

2.2 Schrödinger's Equation

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

1 Introduction

Schrödinger's [time-independent] wave equation for a single particle of mass m and energy ϵ , moving in one dimension in a given [real] potential $v(x)$, is

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

where $\psi(x)e^{-i\epsilon t/\hbar}$ is the time-dependent wave function representing the state of the system, and $2\pi\hbar$ is Planck's constant. If we measure energy in units of ϵ_1 , say, and define a dimensionless co-ordinate $X = \sqrt{2m\epsilon_1} x/\hbar$, then the equation can be simplified to

$$\left[-\frac{d^2}{dX^2} + V(X) \right] Y(X) = E Y(X) \quad (2)$$

where $E = \epsilon/\epsilon_1$ (a constant) and $V(X) = v(x)/\epsilon_1$ are the dimensionless total and potential energies, and $Y(X) = \psi(x)$ is the stationary wave function.

In order to represent a bound state, $Y(X)$ must tend to zero as $|X| \rightarrow \infty$, its real and imaginary parts doing so monotonically for all sufficiently large positive or negative X , and sufficiently fast that the wave function is 'normalisable', i.e. $\int_{-\infty}^{\infty} |Y(X)|^2 dX$ is finite. This is possible only for certain values of E , the 'eigenvalues'. The aim of this project is to determine a few of these eigenvalues, and their corresponding 'eigenfunctions' $Y(X)$, numerically using 'forward shooting' — finding by trial-and-error values of E , $Y(0)$ and $Y'(0)$ which give a solution of (2) with appropriate behaviour as $|X| \rightarrow \infty$.

2 Harmonic oscillator

We first consider the harmonic oscillator potential

$$V(X) = X^2. \quad (3)$$

Two independent analytic solutions of (2) with this potential and any E can be found in the form $\exp(-X^2/2)$ times a series in even or odd powers of X :

$$Y_e(X) \equiv \exp(-X^2/2) \sum_{n=0}^{\infty} c_n X^{2n}, \quad Y_o(X) \equiv \exp(-X^2/2) \sum_{n=0}^{\infty} d_n X^{2n+1}. \quad (4)$$

where

$$c_{n+1} = \frac{4n+1-E}{(2n+2)(2n+1)} c_n, \quad d_{n+1} = \frac{4n+3-E}{(2n+3)(2n+2)} d_n \quad (5)$$

(see for example [1], §13 or [2], §2.3 or [3], chapter 5 G) and without loss of generality $c_0 = d_0 = 1$. If E is not an odd positive integer, neither series terminates and it can be shown that both $Y_e(X)$ and $Y_o(X)$ become unbounded as $X \rightarrow \infty$, asymptoting to $C_{e,o}(E)X^{-(1+E)/2} \exp(X^2/2)^*$

*The analysis between (5-119) and (5-120) of [3] is possibly misleading on this point.

where $C_e(E)$ and $C_o(E)$ are continuous functions of E . On the other hand, if $E = 2p + 1$ with p a non-negative integer, the even (odd) series terminates if p is even (odd) — implying that $C_e(E) = 0$ if and only if $(E - 1)/2$ is a non-negative even integer, and $C_o(E) = 0$ if and only if $(E - 1)/2$ is a non-negative odd integer. It follows that there are bound states with energy eigenvalues $E = 1, 3, 5, \dots$ and corresponding eigenfunctions proportional to $\exp(-X^2/2)$ times the ‘Hermite’ polynomials $1, X, 1 - 2X^2, X - \frac{2}{3}X^3, \dots$

In this part of the project, restrict attention to odd solutions satisfying

$$Y(0) = 0 \text{ and (WLOG) } Y'(0) = 1. \quad (6)$$

Programming Task: Write a program to solve Schrödinger’s equation (2) with the potential (3) by numerical integration, starting from the initial conditions (6). The program should find and (optionally) plot the solution $Y(X)$ for a given value of E and a range of integration $X \in [0, X_{\max}]$, where you will decide on appropriate values for X_{\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 outline 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 $X_{\max} = 5.0$ 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 $X = X_{\max}$, that the solutions found in the previous question will tend monotonically to $\pm\infty$ over the range $[X_{\max}, \infty)$?

