# Postulates of Quantum Mechanics.

Non relativistic quantum Mechanics and its relativistic extension is based on certain postulates which we will now discuss.

## Postulate 1

To every physical system there corresponds a Hilbert space. Each possible state of the system is given by a vector in the Hilbert space.

## Discussions on postulate 1

The first postulate of QM implies the principle of superposition, which states that if $|\psi_1\rangle$ and $|\psi_2\rangle$ are two vectors in the Hilbert space representing two possible states of the system, then a linear combination of $|\psi_1\rangle$ and $|\psi_2\rangle$:

$$|\psi\rangle = c_1 |\psi_1\rangle + c_2 |\psi_2\rangle$$

is also a vector in the Hilbert space and so represents a possible state of the system.

We make a further assumption, namely that by superposing a state with itself we cannot form a new state, but get the original state over again. If the original state is $|\psi_1\rangle$, when it is superposed with itself, the resulting ~~state~~ vector will correspond to

$$c|\psi_1\rangle + c_2|\psi_1\rangle = (c_1 + c_2)|\psi_1\rangle$$

where $c_1$ and $c_2$ are numbers, in general, complex.

Now, we may have $c_1 + c_2 = 0$, in which case result of the superposition process will be the null vector which corresponds to no state of the physical system at all. Apart from this special case, the effect of superposing a vector with itself, is like multiplying the vector by a complex number $c$ $(= c_1 + c_2)$ and therefore $c|\psi_1\rangle$ and $|\psi_1\rangle$ represents the same state of the system.

To repeat, if the vector corresponding to a state of the system is multiplied by any complex number, not zero, the resulting vector will correspond to the same state. Thus a state is specified by the 'direction' of a vector in the Hilbert space, and any 'length' we may assign the vector is irrelevant. Usually we assign a 'length' or norm of unity to the state vector, for convenience, as will be apparent later. In other words, we take $\langle\psi|\psi\rangle = 1$. We may reword the first postulate by saying that the state of a system is given by a ray in the Hilbert space.

The assumption just made shows up very clearly the fundamental difference between the superposition of quantum theory and any kind of classical superposition. In the case of a classical system, for instance a vibrating string or a membrane, ~~system~~, when one superposes a state with itself, the result is a <u>different</u> state with an amplitude double the original amplitude. Again, while there exists a classical state with zero amplitude of oscillation everywhere, namely, the state of rest, there does not exist any corresponding state for a quantum system, the zero or null vector corresponding to no state at all.

Now, even when the state vector is normalized, the vector can be multiplied by a phase factor $e^{i\theta}$ ($\theta$ = real) without affecting the normalization. Thus $e^{i\theta}|\psi\rangle$ is normalized if $|\psi\rangle$ is normalized.

Extreme caution has to be exercised when we superpose states to get a new state. For example, let us assume that

$$|\psi\rangle = \lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle$$

where $\lambda_1$ and $\lambda_2$ are complex numbers. It is true that $e^{i\theta_1}|\psi_1\rangle$ represents, for all real $\theta_1$, the same normalized physical state vector as $|\psi_1\rangle$ and $e^{i\theta_2}|\psi_2\rangle$ the same state as $|\psi_2\rangle$, but

$$|\phi\rangle = \lambda_1 e^{i\theta_1}|\psi_1\rangle + \lambda_2 e^{i\theta_2}|\psi_2\rangle$$

does not describe the same ~~states~~ state as $|\psi\rangle$. However, for the special case where $\theta_2 = \theta_1 + 2n\pi$, we have

$$|\phi\rangle = e^{i\theta_1}\left(\lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle\right)$$
$$= e^{i\theta_1}|\psi\rangle .$$

Now $|\phi\rangle$ represents the same state of the system as $|\psi\rangle$.

In other words, a global (i.e., overall) phase factor does not affect the physical predictions, but the relative phases of the coefficients of an expansion are important.

## Postulate 2

To every physical quantity there corresponds a hermitian operator acting in the Hilbert space of the system. In particular, the operators $\hat{x}$ and $\hat{p}$ corresponding to the coordinate and momentum of the particle, satisfy the commutation relation

$$[\hat{x}, \hat{p}] = i\hbar \hat{\mathbb{1}} .$$

Discussions:

Since any classical physical quantity may be expressed as a function of coordinate and momentum, $Q = Q(x, p)$, the replacement $x \to \hat{x}$ and $p \to \hat{p}$ in the classical expression $Q(x, p)$ yields the operator $\hat{Q} = Q(\hat{x}, \hat{p})$. Thus, a one-to-one correspondence between operators $\hat{Q}$ and physical quantities or observables is established. However, there are also purely quantum operators, such as the spin operators, that cannot be obtained through such substitution.

The operator corresponding to the classical Hamilton function $H(p,x)$ is called the Hamiltonian.

For a conservative system

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + V(\hat{x})$$

where $m$ is the mass of the particle and $V$ the potential.

The recipe

$$\hat{Q} = Q(x \to \hat{x},\ p \to \hat{p})$$

is often ambiguous. If for example, $Q = xp$, we don't know if $\hat{Q} = \hat{x}\hat{p}$ or $\hat{p}\hat{x}$ since $xp = px$ classically but $\hat{x}\hat{p} \neq \hat{p}\hat{x}$.

There is no general method for resolving such ambiguities. In the present case, the rule is to use the symmetric sum, $\hat{Q} = \frac{1}{2}(\hat{x}\hat{p} + \hat{p}\hat{x})$.

Notice incidentally that symmetrization renders $\hat{Q}$ hermitian. Symmetrization is the answer as long as $Q$ does not involve products of two or more powers of $\hat{x}$ with two or more powers of $\hat{p}$. If it does, only experiment can decide the correct prescription. We will not encounter such a situation in this course.

Postulate 3

The only possible result of the measurement of a physical quantity A is one of the eigenvalues of the corresponding hermitian operator $\hat{A}$.

Since the eigenvalues of a hermitian operator are real, it follows that the result of a measurement of a physical quantity is a real number. The eigenvalue spectrum of $\hat{A}$ may be discrete, or continuous, or partly discrete and partly continuous. Thus measurements may yield discrete values or values lying in a continuous range depending on the nature of the operator $\hat{A}$.

The eigenvectors of a hermitian operator $\hat{A}$ representing an observable, form a complete orthonormal set of vectors and therefore form a basis of the Hilbert space.

If the eigenvalue spectrum is discrete, the orthonormality and completeness conditions can be written as

$$\langle a_n, r | a_{n'}, r' \rangle = \delta_{nn'} \, \delta_{rr'}$$

and

$$\sum_n \sum_{r=1}^{g_n} |a_n, r\rangle\langle a_n, r| = \hat{\mathbb{1}} \, ,$$

In the above $|a_n, r\rangle$, $r = 1, 2, \cdots g_n$ are the eigenvectors of $\hat{A}$ with eigenvalue $a_n$. The degeneracy of this eigenvalue is of order $g_n$; i.e., there are $g_n$ linearly independent eigenvectors with eigenvalue $a_n$. In other words, the eigen subspace of $a_n$ is of dimension $g_n$.

The degenerate eigenvectors corresponding to a particular eigenvalue $a_n$ are not necessarily orthogonal to each other. However, by following the ~~Schmi~~ Schmidt orthognalization procedure we can make them orthonormal.

Eigenvectors belonging to different eigenvalues are automatically orthogonal, since $\hat{A}$ is a hermitian operator.

If the eigenvalue spectrum is purely continuous, the orthonormality and completeness conditions of the eigenvectors of $\hat{A}$ are written as

$$\int da \sum_{r=1}^{g_a} |a,r\rangle\langle a,r| = \hat{\mathbb{1}} \quad \text{(completeness)}$$

and

$$\langle a\, r | a'\, r' \rangle = \delta_{rr'}\, \delta(a-a') \; . \; \text{(Orthonormality)}$$

If the eigenvalue spectrum is partly discrete and partly continuous, then

$$\sum_n \sum_{r=1}^{g_n} |a_n\, r\rangle\langle a_n\, r| + \int da \sum_{r=1}^{g_a} |a\, r\rangle\langle a\, r| = \hat{\mathbb{1}}$$

and

$$\langle a_n\, r | a_{n'}\, r' \rangle = \delta_{nn'}\, \delta_{rr'}$$

$$\langle a\, r | a'\, r' \rangle = \delta(a-a')\, \delta_{rr'}$$

$$\langle a_n\, r | a\, s \rangle = 0 \, .$$

The state vector $|\psi\rangle$ of the particle can be expanded as

$$|\psi\rangle = \sum_n \sum_{r=1}^{g_n} |a_n r\rangle\langle a_n r|\psi\rangle + \int da \sum_{r=1}^{g_a} |a\, r\rangle\langle a\, r|\psi\rangle$$

or $$|\psi\rangle = \sum_n \sum_{r=1}^{g_n} c_{nr}\,|a_n r\rangle + \int da \sum_{r=1}^{g_a} c_r(a)\,|a\,r\rangle$$

where $$c_{nr} = \langle a_n r|\psi\rangle$$

and $$c_r(a) = \langle a\,r|\psi\rangle .$$

<u>Note</u>: In our discussions on the eigenvalue spectrum of $\hat{A}$ ~~to~~ the roman letter '$r$' has been used as a discrete index to differentiate between the eigenvectors of a degenerate eigenvalue. The letter $r$ should not be confused with the coordinate $r$ of a particle.

If the state vector $|\psi\rangle$ is normalized, ~~we~~ i.e., if $\langle\psi|\psi\rangle = 1$, then

$$\sum_n \sum_{r=1}^{g_n} |c_{nr}|^2 + \int da \sum_{r=1}^{g_a} |c_r(a)|^2 = 1 .$$

## Postulate 4

When the physical quantity A is measured on a system in the normalized state $|\psi\rangle$, the probability, $P_\psi(a_n)$, of obtaining the eigenvalue $a_n$ of the corresponding hermitian operator $\hat{A}$ is

$$P_\psi(a_n) = |\langle a_n|\psi\rangle|^2.$$

If the eigenvalue $a_n$ is $g_n$-fold degenerate, then

$$P_\psi(a_n) = \sum_{i=1}^{g_n} |\langle a_n, i|\psi\rangle|^2$$

where $\{|a_n, i\rangle; i = 1, 2, \cdots, g_n\}$ are the orthonormalised eigevectors of $\hat{A}$ all belonging to the same eigenvalue $a_n$.

In case of continuously distributed eigenvalues, the probability $dP_\psi(a)$ of obtaining a result between a and $a + da$ is

$$dP_\psi(a) = |\langle a|\psi\rangle|^2 da$$

or, if there is degeneracy

$$dP_\psi(a) = \sum_{i=1}^{g_a} |\langle a, i|\psi\rangle|^2 da.$$

## Discussions on postulate 4

The expectation value of the observable A in the normalized state $|\psi\rangle$ is

$$\langle \hat{A} \rangle = \sum_n{}' a_n P_\psi(a_n) \quad \text{------} (1)$$

where

$$P_\psi(a_n) = |\langle a_n|\psi\rangle|^2 .$$

- The probability amplitude $\langle a_n|\psi\rangle$ is the component of $|\psi\rangle$ along $|a_n\rangle$. We assume that $|\psi\rangle$ is normalized to unity, i.e.,

$$\langle\psi|\psi\rangle = \sum_n \langle\psi|a_n\rangle\langle a_n|\psi\rangle = \sum_n |\langle a_n|\psi\rangle|^2$$

$$= \sum_n P_\psi(a_n) = 1 .$$

Thus, normalisation of the state vector $|\psi\rangle$ to unity ensures that the sum of the probabilities of obtaining the various eigenvalues of $\hat{A}$ is unity.

