

5 Quantum Mechanics

5.3 Bound State Energies for One-Dimensional Potentials (9 units)

This project can be done with knowledge of the course Principles of Quantum Mechanics.

1 Introduction

One-dimensional bound states in quantum mechanics are investigated by using a matrix method to estimate eigenvalues of the Schrödinger operator. Several cases are considered and the answers are compared with theory, including the predictions of perturbation theory and variational methods.

2 The Schrödinger Equation

The Schrödinger equation in 1D (using units where $\hbar = 1 = m$) is

$$-\frac{1}{2} \frac{d^2 \psi_i}{dx^2} + V(x) \psi_i = E_i \psi_i.$$

To obtain approximate solutions to this equation, the real-valued position x is replaced by a discrete set of $2N$ points spaced by ϵ , such that $-N\epsilon \leq x < N\epsilon$. The eigenfunction, $\psi(x)$, is replaced by a $2N$ -dimensional vector, \mathbf{e} , where $\psi(x_n) = e_n$, with $x_n = (n - N)\epsilon$, $0 \leq n < 2N$. The Schrödinger equation becomes the matrix eigenvalue equation

$$M\mathbf{e}_i = \epsilon^2 E_i \mathbf{e}_i,$$

where M is a $2N \times 2N$ symmetric tri-diagonal matrix with

$$\text{diagonal entries} \quad c_n = 1 + \epsilon^2 V(x_n)$$

$$\text{off-diagonal entries} \quad b_n = -\frac{1}{2} \quad \forall n$$

3 Given's Procedure

Given a symmetric tri-diagonal matrix, M , with diagonal entries c_n and off-diagonal entries b_n , consider the sequence q_n , ($0 \leq n < 2N$), for fixed real parameter λ :

$$\begin{aligned} q_0 &= c_0 - \lambda \\ q_n &= (c_n - \lambda) - b_n^2/q_{n-1} \quad n > 0. \end{aligned} \tag{1}$$

Let $s(\lambda)$ be the number of the q_n that are negative. Then **the number of eigenvalues of M whose values are less than λ is $s(\lambda)$** . That is, if the eigenvalues are ordered so that $E_i \leq E_{i+1}$, then

$$\epsilon^2 E_i < \lambda \quad \text{for } 0 \leq i < s(\lambda).$$

$s(\lambda)$ can be computed as a function of λ by starting with a sufficiently small value of λ , incrementing λ in small steps and computing the sequence $\{q_n\}$ for each value. When $s(\lambda)$ increases

in value from one step to the next, λ must have passed through an eigenvalue of M (or through more than one, if $s(\lambda)$ increases by more than one, in which case you should use a smaller stepsize). An accurate value for this eigenvalue can then be determined by bisection before going on to the next eigenvalue.

Once the eigenvalue, E , has been found sufficiently accurately, to at least 3 decimal places, the corresponding eigenvector can be found using the equations

$$\begin{aligned} e_0 &= 1 \\ e_1 &= 2(c_0 - \epsilon^2 E) \\ e_{n+1} &= 2(c_n - \epsilon^2 E)e_n - e_{n-1} \quad n > 0. \end{aligned}$$

Note: for bound states the relevant eigenvectors are required to decay exponentially for large $|x|$. It can be shown that the matrix M only has eigenvectors which satisfy this boundary condition.

There are three cautions:

- (a) In Equation (1) there is a division by q_{n-1} . Should q_{n-1} become too small it is permissible to replace it by a small default value, to avoid numerical instabilities: the results are unaffected by this procedure. For the cases considered below this eventuality has not been found to occur in practice.
- (b) You will compute eigenvectors that are normalised as

$$\epsilon \sum_{n=0}^{2N-1} e_n^2 = 1$$

which corresponds to the physical normalisation $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$. The wavefunction dies away at least exponentially for large $|x|$ so we expect e_0 to be very small indeed. For this reason, it is useful to continually normalise the vector \mathbf{e} , as it is being computed. Specifically, if the e_n have already been calculated for all $n < m$ then it is recommended to normalise them such that

$$\epsilon \sum_{n=0}^{m-1} e_n^2 = 1$$

before computing e_m .

