Zero point energy

$$n_x = 1 \quad n_y = 1 \quad \Rightarrow E_{11} = \frac{h^2}{4m\ell^2}$$

Particle in Three Dimensional Box

Now we will discuss the motion of particle of mass m in a three dimensional box. As in one dimensional box in three dimensional box also, the potential energy is zero with in the box and infinite outside the box.
So three dimensional schrodinger equatioin.

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + \frac{8\pi^2 m}{h^2} E\psi = 0 \qquad ...(1)$$

Where the function ψ will depend upon three independent variable x, y, z to solve the above equation we write the function ψ as the product of three wave function.
Schrodinger wave equation for a particle in three D box.

$$\frac{\partial^2\psi(x,y,z)}{\partial x^2} + \frac{\partial^2\psi(x,y,z)}{\partial y^2} + \frac{\partial^2\psi(x,y,z)}{\partial z^2} + \frac{8\pi^2 m}{\hbar^2}$$

$$\boxed{\psi_{(x,y,z)} = X_{(x)} Y_{(y)} Z_{(z)}}$$

where, $X_{(x)} Y_{(y)} Z_{(z)}$ are three function.

Same as, $\dfrac{\partial^2\psi(x,y,z)}{dy^2} = Z(z)X(x)\dfrac{\partial^2 Y(y)}{\partial y^2}$

$$\frac{\partial^2\psi(x,y,z)}{dz^2} = X(x)Y(y)\frac{\partial^2 Z(z)}{\partial z^2}$$

Put this value in equation (1).

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(XYZ) + \frac{8\pi^2 m}{h^2} E(XYZ) = 0 \qquad ...(2)$$

$$YZ\left(\frac{\partial^2}{\partial x^2} X\right) + XZ\left(\frac{\partial^2}{\partial y^2} Y\right) + XY\left(\frac{\partial^2}{\partial z^2} Z\right) + \frac{8\pi^2 m}{h^2} EXYZ = 0 \qquad ...(3)$$

Dividing by XYZ, we have.

$$\frac{1}{X}\left(\frac{\partial^2}{\partial x^2} X\right) + \frac{1}{Y}\left(\frac{\partial^2}{\partial y^2} Y\right) + \frac{1}{Z}\left(\frac{\partial^2}{\partial z^2} Z\right) = -\frac{8\pi^2 mE_x}{h^2} - \frac{8\pi^2 mE_y}{h^2} - \frac{8\pi^2 mE_z}{h^2} = -\alpha^2 E \qquad ...(4)$$

The term α^2 inthe above equation is a constant quantity. Hence the sum of the three terms on the left hand side of equation (4) must also be a constnat quantity. If we change the value of x (or y or z) keeping the other two variables constants even then the above constancy has to be satisfied. This is possible only when each term is independent of the other terms and each is equal to a constant quantity so that the sum of three constants is equal to α^2.
So we write.

$$\frac{1}{X}\frac{\partial^2}{\partial x^2} X = -\alpha_x^2 \qquad ...(5)$$

$$\frac{1}{Y}\frac{\partial^2}{\partial y^2} Y = -\alpha_y^2 \qquad ...(6)$$

$$\frac{1}{Z}\frac{\partial^2}{\partial z^2}Z = -\alpha_z^2 \qquad ...(7)$$

where, $$\alpha_x^2 = \frac{8\pi^2 m}{h^2}E_x \qquad ...(8)$$

$$\alpha_y^2 = \frac{8\pi^2 m}{h^2}E_y \qquad ...(9)$$

$$\alpha_z^2 = \frac{8\pi^2 m}{h^2}E_Z \qquad ...(10)$$

with, $$\alpha^2 = \alpha_x^2 + \alpha_y^2 + \alpha_z^2 \qquad ...(11)$$

and $$E = E_x + E_y + E_z \qquad ...(12)$$

Now we have three separate equations to be solved each of them has a form of one-domensional box. Thus the normalized wave function of a three-dimensional box is

$$\psi = XYZ = \left(\sqrt{\frac{2}{\ell_1}}\sin\frac{n_x\pi}{\ell_1}x\right)\left(\sqrt{\frac{2}{\ell_2}}\sin\frac{n_y\pi}{\ell_2}y\right)\left(\sqrt{\frac{2}{\ell_3}}\sin\frac{n_z\pi}{\ell_3}z\right)$$

$$\Rightarrow \quad \psi = \sqrt{\frac{8}{\ell_1\ell_2\ell_2}}\sin\left(\frac{n_x\pi}{\ell_1}x\right)\sin\left(\frac{n_y\pi}{\ell_2}y\right)\sin\left(\frac{n_z\pi}{\ell_3}z\right) \qquad ...(13)$$

The constant α_x, α_y *and* α_z will be given by.

$$\alpha_x = \frac{n_x\pi}{l_1}, \alpha_y = \frac{n_y\pi}{l_2} \text{ and } \alpha_z = \frac{n_z\pi}{l_3} \qquad ...(14)$$

and total energy is $$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{l_1^2} + \frac{n_y^2}{l_2^2} + \frac{n_z^2}{l_3^2}\right) \qquad ...(15)$$

There are three quantum numbers one each for energy degree of freedom.

If $\ell_1 = \ell_1 = \ell_3 = \ell$, then $E = \dfrac{h^2}{8m\ell^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

then the energy state will be degenerate.

Degeneracy of 3-D box: