6

The normalized simultaneous eigen fns of L^2 and L_z are

$$Y_{lm}(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}\, P_{lm}(\cos\theta)\, e^{im\phi}$$

$$Y_{l(-m)} = (-1)^m Y^*_{lm}$$

Some eigen fns are

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{20} = \frac{5}{\sqrt{16\pi}}(3\cos^2\theta - 1)$$

$$Y_{11} = -\sqrt{\frac{3}{8\pi}}\, e^{i\phi}\sin\theta$$

$$Y_{21} = -\sqrt{\frac{15}{8\pi}}\, e^{i\phi}\sin\theta\cos\theta$$

$$Y_{22} = \sqrt{\frac{15}{32\pi}}\, e^{2i\phi}\sin^2\theta$$

$$Y_{33} = -\frac{1}{8}\sqrt{\frac{35}{\pi}}\, e^{3i\phi} \sin^3\theta$$

$$Y_{32} = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\, \sin^2\theta \cos\theta\, e^{2i\phi}$$

$$Y_{31} = -\frac{1}{8}\sqrt{\frac{21}{\pi}}\, \sin\theta\, (5\cos^2\theta - 1)\, e^{i\phi}$$

Example: 5.1, 5.2, 5.3, 5.4

Solved Problem: 5.1, 5.2, 5.4, 5.5, 5.6, 5.7, 5.13

Exercise: 5.1, 5.2, 5.3, 5.6, 5.25, 5.35

Ch# 6 3-D Problems.

6.2 The Schrodinger Wave Equation

"The Schrodinger equation is the basic equation of quantum mechanics, which describes the propagation of matter waves."

Let us consider a single free particle of mass "m" moving in a +ve x-direction with momentum "p".

The energy of the particle is,

$$E = K.E = \frac{1}{2}mv^2 = \frac{1}{2}\frac{m^2v^2}{m}$$

$$E = \frac{p^2}{2m}, \quad \text{--- (1)} \quad \because P = mv.$$

In quantum mechanics, a particle is described by a wavefunction $\psi(x,t)$. A typical wave of wave number $K = P/\hbar$ and angular frequency $\omega = E/\hbar$ is

$$\psi(x,t) = A\, e^{i(kx-\omega t)}$$
$$= A\, e^{i(px-Et)/\hbar} \quad \text{--- (2)}$$

where A is constant — amplitude of wave. The angular frequency of matter waves is connected with the wave number by

$$E = \hbar\omega, \quad E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

then $$\hbar\omega = \frac{\hbar^2 k^2}{2m}$$

$$\boxed{\omega = \frac{\hbar k^2}{2m}}$$

describe the effect of dispersion in a medium on the properties of a wave travelling in the medium

Called — dispersion relation. Now differentiating equ. (2) with respect to 't', one gets

$$\frac{\partial\psi}{\partial t} = -i\frac{E}{\hbar}\psi$$

or

$$\boxed{i\hbar\frac{\partial\psi}{\partial t} = E\psi} \quad \text{--- (3)}$$

Again differentiating equation (2) twice with respect to "x", one gets.

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\psi$$

or divided by 2m on both side

$$-\frac{\hbar^2}{2m}\cdot\frac{\partial^2 \psi}{\partial x^2} = \frac{p^2}{2m}\psi$$

or

$$\boxed{-\frac{\hbar^2}{2m}\cdot\frac{\partial^2 \psi}{\partial x^2} = E\psi} \quad \text{--- (4)}$$

by Compare equ. (3) and (4), one get.

$$\boxed{-\frac{\hbar^2}{2m}\cdot\frac{\partial^2 \psi}{\partial x^2} = i\hbar\frac{\partial \psi}{\partial t}} \quad \text{--- (5)}$$

This is time ~~in~~dependent Schrodinger equ. for a particle of mass m. It is a linear and homogeneous 1-dim partial differential equation for wave variable $\psi(x,t)$.

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In particular, it is satisfied by wavepackets of the form,

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} a(p)\, e^{\frac{i}{\hbar}(px - Et)}\, dp$$

which is associated with a localized free particle moving in one dimension

If we make the replacement

$$p \longrightarrow -i\hbar \frac{\partial}{\partial x}$$

$$E \longrightarrow i\hbar \frac{\partial}{\partial t}$$

in Classical equ. 1

$$E = \frac{p^2}{2m}$$

and act all the differential operator on the wave function $\psi(x,t)$, we get equ 5 which represents the quantum mechanical analogue of classical equation.