- (c) The wavefunction also decays exponentially for large positive x . This means that for large n (bigger than N), the values of e_n will become very small. However, if you continue the calculation to very large n , numerical (round-off) errors can lead to exponential growth of the numerical estimates of e_n . The calculation is not accurate in this regime: if this happens you should stop the calculation at some $n_{\max} < 2N$, in order to obtain an accurate estimate of the true eigenvector \mathbf{e} . Alternatively, use the fact that all wavefunctions are either even or odd so the e_n only need to be computed for $0 \leq n \leq N$. (Take care with the normalisation if you use this method).

Programming Task: Write a program to determine the eigenvalues and eigenvectors for the four lowest bound states of a given (symmetric) potential. You should allow the values of N and ϵ and the starting value λ to be input variables.

4 Harmonic Oscillator

[See the Appendix for some theoretical results which may be of use here and in later sections.]

As a check of your code give the four lowest eigenenergies for the potential

$$V(x) = \frac{1}{2}x^2.$$

Adjust N and ϵ to get results to at least 3 decimal places for the eigenvalues and accurate to within 1% for the significant part of the wavefunctions. Make sure that $N\epsilon$ is not too big since the wavefunctions are very small for $x = N\epsilon$ and so nothing is gained. However, if ϵ is too big and/or $N\epsilon$ is too small the results will be inaccurate. A bit of trial and error will yield good values with which to work, but in each case considered you should check that results are insensitive to changes in N and ϵ within the accuracy required. Reasonable values to start with are $N = 50$ and $\epsilon = 0.1$ but you should be able to increase N up to 500 at least.

Question 1 State the values of N and ϵ that you have chosen, to obtain the required accuracy. Justify these choices. For these values, include plots of the wavefunctions corresponding to the two lowest energies and compare with the known analytic form.

Note: throughout this project, you should provide graphs that illustrate clearly the effect of the parameters and the similarities and differences between the wavefunctions. Large numbers of graphs are *very unlikely to be effective* in communicating this information.

5 Anharmonic Oscillator

Now modify the potential energy and take

$$V(x) = \frac{1}{2}x^2 + \frac{b}{6}x^4(x^2 + 1).$$

Question 2 Labeling the harmonic oscillator eigenstates by $|n\rangle$, i.e. $H_0|n\rangle = E_n|n\rangle$ with

$$H_0 = \frac{p^2}{2} + \frac{x^2}{2} = a^\dagger a + \frac{1}{2},$$

explain or show that $\langle n+k|x^6|n\rangle = 0$ for all $k > 6$.

Question 3 Using perturbation theory derive expressions for the lowest two energies to second order in b . You may use without proof, for integer $j \geq 0$, that

$$\int_{-\infty}^{\infty} dz z^{2j} e^{-z^2} = \Gamma(j + \frac{1}{2}),$$

with $\Gamma(\frac{1}{2}) = \sqrt{\pi}$ and $\Gamma(\sigma + 1) = \sigma\Gamma(\sigma)$.

Question 4 Compute (numerically) the four lowest energy eigenvalues and plot the corresponding wavefunctions for $b = 0.02$. Compare the results with your perturbative estimates for the lowest two energies. Try values $b = 0.001$ and 0.1 , as well as any others that you feel might be relevant. You need not plot the wavefunctions for these cases, but you should consider tables and/or plots of the energies vs. b . How well does perturbation theory work here? Is second order perturbation theory an improvement over first order?

6 Double-well potential

Finally consider

$$V(x) = \frac{1}{9d^4}(x^2 - d^2)^2 \left(d^2 + \frac{x^2}{8} \right) \quad (2)$$

This problem is not so easy to study by perturbation theory. Instead we use trial wavefunctions. (This approach is the same as the *variational method* described in the *Applications of Quantum Mechanics* course, but no knowledge of this method is required as full details are given below.)

