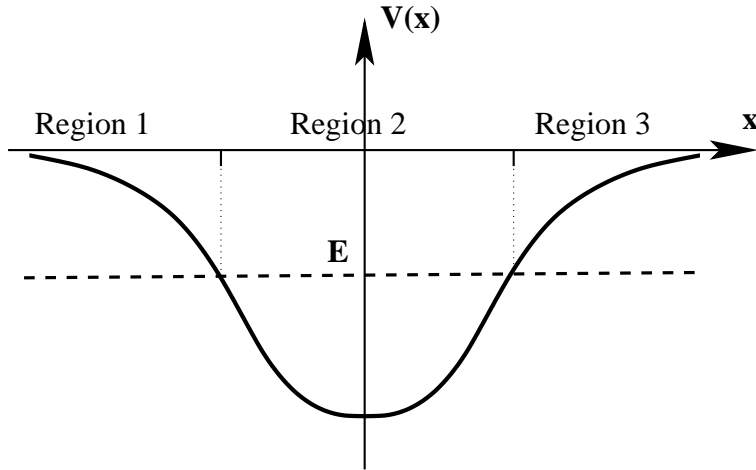


## Physics 115/242

### Eigenvalues of the Schrödinger Equation: the Shooting Method

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



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

$$P(x) = |\psi(x)|^2. \quad (1)$$

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

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

(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

$$\psi(x) \rightarrow 0, \quad (x \rightarrow \pm\infty). \quad (3)$$

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

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x), \quad (4)$$

in which  $\hbar$  is Planck’s constant divided by  $2\pi$ . We require that  $\psi(x)$  satisfy the boundary conditions, Eq. (3), which turns out to be possible only for certain discrete values of  $E$ , the “energy eigenvalues”. The corresponding wavefunctions are called “eigenfunctions” or “eigenstates”.

It is convenient to rewrite Schrödinger's equation as

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi(x) = 0, \quad (5)$$

where

$$k^2(x) = \frac{2m}{\hbar^2}(E - V(x)). \quad (6)$$

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, assume that for large  $x$ ,  $V(x)$  tends to a constant, so  $k^2(x)$  becomes a negative constant which we call  $-\kappa^2$ . The solutions of

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi(x) = 0 \quad (7)$$

are

$$\psi(x) \propto e^{\kappa x}, \quad \psi(x) \propto e^{-\kappa x}. \quad (8)$$

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  $E$ . Even if  $V(x)$  does not tend to a constant for large  $|x|$  there is still a solution which decays to zero (which we want) and a second solution which diverges (which we don't want). The values of  $x$  where  $E = V(x)$ , which separate regions 1 and 2, and 2 and 3, are called "turning points".

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  $\psi'_l(x)/\psi_l(x) = \psi'_r(x)/\psi_r(x)$ . This could be tested at one of the turning points. In the shooting method one adjusts  $E$  (using a root-finding algorithm) until this condition is satisfied.

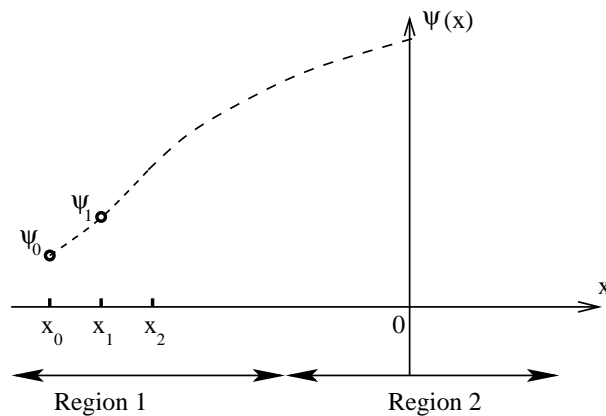
In the problems considered here, we will assume that  $V(x)$  is an even function of  $x$ , i.e.  $V(-x) = V(x)$ , for which the above procedure can be simplified. It is shown in the quantum mechanics books

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  $\psi(-h) = \psi(h)$ .
- Odd eigenfunctions: integrate from region 1 to  $x = 0$  and require that  $\psi(0) = 0$ .

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).

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.



If  $V(x)$  tends to a constant (which we could take to be zero) at large  $|x|$  then this is simple. Choose  $x_0$  to be sufficiently negative that it is the region where  $V(x)$  is constant, and take the decaying solution in Eq. (8), i.e.  $\psi(x) \propto e^{\kappa x}$ , where  $\kappa^2 = 2m|E|/\hbar^2$ . Hence the starting values are

$$\psi_0 \equiv \psi(x_0) = \exp(\kappa x_0), \quad (9)$$

$$\psi_1 \equiv \psi(x_1) = \exp(\kappa x_1), \quad (10)$$

(see the above figure).

However, we are also interested in problems in which  $V(x)$  continues to grow at large  $x$  rather than tends to a constant. A well known example is the simple harmonic oscillator for which

$V(x) = \frac{1}{2}kx^2$ . In these cases one takes  $x_0$  deep in region 1, so  $V(x) \gg E$ , and sets

$$\psi_0 = 0, \tag{11}$$

$$\psi_1 = \text{const.} \tag{12}$$

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 Eqs. (11) and (12) 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 Eqs. (11) and (12) 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.)

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 is another possibility since it is one higher order than RK4 and also simpler.