CHM 6480 - Quantum Mechanics
Handout 2

1. Solution to the particle in an infinite box potential

The simplest Schrodinger equation to solve is that for the particle in an infinite box potential (usually referred to as the particle in a box). We choose $V(x) = 0$ for $0 < |x| < b$, and $V(x) = \infty$ for $|x| \geq b$. Because this is a simple system it is often used to illustrate general properties of the Schrodinger equation and its solutions, such as normalization of wavefunctions, calculation of probabilities, and expectation values for operators. Here we discuss in detail how the solutions to an equation of this type can be found.

The Schrodinger equation for the particle in a box is (for $|x| < b$)

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\,\psi(x) \qquad (2.1.1)$$

Let us represent $\psi(x)$ in terms of an expansion in powers of x

$$\psi(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots = \Sigma_{n=0}^{\infty} a_n x^n \qquad (2.1.2)$$

The second derivative of this function is

$$\frac{d^2}{dx^2}\psi(x) = \psi(x)'' = 1{\cdot}2\, a_2 + 2{\cdot}3\, a_3 x + 3{\cdot}4\, a_4 x^2 + \ldots$$

$$= \Sigma_{n=0}^{\infty} (n+1)(n+2)\, a_{n+2} x^n \qquad (2.1.3)$$

If we substitute these relationships into Eq 2.1.1 we get

$$-\frac{\hbar^2}{2m}(1{\cdot}2\, a_2 + 2{\cdot}3\, a_3 x + 3{\cdot}4\, a_4 x^2 + \ldots) = E\,(a_0 + a_1 x + a_2 x^2 + \ldots) \qquad (2.1.4)$$

or

$$-\frac{\hbar^2}{2m}\Sigma_{n=0}^{\infty} (n+1)(n+2)\, a_{n+2} x^n = E\,\Sigma_{n=0}^{\infty} a_n x^n \qquad (2.1.5)$$

or, bringing the constants over to the right side of the equation

$$\Sigma_{n=0}^{\infty} a_{n+2} x^n = -\frac{2mE}{\hbar^2}\Sigma_{n=0}^{\infty}\frac{a_n x^n}{(n+1)(n+2)} \qquad (2.1.6)$$

For equation 2.1.6 to be true in in general for values of x inside the box the left and right sides of the equation must be equal term by term, that is, the coefficients for each power of x must be the same for the left and right terms. This means

$$a_2 = (-2mE/\hbar^2)\frac{a_0}{(1{\cdot}2)} \qquad (2.1.7)$$

$$a_3 = (-2mE/\hbar^2)\frac{a_1}{(2{\cdot}3)} \qquad (2.1.8)$$

$$a_4 = (-2mE/\hbar^2)\frac{a_2}{(3{\cdot}4)} = (-2mE/\hbar^2)^2\frac{a_0}{(1{\cdot}2{\cdot}3{\cdot}4)} \qquad (2.1.9)$$

$$a_5 = (-2mE/\hbar^2)\frac{a_3}{(4{\cdot}5)} = (-2mE/\hbar^2)^2\frac{a_1}{(1{\cdot}2{\cdot}3{\cdot}4{\cdot}5)} \qquad (2.1.10)$$

We can divide this series of terms for an into two series, one for even a_n and one for odd a_n. The result is the following pair of relationships, called recursion relationships

$$a_{2n} = (-1)^n (2mE/\hbar^2)^n \frac{a_0}{(2n)!} \tag{2.1.11}$$

$$a_{2n+1} = (-1)^n (2mE/\hbar^2)^n \frac{a_1}{(2n+1)!} \tag{2.1.12}$$

If we substitute into Eq 2.1.2, we get

$$\psi(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots = (a_0 + a_2x^2 + a_4x^4 + \ldots) + (a_1x + a_3x^3 + a_5x^5 + \ldots) \tag{2.1.13}$$

$$= a_0 \Sigma_{n=0}^{\infty} (-1)^n (2mE/\hbar^2)^n [x^{2n}/(2n)!] + a_1 \Sigma_{n=0}^{\infty} (-1)^n (2mE/\hbar^2)^n [x^{2n+1}/(2n+1)!] \tag{2.1.14}$$

