

# Chapter 2 Postulates of Quantum Mechanics

In classical mechanics, if we know classical state of system i.e. generalized coordinate  $q_i$  and conjugate momentum of system  $p_i$  we can analyses any physical quantity of system. The time evolution of system can be derived by Hamiltonian equation of motion. For one dimensional

system 
$$\left(\frac{\partial H}{\partial q_i}\right) = -\dot{p}_i$$
 and  $\left(\frac{\partial H}{\partial p_i}\right) = \dot{q}$ 

Similarly, in quantum mechanics the quantum mechanical counterparts to these ideas are specified by postulates, which enable us to understand:

(a) How a quantum state is described mathematically at a given time t,

(b) How to calculate the various physical quantities from this quantum state,

(c) Knowing the system's state at a time t, how to find the state at any later time t'; that is, how to describe the time evolution of a system.

The answers to these questions are provided by the following set of five mathematical hypothesis which are known as postulates of quantum mechanics

# **1. Postulates of Quantum Mechanics**

# Postulates-1: State of Quantum Mechanical System

A quantum mechanical state of system defined by  $|\psi(r,t)\rangle$ , which belong to Hilbert space H associated to the system.

If  $|\psi_1\rangle, |\psi_2\rangle, ..., |\psi_n\rangle$  are state of system then any linear superposition of state will also a state of system.

Mathematically  $|\psi\rangle = c_1 |\psi_1\rangle + c_2 |\psi_2\rangle + ..., c_n |\psi_n\rangle$  is also state of a system.

If  $|\psi\rangle$  is state of system then  $|\psi|^2 = \psi^* \psi$  can be treated as probability density f(x, y, z) if  $\int_{-\infty}^{+\infty} |\psi|^2 d\tau = 1$  (The integration is over all space)

In other words if  $\psi$  is normalized then  $|\psi|^2$  is equivalent to probability density.

# Postulates-2: Physical measurement of state

Any physical quantity  $\mathcal{A}$  is identified as observable, there is an operator  $\hat{A}$  associated to observable  $\mathcal{A}$ . If  $\hat{A}$  is measured on state  $|\psi\rangle$  the physical measurable quantities are the eigen values of operator i.e.  $\hat{A}|\phi_n\rangle = a_n|\phi_n\rangle$  where  $|\phi_n\rangle$  is eigen vector of operator  $\hat{A}$  correspond to eigen value  $a_n$ .

Hence physical measurable quantities are real then eigen value associated to operator  $\hat{A}$  is must real which ensure  $\hat{A}$  must be Hermitian  $\hat{A}^{\dagger} = \hat{A}$ .

One should choose eigen state of operator  $\hat{A}$  must be orthonormal in nature such that they can make complete basis  $\sum_{n} |\phi_n\rangle \langle \phi_n | = I$ .

Every eigen state can be treated as state of system but it is not necessary that every state is eigen state. If  $\hat{A}$  is measurement on state  $|\psi\rangle$  which means  $|\psi\rangle$  can be written in basis of eigen vectors of  $\hat{A}$  as  $|\psi\rangle = I |\psi\rangle \Rightarrow |\psi\rangle = \sum_{n} |\phi_n\rangle \langle \phi_n |\psi\rangle$ 

# Postulates-3: Probabilistic measurement of eigen value $a_n$ on state $\ket{\psi}$

In quantum mechanics the measurement of any physical quantities are nor deterministic so there probability associated to each measurable quantity. From postulates 2 we know  $\hat{A}|\phi_n\rangle = a_n|\phi_n\rangle$ . If

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operator  $\hat{A}$  will measure on state  $|\psi\rangle$  the probability associated with measurement is  $P(a_n)$ 

mathematically 
$$P(a_n) = \frac{\left|\left\langle \phi_n | \psi \right\rangle\right|^2}{\left\langle \psi | \psi \right\rangle}$$

For degenerate eigen state  $P(a_n) = \frac{\sum_{j} |\langle \phi_n^j | \psi \rangle|^2}{\langle \psi | \psi \rangle}$  where *j* is degeneracy of eigen value  $a_n$  and

 $|\phi_n^j\rangle$  are eigen state.

Basic Examples based on postulates 1, 2, 3

(a) If operator  $\hat{A}$  is defined as  $\hat{A} = \begin{bmatrix} a_0 & 0 \\ 0 & 2a_0 \end{bmatrix}$  is measured on  $|\psi_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$  what is measurement

and what will associated probability.

(b) If operator  $\hat{A}$  is defined as  $\hat{A} = \begin{bmatrix} a_0 & 0 \\ 0 & 2a_0 \end{bmatrix}$  is measured on  $|\psi_2\rangle = \begin{pmatrix} 2 \\ 3 \end{pmatrix}$  what is measurement

and what will associated probability.

Solution: According to postulates 2 the measurement is eigen value of operator

$$\hat{A}|\phi_n\rangle = a_n|\phi_n\rangle \text{ where } \hat{A} = \begin{bmatrix} a_0 & 0\\ 0 & 2a_0 \end{bmatrix} , a_1 = a_0, |\phi_1\rangle = \begin{pmatrix} 1\\ 0 \end{pmatrix} \text{ and } a_2 = 2a_0, |\phi_2\rangle = \begin{pmatrix} 0\\ 1 \end{pmatrix}$$

(a) The state is  $|\psi_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$  fortunately it is also eigen state corresponds to eigen value  $a_1 = a_0$ 

from postulates 3 we can measure associated probability as

$$P(a_1) = \frac{\left|\left\langle \phi_1 | \psi_1 \right\rangle\right|^2}{\left\langle \psi_1 | \psi_1 \right\rangle} \Longrightarrow P(a_0) = \frac{\left|\begin{pmatrix} 1 & 0 \\ 0 \end{pmatrix}\right|^2}{\begin{pmatrix} 1 & 0 \\ 0 \end{pmatrix}^2} = 1$$

$$P(a_{2}) = \frac{\left| \left\langle \phi_{2} | \psi_{1} \right\rangle \right|^{2}}{\left\langle \psi_{1} | \psi_{1} \right\rangle} = P(2a_{0}) = \frac{\left| \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right|^{2}}{\left( 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}} = 0$$

Note this is very trivial result because eigen state is also state of system

(b) For  $|\psi_2\rangle = \begin{pmatrix} 2\\ 3 \end{pmatrix}$  from postulates 2 the measurement is eigen value

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$$\hat{A} |\phi_n\rangle = a_n |\phi_n\rangle \text{ where } \hat{A} = \begin{bmatrix} a_0 & 0\\ 0 & 2a_0 \end{bmatrix} , a_1 = a_0, |\phi_1\rangle = \begin{pmatrix} 1\\ 0 \end{pmatrix} \text{ and } a_2 = 2a_0, |\phi_2\rangle = \begin{pmatrix} 0\\ 1 \end{pmatrix}$$

from postulates 3 we can measure associated probability as

$$P(a_{1}) = \frac{\left|\langle \phi_{2} | \psi_{2} \rangle\right|^{2}}{\left\langle \psi_{2} | \psi_{2} \rangle\right|^{2}} = P(a_{0}) = \frac{\left|\begin{pmatrix} 1 & 0 \\ 3 \end{pmatrix}\right|^{2}}{(2 & 3) \begin{pmatrix} 2 \\ 3 \end{pmatrix}} = \frac{4}{13}$$

$$|\langle 4 | \psi_{2} \rangle|^{2} = \frac{\left|\begin{pmatrix} 0 & 1 \\ 2 \end{pmatrix}\right|^{2}}{(2 & 3) \begin{pmatrix} 2 \\ 3 \end{pmatrix}} = \frac{4}{13}$$

$$P(a_2) = \frac{\left| \left\langle \phi_2 \, | \, \psi_2 \, \right\rangle \right|^2}{\left\langle \psi_2 \, | \, \psi_2 \, \right\rangle} = P(2a_0) = \frac{\left| \begin{pmatrix} 0 & 1 \end{pmatrix} \left( 3 \, \right) \right|}{2^2 + 3^2} = \frac{9}{13}$$

Another way we can write state  $|\psi_2\rangle$  can be represented as orthonormal basis of eigen state  $|\phi_1\rangle$ and  $|\phi_2\rangle$  as  $|\psi_2\rangle = 2|\phi_1\rangle + 3|\phi_2\rangle$  (we can use completeness relation)

$$P(a_1 = a_0) = \frac{|\langle \phi_1 | \psi_2 \rangle|^2}{\langle \psi_2 | \psi_2 \rangle} = \frac{2^2}{2^2 + 3^2} = \frac{4}{13} \text{ and } P(a_2 = 2a_0) = \frac{|\langle \phi_2 | \psi_2 \rangle|^2}{\langle \psi_2 | \psi_2 \rangle} = \frac{9}{13}$$

Which means if  $\hat{A}$  will measure on state  $|\psi_2\rangle$  one can get measurement  $a_0$  or  $2a_0$  with respective probability  $\frac{4}{13}$  and  $\frac{9}{13}$ . But nobody can predict what will be next measurement on basis of present measurement.

#### Postulates-4: State just after measurement of eigen value $a_n$

If  $\hat{A}$  is measured in state  $|\psi\rangle$  eigen value  $a_n$  is the measurement at the instantaneous point of time State  $|\psi\rangle$  will collapse (projected) in a direction of eigen state  $|\phi_n\rangle$  corresponding to eigen value  $a_n$ .

$$|\psi\rangle$$
 after measurement of  $a_n$  is  $\frac{P|\psi\rangle}{\sqrt{\langle\psi|P|\psi\rangle}} = \frac{|\phi_n\rangle\langle\phi_n|\psi\rangle}{\sqrt{\langle\psi|\phi_n\rangle\langle\phi_n|\psi\rangle}} = \frac{|\phi_n\rangle\langle\phi_n|\psi\rangle}{\sqrt{(\langle\phi_n|\psi\rangle)^2}} \approx |\phi_n\rangle$ 

If another operator  $\hat{B}$  will measure just after measurement of A on state  $|\psi\rangle$ ,  $\hat{B}$  will measure eigen state  $|\phi_n\rangle$ . After time will evolve during the next measurement any of the eigen value of operator can be measured (according to postulate 2).

**Example:** The operator  $\hat{A}$  is defined as  $\hat{A} |\phi_n\rangle = na_0 |\phi_n\rangle$  n = 1, 2, 3.... the state is given as  $|\psi\rangle = 2|\phi_1\rangle + 3|\phi_2\rangle + 4|\phi_3\rangle$ . Another operator  $\hat{B}$  is defined as  $\hat{B} |\phi_n\rangle = n^2 b_0 |\phi_n\rangle$  n = 1, 2, 3....

(a) After measurement of  $\hat{A}$  when outcome is  $2a_0$  at the same time  $\hat{B}$  will measured on state  $|\psi\rangle$ , what will be the measurement.

(b) After measurement of  $\hat{A}$  when outcome is  $2a_0$  after time evolved  $\hat{B}$  will measured on state  $|\psi\rangle$ , what will be the measurement.

**Solution:** (a) After measurement of  $\hat{A}$  on  $|\psi\rangle$  the measurement is  $2a_0$  means at the time of when we get outcome  $2a_0$ ,  $|\psi\rangle$  is projected in direction of  $|\phi_2\rangle$  at the same time if  $\hat{B}$  will measured actually on  $|\phi_2\rangle$  which is also eigen state of  $\hat{B}$  so measurement is  $2^2b_0 = 4b_0$  only this is outcome according to postulates 4

(b) after measurement of  $\hat{A}$  on  $|\psi\rangle$  the measurement is  $2a_0$  means at the time of when we get outcome  $2a_0$ ,  $|\psi\rangle$  is projected in direction of  $|\phi_2\rangle$  but  $\hat{B}$  will measured after time is evolved so according to postulates 2 again state will be in original state  $|\psi\rangle = 2|\phi_1\rangle + 3|\phi_2\rangle + 4|\phi_3\rangle$  so can outcome  $1^2b_0 = b_0$  or  $2^2b_0 = 4b_0$  or  $3^2b_0 = 9b_0$ 

### Postulates-5: Time evolution of state

In classical mechanics the time evolution of state can be analyze by Hamiltonian equation of motion with will ultimately give force equation  $\vec{F} = \frac{md^2\vec{r}}{dt^2}$ . In quantum mechanics it is not applicable so we find another way named as Schrodinger wave time dependent equation given as

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

A stationary state is a quantum mechanics with all observables independent of time. It is an eigenvector of the Hamiltonian. This corresponds to a state with a single definite energy (instead of a Quantum superposition of different energies). It is also called energy eigenvector, energy eigenstate, energy eigenfunction, or energy eigenket.

Time independent Schrodinger wave equation is given by  $\hat{H} |u_n\rangle = E_n |u_n\rangle$ 

Where  $\hat{H}$  is Hamiltonian of system and  $E_n$  is energy eigenvalue with corresponding energy eigen state  $|u_n\rangle$  n = 1, 2, 3, ..., m...n

$$H|u_n\rangle = \frac{-\hbar^2}{2m} \nabla^2 |u_n\rangle + V|u_n\rangle = E_n |u_n\rangle \text{ where } \langle u_n | u_m\rangle = \delta_{n,m} \text{ and } \sum_n |u_n\rangle \langle u_n| = I$$

Any state  $|\psi(t=0)\rangle = \sum_{n} |u_n\rangle \langle u_n |\psi\rangle$ 

Analogy to solve time dependent Schrödinger wave equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi(x,t)$$
  

$$\psi(x,t) = F(t)u(x) \text{ is solution of } i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi(x,t) \text{ then}$$
  

$$i\hbar u(x)\frac{dF}{dt} = F(t)\left(-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2}\right) + F(t)V(x)u(x) \text{ divided by } F(t)u(x) \text{ both side}$$
  

$$\frac{i\hbar}{F(t)}\frac{dF}{dt} = \frac{1}{u(x)}\left(\left(-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2}\right) + V(x)u(x)\right) \Rightarrow \frac{i\hbar}{F(t)}\frac{dF}{dt} = \frac{\hat{H}u(x)}{u(x)}$$
  

$$\frac{i\hbar}{F(t)}\frac{dF}{dt} = \frac{\hat{H}u(x)}{u(x)} \text{ give guarantee that } \frac{i\hbar}{F(t)}\frac{dF}{dt} = \frac{\hat{H}u(x)}{u(x)} = C$$

where C is constant which is identified as total energy E of system and u(x) is identified as corresponding energy eigen state such that  $\hat{H}u(x) = Eu(x)$ .

$$\frac{i\hbar}{F(t)}\frac{dF}{dt} = E \Longrightarrow \int \frac{dF}{F} = \frac{1}{i\hbar}\int dt \Longrightarrow \ln F(t) = \frac{Et}{i\hbar} + \ln A \Longrightarrow F(t) = A\exp\left(-\frac{iEt}{\hbar}\right)$$

So  $\psi(x,t) = A \exp\left(\frac{-iEt}{\hbar}\right) u(x)$ , where u(x) is the energy eigen state with energy eigen value E

Similarly, we can verify in discrete basis

$$|\psi(t=0)\rangle = \sum_{n} |u_{n}\rangle\langle u_{n}|\psi\rangle$$
$$|\psi(t=t)\rangle = \sum_{n} \exp\left(\frac{-iE_{n}t}{\hbar}\right)|u_{n}\rangle\langle u_{n}|\psi\rangle$$

We can verify  $i \frac{\partial |\psi(t)\rangle}{\partial t} = \sum_{n} i \cdot (-iE_n) \exp\left(\frac{-iE_n t}{\hbar}\right) |u_n\rangle \langle u_n |\psi\rangle$ 

$$\Rightarrow \sum_{n} E_{n} \exp\left(\frac{-iE_{n}t}{\hbar}\right) |u_{n}\rangle \langle u_{n}|\psi\rangle \Rightarrow \sum_{n} \exp\left(\frac{-iE_{n}t}{\hbar}\right) \hat{H} |u_{n}\rangle \langle u_{n}|\psi\rangle$$

 $\Rightarrow \hat{H} | \psi(t) \rangle = i\hbar \frac{\partial | \psi(t) \rangle}{\partial t}$  which is popular Schrödinger wave equation, which is equivalent to

Newton's law of motion in quantum mechanics

The solution of Schrödinger wave equation is  $|\psi(t)\rangle = \left(\exp-\frac{i\hat{H}t}{\hbar}\right)|\psi(0)\rangle$ 

we know 
$$\Rightarrow \langle \psi(t) | = \langle \psi(0) | \left( \exp \frac{i\hat{H}^{\dagger}t}{\hbar} \right)$$
  
 $\hat{H}^{\dagger} = \hat{H} \text{ so } \langle \psi(t) | = \langle \psi(0) | \left( \exp \frac{i\hat{H}t}{\hbar} \right)$ 

**Evolution of norm with time** 

$$\langle \psi(t) | \psi(t) \rangle = \langle \psi(0) | \exp\left(\frac{i\hat{H}t}{2}\right) \exp\left(-\frac{i\hat{H}t}{2}\right) | \psi(0) \rangle = \langle \psi(0) | \exp\left(\frac{i\hat{H}t - i\hat{H}t}{\hbar}\right) \exp\left(\frac{it\left[\hat{H}, -\hat{H}\right]}{2}\right) | \psi(0) \rangle$$

$$\exp\left(\frac{i\hat{H}t - i\hat{H}t}{\hbar}\right) = \exp\hat{O} = I \text{ and } \exp\left(\frac{it\left[\hat{H}, -\hat{H}\right]}{2}\right) = \exp\hat{O} = I$$

$$\langle \psi(t) | \psi(t) \rangle = \langle \psi(0) | I.I | \psi(0) \rangle = \langle \psi(0) | \psi(0) \rangle$$

We can conclude the state will evolve with time but its norms will preserve during the evolution, which means norm of the state will preserve and independent of time.

If we represent any state in orthonormal basis of energy eigen state as  $|\psi(0)\rangle = \sum_{n} c_{n} |u_{n}\rangle$  where

 $c_n = \langle u_n | \psi \rangle$  then it will fulfill two purposes.

(a) We can easily measure associated energy eigen value  $E_n$  with energy eigenstate  $|u_n\rangle$  as we know  $\hat{H}|u_n\rangle = E_n|u_n\rangle$ 

(b) We can analyze time evolution of state  $|\psi(t)\rangle = \sum_{n} c_{n} \exp\left(\frac{-iE_{n}t}{\hbar}\right) |u_{n}\rangle$ 

The solution of Schrodinger equation must be

- (a) Single valued and value must be finite
- (b) Continuous
- (c) Differentiable
- (d) Square integrable.

### **Time Evolution of Probability Density**

The Hamiltonian is defined as  $H |\phi_n\rangle = E_n |\phi_n\rangle$  and  $\hat{H} |\phi_m\rangle = E_m |\phi_m\rangle$ 

It is given as  $\delta_{nm} = \langle \phi_n | \phi_m \rangle$ 

at t = 0 the wave function is  $\psi(0) = c_n \phi_n + c_m \phi_m$  so  $\psi^*(0) = c_n^* \phi_n^* + c_m^* \phi_m^*$ 

Pravegae Education CSIR NET-JRF, GATE, IIT-JAM, JEST, TIFR and GRE for Physics The probability density is given as  $|\psi|^2 = |c_n|^2 |\phi_n|^2 + |c_m|^2 |\phi_m|^2 + 2 \operatorname{Re} c_n^* c_n \phi_n^* \phi_m$ 

After time t state will be 
$$\psi(t) = c_n \exp\left(-\frac{iE_n t}{\hbar}\right)\phi_n + c_m \exp\left(-\frac{iE_m t}{\hbar}\right)\phi_m$$
  
 $\psi^*(t) = c_n^* \exp\left(\frac{iE_n t}{\hbar}\right)\phi_n^* + c_m^* \exp\left(\frac{iE_m t}{\hbar}\right)\phi_m^*$   
 $|\psi(t)|^2 = |c_n|^2 |\phi_n|^2 + |c_m|^2 |\phi_m|^2 + c_n^* \phi_n^* c_m \phi_m e^{\frac{it(E_n - E_m)}{\hbar}} + c_m^* \phi_m^* c_n \phi_n e^{-\frac{it(E_n - E_m)}{\hbar}}$   
 $= |c_n|^2 |\phi_n|^2 + |c_m|^2 |\phi_m|^2 + 2\operatorname{Re} c_n^* c_m \phi_n^* \phi_m \cdot \cos\left(\frac{t(E_n - E_m)}{\hbar}\right)$ 

The condition  $|\psi(t)|^2 = |\psi(0)|^2 \Rightarrow \cos \frac{t(E_n - E_m)}{\hbar} = 1 \Rightarrow \frac{t(E_n - E_m)}{\hbar} = 2\pi$ 

system back to initial  $t = \frac{2\pi\hbar}{|E_n - E_m|}$ , which is also uncertainty in measure of time,  $\Delta t = \frac{2\pi\hbar}{|E_n - E_m|}$ 

# Average value of operator $\hat{A}$

 $|\psi\rangle$  the operator  $\hat{A}$  is defined as  $\hat{A}|\phi_n\rangle = a_n|\phi_n\rangle$ . A state of system is given by  $|\psi\rangle$  where  $P(a_n)$  is probability of measurement on state  $|\psi\rangle$  is given

by 
$$P(a_n) = \frac{\left|\langle \phi_n | \psi \rangle\right|}{\langle \psi | \psi \rangle}$$

The expectation value of  $\hat{A}$  on State  $|\psi\rangle$  which is mean value of  $\hat{A}$ 

i.e. 
$$\langle \hat{A} \rangle = \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle} = \sum_{n} a_{n} P(a_{n}) = \frac{\int_{-\infty}^{+\infty} \psi^{*}(x) \hat{A}(x) \psi(x) dx}{\int_{-\infty}^{+\infty} \psi^{*} \psi dx}$$

The expectation value of  $\hat{A}^2$  on State  $|\psi\rangle$ 

$$\left\langle \hat{A}^{2} \right\rangle = \frac{\left\langle \psi \left| \hat{A} \right| \psi \right\rangle}{\left\langle \psi \left| \psi \right\rangle} = \sum_{n} a_{n}^{2} P(a_{n}) = \frac{\int_{-\infty}^{+\infty} \psi^{*}(x) \hat{A}^{2} \psi(x) dx}{\int_{-\infty}^{+\infty} \psi^{*} \psi dx}$$

The error in measurement of  $\Delta \hat{A} = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2} \qquad \langle \hat{A}^2 \rangle \ge \langle \hat{A} \rangle^2$ 

 $\langle A \rangle$  is equivalent to classical result of measurement.

Pravegae Education CSIR NET-JRF, GATE, IIT-JAM, JEST, TIFR and GRE for Physics **Example:** If eigen value of operator  $\hat{A}$  is 0,  $2a_0$ ,  $2a_0$  and corresponding normalized eigen vector is  $\frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ -i \\ 1 \end{pmatrix}, \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ i \\ 1 \end{pmatrix}$  and  $\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$  respectively *t* system is in state  $\frac{1}{6} \begin{pmatrix} 1 \\ 0 \\ 4 \end{pmatrix}$  then (a) When  $\hat{A}$  is measured on system in state  $\frac{1}{6} \begin{bmatrix} 1 \\ 0 \\ 4 \end{bmatrix}$  then what is probability to getting value 0,  $2a_0$ , respectively. (b) What is the expectation value of  $\hat{A}$ ? **Solution:** For eigen value  $\lambda_1 = 0$  the eigen vector is  $|\phi_1\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} 0 \\ -i \\ 1 \end{vmatrix}$ ,  $P(0) = \frac{|\langle \phi_1 | \psi(t) \rangle|^2}{\langle \psi | \psi \rangle} = \frac{8}{17}$  $\lambda_2 = \lambda_3 = 2a_0$  i.e.,  $\lambda = 2a_0$  is doubly degenerate so two orthonormal eigen states are  $|\phi_2\rangle = \frac{1}{\sqrt{2}} |i|$ and  $|\phi_3\rangle = \begin{pmatrix} 1\\0\\0 \end{pmatrix}$  $P(2a_0) = \frac{|\langle \phi_2 | \psi(t) \rangle|^2}{\langle \psi | \psi \rangle} + \frac{|\langle \phi_3 | \psi(t) \rangle|^2}{\langle \psi | \psi \rangle} = \frac{\frac{2}{9}}{\frac{17}{2}} + \frac{1}{17} = \frac{9}{17}, \ \langle A \rangle = 0 \times \frac{8}{17} + 2a_0 \times \frac{9}{17} = \frac{18a_0}{17}$ 

**Example:** Operator  $\hat{A}$  is defined as  $\hat{A} = \begin{pmatrix} 0 & a_0 \\ a_0 & 0 \end{pmatrix}$ . If A will measure on  $|\psi\rangle = \begin{pmatrix} 3 \\ 4i \end{pmatrix}$ 

(i) What will be the measurement with what probability?

(ii) If  $|\phi_1\rangle$  and  $|\phi_2\rangle$  are orthogonal eigen state of *A*. Prove that  $|\phi_1\rangle$  and  $|\phi_2\rangle$  will make a complete basis

(iii) Write down  $|\psi\rangle$  in the basis of  $|\phi_1\rangle$  and  $|\phi_2\rangle$ . Verify your result.