The expectation (or the average) value of $\hat{A}$ can be written in an alternative form:

$$\langle \hat{A} \rangle = \sum_n a_n P_\psi(a_n)$$

$$= \sum_n a_n \left| \langle a_n | \psi \rangle \right|^2$$

$$= \sum_n a_n \langle \psi | a_n \rangle \langle a_n | \psi \rangle$$

$$= \langle \psi | \left( \sum_n a_n | a_n \rangle \langle a_n | \right) | \psi \rangle$$

$$= \langle \psi | \hat{A} | \psi \rangle \quad \cdots\cdots\cdots \quad (2)$$

We note a few points in connection with this formula for the expectation value.

1. To calculate $\langle \hat{A} \rangle$, one need only be given the state vector $|\psi\rangle$ and the operator $\hat{A}$. There is no need to find the eigenvalues or eigenvectors of $\hat{A}$.

2. If the particle is in an eigenstate of $\hat{A}$, i.e., if $\hat{A}|\psi\rangle = a|\psi\rangle$, then $\langle \hat{A} \rangle = a$.

3. By average value of $\hat{A}$ we mean the average over an ensemble of a large number of particles each in the same state $|\psi\rangle$. Let the number of particles in the ensemble be N where N is a large positive integer number. If we measure the observable A for each particle, we get one or another of the eigenvalues of the operator $\hat{A}$. Suppose the eigenvalue $a_1$ is obtained for $N_1$ of the particles, eigenvalue $a_2$ is obtained for $N_2$ particles and so on. Then, experimentally, the probability for obtaining $a_n$ is

$$P_\psi(a_n) = \frac{N_n}{N} \; ; \; n = 1, 2, 3, \ldots$$

The fourth postulate of quantum mechanics asserts that $P_\psi(a_n) = |\langle a_n|\psi\rangle|^2$.

The quantum mechanical ensemble average is then

$$\langle \hat{A} \rangle = \sum_n a_n P_\psi(a_n) = \sum_n a_n \frac{N_n}{N} .$$

It is this ensemble average that is given by the formula

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle .$$

If the eigenvalue spectrum of $\hat{A}$ is continuous the ensemble average is found in the following way. Suppose we have a very large number $N$ of particles each in the state $|\psi\rangle$. We make a measurement of the observable $A$ for each ~~one~~ of the particles. Suppose after all the ~~measurements~~ measurements are complete, $dn(a)$ particles are found to have values of $A$ lying within a small interval $a$ to $a+da$. Then the probability that the value of $A$ lies in the above range is

$$dP_\psi(a) = \frac{dn(a)}{N}$$

The fourth postulate assumes that

$$dP_\psi(a) = \frac{dn(a)}{N} = |\langle a|\psi\rangle|^2 da .$$

Thus

$$dP_\psi(a) = |\langle a|\psi\rangle|^2 da$$

= probability that a measurement of observable A yields a value lying in the range $a$ to $a + da$ when the state of the system is $|\psi\rangle$.

We can write

$$dP_\psi(a) = \rho(a)\, da$$

where

$$\rho(a) = |\langle a|\psi\rangle|^2.$$

The quantity $\rho(a)$ is called the probability density for the observable A.

Since the total probability is 1, we must have

$$\int \rho(a)\, da = 1$$

or

$$\int |\langle a|\psi\rangle|^2 da = 1$$

or,

$$\int da \, \langle \psi | a \rangle \langle a | \psi \rangle = 1$$

or $\quad \langle \psi | \psi \rangle = 1$

i.e., normalizing the state vector amounts to making the total probability equal to one.

The expectation value of $\hat{A}$ is

$$\begin{aligned}
\langle \hat{A} \rangle_\psi &= \int a \, dP_\psi(a) \\
&= \int a \, |\langle a | \psi \rangle|^2 \, da \\
&= \int a \, \langle \psi | a \rangle \langle a | \psi \rangle \, da \\
&= \int \langle \psi | \hat{A} | a \rangle \langle a | \psi \rangle \, da \\
&= \left( \langle \psi | \hat{A} \right) \underbrace{\int da \, | a \rangle \langle a |}_{= \hat{\mathbb{1}}} \left( | \psi \rangle \right) \\
&= \langle \psi | \hat{A} | \psi \rangle .
\end{aligned}$$

## Reduction of the state vector
## (also called reduction of the wave packet).
### (Fifth postulate)

Assume that we want to measure, at a given instant, the physical quantity A of a system. If the ket $|\psi\rangle$, which represents the state of the system before the measurement, is known, the fourth postulate allows us to predict the probabilities of obtaining the various possible results. But when the measurement is actually made, it is obvious that one of the possible results would be obtained. We would get one of the eigenvalues of $\hat{A}$ (assuming discrete spectrum), say we get $a_n$. After obtaining the result $a_n$, if we repeatedly measure A, we keep getting the same value $a_n$. In other words the system which was in the state $|\psi\rangle$

before the first measurement, is thrown into the eigenstate $|a_n\rangle$ of $\hat{A}$ if the result $a_n$ is obtained.

We postulate that if a measurement of $\hat{A}$ on a system in the state $|\psi\rangle$ yields the value $a_n$ then the state of the system immediately after the measurement is the eigenvector $|a_n\rangle$ associated with $a_n$:

(Postulate 5)

$$\boxed{|\psi\rangle \xRightarrow{(a_n)} |a_n\rangle} \qquad (1)$$

(Assuming $a_n$ is non degenerate)

Thus a measurement process alters the state of the system. The only exception is when the state of the system is already one of the eigenstates of an operator $\hat{A}$, i.e $|\psi\rangle = |a_n\rangle$ say. Then a measurement of A on this state will yield $a_n$ with certainty and the measurement will not alter the state.

The abrupt change of the state $|\psi\rangle$ of the system to an eigenvector of the operator $\hat{A}$ of the measured quantity, is called collapse of the state vector or collapse of the wave packet.

When the eigenvalue $a_n$ obtained by the measurement is degenerate, postulate 5 can be generalised as follows. If the state $|\psi\rangle$ immediately before the measurement is written as

$$|\psi\rangle = \sum_n \sum_{i=1}^{g_n} |a_n i\rangle \langle a_n i|\psi\rangle$$

$$= \sum_n \sum_{i=1}^{g_n} c_n^i \, |a_n i\rangle$$

where

$$c_n^i = \langle a_n i|\psi\rangle ,$$

the state vector immediately after the measurement is

$$|\psi\rangle \xRightarrow{(a_n)} \frac{1}{\sqrt{\sum_{i=1}^{g_n} |c_n^i|^2}} \sum_{i=1}^{g_n} c_n^i \, |a_n, i\rangle \quad -(2)$$

Let us define the projection operator $\hat{P}_n$ onto the eigensubspace ~~of~~ $a_n$, i.e., the subspace $H_{a_n}$ spanned by the degenerate eigenvectors of $\hat{A}$ corresponding to the eigenvalue $a_n$.

We have

$$\hat{P}_n = \sum_{i=1}^{g_n} |a_n\, i\rangle\langle a_n\, i| \quad \cdots\cdots \quad (3)$$

The projection operator has the property

$$\hat{P}_n^2 = \hat{P}_n \quad \cdots\cdots \quad (4)$$

Using $\hat{P}_n$, we can write Eq. (2) as

$$|\psi\rangle \xrightarrow{(a_n)} \frac{\hat{P}_n|\psi\rangle}{\sqrt{\langle\psi|\hat{P}_n|\psi\rangle}} \quad \cdots\cdots (5)$$

We summarize the above discussions in the fifth postulate of quantum mechanics:

> Fifth postulate:
>
> If a measurement of the physical quantity A on a system in the state $|\psi\rangle$ gives the result $a_n$, the state of the system immediately after the measurement is the normalized projection
>
> $$\frac{\hat{P}_n|\psi\rangle}{\sqrt{\langle\psi|\hat{P}_n|\psi\rangle}}$$
>
> of $|\psi\rangle$ onto the eigensubspace associated with $a_n$.

## Time evolution of the system

Postulates 1–5 tell us how to extract information about a system in the state $|\Psi\rangle$ at a particular instant of time. Of course, the state vector evolves with time, i.e., changes with time. The time evolution of the state vector is given by the Schrödinger equation.

**Sixth postulate of quantum mechanics:**

The time evolution of the state vector $|\Psi(t)\rangle$ is governed by the Schrödinger equation

$$i\hbar \frac{d}{dt}|\Psi(t)\rangle = \hat{H}\,|\Psi(t)\rangle$$

where $\hat{H}$ is the operator, called the Hamiltonian, associated with the total energy of the system.

Questions arise how do we construct the Hamiltonian operator for the system. If the system has a classical analog, first we write down the classical Hamiltonian $H(x, p)$ of the system. Then we substitute $x \to \hat{x}$ and $p \to \hat{p}$ to get the Hamiltonian operator.

For example, the Hamiltonian for a classical one-dimensional harmonic oscillator is

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 .$$

The Hamiltonian operator for the quantum mechanical harmonic oscillator would then be

$$H(\hat{x}, \hat{p}) = H(x \to \hat{x}, p \to \hat{p})$$

or

$$H(\hat{x}, \hat{p}) = \frac{\hat{p}^2}{2m} + \frac{1}{2} m \omega^2 \hat{x}^2 .$$

For systems having no classical analog, say problems involving spin, intuition and experiments are the guides that allow us to write down the Hamiltonian operator.

## Discussions on the Schrödinger equation

The Schrödinger equation gives the time evolution of the state vector of a quantum mechanical system. If the state vector of the system is known at some initial instant of time, say at $t = 0$, then the Schrödinger equation allows us to find the state vector uniquely at a later instant of time $t$ provided no measurement of any kind is made on the system. Thus, the state vector of the system evolves in a deterministic manner provided that the system is left undisturbed.

Indeterministic, i.e., probabilistic aspect of quantum mechanics shows up only in the act of measurement. Suppose that the state vector of the system is $|\psi\rangle$ immediately before the measurement of some dynamical variable $A$. If the state $|\psi\rangle$ is a superposition of the various eigenkets $|a_n\rangle$ of the operator $\hat{A}$ ~~repre~~ representing the observable, then immediately after the measurement, the state vector $|\psi\rangle$ changes abruptly and unpredictably to one of the eigenvectors of $\hat{A}$. Thus

$$|\psi\rangle \xrightarrow{\text{measurement}} |a_n\rangle,$$

if the result $a_n$ is obtained in the course of the measurement. Of course, in the special case when the state vector is one of the eigenvectors of $\hat{A}$ corresponding to a particular eigenvalue, say $|\psi\rangle \equiv |a_k\rangle$, then a measurement of $A$ is certain to yield the eigenvalue $a_k$ and the state vectors remains unaltered.

# Solution of the Schrödinger equation (SE)

The Schrödinger equation is

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle . \quad \cdots\cdots (1)$$

The eigenvalue equation for the Hamiltonian operator $\hat{H}$ is written as

$$\hat{H} |E_n\rangle = E_n |E_n\rangle . \quad \cdots\cdots (2)$$

The set of eigenvectors $\{ |E_n\rangle, n = 1, 2, 3, \ldots \}$ form a complete orthonormal set of basis vectors for the Hilbert space. The orthonormality and the completeness conditions for this basis set are written as

$$\langle \psi_n | E_m \rangle = \delta_{nm} \quad (\text{orthonormality}) \cdots (3)$$

$$\sum_n |E_n\rangle\langle E_n| = \hat{\mathbb{1}} \quad (\text{completeness}) \quad \cdots (4)$$

The eigenbasis of $\hat{H}$, i.e., the basis $\{ |E_n\rangle, n=1,2,\cdots \}$ provide a representation for vectors and operators in the Hilbert space. This representation is called the energy representation.

