## **Schrödinger Equation**

In quantum mechanics the wave function  $\psi$  corresponds to the wave variable y of wave motion in general. However,  $\psi$ , unlike y, is not itself a measurable quantity and may therefore be complex. For this reason we assume that  $\psi$  for a particle moving freely in the +x direction is specified by:

$$\psi = Ae^{-i\omega(t-\frac{x}{v})}$$
 (1)

Replacing  $\omega$  in the above function  $\nabla$  For this reason we assume that  $\psi$  for a particle moving freely in the +x direction is specified by:

(2)

$$\psi = Ae^{-i2\pi v(t)\frac{x}{\lambda v}}$$

where  $E = h\upsilon = 2\pi\hbar\upsilon$  and  $\lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$  $\psi = Ae^{-\frac{i}{\hbar}(Et-px)}$  (3)

The total energy E of a particle is the sum of its kinetic energy  $(p^2/2m)$  and its potential energy U, where U is in general a function of position (x) and time (t).

$$\mathbf{E} = \frac{p^2}{2m} + U(x,t) \tag{6}$$

Multiplying both sides of equation (6) by wave function  $\psi$  gives,

$$\mathbf{E}\boldsymbol{\psi} = \frac{p^2\boldsymbol{\psi}}{2m} + U\boldsymbol{\psi}$$
 (7)

Using equation (4) and (5) in equation (7)

$$-\frac{\hbar}{\mathrm{i}}\frac{\partial\psi}{\partial\mathrm{t}} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial\mathrm{x}^2} + U\psi \Longrightarrow i\hbar\frac{\partial\psi}{\partial\mathrm{t}} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial\mathrm{x}^2} + U\psi \qquad (8)$$

This is the time dependant Schrodinger equation in One dimension.

In Three Dimensional case:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + U\psi \qquad (9)$$

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### **Schrödinger Time Independent Equation**

The one dimensional wave function  $\psi$  of an unrestricted particle may be written as,

$$\psi = Ae^{-\frac{i}{\hbar}(Et-px)} = Ae^{\frac{ip}{\hbar}x} \cdot e^{-\frac{iE}{\hbar}t} = \phi e^{-\frac{iE}{\hbar}t}$$
(10)

Evidently  $\psi$  is the product of a time-dependent function and a position dependent function.

Substituting  $\psi$  of equation (10) into the time dependent form of Schrödinger equation (7), we find that:

$$E\varphi e^{-\frac{iE}{\hbar}t} = -\frac{\hbar^2}{2m} e^{-\frac{iE}{\hbar}t} \frac{\partial^2 \varphi}{\partial x^2} + U\varphi e^{-\frac{iE}{\hbar}t} \Longrightarrow E\varphi = -\frac{\hbar^2}{2m} \frac{\partial^2 \varphi}{\partial x^2} + U\varphi$$
$$\Rightarrow \frac{\partial^2 \varphi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U)\varphi = 0 \qquad (11)$$

This is the time independant Schrodinger equation in One dimension.

In Three Dimensional case:

$$\nabla^2 \varphi + \frac{2m}{\hbar^2} (E - U) \varphi = 0$$
 (12)

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### **Eigenfunction and Eigenvalue**

In general, an eigenvalue equation can be written as

$$F_{op}\psi = f\psi$$

 $F_{op}$  is called the Operator,  $\psi$  is the eigenfunction and f is the eigen value. As an example,  $p\psi = -i\hbar \frac{\partial}{\partial x}\psi = -i\hbar \nabla \psi$ Momentum operator  $p = -i\hbar \nabla$ Again,  $E\psi = i\hbar \frac{\partial}{\partial t}\psi$ value.

**Energy operator**  $E = i\hbar \frac{\partial}{\partial t}$ 

Therefore an operator operates on the eigenfunction and give the eigenvalue of the corresponding eigenfunction.

### Application of Schrödinger Equation Particle in a Box

The simplest quantum-mechanical problem is that of a particle trapped in a box with infinitely hard walls. We may specify the particles motion by saying that it is restricted to travelling along the x axis between x = 0 and x = L by infinitely hard walls.