**Solution:** (i) For eigen value  $|\hat{A} - \lambda I| = 0 \Rightarrow \begin{vmatrix} -\lambda & a_0 \\ a_0 & -\lambda \end{vmatrix} = 0 \Rightarrow (\lambda^2 - a_0^2) = 0 \Rightarrow \lambda_1 = a_0, \lambda_2 = -a_0$ 

So, the measurement is  $\lambda_1 = a_0$  and  $\lambda_2 = -a_0$ .

Now let  $|\phi_1\rangle = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$  will be the eigen state corresponding to  $a_1 = a_0$ 

 $\hat{A} |\phi_1\rangle = a_0 |\phi_1\rangle \Longrightarrow \begin{pmatrix} 0 & a_0 \\ a_0 & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = a_0 \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \Longrightarrow a_1 = a_2 \Longrightarrow |\phi_1\rangle = \begin{pmatrix} a_1 \\ a_1 \end{pmatrix}$ We normalized  $|\phi_1\rangle$  to get a single state  $\langle \phi_1 | \phi_1 \rangle = 1$  $\left(a_1^* \quad a_1^*\right) \left(a_1 \\ a_2\right) = 1 \Longrightarrow 2a_1^2 = 1 \Longrightarrow a_1 = \frac{1}{\sqrt{2}} \Longrightarrow \left|\phi_1\right\rangle = \frac{1}{\sqrt{2}} \left(1 \\ 1\right)$ For the eigen value  $a_2 = -a_0$ ,  $|\phi_2\rangle = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}$  $\hat{A} | \phi_2 \rangle = -a_0 | \phi_2 \rangle \Rightarrow \begin{pmatrix} 0 & a_0 \\ a_0 & 0 \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = -a_0 \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \Rightarrow b_1 = -b_2 \Rightarrow | \phi_2 \rangle = \begin{pmatrix} b_1 \\ -b_1 \end{pmatrix}$  $\langle \phi_2 | \phi_2 \rangle = 1 \Rightarrow \begin{pmatrix} b_1^* & -b_1^* \end{pmatrix} \begin{pmatrix} b_1 \\ -b_1 \end{pmatrix} = 1 \Rightarrow b_1 = \frac{1}{\sqrt{2}} \Rightarrow | \phi_2 \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$  $P(a_{0}) = \frac{\left|\langle \phi_{1} | \psi \rangle\right|^{2}}{\langle \psi | \psi \rangle} = \frac{\left|\left(\frac{1}{\sqrt{2}} \ \frac{1}{\sqrt{2}}\right)\left(\frac{3}{4i}\right)\right|^{2}}{\left(3-4i\right)\left(\frac{3}{4i}\right)} = \frac{\left|\frac{3}{\sqrt{2}}+i\frac{4}{\sqrt{2}}\right|^{2}}{3^{2}+4^{2}} = \frac{\left|\frac{3}{\sqrt{2}}\right|^{2}+\left|\frac{4}{\sqrt{2}}\right|^{2}}{3^{2}+4^{2}} = \frac{\frac{25}{2}}{25} = \frac{1}{2}$  $P(-a_{0}) = \frac{\langle \phi_{2} | \psi \rangle^{2}}{\langle \psi | \psi \rangle} = \frac{\left| \left( \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} \right) \left( \frac{3}{4i} \right) \right|^{2}}{(3 - 4i) \left( \frac{3}{4i} \right)^{2}} = \frac{\left| \frac{3}{\sqrt{2}} - i \frac{4}{\sqrt{2}} \right|^{2}}{3^{2} + 4^{2}} = \frac{\left| \left( \frac{3}{\sqrt{2}} \right)^{2} + \left( \frac{-4}{\sqrt{2}} \right)^{2} \right|}{25} = \frac{25}{25} = \frac{1}{2}$   $P(a_{0}) + P(-a_{0}) = 1$   $(\text{ii}) |\phi_{1}\rangle\langle\phi_{1}| + |\phi_{2}\rangle\langle\phi_{2}| = \left( \frac{1}{\sqrt{2}} \right) \otimes \left( \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} \right) + \left( \frac{1}{\sqrt{2}} \right) \otimes \left( \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} \right) \otimes \left( \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} \right)$  $= \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} + \begin{pmatrix} \frac{1}{2} & \frac{-1}{2} \\ \frac{-1}{2} & \frac{1}{2} \\ \frac{-1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = 1 \text{ so } |\phi_1\rangle \text{ and } |\phi_2\rangle \text{ will make a complete basis}$  $(iii) |\psi\rangle = \{\langle \phi_1 |\psi\rangle\} |\phi_1\rangle + \{\langle \phi_2 |\psi\rangle\} |\phi_2\rangle = \frac{3+4i}{\sqrt{2}} |\phi_1\rangle + \frac{3-4i}{\sqrt{2}} |\phi_2\rangle$   $P(a_0) = \frac{|\langle \phi_1 |\psi\rangle|^2}{\langle \psi |\psi\rangle} = \frac{\left|\frac{3+4i}{\sqrt{2}}\right|^2}{\frac{1}{2}(3^2+4^2) + \frac{1}{2}(3^2+4^2)} = \frac{\left(\frac{3}{\sqrt{2}}\right)^2 + \left(\frac{4}{\sqrt{2}}\right)^2}{3^2+4^2} = \frac{1}{2}$   $P(-a_0) = \frac{|\langle \phi_2 |\psi\rangle|^2}{\langle \psi |\psi\rangle} = \frac{\frac{1}{2}|3-4i|^2}{3^2+4^2} = \frac{1}{2}\left(\frac{3^2+4^2}{3^2+4^2}\right) = \frac{1}{2} \Rightarrow P(a_0) + P(-a_0) = 1$ 

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Example: An operator  $\hat{A}$  is given by  $\hat{A} = \begin{pmatrix} a_0 & 0 & 0 \\ 0 & a_0 & 0 \\ 0 & 0 & -a_0 \end{pmatrix}$  If  $\hat{A}$  will measured on a state  $|\psi\rangle = \begin{pmatrix} 3 \\ 4i \\ 5 \end{pmatrix}$ , then what will be the measurement with what probability? Solution: As here A is a diagonal matrix the eigen value of A will be  $\lambda_1 = a_0, \lambda_2 = a_0, \lambda_3 = -a_0$  Corresponding eigen state is  $|\phi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, |\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, |\phi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$ Now the probability of degenerate eigen value  $P(a_0) = \frac{|\langle \phi_1 | \psi \rangle|^2}{\langle \psi | \psi \rangle} \oplus \frac{|\langle \phi_2 | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{|3|^2}{|3|^2 + |4i|^2 + |5|^2} \oplus \frac{|4i|^2}{|3|^2 + |4i|^2 + |5|^2} = \frac{9}{50} + \frac{16}{50} = \frac{25}{50} = \frac{1}{2}$   $P(-a_0) = \frac{|\langle \phi_1 | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{\left| \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 3 \\ 4i \\ 5 \end{pmatrix} \right|^2}{(3 & -4i & 5) \begin{pmatrix} 3 \\ 4i \\ 5 \end{pmatrix}} = \frac{5^2}{3^2 + 4^2 + 25} = \frac{25}{50} = \frac{1}{2}$  $\therefore P(-a_0) + P(a_0) = 1$ 

Example:  $\hat{A} = \begin{bmatrix} a_0 & 0 & 0 \\ 0 & 0 & a_0 \\ 0 & a_0 & 0 \end{bmatrix}$ . If A will measured on a state  $|\psi\rangle = \begin{pmatrix} 3 \\ 4i \\ 5 \end{pmatrix}$ , what will be

measurement and what is probability?

Solution: From eigen value

$$\begin{vmatrix} \hat{A} - \lambda I \end{vmatrix} = 0 \Longrightarrow \begin{vmatrix} a_0 - \lambda & 0 & 0 \\ 0 & -\lambda & a_0 \\ 0 & a_0 & -\lambda \end{vmatrix} = 0 \Longrightarrow (a_0 - \lambda) (\lambda^2 - a_0^2) = 0$$

$$(a_0 - \lambda)(\lambda + a_0)(\lambda - a_0) = 0 \Longrightarrow \lambda_1 = -a_0, \lambda_2 = a_0, \lambda_3 = a_0,$$

The measurement is  $-a_0$  or  $a_0$ 

For  $\lambda_1 = -a_0$  Let the eigen state be  $|\phi_1\rangle = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$ 

$$A|\phi_{1}\rangle = -a_{0}|\phi_{1}\rangle \Rightarrow \begin{pmatrix} a_{0} & 0 & 0\\ 0 & 0 & a_{0}\\ 0 & a_{0} & 0 \end{pmatrix} \begin{pmatrix} a_{1}\\ a_{2}\\ a_{3} \end{pmatrix} = -a_{0} \begin{pmatrix} a_{1}\\ a_{2}\\ a_{3} \end{pmatrix}$$
$$a_{1} = -a_{1} \Rightarrow a_{1} = 0$$
$$a_{3}.a_{0} = -a_{2}a_{0} \Rightarrow a_{2} = -a_{3} \text{ and } a_{2}a_{0} = -a_{3}a_{0} \Rightarrow a_{2} = -a_{3} \text{ so } |\phi_{1}\rangle = \begin{pmatrix} 0\\ a_{2}\\ -a_{2} \end{pmatrix}$$

using normalization condition  $\langle \phi_1 | \phi_1 \rangle = 1$ 

$$\begin{pmatrix} 0 & a_2^* & -a_3^* \end{pmatrix} \begin{pmatrix} 0 \\ a_2 \\ -a_2 \end{pmatrix} = 1 \Longrightarrow a_2^2 + a_2^2 - 1 \Longrightarrow a_2 = \frac{1}{\sqrt{2}} \qquad \Rightarrow |\phi_1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}$$

Now we will calculate eigen vector corresponds to for  $\lambda_2 = a_0$ . Let corresponding eigen state be

$$\begin{aligned} |\phi_{2}\rangle &= \begin{pmatrix} b_{1} \\ b_{2} \\ b_{3} \end{pmatrix} \\ \hat{A}|\phi_{2}\rangle &= a_{0}|\phi_{2}\rangle \Rightarrow \begin{pmatrix} a_{0} & 0 & 0 \\ 0 & 0 & a_{0} \\ 0 & a_{0} & 0 \end{pmatrix} \begin{pmatrix} b_{1} \\ b_{2} \\ b_{3} \end{pmatrix} = a_{0} \begin{pmatrix} b_{1} \\ b_{2} \\ b_{3} \end{pmatrix} \\ b_{1}a_{0} &= b_{1}a_{0} \Rightarrow b_{1} = b_{1}, b_{3}a_{0} = b_{2}a_{0} \Rightarrow b_{2} = b_{3}, b_{2}a_{0} \Rightarrow b_{2} = b_{3}a_{0} \Rightarrow b_{2} = b_{3} \therefore |\phi_{2}\rangle = \begin{pmatrix} b_{1} \\ b_{2} \\ b_{3} \end{pmatrix} \end{aligned}$$

We choose any arbitrary value  $b_1 = 0$  to make  $|\phi_2\rangle$ 

$$|\phi_{2}\rangle = \begin{pmatrix} 0\\b_{2}\\b_{2} \end{pmatrix}. \text{ Using normalisation condition } \langle \phi_{2} | \phi_{2} \rangle = 1 \Rightarrow \begin{pmatrix} 0&b_{2}^{*}&b_{2}^{*} \end{pmatrix} \begin{pmatrix} 0\\b_{2}\\b_{2} \end{pmatrix}.$$
$$2b_{2}^{2} = 1 \Rightarrow b_{2} = \frac{1}{\sqrt{2}} \Rightarrow |\phi_{2}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0\\1\\1 \end{pmatrix}$$
For  $\lambda_{3} = a_{0} \hat{A} | \phi_{3} \rangle = a_{0} | \phi_{3} \rangle \Rightarrow \begin{pmatrix} a_{0} & 0 & 0\\0 & 0 & a_{0}\\0 & a_{0} & 0 \end{pmatrix} \begin{pmatrix} c_{1}\\c_{2}\\c_{3} \end{pmatrix} = a_{0} \begin{pmatrix} c_{1}\\c_{2}\\c_{3} \end{pmatrix}$ Now we find  $\begin{pmatrix} c_{1}\\c_{2}\\c_{3} \end{pmatrix}$  in the form of  $|\phi_{3}\rangle = \begin{pmatrix} c_{1}\\c_{2}\\c_{2} \end{pmatrix}$  such that  $\langle \phi_{2} | \phi_{3} \rangle = 0$ 

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$$\begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_2 \end{pmatrix} = 0 \Longrightarrow c_2 = 0$$

from normalization condition  $\langle \phi_3 | \phi_3 \rangle = 1 \Longrightarrow c_1 = 1$  so  $| \phi_3 \rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ 

$$P(-a_{0}) = \frac{\left|\langle \phi_{1} | \psi \rangle\right|^{2}}{\langle \psi | \psi \rangle} = \frac{\left|\begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} 3\\4i\\5 \end{pmatrix} \right|^{2}}{(3-4i\ 5) \begin{pmatrix} 3\\4i\\5 \end{pmatrix}} = \frac{\frac{1}{2}|4i-5|^{2}}{|3|^{2}+|4i|^{2}+|3|^{2}} = \frac{1}{2}\frac{|4|^{2}+|5|^{2}}{50} = \frac{41}{100}$$

$$P(a_{0}) = \frac{\left|\langle \phi_{2} | \psi \rangle\right|^{2}}{(3-4i\ 5) \begin{pmatrix} 4\\5 \end{pmatrix}} = \frac{|\langle \phi_{3} | \psi \rangle|^{2}}{(5-2i)^{2}} = \frac{1}{2}\frac{|\psi|^{2}+|5|^{2}}{(5-2i)^{2}} = \frac{1}{2$$

$$P(a_{0}) = \frac{1}{\langle \psi | \psi \rangle} \oplus \frac{1}{\langle \psi | \psi \rangle} \oplus$$

**Example:** Operation  $\hat{A}$  is defined as  $\hat{A} |\phi_n\rangle = n^2 a_0 |\phi_n\rangle$  where n = 1, 2, 3, ... it is also given  $\langle \phi_m | \phi_n \rangle = \delta_{n,m}$ 

Any state  $|\psi\rangle$  at t = 0 is given as  $|\psi\rangle = 3|\phi_1\rangle - 2i|\phi_2\rangle + (3+4i)|\phi_4\rangle$ If  $\hat{A}$  will measured on the state  $|\psi\rangle$  then what will be the measurement with what probability? **Solution:** When  $\hat{A}$  will measured on  $|\phi_n\rangle$  it will give the eigen value  $n^2a_0$ 

$$\hat{A} |\phi_n\rangle = n^2 a_0 |\phi_n\rangle, A |\phi_1\rangle = 1^2 a_0 |\phi_1\rangle, A |\phi_2\rangle = 2^2 a_0 |\phi_2\rangle, A |\phi_4\rangle = 4^2 a_0 |\phi_4\rangle$$
  
So, that measurement is  $a_0, 4a_0, 16a_0 |\psi\rangle = 3 |\phi_1\rangle - 2i |\phi_2\rangle + (3+4i) |\phi_4\rangle$ 

Here  $|\psi\rangle$  is given in terms of  $|\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle$ 

$$P(a_{0}) = \frac{\langle \phi_{1} | \psi \rangle^{2}}{\langle \psi | \psi \rangle} = \frac{|3|^{2}}{|3|^{2} + |-2i|^{2} + |3 + 4i|^{2}} = \frac{|3|^{2}}{9 + 4 + 9 + 16} = \frac{9}{38}$$

$$P(4a_{0}) = \frac{|\langle \phi_{2} | \psi \rangle|^{2}}{\langle \psi | \psi \rangle} = \frac{|-2i|^{2}}{38} = \frac{4}{38}, P(16a_{0}) = \frac{|\langle \phi_{4} | \psi \rangle|^{2}}{\langle \psi | \psi \rangle} = \frac{|3 + 4i|^{2}}{38} = \frac{3^{2} + 4^{2}}{38} = \frac{25}{38}$$

$$P(a_{0}) + P(4a_{0}) + P(16a_{0}) = \frac{9}{38} + \frac{4}{38} + \frac{25}{38} = 1$$

**Example:** The Hamiltonian operator is defined as  $\hat{H} |\phi_n\rangle = E_n |\phi_n\rangle$ , where n = 1, 2, 3, ..., n at  $t = 0, |\psi\rangle = c_n |\phi_n\rangle + c_m |\phi_m\rangle \langle \phi_n |\phi_m\rangle = \delta_{nm}$ (a) At t = 0, if H is measured on state  $|\psi\rangle$ , what will be measurement with what probability? (b) Find the angular value of H and  $H^2$  on state  $|\psi\rangle$  at t=0. (c) After what time  $t, |\psi(t)\rangle$  is orthogonal to  $|\psi(0)\rangle$ ? (d) After what time t,  $|\psi(t)|^2 = |\psi(0)|^2$ ? (e) Find the value of  $\Delta t$  if H is measured on  $|\psi\rangle$  at  $t = t_0$  what will be measurement with what probability? (f) Find the angular value of H and  $H^2$  on state  $|\psi(t)\rangle$  where  $t = t_0$ . **Solution:** (a) Measurement: at  $t = 0 |\psi\rangle = c_n |\phi_n\rangle + c_m |\phi_m\rangle$  $\hat{H} | \phi_n \rangle = E_n | \phi_n \rangle$  and  $\hat{H} | \phi_m \rangle = E_m | \phi_m \rangle$ , so measurement is either  $E_n$  or  $E_m$  $P(E_n) = \frac{|c_n|^2}{|c_n|^2 + |c_n|^2}, \ P(E_m) = \frac{|c_m|^2}{|c_n|^2 + |c_n|^2}$ (b)  $\langle H \rangle = E_n P(E_n) + E_m P(E_m) = \frac{E_n |c_n|^2}{|c_n|^2 + |c_m|^2} + \frac{E_m |c_m|^2}{|c_n|^2 + |c_m|^2}$  $\left\langle \hat{H}^{2} \right\rangle = E_{n}^{2} P(E_{n}) + E_{m}^{2} P(E_{m}) = \frac{E_{n}^{2} |c_{n}|^{2}}{|c_{n}|^{2} + |c_{m}|^{2}} + \frac{E_{m}^{2} |c_{m}|^{2}}{|c_{n}|^{2} + |c_{m}|^{2}}$ we can solve it with using formula  $\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$ if  $|\psi\rangle = c_n |\phi_n\rangle + c_m |\phi_m\rangle$  then  $\langle\psi| = c_n^* \langle\phi_n| + c_m^* \langle\phi_m|$  $H |\psi\rangle = c_n E_n |\phi_n\rangle + c_m E_m |\phi_m\rangle \Longrightarrow \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{|c_n|^2 E_n + E_m |c_m|^2}{|c_n|^2 + |c_m|^2}$   $(c) |\psi(0)\rangle = c_n |\phi_n\rangle + c_m |\phi_m\rangle$   $|\psi(t)\rangle = c_n \exp\left(-\frac{iE_n t}{\hbar}\right) |\phi_n\rangle + c_m \exp\left(-\frac{iE_m t}{\hbar}\right) |\phi_m\rangle$   $\langle \psi(0) |\psi(t)\rangle = 0 \Longrightarrow |c_n|^2 \exp\left(-\frac{iE_n t}{\hbar}\right) + |c_m|^2 \exp\left(-\frac{iE_m t}{\hbar}\right) = 0$  $=\frac{|c_n|^2}{|c_n|^2} = -\exp\left(\frac{i(E_n - E_m)t}{\hbar}\right) \Longrightarrow \cos\frac{(E_n - E_m)t}{\hbar} = -\frac{|c_n|^2}{|c_n|^2}$  $t = \frac{\hbar}{|E_n - E_n|} \cos^{-1} \left( -\frac{|c_n|^2}{|c_n|^2} \right) \text{ where } 0 \le \frac{|c_n|^2}{|c_n|^2} \le 1$ (d)  $|\psi(t)|^2 = |\psi(0)|^2$  $\cos\frac{\left(E_{n}-E_{m}\right)t}{\hbar} = 1 \Longrightarrow t = \frac{2\pi\hbar}{|E_{n}-E_{n}|} \Longrightarrow \Delta t \simeq \frac{2\pi\hbar}{|E_{n}-E_{n}|}$ 

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$$(e) |\psi'(t = t_0)\rangle = c_n \exp\left(-\frac{iE_n t_0}{\hbar}\right) |\phi_n(0)\rangle + c_m \exp\left(-\frac{iE_m t_0}{\hbar}\right) |\phi_m\rangle$$

$$= c'_n |\phi_n(0)\rangle + c'_m |\phi_m(0)\rangle$$

$$P(E_n) = \frac{|c'_n|^2}{|c'_n|^2 + |c'_m|^2} = \frac{|c_n|^2}{|c_n|^2 + |c_m|^2} \quad \text{and} \ P(E_m) = \frac{|c'_m|^2}{|c'_n|^2 + |c'_m|^2} = \frac{|c_m|^2}{|c_n|^2 + |c_m|^2}$$
(f) Hence after time t measurement of energy and associated probability is same as  $t = 0$ 

$$\langle H \rangle = E_n P(E_n) + E_m P(E_m) = \frac{E_n |c_n|^2}{|c_n|^2 + |c_m|^2} + \frac{E_m |c_m|^2}{|c_n|^2 + |c_m|^2}$$

$$\langle \hat{H}^2 \rangle = E_n^2 P(E_n) + E_m^2 P(E_m) = \frac{E_n^2 |c_n|^2}{|c_n|^2 + |c_m|^2} + \frac{E_m^2 |c_m|^2}{|c_n|^2 + |c_m|^2}$$

**Example:** A state function is given by

$$|\psi\rangle = |\phi_1\rangle + \frac{1}{\sqrt{2}}|\phi_2\rangle$$

It is given that  $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ 

(a) check  $|\psi\rangle$  is normalized or not

(b) write down normalized wavefunction  $\langle \psi |$ .

(c) It is given  $\hat{H} | \phi_n \rangle = (n+1)\hbar \omega | \phi_n \rangle$  n = 0, 1, 2, 3, ...

If  $\hat{H}$  will measured on  $|\psi\rangle$ , what will be measurement with what probability.

(d) Find the expectation value at  $\hat{H}$  i.e.,  $\langle \hat{H} \rangle$ 

(e) Find the error in the measurement in  $\hat{H}$  ie  $\Delta \hat{H}$ .

**Solution:** (a)  $|\psi\rangle = |\phi_1\rangle + \frac{1}{\sqrt{2}} |\phi_2\rangle$ 

To check normalization, one should verify.  $\langle \psi | \psi \rangle = 1$ 

$$|\psi\rangle = |\phi_1\rangle + \frac{1}{\sqrt{2}} |\phi_2\rangle$$
  
$$\langle\psi|\psi\rangle = \langle\phi_1|\phi_1\rangle + \langle\phi_1|\phi_2\rangle \frac{1}{\sqrt{2}} \langle\phi_2|\phi_1\rangle + \frac{1}{\sqrt{2}} \langle\phi_2+\phi_2\rangle \left(\frac{1}{\sqrt{2}}\right)^2 = 1 + 0 + 0 + \frac{1}{2} = \frac{3}{2}$$

The value of  $\langle \psi | \psi \rangle = \frac{3}{2}$  so  $|\psi\rangle$  is not normalized.

(b) Now we need to find normalized  $|\psi\rangle$  let A be normalization constant.

$$|\psi\rangle = A\left(|\phi_1\rangle + \frac{1}{\sqrt{2}}|\phi_2\rangle\right)$$
$$\langle\psi|\psi\rangle = A^2 + \frac{A^2}{2} = 1 \implies \frac{3A^2}{2} = 1 \implies A = \sqrt{\frac{2}{3}}$$

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So 
$$|\psi\rangle = \sqrt{\frac{2}{3}} |\phi\rangle + \frac{1}{\sqrt{3}} |\phi_2\rangle$$
  
