Ex2: Calculate P_x^2 for the particle in a box the operator of P_x^2 is: $p_x^2 = -\hbar^2 \frac{d^2}{dx^2}$

The wavefunction Ψ is $\Psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ is an eigenfunction of P_x^2 $\therefore$ we can calculate the precise value of P_x

The equation to be solve is: $\hat{P}_x^2 \Psi = P_x^2 \Psi$

$$-\hbar^2 \frac{d^2\Psi}{dx^2} = p_x{}^2\Psi \quad \text{eigenvalue equation}$$

$$\frac{\mathrm{d}\Psi}{\mathrm{dx}} = \frac{d}{dx}\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} = \sqrt{\frac{2}{a}}\cos\frac{n\pi x}{a}\left(\frac{n\pi}{a}\right)$$

$$\frac{d^2\Psi}{dx^2} = \sqrt{\frac{2}{a}}\left(\frac{n\pi}{a}\right)^2\left(-\sin\frac{n\pi x}{a}\right) = -\left(\frac{n\pi}{a}\right)^2\sqrt{\frac{2}{a}}\left(\sin\frac{n\pi x}{a}\right)$$

$$\therefore -\hbar^2 \frac{d^2\Psi}{dx^2} = \frac{n^2\pi^2\hbar^2}{a^2}\Psi$$

$$p_x{}^2 = \frac{n^2\pi^2\hbar^2}{a^2} = \frac{n^2h^2}{4a^2} = 2mE_n$$

$$\therefore p_x{}^2 = \pm\sqrt{2mE_n} = \pm\frac{nh}{2a}$$

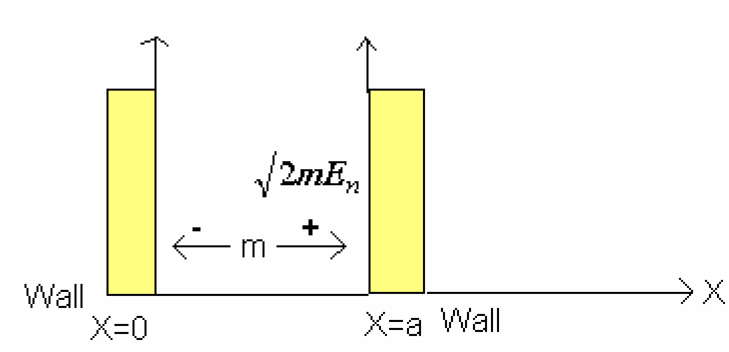
The paradox between the results of exercise (1) and (2) is resolved when we realize that the energy of $+\sqrt{2mE_n}$ and $-\sqrt{2\mathrm{mE_n}}$ *is Zero*

Thus the maximum uncertainty in momentum is $2\sqrt{2mE_n}$ similarly the maximum uncertainty in the position of the particle is a ⟶

$$\therefore \Delta X \Delta P_x = a\left(2\sqrt{2mE_n}\right)$$

$$= 2a\frac{nh}{2a}$$
$$= nh$$
$$= h(\ for\ n = 1)$$

ΔX is uncertainty in position and ΔP_x is uncertainty in momentum



This is a form of " Heisenberg uncertainty principle" Which stated that the simultaneous measurement of both the position and momentum of a particle cannot be made to an accuracy greater than Planck's constant h. If one of these is measured with high accuracy the uncertainty in the other will be greater.

Ex-3: Evaluate the integral $\int_0^a \Psi_1 \Psi_2 dx$ For a particle in a box

$$\int_0^a \sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}dx$$

$$= \frac{2}{a}\int_0^a \sin\frac{\pi x}{a}\left(2\sin\frac{\pi x}{a}\cos\frac{\pi x}{a}\right)dx$$

$$= \frac{4}{a}.\frac{a}{\pi}\int\left(\sin\frac{\pi x}{a}\right)^2\cos\frac{\pi x}{a}\left(\frac{\pi}{a}\right)dx$$

$$= \frac{4}{a}.\frac{1}{3}\left[\sin^3\frac{n\pi}{a}\right]_0^a = 0$$

This is another feature of the solution of the particle in a box problem. It can be shown that:

$$\int_{\text{all space}} \Psi i \Psi j d\tau = 0 \ \text{ For } i \neq j$$

ΨI and Ψj are said to be orthogonal. Orthogonally is very important property in quantum mechanics.

$$\langle p_x \rangle = \frac{\int \Psi \hat{p}_x \Psi dx}{\int \Psi_1 \Psi_1 dx}$$

In general

$$\int_{all\ space} \Psi i \Psi j d\tau = \delta ij$$

$$\delta ij = 1 \quad for \quad i = j \quad and \quad \delta ij = 0 \quad for \quad i \neq j$$

δ_{ij} is called Kronecker delta. The above equation is true for a set of quantum mechanical function the set is said to be orthonormal.

Particle In three Dimensional Box:

It is to illustrate the : (a) The technique of separation of variables which is widely used in Q.Ms. (b) To illustrate how degenerate states (states with equal energy) arise.

The Schrödinger equation for a particle in a 3-D box is:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi = E\Psi$$

$$or\ \nabla^2\Psi = \frac{-2mE}{\hbar^2}\Psi \ \text{ or } \frac{d^2}{dx^2}\Psi + \frac{d^2}{dy^2}\Psi + \frac{d^2}{dz^2}\Psi = \frac{-2mE}{\hbar^2}\Psi$$

The technique of separation of variables involves finding a solution of the box:

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

Where each of the wavefunction X, Y, Z is function of a single coordinate, i.e. X is a function of X only and so on.

