta outine you wrote for the Ordinary Differential Equations core project.

**Question 1** Run the program with E = 2.9 to obtain the value of Y(5) correct to 8 significant figures. Explain how you have tested that the input parameters of the ODE solver (tolerances or steplength) are appropriate for this purpose, and present evidence that the required accuracy has been achieved.

**Question 2** Run the program with  $X_{\text{max}} = 5.0$  and E = 2.9995 and 3.0005 in turn, and plot *one* graph with both solutions Y(X) superposed. Why are you satisfied that the numerical results are correct?

**Question 3** Why can you be sure, without integrating beyond  $X = X_{\text{max}}$ , that the solutions found in the previous question will tend monotonically to  $\pm \infty$  over the range  $[X_{\text{max}}, \infty)$ ?

**Question 4** How will a *numerical* solution of (2)–(4) with E = 3 behave as  $X \to \infty$ , and why? (It may be instructive to vary the parameters of the ODE solver.)

## 3 Nearly-square potential well

**Programming Task:** Modify your program so that V(X) is given by

$$V(X) = -\frac{\Delta V}{1 + X^4} \tag{5}$$

where  $\Delta V$  is a strictly positive constant. Also modify your program so that you can use initial conditions appropriate to either even or odd solutions. Be sure to specify these initial conditions in your write-up.

**Question 5** For bound states of this V(X), why is there no loss of generality in restricting to solutions which are either even or odd in X?

#### **3.1** Shallow potential : $\Delta V = 1$

The potential (5) has at least one bound state for any  $\Delta V > 0$ , and more for larger  $\Delta V$ . For  $\Delta V = 1$ , it turns out that there is exactly one bound state.

**Question 6** Use your program to verify that the potential (5) with  $\Delta V = 1$  has only one bound state, at least to the extent of trying E = -1, E = 0 and a few judiciously chosen values of E between -1 and 0. You should check for both even and odd solutions. Present plots of these solutions over a suitable range  $[0, X_{\text{max}}]$ , explaining your choice(s) for  $X_{\text{max}}$  and the input parameters of the ODE solver.

**Question 7** Why is there no need to consider values of E greater than 0 or less than  $-\Delta V$  when seeking bound-state solutions for the potential (5)? Argue carefully why your numerical results indicate that for  $\Delta V = 1$  there can be no more than one bound state.

**Question 8** Determine the single [negative] energy eigenvalue, correct to 3 significant figures, by interval-halving (or otherwise). Be sure to use appropriate value(s) of  $X_{\text{max}}$  (with justification). Include in your write-up a graph with superimposed plots of Y(X) for a final pair of integrations which bracket the eigenvalue sufficiently closely, remembering to identify them with the values of E used.

**Question 9** Explain why there must be a bound state with energy between these values. [*Hint*: what is the asymptotic behaviour of Y(X) as  $X \to \infty$ ?]

#### 3.2 Stronger potentials

For larger  $\Delta V$ , there tend to be more bound states. To understand this, two theoretical results can be useful.

1. Consider a 'square' potential well of width 2L:

$$V_{\text{square}}(X) = \begin{cases} -\Delta V & \text{if } |X| < L\\ 0 & \text{if } |X| > L \end{cases}$$
(6)

As discussed in textbooks such as Refs. [1,2,3], this potential has exactly N bound states if

$$\frac{2L}{\pi}\sqrt{\Delta V} \in (N-1,N] .$$
(7)

Bound states for the square potential and the potential of Eq. (5) turn out to be qualitatively similar, but one must choose L appropriately. For example, one might estimate the 'width' of the potential (5) as

$$L = \left(\frac{\int_0^\infty X^2 V(X) dX}{\int_0^\infty V(X) dX}\right)^{1/2} = 1.$$
 (8)

2. The WKB approximation (discussed in Refs. [1,2,3]) can be used to analyse situations where  $\Delta V$  is very large. Specifically, as  $\Delta V \to \infty$  then the bound state energies asymptote to  $\tilde{E}_n = -\Delta V/(1 + X_n^4)$  for n = 0, 1, 2, ..., N - 1, where N is the number of bound states and  $X_n$  is determined by

$$\int_{-X_n}^{X_n} \sqrt{\tilde{E}_n - V(X)} \, \mathrm{d}X = \left(n + \frac{1}{2}\right)\pi \tag{9}$$

Also, N is determined (asymptotically) by the condition that

$$\frac{2\tilde{L}}{\pi}\sqrt{\Delta V} \in \left(N - \frac{1}{2}, N + \frac{1}{2}\right].$$
(10)

where

$$\tilde{L} = \frac{1}{2} \int_{-\infty}^{\infty} \sqrt{\frac{-V(X)}{\Delta V}} \, \mathrm{d}X = \int_{0}^{\infty} \frac{\mathrm{d}X}{\sqrt{1+X^4}} \approx 1.85 \tag{11}$$

**Question 10** For the potential (5) with  $\Delta V = 36$ , find all possible bound-state energy eigenvalues correct to at least 3 significant figures and display plots of the corresponding eigenfunctions, recording the number of times each takes the value zero.

Explain carefully why you are satisfied that there are no other bound states. Mention any precautions needed to ensure that all eigenvalues are obtained to the required accuracy.

Discuss the relationship between your results and the theories for the square well and the WKB approximation.

### References

- [1] LI Schiff, Quantum Mechanics, 3rd edition, McGraw-Hill 1968.
- [2] DJ Griffiths, Introduction to Quantum Mechanics, Prentice Hall 1995.
- [3] S Gasiorowicz, Quantum Physics, Wiley 2003.