Wavefunction in a 1D or 3D Box

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A "box" is a region (between x = 0 and x = L) where the potential is zero, but such that the potential becomes infinite at the walls, i.e., at x = 0 and x = L. This means that the wavefunction must become zero at x = 0 and x = L. But for $0 < x < L$ the wavefunction must obey the 'free particle' Schrodinger equations, i.e., with zero potential, which in 1D is simply,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi \tag{1}$$

The general solution to (1) is $\psi = Ae^{ikx} + Be^{-ikx}$, where,

$$E = \frac{\hbar^2 k^2}{2m} \qquad \text{or,} \qquad k = \frac{\sqrt{2mE}}{\hbar} \tag{2}$$

The requirement that the wavefunction vanish at at x = 0 and x = L gives us,

$$A + B = 0 \qquad \text{and} \qquad Ae^{ikL} + Be^{-ikL} = 0 \tag{3}$$

These give

$$Ae^{ikL} - Ae^{-ikL} = 0 \tag{4}$$

Since $e^{i\theta} = \cos\theta + i\sin\theta$ this becomes $\sin 2kL = 0$, the solution to which is,

$$k = \frac{n\pi}{L} \qquad \text{for } n = 1, 2, 3, \ldots. \tag{5}$$

Substitution into (2) gives the energy levels,

$$E_n = \frac{1}{2m}\left(\frac{\pi \cdot n \cdot \hbar}{L}\right)^2 \tag{6}$$

This is the simplest example of how discrete quantum states arise, with only certain discrete energy levels being permitted. The lowest possible energy of a particle which has been confined in a box of size L is,

$$E_1 = \frac{1}{2m}\left(\frac{\pi \cdot \hbar}{L}\right)^2 \tag{7}$$

So, in quantum mechanics, it is contradictory to think that a particle can have zero energy if you've confined it in a small space. For example, confining an electron in a box the size of an atom, (7) implies a minimum energy of ~38eV.

[*The actual energy of an electron in an atom is negative, of course, due to the electrostatic attraction to the nucleus – its not 'free' inside the 'box'*].

The wavefunction is $\psi = Ae^{ikx} - Ae^{-ikx} = 2iA\sin kx = \tilde{A}\sin kx$. The constant is found from the normalisation condition, i.e.,

$$\int_0^L |\psi|^2 dx = 1 = \int_0^L |\tilde{A}|^2 \sin^2 kx \cdot dx \tag{8}$$

The integral can be evaluated with the help of a trigonometric identity,

$$\cos 2\theta \equiv 1 - 2\sin^2\theta \qquad \text{which gives} \qquad \sin^2\theta = \frac{1-\cos 2\theta}{2} \tag{9}$$

Hence, $\int_0^L \left|\tilde{A}\right|^2 \sin^2 kx \cdot dx = \left|\tilde{A}\right|^2 \int_0^L \left(\frac{1-\cos 2kx}{2}\right) \cdot dx = \left|\tilde{A}\right|^2 \left[\frac{x}{2} - \frac{\sin 2kx}{4k}\right]_0^L = \left|\tilde{A}\right|^2 \frac{L}{2} = 1$ (10)

The last step follows because $\sin 2kL = 0$ by virtue of (5). So we get,

$$\left|\tilde{A}\right| = \sqrt{\frac{2}{L}} \qquad (11)$$

Note that only the magnitude of the normalisation constant is defined. The phase is irrelevant – but we can take it to be real. So finally the normalised wavefunction is,

$$\psi = \sqrt{\frac{2}{L}} \sin kx \qquad (12)$$

Inserting (5), the n'th energy state is,

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) \qquad (13)$$

for n = 1, 2, 3,….

The lowest energy state (*n* = 1) has half a wavelength within the box.

The next state (*n* = 2) has a whole wavelength within the box.

The next (*n* = 3) has one-and-a-half wavelengths within the box, etc.

This easily generalised to a **3D box**, which gives an overall wavefunction which is the product of three factors, each of which is just like (13), giving,

$$\psi_{nmq} = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n\pi}{L} x\right) \sin\left(\frac{m\pi}{L} y\right) \sin\left(\frac{q\pi}{L} z\right) \qquad (14)$$

where each of *n, m* and *q* are quantum numbers which can take values 1, 2, 3…

The fact that there are 3 quantum numbers in 3D is something that you will see again for atoms. These three *n, m, q* quantum numbers become the three *n, l, m* quantum numbers for atomic electrons.