If we compare the above to the power series expansions for cosine and sine

$$\cos\phi = 1 - (\phi^2/2!) + (\phi^4/4!) - \ldots = \Sigma_{n=0}^{\infty} (-1)^n [\phi^{2n}/(2n)!] \tag{2.1.15}$$

$$\sin\phi = \phi - (\phi^3/3!) + (\phi^5/5!) - \ldots = \Sigma_{n=0}^{\infty} (-1)^n [\phi^{2n+1}/(2n+1)!] \tag{2.1.16}$$

we see that they have the same form. If we set $\phi = (2mE/\hbar^2)^{1/2}\, x = kx$, where $k = (2mE/\hbar^2)^{1/2}$, then Eq 2.1.14 can be rewritten to give

$$\psi(x) = a_0 \cos kx + a_1 \sin kx \tag{2.1.17}$$

Possible values for E are found from the boundary conditions

$$\psi(-b) = \psi(b) = 0 \tag{2.1.18}$$

The first boundary condition requires

$$\psi(-b) = 0 = a_0 \cos(-kb) + a_1 \sin(-kb) = a_0 \cos(kb) - a_1 \sin(kb) \tag{2.1.19}$$

where we have used the fact that cos(x) is an even function and sin(x) is an odd function to rewrite Eq 2.1.19. The second boundary condition requires

$$\psi(b) = 0 = a_0 \cos(kb) + a_1 \sin(kb) \tag{2.1.20}$$

There are only two cases where Eq 2.1.19 and 2.1.20 can be satisfied, corresponding to even and odd solutions to the particle in a box

Even solutions

$$a_1 = 0 \,;\ \cos(kb) = 0 \qquad \text{and so } kb = (s + \tfrac{1}{2})\pi \,;\ s = 0, 1, 2, \ldots \tag{2.1.21}$$

Odd solutions

$$a_0 = 0 \,;\ \sin(kb) = 0 \qquad \text{and so } kb = s'\pi \,;\ s' = 1, 2, \ldots \tag{2.1.22}$$

We may write the above wavefunctions and their corresponding energy eigenvalues in terms of a single quantum number n. The normalized wavefunctions and allowed values of energy are then given by the following

Even solutions (|x| < b)

$$\psi_n(x) = (1/b)^{1/2} \cos(n\pi x/2b) \qquad n = 1, 3, 5, ... \tag{2.1.23}$$

Odd solutions (|x| < b)

$$\psi_n(x) = (1/b)^{1/2} \sin(n\pi x/2b) \qquad n = 2, 4, 6, ... \tag{2.1.24}$$

Eigenvalues (allowed values for energy)

$$E_n = \frac{n^2\pi^2\hbar^2}{8mb^2} = \frac{n^2h^2}{32mb^2} \qquad n = 1, 2, 3, ... \tag{2.1.25}$$

Properties of the solution to the particle in a box and their use in illustrating general concepts in quantum mechanics are discussed in undergraduate texts.

2. Even and odd functions

A function is an even function if f(-x) = f(x) for all x, and an odd function if f(-x) = - f(x) for all x. Examples of even functions include x^2, cos(x), and exp($-ax^2$). Examples of odd functions include x and sin(x). Some functions are neither even nor odd, as, for example, $x^2 + x$ and exp(x).

A useful property for integrals of even and odd functions is the following:

$$\int_{-a}^{a} f(x)\, dx = 2 \int_0^a f(x)\, dx \text{ if f(x) is an even function} \tag{2.2.1}$$

$$\int_{-a}^{a} f(x)\, dx = 0 \text{ if f(x) is an odd function} \tag{2.2.2}$$

3. General solution to the Schrodinger equation for a step potential

A one dimensional step potential is a potential where the potential energy V_0 is constant over some region of x. The general solution to the Schrodinger equation for such a potential depends on whether $E > V_0$ or $E < V_0$.

If $E > V_0$, then

$$\psi(x) = A \exp(ikx) + B \exp(-ikx) \tag{2.3.1}$$

where $k = [2m(E-V_0)/\hbar^2]^{1/2}$, and A and B are constants.

If $E < V_0$, then

$$\psi(x) = C \exp(Kx) + D \exp(-Kx) \tag{2.3.2}$$

where $K = [2m(V_0-E)/\hbar^2]^{1/2}$, and C and D are constants.

Note that we have defined k and K such that they take on positive values. Both k and K have dimensions of 1/(length). Also note that k and K are related to the momentum of the particle. For $E > V_0$, $p^2 = \hbar^2 k^2$, while for $E < V_0$, $p^2 = - \hbar^2 K^2$. Notice that in the second case we get an imaginary value for momentum, not really surprising, since it corresponds to the particle being in a region where the potential energy is greater than the total energy, which requires the kinetic energy to be negative. Such regions are inaccessible according to classical mechanics but not according to quantum mechanics.

4. Solution to the particle in a finite box potential

In 2.1 we discussed the Schrodinger equation for a particle in an infinite box potential (Fig 2.4.1). Here we consider the case of a particle in a finite box potential, that is, a potential that is zero inside the box and a constant value V_0 outside the box.

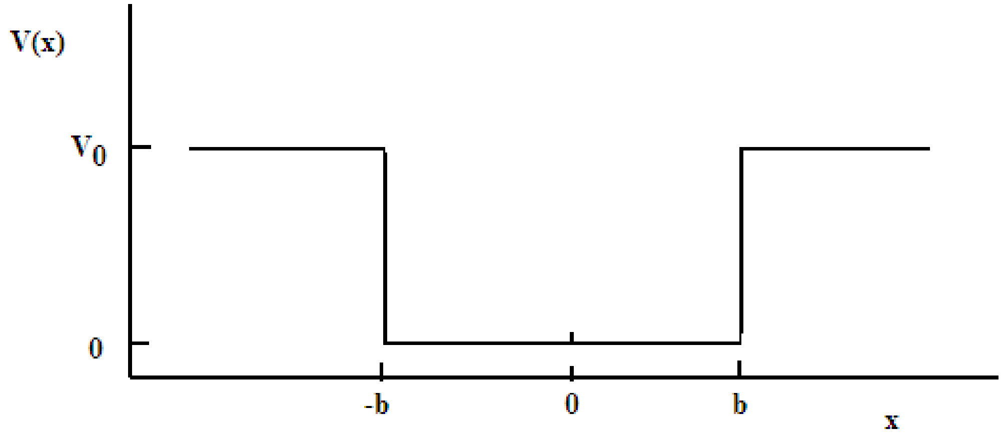

Figure 2.4.1. Particle in a finite box potential.

To take advantage of the symmetry of the potential we define our system as follows

$V_0 = 0$ for $|x| < b$; V_0 = constant for $|x| \geq b$. (2.4.1)

Note that the size of the box is 2b.

We will first focus on the bound solutions to this problem. Using the general solutions that apply for step potentials (section 2.3) we can write down the solutions as follows

$x \leq -b$

$\psi(x) = A \exp(Kx) + B \exp(-Kx)$ (2.4.2)

$-b < x < b$

$\psi(x) = C \exp(ikx) + D \exp(-ikx)$ (2.4.3)

$x \geq b$

$\psi(x) = F \exp(Kx) + G \exp(-Kx)$ (2.4.4)

where $K = [2m(V_0-E)/\hbar^2]^{1/2}$, $k = [2mE/\hbar^2]^{1/2}$, and A, B, C, D, F, and G are constants.

Constraints on the values of the above constants can be found from the limiting behavior of the wavefunction. Since $\psi(x) \to 0$ as $x \to \pm \infty$ (from the normalizability requirement) it follows that B = F = 0.

The requirement that the wavefunction and its first derivative are continuous places additional constraints on the values for the constants. At x = -b, we get, from continuity of the wavefunction and its first derivative, that

$A \exp(-Kb) = C \exp(-ikb) + D \exp(ikb)$ (2.4.5)

$KA \exp(-Kb) = ikC \exp(-ikb) - ikD \exp(ikb)$ (2.4.6) while at x = b, we get, from continuity of the wavefunction and its first derivative, that

$$G \exp(-Kb) = C \exp(ikb) + D \exp(-ikb) \qquad (2.4.7)$$

$$- KG \exp(-Kb) = ikC \exp(ikb) - ikD \exp(-ikb) \qquad (2.4.8)$$

Eq 2.4.5 and 2.4.6 can be combined to show that

$$C/D = - [(K + ik)/(K - ik)] \exp(2ikb) \qquad (2.4.9)$$

while Eq 2.4.7 and 2.4.8 can be combined to show that

$$C/D = - [(K - ik)/(K + ik)] \exp(-2ikb) \qquad (2.4.10)$$

If we take the product of Eq 2.4.9 and 2.4.10 we get $C^2/D^2 = 1$, from which it follows that $D = \pm C$. For the case D = C the wavefunctions that are solutions to this system are even functions, with G = A, while for the case D = - C the wavefunctions are odd functions, with G = -A.

