Topic: Particle in a Three Dimensional Box

Wave function

In quantum physics, a wave function is a mathematical description of a quantum state of a particle as a function of momentum, time, position and spin. The symbol used for a wave function is a Greek letter called psi, ψ. It helps us to know the probability of finding particle within the matter

Some properties of wave function

- All measurable information about the particle is available.
- ψ should be continuous and single-valued.
- It should be finite.
- It should be square Integrable.
- ψ^2 gives us probability of finding the particle.

Normalization and Probability

- The probability $P(x)\,dx$ of a particle being between x and $x + dx$ was given in the equation

$$P(x)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx$$

- The probability of the particle being between x_1 and x_2 is given by

$$P = \int_{x_1}^{x_2} \Psi^* \Psi \, dx$$

- The wave function must also be normalized so that the probability of the particle being somewhere on the x axis is 1.

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx = 1$$

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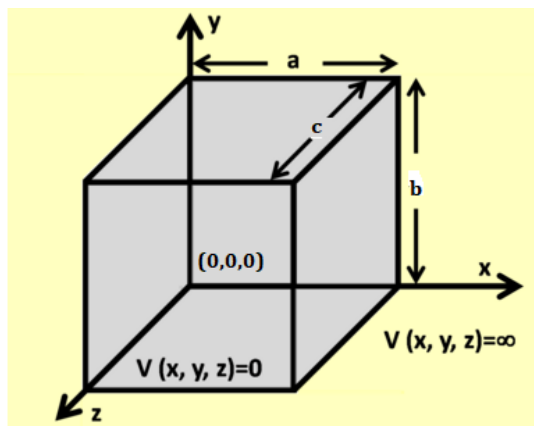
Boundary conditions

1) In order to avoid infinite probabilities, the wave function must be finite everywhere.
2) In order to avoid multiple values of the probability, the wave function must be single valued.
3) For finite potentials, the wave function and its derivative must be continuous. This is required because the second-order derivative term in the wave equation must be single valued. (There are exceptions to this rule when *V* is infinite.)
4) In order to normalize the wave functions, they must approach zero as *x* approaches infinity.

- Solutions that do not satisfy these properties do not generally correspond to physically realizable circumstances.

Particle in a 3D Box

A real box has three dimensions. Consider a particle which can move freely with in rectangular box of dimensions a × b × c with impenetrable walls. The potential can be written mathematically as;



$$V = \begin{cases} 0 & \text{Inside} \\ \infty & \text{At surfaces and outside} \end{cases}$$

Since the wavefunction ψ should be well behaved, so, it must vanish everywhere outside the box. By the continuity requirement, the wavefunction must also vanish in the six surfaces of the box. Orienting the box so its edges are parallel to the cartesian axes, with one corner at (0,0,0), the following boundary conditions must be satisfied:

ψ(x,y, z) = 0 when x = 0, x = a, y = 0, y = b, z = 0 or z = c

Inside the box, where the potential energy is everywhere zero, the Hamiltonian is simply the three-dimensional kinetic energy operator and the Schrodinger equation reads

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E(x,y,z) \qquad (1)$$

Since we can write ψ(x,y, z) = X(x)Y(y)Z(z), with condition X(x) is independent of y and z coordinates. Also, Y(y) and Z(z) are only functions of y and z, respectively. The boundary conditions are

X(0) = X(a) = 0, Y (0) = Y (b) = 0, Z(0) = Z(c) = 0 (2)

So, on substituting (x,y, z) = X(x)Y(y)Z(z) into Schrodinger equation we obtain

$$\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)} + \frac{2mE}{\hbar^2} = 0 \qquad (3)$$

Each of the first three terms depends on one variable only, independent of the other two. We can write it as;

$$\frac{X''(x)}{X(x)} = -\left[\frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)} + \frac{2mE}{\hbar^2}\right]$$

Now on left hand side (LHS) we have only function of x, while right hand side (RHS) contains functions of y and z. This is possible only if each term separately equals a constant, say, $-\alpha^2$. So,

$$\frac{X''(x)}{X(x)} = -\left[\frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)} + \frac{2mE}{\hbar^2}\right] = -\alpha^2.$$

$$\Rightarrow \frac{X''(x)}{X(x)} = -\alpha^2 \qquad (4)$$

That implies $\left[\frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)} + \frac{2mE}{\hbar^2}\right] = \alpha^2$ which can be transformed into $\frac{Y''(y)}{Y(y)} = \alpha^2 - \left[\frac{Z''(z)}{Z(z)} + \frac{2mE}{\hbar^2}\right]$; Using similar argument as above both sides of eqution should be equal to a constant, say, $-\beta^2$;

