1 Particle in a Box

1.1 Infinite Square Well

So far we have considered only the case in which the potential energy is zero, i. e., there is no force acting on a particle. The general treatment of arbitrary potentials in quantum mechanics is mathematically involved. However, the case in which the potential takes on the form

$$U(x) = \begin{cases} 0 & x > 0 \text{ and } x < a \\ \infty & \text{otherwise} \end{cases}, \tag{1}$$

where a is a constant, is easy to solve. This potential is called the *infinite square well*, and the solution for $0 < x < a$ is the same as that for a free particle, namely some superposition of plane waves. At $x = 0,\ a$ we must have $\psi = 0$. This tells us which plane waves are allowed in the superposition.

A single plane wave moving the the positive x direction, $\psi = \exp[i(kx - \omega t)]$, is clearly unable to satisfy the condition $\psi = 0$ at $x = 0,\ a$. However, note that subtracting from this wave one moving in the negative x direction, $\psi = \exp[i(-kx - \omega t)]$, results in the following waveform:

$$\psi(x,t) = \exp[i(kx - \omega t)] - \exp[i(-kx - \omega t)] = 2i\exp(-i\omega t)\sin(kx). \tag{2}$$

This wavefunction is automatically zero when $x = 0$. (Would this have been true if we had added the two waves rather than subtracting them?) It is zero at $x = a$ if $ka = n\pi$, where $n = 0,\ 1,\ 2,\ \ldots$. We omit $n = 0$ because this would cause $\psi = 0$ *everywhere* — a not very interesting case!

Solving for k, and calling it k_n, we find that $k_n = n\pi/a$. However, recalling the de Broglie relationship, $p = \hbar k$, we see that the wavefunction is composed of two plane waves with momenta $p_n = \pm n\pi\hbar/a$. We finally note that both waves have the same total energy, E, given in this case by $E = K = p^2/2m$, where K is the kinetic energy and m is the mass of the particle. Thus, a particle in an infinite square well potential can take on only discrete values of the energy given by

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \qquad n = 1,\ 2,\ 3,\ \ldots. \tag{3}$$

Figure 1 shows the energy levels and wavefunctions for the first three states of the infinite square well.

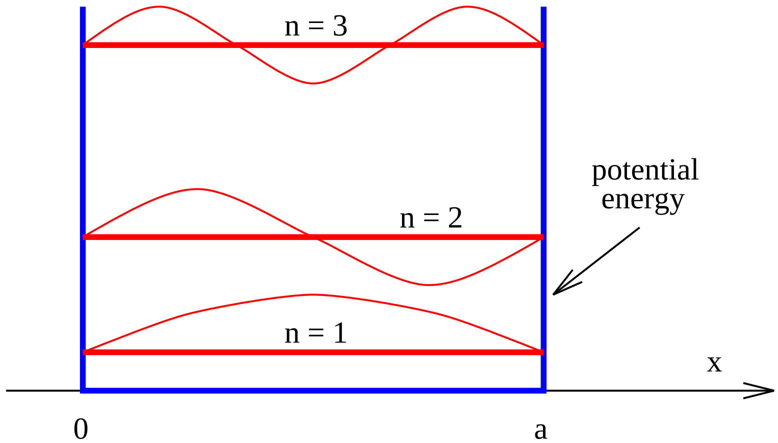

Figure 1: Energy levels and wavefunctions for the first three energy levels of the infinite square well.

Note that the spacing between energy levels varies inversely as the square of the size, a, of the potential well. Since $\hbar$ is so small, the spacing between levels will only be significant for very small masses and well dimensions. For everyday objects and potentials in particular, the spacing will be undetectably small. Nevertheless this "quantization" of the energy is extremely important on the atomic level, as it means that the electrons in an atom cannot take on arbitrary energy values, but are limited to those allowed by quantum mechanics. Note in particular that the lowest energy is not zero, but is some value higher than would be allowed by classical mechanics.

1.2 Finite Square Well

A slightly more interesting problem is that of the finite square well. Figure 2 shows the potential energy function $U(x)$ for this case. If a particle of mass m has a negative total energy $E = -E_B$, where the *binding energy* $E_B > 0$, then the wave function $\psi(x)$ turns out to be either symmetric or antisymmetric about $x = 0$, i. e., either $\psi(-x) = \psi(x)$ or $\psi(-x) = -\psi(x)$. This is a consequence of the symmetry of the potential energy function about $x = 0$. The symmetric solutions are of the form

$$\psi(x) = A\cos(kx), \quad 0 < x < a/2 \tag{4}$$

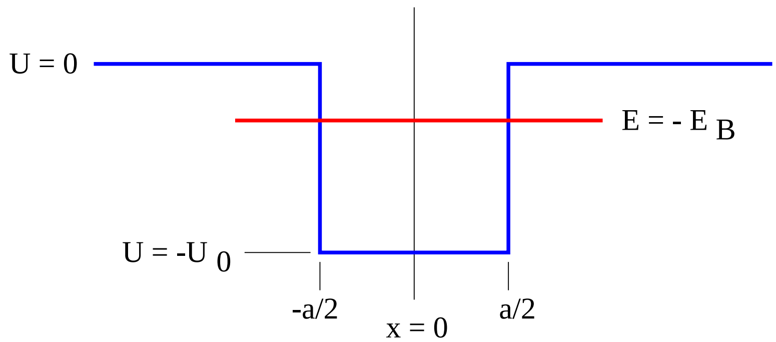

Figure 2: Definition sketch for the finite square well.