 $\langle \psi = \langle \phi_1 | \sqrt{\frac{2}{3}} + \langle \phi_2 | \frac{1}{\sqrt{3}}$   
(c) It is given that  
 $\hat{H} | \phi_2 \rangle = 2\hbar\omega$   $\hat{H} | \phi_2 \rangle = 3\hbar\omega$   
When H will measured  $|\psi\rangle$  it will measured either  $2\hbar\omega$  or  $3\hbar\omega$   
The probability of measured  $2\hbar\omega$  is  $P(2\hbar\omega)$  is given by  
 $P(2\hbar\omega) = \frac{|\langle \phi_1 | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{2}{3}$   $P(3\hbar\omega) = \frac{|\langle \phi_1 | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{1}{3}$   
So when  $\hat{H}$  will measure state  $|\psi\rangle$  the following outcome will come.  
Measurement  $i = 2\hbar\omega$   $3\hbar\omega$   
Probability  $: \frac{2}{3} = \frac{1}{3}$   
(d)  $\langle \hat{H} \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \sum_{n} P_n (E_n) E_n = 2\hbar\omega \times \frac{2}{3} + 3\hbar\omega \times \frac{1}{3} \Rightarrow \langle H \rangle = \frac{7\hbar\omega}{3}$   
 $\langle \hat{H}^2 \rangle = \frac{\langle \psi | \hat{H}^2 | \psi \rangle}{\langle \psi | \psi \rangle} = \Sigma P_n (E_n) E_n^2 \Rightarrow \langle \hat{H}^2 \rangle = \frac{2}{3} \times (2\hbar\omega)^2 + \frac{1}{3} \times (3\hbar\omega)^2$   
 $= \frac{8\hbar^2 \omega^2}{3} + \frac{9\hbar^2 \omega^2}{3} = \frac{17\hbar^2 \omega^2}{3}$   
(e) The error in measurement in  $\hat{H}$  is given as  
 $\Delta \hat{H} = \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2}$   $\langle \hat{H}^2 \rangle = \frac{17\hbar^2 \omega^2}{3}$   $\langle \hat{H} \rangle^2 = (\frac{7\hbar\omega}{3})^2 = \frac{49\hbar^2 \omega^2}{9}$   
 $\Delta \hat{H} = \sqrt{\frac{17}{3} - \frac{49}{9}} \hbar\omega \Rightarrow \Delta \hat{H} = \sqrt{\frac{51-49}{9}} \hbar\omega = \frac{\sqrt{2}}{3} \hbar\omega$ 

**Example:** Operator  $\hat{A}$  is defined as  $\hat{A}|a_1\rangle = a_1|a_1\rangle$  and  $\hat{A}|a_2\rangle = a_2|a_2\rangle$ 

If A will measured on a state  $|\psi\rangle$  which is defined as  $|\psi\rangle = 3|a_1\rangle + 4|a_2\rangle$  where  $|a_1\rangle$  and  $|a_2\rangle$  are orthonormal vectors

(i) What will be the measurement and what is probability?

(ii) If A will measured on a state  $|\psi\rangle$  the measurement is  $a_2$ . Just after the measurement of  $\hat{A}$ , again operator  $\hat{B}$  will measured on a state,  $|\psi\rangle$ , where  $\hat{B}$  is defined as  $\hat{B}|b_1\rangle = b_1|b_1\rangle$ ,  $\hat{B}|b_2\rangle = b_2|b_2\rangle$  where  $|b_1\rangle$  and  $|b_2\rangle$  are orthonormal vectors

It is also given that  $|a_1\rangle = \frac{1}{\sqrt{2}} (|b_1\rangle + |b_2\rangle)$  and  $|a_2\rangle = \frac{1}{\sqrt{2}} (|b_1\rangle - |b_2\rangle)$ 

Then what will be the measurement and what is probability.

(iii) After evolving time again  $\hat{B}$  will measured on  $|\psi\rangle$ . What will measurement and what is probability?

Solution: (i) According to postulates 2 and postulates 2

 $\hat{A}|a_1\rangle = a_1|a_1\rangle \ \hat{A}|a_2\rangle = a_2|a_2\rangle$  The measurement is eigen value  $a_1$  or  $a_2$ 

$$P(a_1) = \frac{|\langle a_1 | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{|3|^2}{|3|^2 + |4|^2} = \frac{9}{25} \text{ and } P(a_2) = \frac{|\langle a_2 | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{|4|^2}{|3|^2 + |4|^2} = \frac{16}{25}$$
  
$$\therefore P(a_1) + P(a_2) = \frac{9}{25} + \frac{16}{25} = 1$$

(ii) According to postulates 4 if  $\hat{A}$  will measured on a state  $|\psi\rangle$  and the measurement is  $a_2$ , that means  $|\psi\rangle$  will projected in the direction of  $|a_2\rangle$ 

Just after measurement of  $\hat{A}$ , if  $\hat{B}$  will measure on the state  $|\psi\rangle$   $\hat{B}$  will measured on eigen state corresponds to eigen value  $a_2$  i.e.  $|a_2\rangle$ 

As 
$$\hat{B}|b_1\rangle = b_1|b_1\rangle$$
,  $\hat{B}|b_2\rangle = b_2|b_2\rangle$  and  $|a_2\rangle = \frac{1}{\sqrt{2}}(|b_1\rangle - |b_2\rangle)$ 

Now the measurement is  $b_1$  or  $b_2$ 

$$P(b_1) = \frac{|\langle b_1 | a_2 \rangle|^2}{\langle a_2 | a_2 \rangle} = \frac{\left|\frac{1}{\sqrt{2}}\right|^2}{\left|\frac{1}{\sqrt{2}}\right|^2 + \left|\frac{1}{\sqrt{2}}\right|^2} = \frac{1}{2} \text{ and } P(b_2) = \frac{|\langle b_2 | a_2 \rangle|^2}{\langle a_2 | a_2 \rangle} = \frac{\left|\frac{1}{\sqrt{2}}\right|^2}{\frac{1}{2} + \frac{1}{2}} = \frac{1}{2}$$

(iii) When time is evolved sufficiently then the state become again  $|\psi\rangle$ . Now  $\hat{B}$  will measured on  $|\psi\rangle$ 

Now we write  $|\psi\rangle$  in terms of  $|b_1\rangle$  and  $|b_2\rangle$ 

$$|\psi\rangle = 3|a_1\rangle + 4|a_2\rangle = \frac{3}{\sqrt{2}}(|b_1\rangle + |b_2\rangle) + \frac{4}{\sqrt{2}}(|b_1\rangle - |b_2\rangle)$$
$$|\psi\rangle = \frac{7}{\sqrt{2}}|b_1\rangle - \frac{1}{\sqrt{2}}|b_2\rangle$$

Here the measurement is again  $b_1$  or  $b_2$  as this is the eigen value.

$$P(b_{1}) = \frac{\left|\langle b_{1} | \psi \rangle\right|^{2}}{\left\langle \psi | \psi \rangle} = \frac{\left|7 / \sqrt{2}\right|^{2}}{\left|7 / \sqrt{2}\right|^{2} + \left|1 / \sqrt{2}\right|^{2}} = \frac{49}{50}$$
$$P(b_{2}) = \frac{\left|\langle b_{2} | \psi \rangle\right|^{2}}{\left\langle \psi | \psi \rangle} = \frac{\left|1 / \sqrt{2}\right|^{2}}{\left|7 / \sqrt{2}\right|^{2} + \left|1 / \sqrt{2}\right|^{2}} = \frac{1}{50}$$
$$P(b_{1}) + P(b_{2}) = 1$$

**Example:** A time t = 0 the state vector  $|\psi(0)\rangle$  where  $|\psi(0)\rangle = \frac{1}{\sqrt{2}} (|\phi_1\rangle + |\phi_2\rangle)$ 

It is given as Hamiltonian is defined as  $\hat{H} | \phi_n \rangle = n^2 \in_0 | \phi_n \rangle$  where n = 1, 2, 3... it is given as  $\langle \phi_m | \phi_n \rangle = \delta_{m,n}$ 

- (a) What is wave function  $|\psi(t)\rangle$  at later time *t*.
- (b) Write down expression of evolution of  $|\psi(x, t)|^2$
- (c) Find  $\Delta \hat{H}$

(d) Find the value of  $\Delta \hat{H}.\Delta t$ 

Solution: (a) 
$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} \left[ \exp\left(\frac{-i \in_0 t}{\hbar}\right) |\phi_1\rangle + \exp\left(\frac{-i4 \in_0 t}{\hbar}\right) |\phi_2\rangle \right]$$
  
 $|\psi(t)\rangle \propto \left[ |\phi_1\rangle + e^{-\omega_{21}t} |\phi_2\rangle \right]$   
Where  $\omega_{21} = \frac{E_2 - E_1}{\hbar} = \frac{3 \in_0}{\hbar}$   
(b) Evolution of shape of the wave packet  
 $|\psi(x,t)|^2 = \frac{1}{2} |\phi_1(x)|^2 + \frac{1}{2} |\phi_2(x)|^2 + \phi_1 \phi_2 \cos \omega_{21} t$ 

(c)  $\Delta \hat{H} = \left(\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2\right)^{1/2}$ 

$$\langle \hat{H} \rangle = \frac{1}{2} E_1 + \frac{1}{2} E_2 = \frac{1}{2} \epsilon_0 + \frac{1}{2} 4 \epsilon_0 = \frac{3}{2} \epsilon_0$$
  
$$\langle \hat{H}^2 \rangle = \frac{1}{2} E_1^2 + \frac{1}{2} E_2^2 = \frac{1}{2} (\epsilon_0)^2 + \frac{1}{2} (4 \epsilon_0)^2 = \frac{17}{2} \epsilon_0^2$$
  
$$\Delta \hat{H} = \left( \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 \right)^{1/2} = \sqrt{\left(\frac{17}{2} - \frac{25}{4}\right)} \epsilon_0 = \sqrt{\frac{9}{4}} \epsilon_0 \Rightarrow \Delta \hat{H} = \frac{3}{2} \epsilon_0$$
  
(d) 
$$\Delta \hat{H} = \frac{3}{2} \epsilon_0 \text{ and } \Delta t = \frac{2\pi\hbar}{E_2 - E_1} = \frac{2\pi\hbar}{3\epsilon_0} \text{ so } \Delta \hat{H} \cdot \Delta t = \frac{3}{2} \epsilon_0 \times \frac{2\pi\hbar}{3\epsilon_0} = \frac{\hbar}{2}$$

**Example:** A state 
$$|\psi\rangle$$
 is written in the form  $|\psi(0)\rangle = \frac{1}{\sqrt{2}}|\psi_+\rangle + \frac{1}{\sqrt{2}}|\psi_-\rangle$ 

The energy eigen value is (E) and (-E) associated to  $\ket{\psi_+}$  and  $\ket{\psi_-}$ 

(i) If *H* will measured on state  $|\psi(0)\rangle$  then what will be the measurement and what probability? (ii) After what time  $t, |\psi(t)\rangle$  is orthogonal to  $|\psi(0)\rangle$ ?

- (iii) After what time  $|\psi(t)|^2 = |\psi(0)|^2$
- (iv) Write down the expression of state after time  $t = \frac{h}{6E}$
- (v) Find  $\langle H \rangle$  and  $\langle H^2 \rangle$  at time  $t = \frac{h}{6E}$  on  $|\psi(H)\rangle$ .

(vi) Find the probability that the system will be in the state at  $t = \frac{h}{6E}$  i.e., the probability that  $|\psi(0)\rangle$  will be in the state  $|\psi(H)\rangle$ .

**Solution:** (i) A state  $|\psi\rangle$  is written in the form  $|\psi(0)\rangle = \frac{1}{\sqrt{2}}|\psi_+\rangle + \frac{1}{\sqrt{2}}|\psi_-\rangle$ If *H* will measured on state  $|\psi(0)\rangle$  then the measurement is *E* or -E

$$P(E) = \frac{\left| \langle \psi_{+} | \psi(0) \rangle \right|^{2}}{\left\langle \psi(0) | \psi(0) \rangle} = \frac{\left| \frac{1}{\sqrt{2}} \right|^{2}}{\left| \frac{1}{\sqrt{2}} \right|^{2} + \left| \frac{1}{\sqrt{2}} \right|^{2}} = \frac{1}{2}$$

$$P(-E) = \frac{\left| \langle \psi_{-} | \psi(0) \rangle \right|^{2}}{\left\langle \psi(0) | \psi(0) \rangle} = \frac{\left| \frac{1}{\sqrt{2}} \right|^{2}}{\left| \frac{1}{\sqrt{2}} \right|^{2} + \left| \frac{1}{\sqrt{2}} \right|^{2}} = \frac{1}{2}$$
(ii)  $|\psi(0)\rangle = \frac{1}{\sqrt{2}} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} |\psi_{-}\rangle \langle \psi(0)| = \frac{1}{\sqrt{2}} \langle \psi_{+}| + \frac{1}{\sqrt{2}} \langle \psi_{-}|$ 

$$\begin{split} |\psi(t)\rangle &= \frac{1}{\sqrt{2}} |\psi_{-}\rangle \exp\left(\frac{-iEt}{\hbar}\right) + \frac{1}{\sqrt{2}} |\psi_{-}\rangle \exp\left(\frac{iEt}{\hbar}\right) \\ \langle\psi(0)|\psi(t)\rangle &= 0 \Rightarrow t = \frac{\hbar}{|E_{-}-E_{-}||} \cos^{-1}\left\{\frac{-|C_{+}|^{2}}{|C_{-}|^{2}}\right\} \text{ here } E_{-} = E_{-} E_{-} \text{ and } |C_{+}|^{2} = \left|\frac{1}{\sqrt{2}}\right|^{2} = \frac{1}{2} \text{ and } \\ |C_{+}|^{2} = \left|\frac{1}{\sqrt{2}}\right|^{2} = \frac{1}{2} \Rightarrow t = \frac{\hbar}{|E_{+}E|} \cos^{-1}(-1) = \frac{\hbar}{2E} \pi t = \frac{\pi\hbar}{2E} \\ (\text{iii) Now for } |\psi(t)|^{2} = |\psi(0)|^{2} \text{ where} \\ t = \frac{2\pi\hbar}{2E} = \frac{2\pi\hbar}{2E} = \frac{\pi\hbar}{E} \Rightarrow \Delta t = t = \frac{\pi\hbar}{E} \\ (\text{iv) We have } |\psi(0)\rangle = \frac{1}{\sqrt{2}} |\psi_{-}\rangle + \frac{1}{\sqrt{2}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{\frac{iE_{-}}{\hbar}} |\psi_{-}\rangle + \frac{1}{\sqrt{2}} e^{\frac{iE_{-}}{\hbar}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{\frac{iE_{-}}{\hbar}} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} e^{\frac{iE_{-}}{\hbar}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} e^{-\frac{i\pi}{\hbar}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{\hbar}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{\hbar}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{\hbar}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{\hbar}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{\hbar}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{4}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{4}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{3}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{3}} |\psi_{-}\rangle \\ |\psi(t)\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle + \frac{1}{\sqrt{2}} \exp^{-\frac{i\pi}{3}} |\psi_{-}\rangle \\ \langle t\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle \\ \langle t\rangle = \frac{1}{\sqrt{2}} \exp\frac{i\pi}{3} |\psi_{+}\rangle \\ \langle t\rangle = \frac{1}{\sqrt{2}} \exp\left(-\frac{1}{\sqrt{2}} |\psi_{-}\rangle\right \\ \langle t\rangle = \frac{1}{\sqrt{2}} \exp\left(-\frac{1}{\sqrt{2}} |\psi_{-}\rangle\right) \\ \langle t\rangle = \frac{1}{\sqrt{2}} \exp\left$$

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(vi) The probability that the system will be in the state at  $t = \frac{h}{6E}$  $P = \frac{\left| \langle \psi(t) | \psi(0) \rangle \right|^2}{\langle \psi(0) | \psi(0) \rangle}$   $\langle \psi(t) | = \frac{1}{\sqrt{2}} \exp \frac{-i\pi}{3} \langle \psi_+ | + \frac{1}{\sqrt{2}} \exp \frac{i\pi}{3} \langle \psi_- |$ Probability *P* that state  $| \psi(t) \rangle$  is in direction of state  $| \psi(0) \rangle = \frac{\left| \langle \psi(t) | \psi(0) \rangle \right|^2}{\langle \psi(0) | \psi(0) \rangle}$ where  $\langle \psi(t) | \psi(0) \rangle = \left| \frac{1}{\sqrt{2}} \right|^2 \exp \frac{i\pi}{3} + \left| \frac{1}{\sqrt{2}} \right|^2 \exp \frac{-i\pi}{3}$   $P = \frac{\left| \frac{1}{2} \left( \exp \frac{i\pi}{3} + \exp \frac{-i\pi}{3} \right) \right|^2}{1} = \left| \frac{1}{2} \cdot 2 \cos \frac{\pi}{3} \right|^2 \Rightarrow P = \frac{1}{4}$ 

**Example:** Consider a one-dimensional particle which is confined within the region  $0 \le x \le a$  and whose wave function is  $\psi(x,t) = \sin\left(\frac{\pi x}{a}\right)e^{i\omega t}$ . Find the potential V(x). **Solution:** From the fifth postulate.

$$H\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad H = \frac{P^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$
$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = i\hbar\frac{\partial\psi}{\partial t}$$
$$\frac{\pi^2\hbar^2}{2ma^2}\sin\frac{\pi x}{a}e^{i\omega t} + V(x)\frac{\sin\pi x}{a}e^{i\omega t} = i\hbar\sin\frac{\pi x}{a}(-i\omega)e^{i\omega a}$$
$$\frac{\pi^2\hbar^2}{2ma^2} + V(x) = -\hbar\omega \quad V(x) = -\hbar\omega - \frac{\pi^2\hbar^2}{2ma^2} \quad V(x) = -\left(\hbar\omega + \frac{\pi^2\hbar^2}{2ma^2}\right)$$