Question 5 Change variable to $y = x - d$ and show that

$$V = \frac{1}{2}y^2 + V_3y^3 + \frac{7}{24d^2}y^4 + V_5y^5 + \frac{1}{72d^4}y^6.$$

where V_3 and V_5 are constants that you should express as real numbers times d to some (negative) power.

Observe that for small y , the potential V resembles the harmonic oscillator from question 1. A similar result occurs if we change variable to $y = x + d$ instead: the potential is symmetric in x so this must happen. Based on this observation we introduce two wavefunctions that are ground states of the relevant harmonic oscillators:

$$\begin{aligned} \psi_+(x) &= \frac{1}{\pi^{1/4}} e^{-\frac{1}{2}(x-d)^2} \\ \psi_-(x) &= \frac{1}{\pi^{1/4}} e^{-\frac{1}{2}(x+d)^2}. \end{aligned}$$

Define two trial wavefunctions as

$$\phi_{\pm} = C_{\pm}(\psi_+ \pm \psi_-)$$

You will investigate how close are these wavefunctions to the solutions of the Schrödinger equation.

Question 6 Determine the normalization constants C_{\pm} and show that the expectation values of the Hamiltonian, $E_{\pm} = \langle \phi_{\pm} | H | \phi_{\pm} \rangle$ are

$$E_{\pm} = \frac{(A \pm B)}{(1 \pm e^{-d^2})},$$

where

$$A = \frac{1}{2} + \frac{7}{32d^2} + \frac{5}{192d^4} \quad \text{and} \quad B = e^{-d^2} \left(-\frac{7d^2}{18} + \frac{7}{48} + \frac{1}{16d^2} + \frac{5}{192d^4} \right).$$

Question 7 What is the physical interpretation of the situation where $d \gg 1$, and what happens to the energy in this case? We focus on large d and define $\beta = 1/(9d^4)$ which is a small parameter in this situation. Use your program to compute the energies of the two lowest eigenstates for various values of β including $\beta = 1.0, 0.1, 0.01$, and 0.001 . How accurate are these numerical estimates? Compare them with the theoretical estimates E_{\pm} .

Question 8 What are the symmetry properties of the ground state eigenvector and the first excited state? Explain your answer. By expanding ϕ_{\pm} on the complete set of eigenstates of the Hamiltonian, show that E_{\pm} are upper bounds for the energies of the ground state and first excited state. You will need to consider the symmetries of the wavefunctions.

Question 9 For the cases considered in question 7, how close are the bounds E_{\pm} to the true energies? For two interesting values of d , plot the potential and indicate the four lowest lying energy levels on the same plot. Is it possible for some of the energy levels to be **lower** than the height of the central peak, i.e. than V at $x = 0$?

Question 10 How well does the trial wavefunction method estimate the energy difference, ΔE , between the first excited state and the ground state? What happens to ΔE as $\beta \rightarrow 0$?

Appendix

You are given that the harmonic oscillator wavefunctions are

$$\psi_n(x) = \frac{C_n}{\pi^{1/4}} H_n(x) e^{-x^2/2}$$

where

$$\begin{aligned} H_0 &= 1, & C_0 &= 1 \\ H_1 &= 2x, & C_1 &= \frac{1}{\sqrt{2}} \\ H_2 &= 2(2x^2 - 1), & C_2 &= \frac{1}{2\sqrt{2}} \\ H_3 &= 4x(2x^2 - 3), & C_3 &= \frac{1}{4\sqrt{3}} \\ H_4 &= 4(4x^4 - 12x^2 + 3), & C_4 &= \frac{1}{8\sqrt{6}} \\ H_5 &= 8x(4x^4 - 20x^2 + 15), & C_5 &= \frac{1}{16\sqrt{15}} \\ H_6 &= 8(8x^6 - 60x^4 + 90x^2 - 15), & C_6 &= \frac{1}{96\sqrt{5}} \\ H_7 &= 16x(8x^6 - 84x^4 + 210x^2 - 105), & C_7 &= \frac{1}{96\sqrt{70}} \end{aligned}$$

and so on.