Schrödinger equation becomes:

$$yz\frac{d^2x}{dx^2} + xz\frac{d^2y}{dy^2} + xy\frac{d^2z}{dz^2} = \frac{-2mE}{\hbar^2}xyz$$

Dividing both sides of the equation by xyz we get →

$$\frac{1}{x}\frac{d^2x}{dx^2}+\frac{1}{y}\frac{d^2y}{dy^2}+\frac{1}{z}\frac{d^2z}{dz^2}=\frac{-2mE}{\hbar^2}$$

$$\frac{1}{x}\frac{d^2x}{dx^2}+\frac{1}{y}\frac{d^2y}{dy^2}+\frac{2mE}{\hbar^2}=-\frac{1}{z}\frac{d^2z}{dz^2}$$

The right hand side is a function of z only whereas the left side is a function of x and y. Therefore, for this equation to be true for all values of x,y and z both sides of the equation must be equal to a constant. We at this point call this constant

$\frac{2mE_z}{\hbar^2}$ thus:

$$-\frac{1}{z}\frac{d^2z}{dz^2}=\frac{2mE_z}{\hbar^2}$$

Now the main equation could be arranged to gives:

$$\frac{1}{x}\frac{d^2x}{dx^2}+-\frac{1}{z}\frac{d^2z}{dz^2}+\frac{2mE_z}{\hbar^2}=-\frac{1}{y}\frac{d^2y}{dy^2}=Cons.$$

Applying the same argument as above both sides of this equation must be equal a constant, which in this case will be equal to $\frac{2mE_y}{\hbar^2}$

Finally the main equation rearranged to give

$$\frac{1}{y}\frac{d^2y}{dy^2}+\frac{1}{z}\frac{d^2z}{dz^2}+\frac{2mE}{\hbar^2}=-\frac{1}{x}\frac{d^2x}{dx^2}=\frac{2mE_x}{\hbar^2}$$

Thus the 3-D problem has been split into three unidimensional problems which are:

$$\frac{d^2x}{dx^2} = \frac{-2mE_x}{\hbar^2}X \qquad \frac{d^2y}{dy^2} = \frac{-2mE_y}{\hbar^2}Y \qquad \frac{d^2z}{dz^2} = \frac{-2mE_z}{\hbar^2}Z$$

This equations are of the same form as the equation of a particle in 1-D box except that Ψ has been replaced by E_x, E_y and E_z, therefore, similar solution if a, b and c are the dimensional of the box in the x, y and z directions respectively then:

$$X = \sqrt{\frac{2}{a}}\sin\frac{n_x\pi x}{a}\ ,\ E_x = \frac{n^2{}_x h^2}{8ma^2}$$

$$Y = \sqrt{\frac{2}{b}}\sin\frac{n_y\pi y}{b}\ ,\ E_y = \frac{n^2{}_y h^2}{8mb^2}$$

$$Z = \sqrt{\frac{2}{c}}\sin\frac{n_z\pi z}{c}\ ,\ E_z = \frac{n^2{}_z h^2}{8mc^2}$$

$$\Psi = XYZ = \sqrt{\frac{8}{abc}}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\sin\frac{n_z\pi z}{c}$$

$$E = E_x + E_y + E_z$$

$$E = \frac{h2}{8m}\left(\frac{n_x{}^2}{a^2} + \frac{n_y{}^2}{b^2} + \frac{n_z{}^2}{c^2}\right)$$

If all three dimensions of the box are equal, i.e. a =b=c then:

$$E = \frac{h^2}{8ma^2}\left(n_x{}^2 + n_y{}^2 + n_z{}^2\right)$$

The ground state (i.e. state of lowest energy of a system is the state when $n_x=n_y=n_z=1$

The energy will be: $E = \frac{3h^2}{4ma^2}$

Suppose we consider the state with next to lowest energy. This state arises when one of the quantum numbers is 2 and the other two are 1 and $E = \frac{3h^2}{4ma^2}$

There are three different combinations of quantum numbers which will give this energy, however, if the values of three quantum numbers n_x, n_y and n_z are listed in parentheses after the energy, we can express this as

E(2 ,1,1)= E(1, 2, 1) = E(1, 1, 2)= $E = \frac{3h^2}{4ma^2}$

Such states of equal energy are called degenerate states, thus the second state for a particle in a cubical box is said to be three-fold degenerate.

Postulate VI:

The wavefunction Ψ(x, y, z, t) describing the state of a system is obtained for a solution to

$$\frac{-\hbar}{i}\frac{d}{dt}\Psi_{(x,y,z,t)} = \hat{H}\,\Psi_{(x,y,z,t)}$$

And this equation gives the time development of the wavefunction and thus of the state of the system.

For systems which do not change with time, this reduces tro the Schrödinger equation

$$H\Psi_{(x,y,z)} = E\Psi_{(x,y,z)}$$

Conclusion

Postulates of quantum mechanics

I- Wavefunction

II- Operators

III- Measyrable values

IV- Completeness

V- Average Expectation value

VI- Calculation of wavefunctions and its time evolution.