# Physics 115/242

## Eigenvalues of the Schrödinger Equation: the Shooting Method

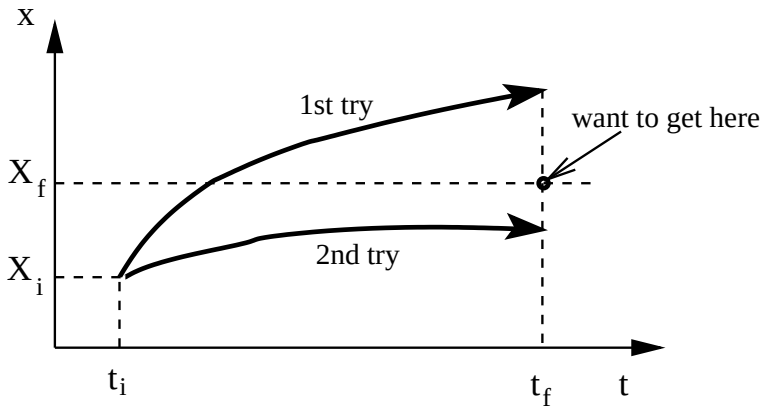
Peter Young

(Dated: April 24, 2007)

## I. INTRODUCTION

So far, we have considered *initial value* problems in which all the boundary conditions are specified at the *same* value of the independent variable. For example we may want to solve Newton's equation of motion (which is second order and so two boundary conditions are needed) in which $x$ and $v$ are specified at some initial time $t_0$ (so $t$ is the independent variable here). We then integrate forward in time to determine $x$ and $v$ at a later time.

However, we sometimes have to solve *two-point* boundary value problems, in which the boundary conditions are specified at two *different* values of the independent variable. For example, we may need to solve Newton's equations of motion in which $x$ is specified at two different times $t_i$ and $t_f$, i.e. $x(t_i) = X_i$, $x(t_f) = X_f$, and we want to find the motion at intermediate times. The problem is that to integrate from $t_i$ we need to know *both* $x(t_i)$ and $v(t_i)$. We do know $x(t_i)\,(= X_i)$ but not $v(t_i)$, so how do we proceed? The only way to start is to *guess* a value for $v(t_i)$ and do the integration. This is the upper trajectory in the figure below. $v(t_i)$ is, of course, the slope of the curve at $t_i$.



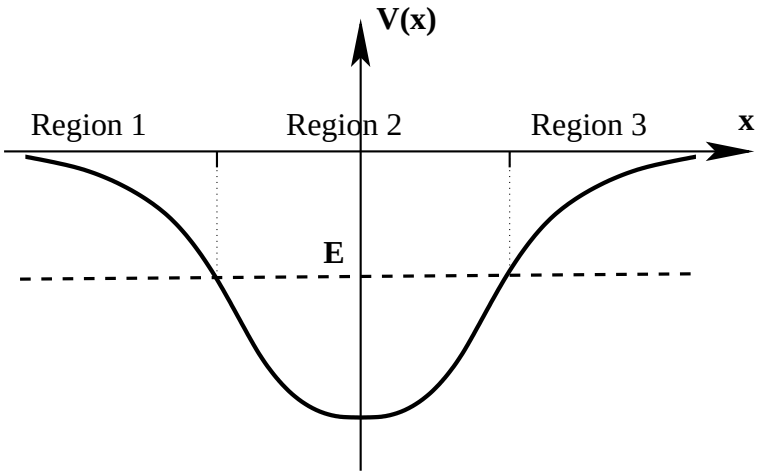

The resulting value of $x(t_f)$ will not, in general, equal the desired result, $X_f$. We therefore choose a *new value* for $v(t_i)$ and integrate again, shown as the lower trajectory in the figure. We continue to adjust the initial value of $v(t_i)$ until

$$x(t_f) - X_f = 0 \tag{1}$$

**using a root finding algorithm**. In other words we regard $x(t_f)$ as a function of $v(t_i)$. Since we don't know the derivative of this function, we can not use Newton-Raphson, and a safe method like bisection is recommended.

An important example of two point boundary value problems is the *eigenvalue* problem in quantum mechanics, which we discuss in the remainder of this handout. The independent variable will now be $x$, rather than $t$.

Consider a quantum mechanical particle of mass $m$ in one dimension moving in an attractive potential $V(x)$, see the figure below:




We shall assume in this handout that $\mathbf{V(x)}$ **is an even function of** $\mathbf{x}$, i.e. $V(-x) = V(x)$. This leads to certain simplifications, but the methods we describe can be extended to non-symmetric potentials without much additional difficulty.

The particle is described by a wavefunction $\psi(x)$, such that the probability the particle is between $x$ and $x + dx$ is given by $P(x)dx$ where

$$P(x) = |\psi(x)|^2 \,. \tag{2}$$

The probability distribution $P(x)$ is normalized to unity, i.e.

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1, \tag{3}$$

(since the particle must be somewhere). Here we shall consider only "bound states" where the particle is bound in the vicinity of the minimum of the potential, so $\psi$ must satisfy the boundary conditions

$$\psi(x) \to 0, \qquad (x \to \pm\infty). \tag{4}$$

Hence the boundary conditions are specified at two different values of $x$ so this is a two-point boundary value problem.

The allowed energy levels of the particle, $E$, are determined from the Schrödinger equation

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x),} \tag{5}$$

in which $\hbar$ is Planck's constant divided by $2\pi$. We require that $\psi(x)$ satisfy the boundary conditions, Eq. (4), which turns out to be possible only for certain discrete values of $E$, the "energy eigenvalues". The corresponding wavefunctions are called "eigenfunctions" or "eigenstates". All the problems we shall study have real Hamiltonians, as a result of which the wavefunctions can be chosen to be real.

It is convenient to rewrite Schrödinger's equation as

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

where

$$k^2(x) = \frac{2m}{\hbar^2}(E - V(x)). \tag{7}$$

In region 2 in the figure, where $E > V(x)$, we have $k^2(x) > 0$ and $\psi(x)$ oscillates. In regions 1 and 3, where $E < V(x)$, there are two independent solutions one of which tends to zero at large $x$ and the other of which diverges. To see this, we consider two possible behaviors for the potential at large $|x|$:

1. ***V*(*x*) tends to a constant**.

   This is the simplest case. We see that $k^2(x)$ becomes an negative constant which we call $-\kappa^2$. The solutions of

   $$\frac{d^2\psi}{dx^2} - \kappa^2\psi(x) = 0 \tag{8}$$

   are

   $$\psi(x) \propto e^{\kappa x}, \qquad \psi(x) \propto e^{-\kappa x}. \tag{9}$$

   We require that in both regions 1 and 3, only the decaying exponential is present. This is not possible in general and only occurs for certain discrete values of $E$.

2. ***V*(*x*) tends to $\infty$**.

   This is more complicated but there is still a solution which decays to zero (which we want)

and a second solution which diverges (which we don't want). A familiar example is the harmonic oscillator for which $V(x) \propto x^2$. It is shown in textbooks on quantum mechanics that the solutions at large $|x|$ have the form $\exp(-cx^2)$ and $\exp(+cx^2)$, where $c$ is a constant.

The values of $x$ where $E = V(x)$, which separate regions 1 and 2, and 2 and 3, are called "turning points".

## II. SHOOTING METHOD

### A. The basics

The standard technique for finding the energy levels $E$ is called the "shooting method". The basic idea is to start in region 1, say, and integrate through the turning point to region 2. We need to provide the value of $\psi(x)$ for two starting values of $x$, since Schrödinger's equation is second order, and will discuss in a moment how we do this. Let's call the resulting function $\psi_l(x)$. Next we repeat the procedure starting from region 3 and again integrate through the turning point (this time moving to the left). We call the resulting function $\psi_r(x)$.

The wavefunction and its derivative must be continuous, so we require $\psi_l(x) = \psi_r(x)$ and $\psi_l'(x) = \psi_r'(x)$ in region 2. However, since Schrödinger's equation is linear we can multiply $\psi_l$ and $\psi_r$ by a constant and the equation is still satisfied. Hence there is really only one matching condition which we could take to be

$$\boxed{\frac{\psi_l'(x)}{\psi_l(x)} = \frac{\psi_r'(x)}{\psi_r(x)}.} \tag{10}$$

In the general form of the shooting method one

**adjusts E (using a root-finding algorithm) until Eq. (10) is satisfied**

at some point in region 2, which is often taken to be one of the turning points.

However, as mentioned, we assume here that $V(x)$ is an even function of $x$, for which the **above procedure can be simplified**. It is shown in quantum mechanics books that the eigenfunctions $\psi(x)$ are either even or odd functions of $x$. Hence the criterion that $E$ is an eigenvalue simplifies to:

- Even eigenfunctions: integrate from region 1 to $x = 0$ and require that $\psi'(0) = 0$. Since we don't directly compute the derivative, but know the values of $\psi(x)$ at discrete values of $x$

separated by $h$, the criterion that the wavefunction is even will actually be $\psi(-h) = \psi(h)$. We then vary $E$ to make

$$\boxed{\psi(h) - \psi(-h) = 0, \qquad \text{(even eigenfunctions)}} \tag{11}$$

using a root finding algorithm such as bisection. The value of $E$ where Eq. (11) is satisfied is an eigenvalue, and the solution for $\psi(x)$ is the corresponding eigenfunction (which has even symmetry in this case).