The values for E (energy) for the bound state solutions can be found using either Eq 2.4.9 or 2.4.10. For the even solutions (C/D = 1) substitution into Eq 2.4.9 gives the requirement that

$$\alpha \tan(\alpha) = \beta \qquad (2.4.11)$$

while for the odd solutions (C/D = -1) substitution into Eq 2.4.9 gives the requirement that

$$\alpha \cot(\alpha) = - \beta \qquad (2.4.12)$$

where α and β are dimensionless parameters defined by the expressions $\alpha = kb$ and $\beta = Kb$. We may also show that

$$\alpha^2 + \beta^2 = 2mV_0b^2/\hbar^2 \qquad (2.4.13)$$

Possible values for energy are found by determining values for α and β that are simultaneous solutions to Eq 2.4.11 and 2.4.13 (for the even solutions) or Eq 2.4.12 and 2.4.13 (for the odd solutions). This is most conveniently done graphically by plotting Eq 2.4.11, 2.4.12 and 2.4.13 as illustrated below. The points where the plot of Eq 2.4.11 or 2.4.12 intersects with the plot of Eq 2.3.13 correspond to the values for α and β for even and odd solutions respectively. Values for E can be determined from the values of α found by this procedure, as shown in Fig 2.4.2. Close examination of Fig 2.4.2 shows that there must be at least one bound solution to the particle in a finite box, even for a shallow potential.

Wavefunctions may also be found for states with $E > V_0$. These are basically free particle wavefunctions modified by the potential well. As is the case for the free particle wavefunction there are two solutions for every value of energy.

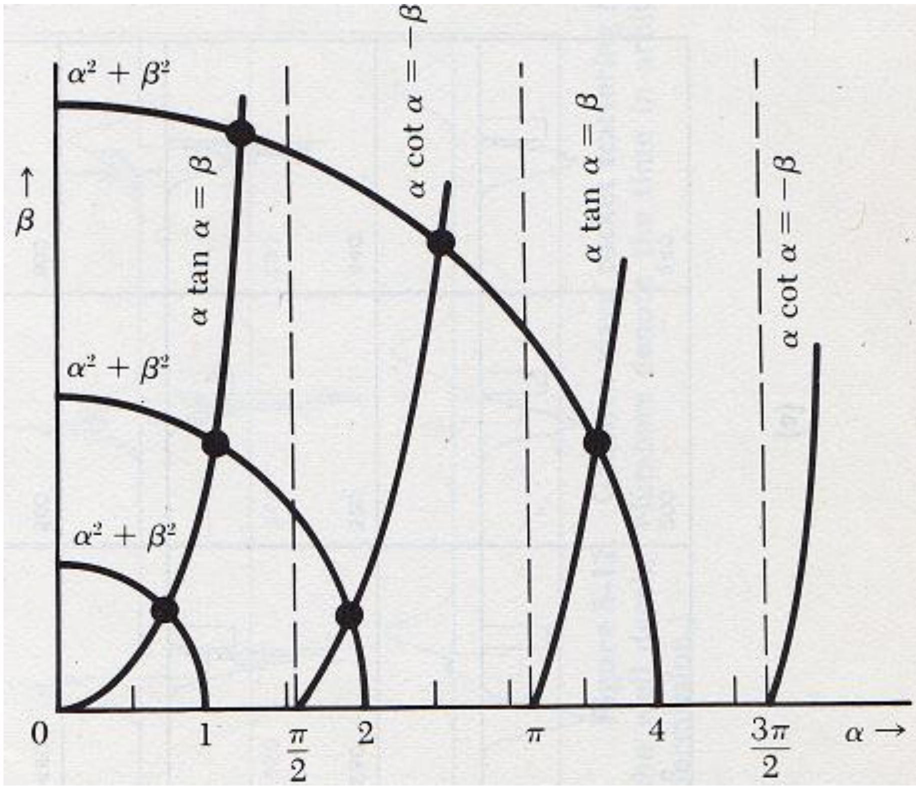

Figure 2.4.1. Graphical method for determining eigenvalues for the particle in a finite box. Points where the plot of $\alpha^2 + \beta^2$ = (constant) intersect with a plot of $\alpha \tan(\alpha) = \beta$ correspond to even solutions, while intersections with a plot of $\alpha \cot(\alpha) = -\beta$ correspond to odd solutions. Notice that there must be at least one bound even solution to this system.

5. Scattering and tunneling

Consider a potential barrier where (Fig 2.5.1)

$$V_0 = 0 \text{ for } |x| \geq b;\ V_0 = \text{constant for } |x| < b \qquad (2.5.1)$$

We may use the same methods used in 2.4 to find solutions to the Schrodinger equation corresponding to this system. However, here we will simply discuss some of the general properties of the solution.

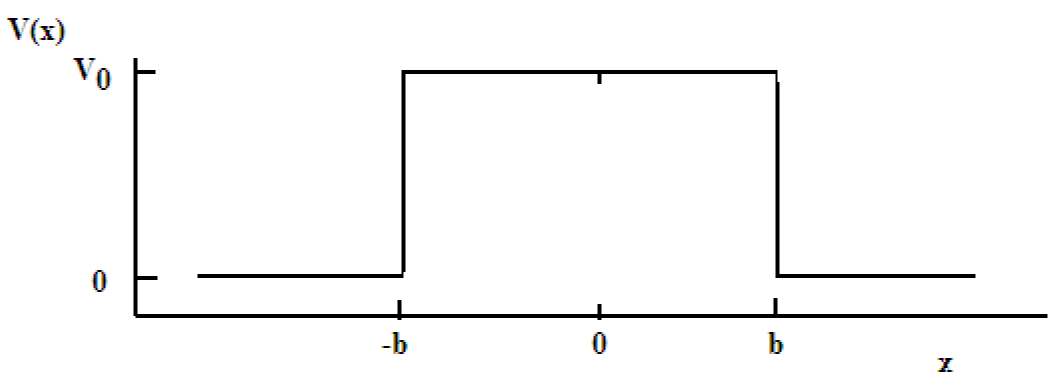

Figure 2.5.1. Finite potential barrier.

Consider a particle approaching a potential of the form shown in Fig 2.5.1 from the left. Classically, the particle will bounce back (reflect) from the potential if $E < V_0$, and will pass (transmit) over the potential if $E > V_0$, where V_0 is the height of the barrier. If we define the transmission coefficient T as probability the particle will pass over the barrier, and the reflection coefficient R as the probability that the particle will be reflected off of the potential, we can say that classically T = 0 (and R = 1) when $E < V_0$, and T = 1 (and R = 0) when $E > V_0$.

The behavior seen in the quantum mechanical analogue to this system is different than what is observed classically, particularly when $E \sim V_0$ and when the width of the barrier is small. In those cases the transmission coefficient will be larger than zero even when $E < V_0$ and will be less than 1 even when $E > V_0$. The transmission coefficient will also show fluctuations, called resonances, in the region where the energy of the particle is slightly larger than the height of the barrier, as seen in Fig 2.5.2. The passage of particles through the potential barrier when $E < V_0$, which is classically forbidden, is called tunneling. Tunneling is important in the movement of electrons through potential barriers and of hydrogen atoms through potential barriers in some chemical reactions. Tunneling can also be used to explain α emission by radioactive nuclei. Equations for the transmission coefficient and its dependence on energy can be found using the same methods used to find solutions to the particle in a finite box.

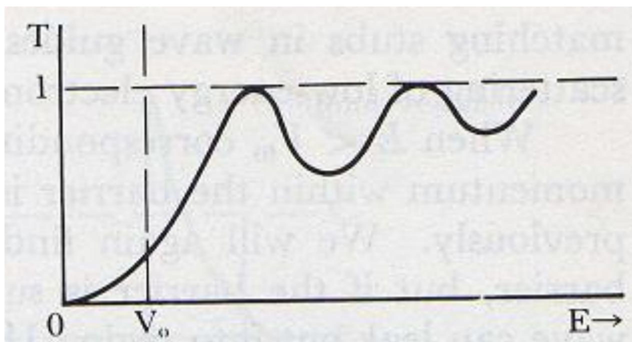

Figure 2.5.2. Transmission coefficient (T) vs particle energy for a potential barrier of the form given in Fig 2.5.1. Classically T = 0 when $E < V_0$ and T = 1 when $E > V_0$. The quantum mecanical behavior is different, showing both tunneling (for $E < V_0$) and resonances (for $E > V_0$).