In 3D, the time-dependent Schrodinger equation is.

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right)$$

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In three dimensions, the wave-packet associated with a localized free particle is

$$\psi(\underline{x}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} a(\underline{p})\, e^{i(\underline{p}\cdot\underline{x} - Et)/\hbar}\, d\underline{p}$$

In classical mechanics, the quantity $\frac{p^2}{2m}$ called the Hamiltonian of a particle.

In quantum mechanics, the Hamiltonian of a free particle is represented by the differential operator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \quad \text{— 1D.}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 \quad \text{— 3D.}$$

Known as the Hamiltonian operator of a free particle of mass m.

The time-dependent Schrodinger equation can be written as.

$$\hat{H}\psi = E\psi$$

The free particle Schrodinger equ can be generalized to the case of a particle moving in an external ~~field~~ field of force,

$$F(x,t) = -\nabla V(x,t)$$

In this case the total energy of the particle is

$$E = \frac{p^2}{2m} + V(x,t)$$

The replacement

$$E \longrightarrow i\hbar \frac{\partial}{\partial t}$$

$$\underline{p} \longrightarrow -i\hbar \nabla$$ (4)

gives

$$i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\underline{x}, t) \right] \psi$$

This is time dependent Schrodinger wave Equation for a particle moving in a potential $V(\underline{x}, t)$ and

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{x}, t)$$

is the corresponding Hamiltonian operator.

6.2.2 The Free Particle:

The Schrodinger wave equ. for a particle of mass "m" can be written as:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + (V_x + V_y + V_z) \psi = E \psi \quad (1)$$

For a free Particle, $V_x = V_y = V_z = 0$,

then equ (1) reduces to.

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

In one dimension $- \underline{x}$

$$-\frac{\hbar^2}{2m}\cdot\frac{\partial^2}{\partial x^2}\psi(x) = E_x\psi(x).$$

$$\frac{\partial^2}{\partial x^2}\psi(x) = -\frac{2mE_x}{\hbar^2}\psi(x)$$

$$\frac{\partial^2}{\partial x^2}\psi(x) = -K_x^2\psi(x).$$

Hence, the normalized solution of above equ. is.

$$\boxed{\psi(x) = \frac{1}{\sqrt{2\pi}} e^{iK_x x}} \quad \text{--- (1)}$$

Thus, the solution to 3D - Schrodinger equation is given by

$$\psi(x,y,z) = \frac{1}{(2\pi)^{3/2}} e^{iK_x x} \cdot e^{iK_y y} \cdot e^{iK_z z}.$$

$$\boxed{\psi(\underline{r}) = \frac{1}{(2\pi)^{3/2}} e^{i\bar{k}\cdot\bar{r}}} \quad \text{--- (2)}$$

where $\bar{k}$ and $\bar{r}$ are the wave and position vectors of the particle, respectively.

The total energy of the particle is equal to the sum of the eigenvalues of the three one dimensional equations.

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}(K_x^2 + K_y^2 + K_z^2)$$

$$\boxed{E = \frac{\hbar^2}{2m}\bar{K}^2}$$

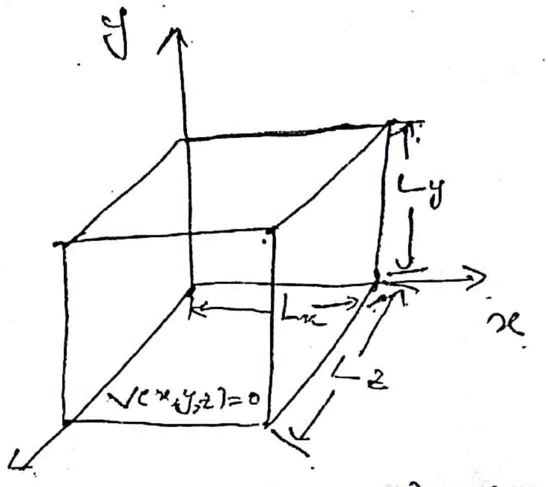
Since, the energy depends only on the magnitude of $\bar{K}$, ~~which~~ All the different orientations of $\bar{k}$ subjected to the condition

$$|\bar{k}| = \sqrt{K_x^2 + K_y^2 + K_z^2} = \text{Constant}.$$

It means constant wave number generate different eigenfunction in equation (2) without change in energy.