A particle does not loss energy when it collides with such walls., so that its total energy stays constant. From a formal point of view the particle energy U of the particle is infinite on both sides of the box, while U is constant – say 0 for convenience on the inside.

Because the particle cannot have an infinite amount of energy, it cannot exist outside the box, and so its wave function  $\psi$  is 0 for  $x \le 0$  and  $x \ge L$ . Our task is to find what  $\psi$  is within the box., namely between x =0 and x = L.

Within the box the potential energy U = 0 because the particle act as a free particle. Therefore the Schrödinger equation within the box can be written as:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - 0)\psi = 0 \Longrightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E\psi = 0$$
(1)

Equation (1) has the solution

$$\psi = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x$$

A and B are constants.  $\psi$  =0 for x =0 and x =L:

$$0 = A \sin \frac{\sqrt{2mE}}{\hbar} (0) + B \cos \frac{\sqrt{2mE}}{\hbar} (0)$$
  

$$\Rightarrow 0 = 0 + B \Rightarrow B = 0$$
  
Solution becomes,  $\psi = A \sin \frac{\sqrt{2mE}}{\hbar} x$  (3)

(2)

# Using another boundary condition $\psi = 0$ at x = L, equation (3) becomes

$$0 = A \sin \frac{\sqrt{2mE}}{\hbar} L \Rightarrow \sin \frac{\sqrt{2mE}}{\hbar} L = 0$$
$$\Rightarrow \frac{\sqrt{2mE_n}}{\hbar} L = n\pi \qquad (4)$$

n = 1, 2, 3.....This result comes about because the sin of the angles  $\pi$ ,  $2\pi$ ,  $3\pi$ .....are all 0.

From equation (4) it is clear that the energy of the particle can have only certain values, which are the eigenvalues. These eigenvalues, constituting the energy levels of the system, are found by solving equation (4) of  $E_n$ , which gives,

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \qquad n = 1, 2, 3.....$$
(5)

Equation (5) is called the energy equation of the particle in a box.

### Wave function of a particle in a box:

The wave function of a particle in a box whose energies are  $E_n$ , from equation (3) becomes

$$\psi = A\sin\frac{\sqrt{2mE_n}}{\hbar}x = A\sin\frac{n\pi x}{L}$$
 (6)

for the eigenfunctions corresponding to the energy eigenvalues  $E_{n.}$ 

For each quantum number *n*,  $\psi_n$  is a finite single-valued fuunction of x, and the derivative of  $\psi_n$  are continuous (except at the ends of the box). Furthermore, the integral of  $|\psi_n^2|$  over all space is finite, as we can see by integrating  $|\psi_n^2|$  dx from x =0 to x =L.

$$\therefore \int_{-\infty}^{\infty} |\psi_n|^2 dx = \int_{0}^{L} |\psi_n|^2 dx = A^2 \int_{0}^{L} \sin^2(\frac{n\pi x}{L}) dx$$
$$= \frac{A^2}{2} \left[ \int_{0}^{L} dx - \int_{0}^{L} \cos(\frac{2n\pi x}{L}) dx \right] = \frac{A^2}{2} \left[ x - \frac{L}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{0}^{L} = A^2 \frac{L}{2}$$
(7)

For normalization the wave function,

$$\therefore \int_{-\infty}^{\infty} |\psi_n|^2 dx = \int_{0}^{L} |\psi_n|^2 dx = 1$$
$$\Rightarrow A^2 \frac{L}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{L}}$$
(8)

The normalized wave functions of the particle are therefore,

$$\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$
  $n = 1, 2, 3.....$  (9)

The normalized wave functions  $\psi_1$ ,  $\psi_2$ ,  $\psi_3$  together with the probability density  $| \psi_1 |^2$ ,  $| \psi_2 |^2$  and  $| \psi_{13} |^2$  are plotted in the following page.

