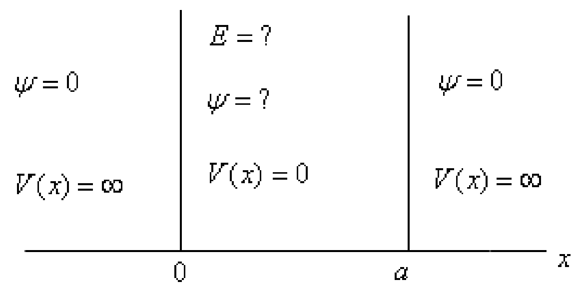
3-4 Particle in a box

Let's now try to investigate a free particle moves in a potential distribution as shown below;

$$V(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & 0 \ge x \ge a \end{cases}$$



It is seen that for such a system the particle is restricted to move in the confined region $0 \le x \le a$ due to the infinite potential value that prevents the particle to penetrate the barrier at $x = 0$ and $x = a$. This system looks like a molecule in a gas cylinder that can't escape out due to the solid walls of the cylinder. In addition, this system is similar to a free electron in metals.

H.W: Prove mathematically that ψ=0 in the regions $0 \ge x \ge a$ and state the physical meaning for that.

Anyway Schrodinger equation in the region under consideration is given by;

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \qquad \text{.............(3-23)}$$

Keeping in mind that $k^2 = \frac{2mE}{\hbar^2}$, the solution of this equation is;

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad \text{.............(3-24)}$$

The constants A and B can found as before with aid of the boundary condition as in below. Indeed, at x=0 the wave function in (3-24) vanishes, i.e. $\psi(x=0)=0$. So, $A+B=0$ and hence $A=-B$, therefore;

$$\psi(x) = A(e^{ikx} - e^{-ikx})$$

Using Euler's method last equation becomes; $e^{\pm i\theta} = \cos\theta \pm i\sin\theta$

$$\psi(x) = A(\cos kx + i\sin kx - \cos kx + i\sin kx) \longrightarrow$$

$$\psi(x) = 2iA\sin kx$$

$$\psi(x) = C\sin kx$$

Where $C = 2iA$, and similarly at $x=a$ the wave function is also vanishes, i.e. $\psi(x=a) = 0$, therefore;

$$\psi(x=a) = C\sin ka = 0$$

This requires that; $\sin ka = 0$, which leads to $ka = n\pi$ and thus;

$$k = \frac{n\pi}{a}$$

Consequently, the energy eigen values and eigen wave functions of a particle moving in a potential box becomes respectively as follows;

$$E_n = \frac{\pi^2\hbar^2 n^2}{2ma^2} \quad \text{and} \quad \psi_n(x) = C\sin(n\pi x/a)$$

It is obvious that the energy of this system is quantize because the particle is confine in a limited region by means of the potential. Accordingly, we may draw the following;

$n = 4$ ______________________ $E_4 = 16E_1$

$n = 3$ ______________________ $E_3 = 9E_1$

$n = 2$ ______________________ $E_2 = 4E_1$

$n = 1$ ______________________ $E_1 = \dfrac{\pi^2\hbar^2}{2ma^2}$

Indeed, the energy of ground state, $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$ call Zero Point Energy. Concerning with the wave function ($\psi_n(x) = C\sin(n\pi x/a)$) the normalization constant C can found as follows;

$$\int \psi_n^*(x)\psi_n(x)\ dx = 1$$

$$\int C^* \sin(n\pi x/a)\ C\ \sin(n\pi x/a)\ dx = 1$$

$$C^2 \int_0^a \sin^2(n\pi x/a)\ dx = 1$$

Using the identity; $\sin^2\theta = \frac{1}{2}(1-\cos 2\theta)$,we get;

$$\frac{1}{2}C^2\left\{\int_0^a dx - \int_0^a \cos(2n\pi x/a)\ dx\right\} = 1$$

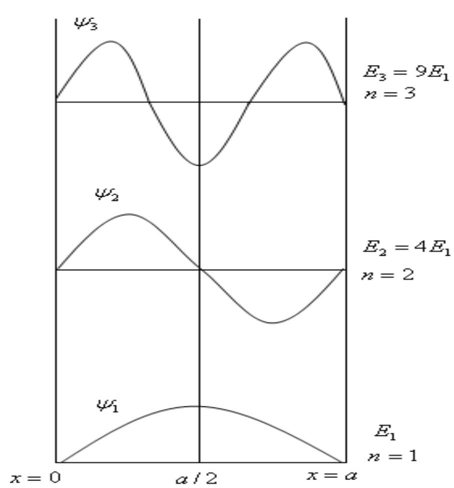
$$\tfrac{1}{2}C^2\left\{x\Big|_0^a - (\frac{a}{2n\pi})\sin(2n\pi x/a)\Big|_0^a\right\} = 1$$

$$\tfrac{1}{2}C^2\{(a-0) - (a/2n\pi)(0-0)\} = 1$$

$$\tfrac{1}{2}C^2 a = 1 \longrightarrow \quad C = \sqrt{\tfrac{2}{a}}$$

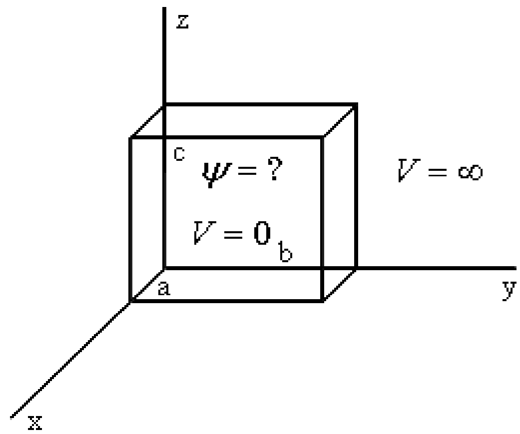
$$\therefore \quad \psi_n(x) = \sqrt{\tfrac{2}{a}}\sin(n\pi x/a)$$

The figure below shows the first three eigen wave functions ψ_1, ψ_2, ψ_3.



3.5 Particle in potential box in three dimensions

The same procedure used in last section repeats here but in three dimensions *x,y* and *z* instead of one. So, the particle now moves freely in a box of dimensions *a,b* and *c* as shown in figure below.



The Schrödinger equation for this system must written as follows;

$$\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}\frac{\partial^2\psi(x,y,z)}{\partial z^2}+k^2\,\psi(x,y,z)=0 \quad \ldots\ldots\ldots\ldots..(3\text{-}25)$$

Keeping in mind that; $k^2=\frac{2mE}{\hbar^2}$. However, to solve this equation the method of separating of variables must be use. Accordingly, we may write;

$$\psi(x,y,z)=\psi(x)\cdot\psi(y)\cdot\psi(z) \quad \ldots\ldots\ldots\ldots..(3\text{-}26)$$

The substitution of equation (3-26) into equation (2-25) and dividing the resultant expression on equation (3-26) leads to;

$$\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+\frac{1}{\psi(y)}\frac{d^2\psi(y)}{dy^2}+\frac{1}{\psi(z)}\frac{d^2\psi(z)}{dz^2}+k^2=0 \quad \ldots\ldots\ldots\ldots..(3\text{-}27a)$$

Or;

$$\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+k_x^2+\frac{1}{\psi(y)}\frac{d^2\psi(y)}{dy^2}+k_y^2+\frac{1}{\psi(z)}\frac{d^2\psi(z)}{dz^2}+k_z^2=0 \quad \ldots\ldots..(3\text{-}27b)$$

Which is equivalent to;

$$\frac{d^2\psi(x)}{dx^2} + k_x^2\psi(x) = 0$$
$$\frac{d^2\psi(y)}{dy^2} + k_y^2\psi(y) = 0 \qquad \text{…………..(3-27c)}$$
$$\frac{d^2\psi(z)}{dz^2} + k_z^2\psi(z) = 0$$

The solution of each of thses three equations is as shown below respectively;

$$\psi(x) = A_x e^{ik_x} + B_x e^{-ik_x}$$
$$\psi(y) = A_y e^{ik_y} + B_y e^{-ik_y} \qquad \text{…………..(3-28)}$$
$$\psi(x) = A_z e^{ik_x} + B_z e^{-ik_z}$$

By using the boundary conditions [$\psi(x=0, x=a) = 0$, $\psi\ (y=0, y=b) = 0$, $\psi(z=0, z=c)$ $= 0$], we can get;

$$\psi(x) = C_x\ sink_x x$$
$$\psi(y) = C_y\ sink_y y \qquad \text{…………..(3-29)}$$
$$\psi(z) = C_z\ sink_z z$$

Therefore the wave function of this system is as follows;

$$\psi(x,y,z) = C_x\ sin(k_x x). C_y\ sin(k_y y). C_z\ \sin(k_z z) \qquad \text{………..(3-30)}$$

Remember that; $k_x = n_x\pi/a$, $k_y = n_y\pi/b$ and$k_z = n_z\pi/c$ one get;

$$\psi(x,y,z) = C\ \sin(\frac{n_x\pi}{a}x).\sin(\frac{n_y\pi}{b}y).\sin(\frac{n_z\pi}{c}z) \qquad \text{…..……..(3-31)}$$

H.W: Show that; $C = \sqrt{\frac{8}{abc}}$

Concerning with energy eigen values we have that; $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$, so;

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2).$$

The substituation of thevalues of $k_x = n_x\pi/a$, $k_y = n_y\pi/b$ and $k_z = n_z\pi/c$ leads to;

$$E = \frac{\hbar^2\pi^2}{2m}(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}) \qquad \text{…..……..(3-32)}$$

For the case when $a=b=c$ last formula becomes;

$$E = \frac{\hbar^2 \pi}{2ma^2}(n_x^2 + n_y^2 + n_z^2) \qquad \text{…..……..(3-33)}$$

Or equvilently;

$$E = E_1\left(n_x^2 + n_y^2 + n_z^2\right) = E_1 n^2 \qquad \text{…..……..(3-34)}$$

Equation (3-34) represent the the allowable energies eigen values, however it indicates that all of the states characterized by (n_x,n_y,n_z) that gives the same value of N have the same value of energy. Indeed, this is directly shows to the degeneracy where there are more than one wave function describe the same state, see the table below.

Degeneracy	Combination of (n_x,n_y,n_z)	Energy
1	(1,1,1)	$3E_1$
3	(1,1,2) (1,2,1) (2,1,1)	$6E_1$
3	(1,2,2) (2,1,2) (2,2,1)	$9E_1$
3	(3,1,1) (1,3,1) (1,1,3)	$11E_1$
1	(2,2,2)	$12E_1$
6	(1,2,3) (3,2,1) (2,3,1) (1,3,2) (2,1,3) (3,1,2)	$14E_1$