$$\psi(x) = B \exp(-\kappa x), \quad x > a/2. \tag{5}$$

Schrödinger's equation demands that ψ and $d\psi/dx$ be continuous at $x = a/2$, which leads to the equation

$$\begin{pmatrix} \cos(ka/2) & \exp(-\kappa a/2) \\ k \sin(ka/2) & -\kappa \exp(-\kappa a/2) \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = 0. \tag{6}$$

This only has a non-trivial solution if

$$-\kappa \cos(ka/2) \exp(-\kappa a/2) + k \sin(ka/2) \exp(-\kappa a/2) = 0, \tag{7}$$

which simplifies to

$$\kappa/k = \tan(ka/2). \tag{8}$$

The wavenumber k inside the well is $k = [2m(U_0 - E_B)]^{1/2}/\hbar$. Outside the well the wavenumber is imaginary. We write $k = i\kappa$ there and find that $\kappa = (2mE_B)^{1/2}/\hbar$. If we let $\epsilon = E_B/U_0$ and $\alpha = a(mU_0/2)^{1/2}/\hbar$, then the above equation can be written

$$\left(\frac{\epsilon}{1-\epsilon}\right)^{1/2} - \tan[\alpha(1-\epsilon)^{1/2}] = 0. \tag{9}$$

The parameter ϵ is a non-dimensionalized binding energy, while α is a combination of constants which characterizes the behavior of the particle in the well.

We can obtain a graphical solution to this equation by plotting the left side as a function of ϵ for a given value of α. The solutions occur where the

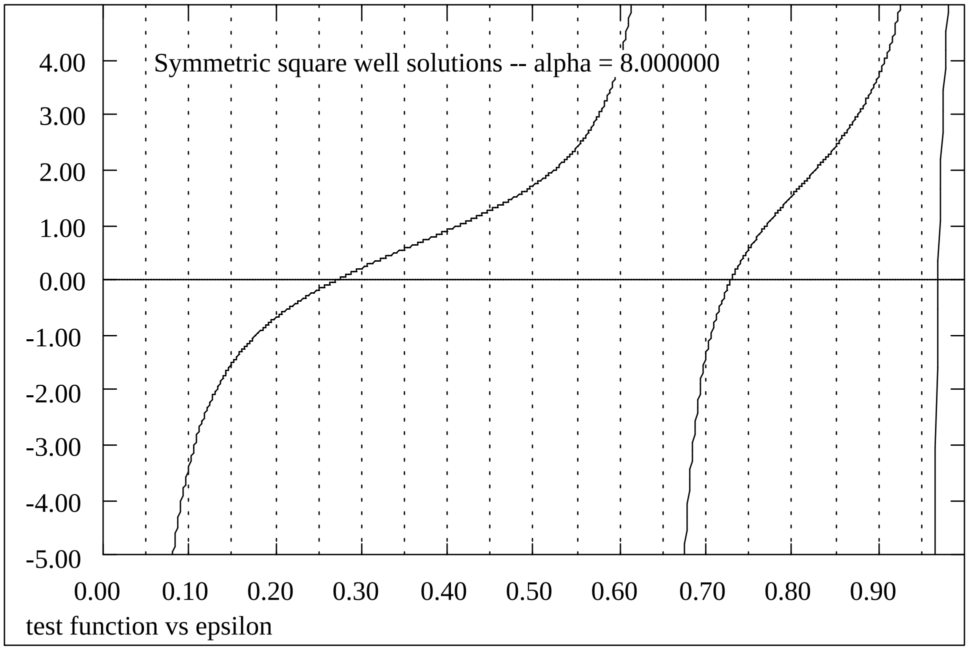

Figure 3: Example of numerical solution to equation (9). The allowed values of the dimensionless binding energy $\epsilon = E_B/U_0$ occur where the function crosses the horizontal axis.

α	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	ϵ_6	ϵ_7
1	0.45		—		—		—
2	0.73		—		—		—
3	0.85		—		—		—
4	0.90		0.19		—		—
5	0.93		0.41		—		—
6	0.95		0.56		—		—
7	0.96		0.66		0.11		—
8	0.97		0.73		0.27		—
9	0.98		0.78		0.40		—
10	0.98		0.82		0.50		0.07

Table 1: Scaled binding energies for the symmetric solutions of the finite square well. Space is left to insert the energies for the antisymmetric solutions.

function is zero. Figure 3 shows an example of this technique for $\alpha = 8$. Solutions occur near $\epsilon = 0.27$, $\epsilon = 0.73$, and $\epsilon = 0.97$.

Table 1 shows the approximate scaled binding energies as a function of α for the symmetric solutions to the finite square well. Unlike the infinite well, the finite well exhibits only a finite number of bound states. This number depends on α, but a minimum of one symmetric solution always exists. The antisymmetric solutions can be found by a similar technique — however, this is left as an exercise for the reader.