Therefore, $\frac{Y''(y)}{Y(y)} = \alpha^2 - \left[\frac{Z''(z)}{Z(z)} + \frac{2mE}{\hbar^2}\right] = -\beta^2$

$$\Rightarrow \frac{Y''(y)}{Y(y)} = -\beta^2 \qquad (5)$$

And

$$\alpha^2 - \left[\frac{Z''(z)}{Z(z)} + \frac{2mE}{\hbar^2}\right] = -\beta^2$$

$$\Rightarrow \frac{Z''(z)}{Z(z)} = \alpha^2 + \beta^2 - \frac{2mE}{\hbar^2}$$

Now, LHS of above equation is just a constant so we can write it as a $\frac{Z''(z)}{Z(z)} = -\gamma^2$ (6)

Thereby we have transformed a single Schrodinger equation (1) into three ordinary differential equations

$X'' + \alpha^2 X = 0\,; Y'' + \beta^2 Y = 0$ and $Z'' + \gamma^2 Z = 0$

The constants α, β and γ are related by

$$\frac{2mE}{\hbar^2} = \alpha^2 + \beta^2 + \gamma^2 \qquad (7)$$

Each of the equations (4, 5 and 6) with its associated boundary conditions in (2) is equivalent to the one-dimensional problem. The normalized solutions X(x), Y (y), Z(z) can therefore be written down in complete analogy with one dimensional box

$$X_{n1}(x) = \left(\frac{2}{a}\right)^{1/2} Sin\,\frac{n_1 \pi x}{a}\,; \qquad n_1 = 1,2,3\ldots.. \qquad (8)$$

$$Y_{n2}(x) = \left(\frac{2}{a}\right)^{1/2} Sin\,\frac{n_2 \pi y}{b}\,; \qquad n_2 = 1,2,3\ldots. \qquad (9).$$

$$Z_{n3}(x) = \left(\frac{2}{a}\right)^{1/2} Sin\,\frac{n_2 \pi z}{c}\,; \qquad n_3 = 1,2,3\ldots.. \qquad (10)$$

The constants in Eq (7) are given by

$$\alpha = \frac{n_1 \pi}{a}\,;\ \beta = \frac{n_2 \pi}{b} \text{ and } \gamma = \frac{n_3 \pi}{c}$$

and the allowed energy levels are therefore

$$E_{n_1,n_2,n_3} = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right), \qquad n_1, n_2, n_3 = 1, 2\ldots \qquad (11)$$

Three quantum numbers are required to specify the state of this three dimensional system. The corresponding eigen-functions are

$$\psi_{n_1,n_2,n_3}(x,y,z) = \left(\frac{8}{V}\right)^{1/2} Sin\,\frac{n_1 \pi x}{a}\, Sin\,\frac{n_2 \pi x}{b}\, Sin\,\frac{n_3 \pi x}{c} \qquad (12)$$

where V = abc, the volume of the box. These eigen-functions form an ortho-normal set such that

$$\int_0^a\int_0^b\int_0^c \psi_{n'_1,n'_2,n'_3}(x,y,z)\psi_{n_1,n_2,n_3}(x,y,z)\,dxdydz = \delta_{n'_1,n_1}\delta_{n'_2,n_2}\delta_{n'_3,n_3}$$

Note that two eigen-functions will be orthogonal unless all three quantum numbers match.

When the box has the symmetry of a cube, with a = b = c, the energy formula (11) simplifies to

$$E_{n_1,n_2,n_3} = \frac{h^2}{8ma^2}\left(n_1^2 + n_2^2 + n_3^2\right), \qquad n_1, n_2, n_3 = 1, 2\ldots \qquad (13)$$

Quantum systems with symmetry generally exhibit degeneracy in their energy levels. This means that there can exist distinct eigenfunctions which share the same eigenvalue. An eigenvalue which corresponds to a unique eigenfunction is termed nondegenerate while one which belongs to n different eigenfunctions is termed n-fold degenerate. As an example, we enumerate the first few levels for a cubic box, with E_{n_1,n_2,n_3} expressed in units in units of $h^2/8ma^2$.

$E_{1,1,1} = 3$ (nondegenerate)
$E_{1,1,2} = E_{1,2,1} = E_{2,1,1} = 6$ (3-fold degenerate)
$E_{1,2,2} = E_{2,1,2} = E_{2,2,1} = 9$ (3-fold degenerate)
$E_{1,1,3} = E_{1,3,1} = E_{3,1,1} = 11$ (3-fold degenerate)
$E_{2,2,2} = 12$ (nondegenerate)
$E_{1,2,3} = E_{1,3,2} = E_{2,1,3} = E_{2,3,1} = E_{3,1,2} = E_{3,2,1} = 14$ (6-fold degenerate)