19.2: The Particle in a Box

Now we can consider a particle constrained to move in a single dimension, under the influence of a potential $V(x)$ which is zero for $0 \leq x \leq a$ and infinite elsewhere. Since the wavefunction is not allowed to become infinite, it must have a value of zero where $V(x)$ is infinite, so $\psi(x)$ is nonzero only within $[0, a]$. The Schrödinger equation is thus:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x) \qquad 0 \leq x \leq a. \tag{19.2.1}$$

In other words, inside the box $\psi(x)$ describes a free particle, but outside the box $\psi(x) = 0$. Since the Schrödinger equation involves derivatives, the function that solves it, $\psi(x)$, must be everywhere continuous and everywhere continuously differentiable. This fact means that the value of the wave function at the two extremes must be equal to zero:

$$\psi(0) = \psi(a) = 0. \tag{19.2.2}$$

Inside the box we can use Euler's formula to write the wave function as a linear combination of the positive and negative solutions:

$$\psi(x) = A\exp(\pm ix) = A\sin kx + B\cos kx, \tag{19.2.3}$$

where A and B are constants that we need to determine using the two constraints in Equation 19.2.2. For B it is straightforward to see that:

$$\psi(0) = 0 + B = 0 \implies B = 0. \tag{19.2.4}$$

For A we have:

$$\psi(a) = A\sin ka = 0, \tag{19.2.5}$$

which is trivially solved by $A = 0$, or by the more interesting condition of $ka = n\pi$. The trivial solution corresponds to a wave function uniformly equal to zero everywhere. This wave function is uninteresting, since it describes no particles in no boxes. The second set of solutions, however, is very interesting, since we can write it as:

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right) \quad n = 1, 2, \ldots, \infty, \tag{19.2.6}$$

which represents an infinite set of functions, $\psi_n(x)$, determined by a positive integer number n, called *quantum number*. Since these functions solve the TISEq, they are also called *eigenfunctions*, but they are not a continuous set, unlike in the previous case. To calculate the energy eigenvalues, we can replace 19.2.6 into Equation 19.2.1, to obtain:

$$E_n = \frac{h^2 n^2}{8ma^2} \quad n = 1, 2, \ldots, \infty. \tag{19.2.7}$$

A few interesting considerations can be made from the results of Equation 19.2.7. First, although there is an infinite number of acceptable values of the energy (eigenvalues), these values are not continuous. Second, the lowest value of the energy is not zero, and it depends on the size of the box, a, since:

$$E_1 = \frac{h^2}{8ma^2} \neq 0. \tag{19.2.8}$$

This value is called *zero-point energy (ZPE)*, and is a purely quantum mechanical effect. Notice that we did not solve for the constant A. This task is not straightforward, and it can be achieved by requiring the wave function to describe one particle exclusively (we will come back to this task after chapter 23). Extending the problem to three dimensions is relatively straightforward, resulting in a set of three separate quantum numbers (one for each of the 3-dimensional coordinate n_x, n_y, n_z).