Although  $\psi_n$  may be negative as well as positive,  $|\psi_n|^2$  is always positive and, since  $\psi_n$  is normalized, its value at a given x is equal to the probability density of finding the particle there. In every case,  $|\psi_n|^2 = 0$  at x =0 and x =L, the boundaries of the box. At a particular place in the box the probability of the particle being present may be very different for different quantum numbers.



For instance,  $|\psi_1|^2$  has its maximum value at L/2 in the middle of the box, while  $|\psi_2|^2 = 0$  there. A particle in the lowest energy level of n=1 is most likely to be in the middle of the box. While a particle in the next higher state n=2 is never there! Classical physics, of course suggest the same probability for the particle being anywhere in he box.

## **Problems**

Find the probability that a particle trapped in a box of length L can be found between 0.45L and 0.55L for the ground and first excited state.

Solution: The probability of finding the particle in the box

$$P = \int_{0.45L}^{0.55L} |\psi_n|^2 dx = \int_{0.45L}^{0.55L} \left( \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \right)^2 dx = \frac{2}{L} \int_{0.45L}^{0.55L} \sin^2 \frac{n\pi x}{L} dx$$
$$= \frac{2}{L} \left[ \frac{x}{L} - \frac{1}{2nx} \sin \frac{2n\pi x}{L} \right]_{0.45L}^{0.55L}$$

For the ground state, which correspond to n=1, we have probability = 0.198 = 19.8%. This is about twice the classical probability.

For the first excited state, which corresponds to n = 2, probability = 0.0065 = 0.65%

Show that the normalization of wave function is independent of time.

Solution: The wave function  $\psi$  (x, t) can be written as a product of two functions as

$$\psi(\mathbf{x}, \mathbf{t}) = \mathbf{A} \mathbf{e}^{-\frac{\mathbf{i}}{\hbar}(\mathbf{E}\mathbf{t}-\mathbf{p}\mathbf{x})} = \mathbf{A} \mathbf{e}^{-\frac{\mathbf{i}\mathbf{E}}{\hbar}\mathbf{x}} \cdot \mathbf{e}^{-\frac{\mathbf{i}\mathbf{E}}{\hbar}\mathbf{t}} = \mathbf{\phi} \mathbf{e}^{-\frac{\mathbf{i}\mathbf{E}}{\hbar}\mathbf{t}}$$
  
Complex conjugate of  $\psi$  (x, t) is  $\psi^*(\mathbf{x}, \mathbf{t}) = \phi^* \mathbf{e}^{\frac{\mathbf{i}\mathbf{E}}{\hbar}\mathbf{t}}$ 

Normalization condition states that

$$\int_{-\infty}^{\infty} \psi(x,t)\psi^{*}(x,t)dx = 1$$
  
$$\Rightarrow \int_{-\infty}^{\infty} \varphi(x)e^{-\frac{iEt}{\hbar}}\varphi^{*}(x)e^{\frac{iEt}{\hbar}}dx = 1 \Rightarrow \int_{-\infty}^{\infty} \varphi(x)\varphi^{*}(x)dx = 1$$

#### This is independent of time.

A particle is moving in a one-dimensional box (of infinite height) of width 10 Å. Calculate the probability of finding the particle within an interval of 1 Å at the centre of the box, when it is in its state of least energy.

Solution: The wave function  $\psi$  (x, t) of the particle in the ground state (n=1), is

$$\psi_1 = \sqrt{\frac{2}{L}\sin\frac{\pi x}{L}}$$

Probability of finding the particle in unit interval at the centre of the box (x = L/2) is  $\pi(L/2)^2 = 2\pi - 2\pi - 2$ 

$$P = \psi_1^2 = \left(\sqrt{\frac{2}{L}} \sin \frac{\pi(L/2)}{L}\right)^2 = \frac{2}{L} \sin^2 \frac{\pi}{2} = \frac{2}{L}$$

Probability of finding the particle within an interval of  $\Delta x$  at the centre of the box

$$=\psi_1^2 \Delta x = \frac{2}{L} \Delta x = \frac{2}{10 \times 10^{-10}} \times 10^{-10} = 0.2$$

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