6.2.3 The Box Potential

6.2.3.1: The Rectangular Box Potential



Consider a particle of mass "m" and energy "E" constrained to move in a 3D rectangular potential well having sides of length equal to L_x, L_y, and L_z parallel to the x, y, and z-axes, respectively. Suppose there is no force acting on the particle in the box. Here, the appropriate potential is defined as

$$V(x,y,z) = \begin{cases} 0, & 0<x<L_x,\ 0<y<L_y,\ 0<z<L_z \\ \infty, & \text{elsewhere (outside the box)} \end{cases}$$

which can be written as

$$V(x,y,z) = V_x(x) + V_y(y) + V_z(z).$$

~~with~~

$$V_x(x) = \begin{cases} 0, & 0<x<L_x \\ \infty, & \text{elsewhere.} \end{cases} \text{— 1D.}$$ (6)

The Potentials $V_y(x)$ and $V_z(z)$ have similar forms

Quantum mechanically, we assumed that the particle do have only bound state solutions and a discrete non-degenerate energy spectrum.

Since the particle can not exist outside the well due to the infinite barriers, so $\psi_{out} = 0$, for ~~0<x<Lx~~
$0<x<L_x$
$0<y<L_y$
$0<z<L_z$

and also wavefns $\psi(x,y,z)$ must vanish at the walls of the box.

for $0<x<L_x$, the solution of the Schrodinger equ. is of the form

$$\frac{d^2}{dx^2}\psi_x(x) + K_x^2\psi_x(x) = 0$$

$$K_x = \sqrt{\frac{2mE_x}{\hbar}}$$

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After applying the boundary conditions, we know.

$$K_x L_x = n_x \pi \; , \; n_x = 1, 2, 3, 4, \ldots$$

$$K_x = \frac{n_x \pi}{L_x}.$$

and the normalized solution is.

$$\boxed{\psi_x(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi}{L_x} x\right)}$$

The solution for y and z axes have the same form. The corresponding energy eigenvalues are

$$\boxed{E_{n_x} = \frac{\hbar^2 \pi^2}{2 m L_x^2} n_x^2} \quad \text{— 1D.}$$

$$E = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$\to$ 3D

These eigenvalues of the energy are called as the energy levels of the particle.

They form quantized or discrete energy spectrum.

The normalized 3D eigenfunctions ~~and~~ are:

$$\boxed{\psi_n(x,y,z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi}{L_z} z\right)}$$

5.2.3.2 The Cubic potential:

Consider a cubic box of side L, then

$$L_x = L_y = L_z = L$$

The energy eigenvalue becomes

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

$$= \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2}\right)$$

$$= \frac{\hbar^2 \pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$n_x, n_y, n_z = 1, 2, 3, \ldots$

The ground state corresponds to

$n_x = n_y = n_z = 1$, which gives

$$E_{111} = \frac{\hbar^2 \pi^2}{2mL^2}(1+1+1)$$

$$= \frac{3\hbar^2 \pi^2}{2mL^2}$$

we know that the zero-point energy of a particle in one dimensional box is

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2},$$

So

$$\boxed{E_{111} = 3E_1}$$

Thus the zero-point energy for a particle in a 3D box is three times that in a 1D box

→ The first excited state has three possible sets of quantum numbers,

$(n_x, n_y, n_z) = (2,1,1), (1,2,1), (1,1,2)$

correspond to three different states,

$\psi_{211}(x,y,z)$, $\psi_{121}(x,y,z)$, and $\psi_{112}(x,y,z)$

where
$$\boxed{\psi_{211}(x,y,z) = \sqrt{\frac{8}{L^3}}\, \sin\left(\frac{2\pi}{L}x\right)\sin\left(\frac{\pi}{L}y\right)\sin\left(\frac{\pi}{L}z\right)}$$

Notice that all three excited states have the same energy eigen value

$$\boxed{E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2mL^2} = 6E_1}$$

Hence, the first excited state is three fold degenerate.

Degeneracy comes into the picture only when system contain symmetry.

→ for cubic system, there is a perfect symmetry, $a=b=c$

→ But in rectangular box, all three sides are not equivalent - since there is no degeneracy.

The second excited state also has three different states, and hence it is 3-fold degenerate, $\boxed{\text{i.e. } E_{221} = E_{212} = E_{122} = 9E_1}$