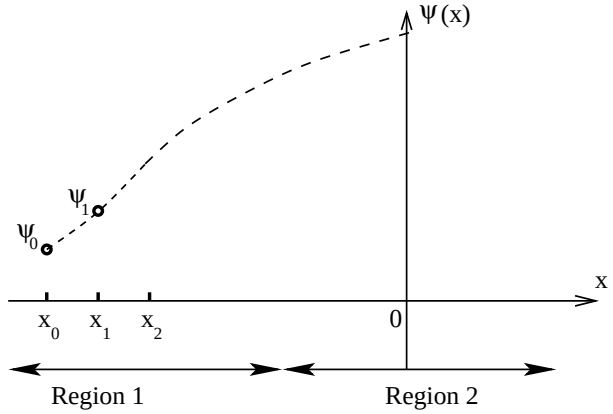
- Odd eigenfunctions: integrate from region 1 to $x = 0$ and vary $E$ using a root finding algorithm until

$$\boxed{\psi(0) = 0, \qquad \text{(odd eigenfunctions).}} \tag{12}$$

In one-dimension, one can show quite generally that the ground state wavefunction has no zeroes (nodes), the first excited state has 1 node, the second excited state 2 nodes, and so on. Hence the ground state must be even, the 1st excited state odd, the 2nd excited state even, etc. In the problems considered in this course we will generally have to calculate the ground state and 1st excited state (the lowest even and lowest odd states respectively).

### B. The starting values

There remains the question of how to specify the starting values, $\psi(x_0)$ and $\psi(x_1)$, where $x_0$ is well in region 1, and $x_1 = x_0 + h$. We want these to represent the solution which decays exponentially as one goes deeper into region 1.




The procedure is somewhat simpler if $V(x)$ tends to a constant at large $|x|$, so we consider the two possibilities:

1. **$V(x)$ tends to a constant**.

   If $V(x)$ tends to a constant (which we could take to be zero) at large $|x|$ we choose $x_0$ to be sufficiently negative that it is the region where $V(x)$ is constant, and take the decaying solution in Eq. (9), i.e. $\psi(x) \propto e^{\kappa x}$, where $\kappa^2 = 2m|E|/\hbar^2$. Hence the starting values are

$$\boxed{\psi_0 \equiv \psi(x_0) = \exp(\kappa x_0),} \tag{13a}$$

$$\boxed{\psi_1 \equiv \psi(x_1) = \exp(\kappa x_1),} \tag{13b}$$

   (see the above figure). Note that we have been able to choose the two initial conditions to match on to the (desired) decaying solution and eliminate the growing solution.

2. **$V(x)$ tends to $\infty$**.

   Here we do not know the exact form of the decaying solution, and so, unlike in the previous case, we don't know how to choose boundary conditions to match on to it. However, in the end, this does not matter, as we shall see. We take $x_0$ *deep* in region 1, so $V(x) \gg E$, and set

$$\boxed{\psi_0 = 0,} \tag{14a}$$

$$\boxed{\psi_1 = \text{const.}} \tag{14b}$$

   The value of the constant is unimportant since the equation is linear, but can conveniently be taken to be the step size $h$. The starting values in Eq. (14) do not correspond to just the decaying solution, but represent a linear combination of the decaying and increasing solutions. Since we want only the decaying solution, how can Eq. (14) be justified? The reason is that the unwanted solution increases when we go the left ($x$ more negative). However, we are integrating to the right where it *decreases* relative to the solution we want. Hence, if we start deep enough in region 1, the unwanted solution will have become negligible before we get to the turning point.

   By the same argument one should not integrate from region 2 into region 1 or 3, since any small piece of the unwanted solution will grow. (Hence the algorithm is unstable.) Instead, in the shooting method, one always integrates from region 1 or 3 into region 2, since the unwanted solution then diminishes. (This algorithm is therefore stable.)

## III. METHOD FOR DOING THE NUMERICAL INTEGRATION

To perform the numerical integration with sufficient accuracy one choice is fourth order Runge-Kutta. However, as we discuss in a separate handout, the **Numerov method**, which takes advantage of some special features of the Schrödinger equation, is perhaps to be preferred since it is one higher order than RK4 and also simpler.

## IV. SUMMARY

The eigenvalue problem discussed here is an example of a *two-point* boundary value problem, in which the boundary conditions are specified at two *different* points. In the present case these points are $x = \pm\infty$ and the boundary conditions there are that the wavefunction vanishes. This class of problem is more complicated than an *initial value* problem in which all the boundary conditions are at the *same point*. For two point boundary value problems we not only have to integrate numerically the equation, but the result of that integration has to be viewed as a function which is then put into a root finding algorithm to determine the eigenvalue (more generally to ensure that the second boundary condition is satisfied when integrating from the location of the first boundary condition).