The asymptote can be established by substituting

$$Y(X) = e^{S(X)} \Rightarrow (S')^2 + S'' = X^2 - E$$

and noting that this is satisfied [formally] by the infinite series

$$S' \sim a_0 X + \sum_{n=1}^{\infty} a_n X^{-2n+1} \Rightarrow S \sim \frac{1}{2}a_0 X^2 + a_1 \ln X [+a \text{ constant, } = 0 \text{ WLOG}] - \frac{1}{2}a_2 X^{-2} + \dots$$

with

$$a_0 = -1, \quad a_1 = \frac{1}{2}(E - 1), \quad a_2 = \frac{1}{8}(E - 1)(E - 3), \quad \dots$$

or

$$a_0 = 1, \quad a_1 = -\frac{1}{2}(E + 1), \quad a_2 = -\frac{1}{8}(E + 1)(E + 3), \quad \dots,$$

implying that equation (2)–(3) has a solution $Y_-(X)$ with exponential decay as $X \rightarrow \infty$,

$$\begin{aligned} Y_- &= \exp \left[-\frac{1}{2}X^2 + \frac{1}{2}(E - 1) \ln X - \frac{1}{16}(E - 1)(E - 3)X^{-2} + \dots \right] \\ &= \exp \left(-\frac{1}{2}X^2 \right) X^{(E-1)/2} \left[1 - \frac{1}{16}(E - 1)(E - 3)X^{-2} + \dots \right], \end{aligned}$$

and an independent solution $Y_+(X)$ with exponential growth,

$$Y_+ = \exp \left(\frac{1}{2}X^2 \right) X^{-(E+1)/2} \left[1 + \frac{1}{16}(E + 1)(E + 3)X^{-2} + \dots \right],$$

the general linear combination being dominated for large X by the second (unless that is completely absent).

Question 4 How will a *numerical* solution of (2)–(6) with $E = 3$ behave as $X \rightarrow \infty$, 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

$$V(X) = -\frac{\Delta V}{(1 + X^2)^2} \quad (7)$$

where ΔV 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 Why, when looking for bound states for this $V(X)$, is there no loss of generality in restricting attention to solutions which are either even or odd in X ?

The potential (7) has at least one bound state for any $\Delta V > 0$, and more for larger ΔV . Naively it might be expected to behave something like the ‘square’ potential well $V_{\text{square}}(X)$ with the same dimensionless depth and comparable half-width[†], i.e.

$$V_{\text{square}}(X) = \begin{cases} -\Delta V & \text{if } |X| < L \\ 0 & \text{if } |X| > L \end{cases} \quad \text{with (say) } L = \left(\frac{\int_0^\infty X^2 V(X) dX}{\int_0^\infty V(X) dX} \right)^{1/2} = 1, \quad (8)$$

which has exactly N bound states if $(N - 1)\pi < 2L\sqrt{\Delta V} \leq N\pi$ (see for example [1], §9 or [2], §2.6 or [3], chapter 5 B).

Alternatively we might appeal to the *WKB approximation*, which is based on the [non-trivial!] observation (see for example [1], §34 or [2], chapter 8) that in the limit $\Delta V \rightarrow \infty$ the bound-state energy eigenvalues asymptote to $\tilde{E}_n \equiv -\Delta V / (1 + X_n^2)^2$ where X_n is determined from

$$\int_{-X_n}^{X_n} \sqrt{\tilde{E}_n - V(X)} dX \equiv \sqrt{\Delta V} \int_{-X_n}^{X_n} \left[\frac{1}{(1 + X^2)^2} - \frac{1}{(1 + X_n^2)^2} \right]^{1/2} dX = (n + \tfrac{1}{2})\pi \quad (9)$$

for $n = 0, 1, 2, \dots, N - 1$ [cf. the ‘Bohr-Sommerfeld quantisation rule’ of the ‘old quantum theory’], the number of bound states N being determined (asymptotically) by

$$(N - \tfrac{1}{2})\pi < \int_{-\infty}^{\infty} \sqrt{-V(X)} dX \equiv 2\tilde{L}\sqrt{\Delta V} \leq (N + \tfrac{1}{2})\pi \quad \text{with} \quad \tilde{L} = \int_0^\infty \frac{dX}{1 + X^2} = \tfrac{1}{2}\pi. \quad (10)$$

Question 6 Both these arguments *suggest* – correctly as it happens – that the potential (7) with $\Delta V = 1$ has only one bound state. Verify that this is indeed the case, at least to the extent of trying $E = -1$, $E = 0$ and a few judiciously chosen values of E between -1 and 0 , 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_{max} and the input parameters of the ODE solver.

[†]This cannot be defined unambiguously, e.g. we might use $L = \int_0^\infty XV(X)dX / \int_0^\infty V(X)dX = 2/\pi$ instead of (8).

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(7)? 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_{\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 $X \rightarrow \infty$?]

Question 10 For the potential (7) with $\Delta V = 49$, 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.

References

- [1] LI Schiff, *Quantum Mechanics*, 3rd edition, McGraw-Hill 1968.
[https : //archive.org/details/QuantumMechanics_500](https://archive.org/details/QuantumMechanics_500)
- [2] DJ Griffiths, *Introduction to Quantum Mechanics*, Prentice Hall 1995.
[https : //archive.org/details/IntroductionToQuantumMechanics_718](https://archive.org/details/IntroductionToQuantumMechanics_718)
- [3] S Gasiorowicz, *Quantum Physics*, Wiley 2003.