Now, suppose that we know the state vector $|\psi(0)\rangle$ at $t=0$. How do we find the state vector $|\psi(t)\rangle$ at a later time by solving the Schrödinger equation? We start by expanding $|\psi(0)\rangle$ in the eigenbasis of $\hat{H}$. Write

$$|\psi(0)\rangle = \sum_n c_n(0)\,|E_n\rangle \quad \cdots\cdots (5)$$

where the expansion coefficients $c_n(0)$ are assumed to be known. If $|\psi(0)\rangle$ is normalized to unity, the expansion coefficients must satisfy the relation

$$\langle\psi(0)|\psi(0)\rangle = \sum_n |c_n(0)|^2$$

$$= \sum_n |\langle E_n|\psi(0)\rangle|^2 = 1 \quad \cdots (6)$$

where we have used

$$c_n(0) = \langle E_n|\psi(0)\rangle.$$

Next, we write

$$|\Psi_n(t)\rangle = \sum_n c_n(t)\,|E_n\rangle \quad \cdots\cdots (7).$$

We have to find the expansion coefficients $c_n(t)$. Substitute Eq.(7) into the Schrödinger equation (Eq.(1)). We get

$$i\hbar \frac{d}{dt}\sum_n c_n(t)\,|E_n\rangle = \hat{H}\sum_n c_n(t)\,|E_n\rangle$$

or

$$i\hbar \sum_n \frac{dc_n(t)}{dt}\,|E_n\rangle = \sum_n c_n(t)\,\hat{H}\,|E_n\rangle$$

or
$$i\hbar \sum_n \frac{dc_n(t)}{dt}\,|E_n\rangle = \sum_n c_n(t)\,E_n\,|E_n\rangle. \quad \cdots (8)$$

Since the eigenkets $\{|E_n\rangle\}$ are orthonormal, it follows from Eq.(8) that for each $c_n(t)$ we must have

$$i\hbar \frac{dc_n(t)}{dt} = E_n\,c_n(t), \quad \cdots\cdots (9)$$

Eq.(9) can be solved easily. We have

$$c_n(t) = c_n(0)\,e^{-iE_n t/\hbar} \quad \cdots\cdots (10)$$

Here $c_n(0)$ are known, and we find $c_n(t)$ by using Eq.(10). The state ket $|\Psi(t)\rangle$ (Eq.(7)) can then written as

$$\boxed{|\psi(t)\rangle = \sum_n c_n(0)\, e^{-iE_n t/\hbar} |E_n\rangle} \quad \cdots\cdots (11)$$

This is the solution of the Schrödinger equation giving us the state vector at an arbitrary time $t$ given the state vector at $t=0$. From Eq. (11) we note that, to obtain $|\psi(t)\rangle$ each expansion coefficient $c_n(0)$ of the initial state vector $|\psi(0)\rangle$ is modified by the multiplicative phase factor $e^{-iE_n t/\hbar}$.

From Eq. (11) we also note that $|\psi(t)\rangle$ is normalized to unity if the initial state vector $|\psi(0)\rangle$ is normalized to unity:

$$\langle\psi(t)|\psi(t)\rangle = \sum_n \left| c_n(0)\, e^{-iE_n t/\hbar} \right|^2$$

$$= \sum_n |c_n(0)|^2 = \langle\psi(0)|\psi(0)\rangle = 1.$$

Thus the Schrödinger equation does not alter the normalization of the state vector.

## Stationary States

Suppose that the state vector of the system at $t=0$ is one of the eigenstates of $\hat{H}$, say

$$|\psi(0)\rangle = |E_n\rangle \quad \text{. . . . . . . . . (12)}$$

This state of the system is a state where the system has a definite energy $E_n$. Here we have taken $c_n(0) = 1$ and $c_m(0) = 0$ if $m \neq n$ in Eq. (5). Then according to Eq. (11), the state vector of the system at a later time $t$ is

$$|\psi(t)\rangle = e^{-iE_n t/\hbar}\,|E_n\rangle \quad \text{. . . . . . . (13)}$$

From Eqs. (12) and (13) we see that both the the vectors $|\psi(0)\rangle$ and $|\psi(t)\rangle$ represent the same state of definite energy $E_n$, because the two vectors only differ by an overall phase factor.

The states of the system with definite energy are called ~~stationary~~ stationary states because in such states the expectation value of any observable $\hat{A}$ is time-independent;

$$\langle \hat{A} \rangle = \langle \psi(t) | \hat{A} | \psi(t) \rangle$$

$$= \langle \psi(0) | e^{iE_n t/\hbar} \hat{A} \, e^{-iE_n t/\hbar} | \psi(0) \rangle$$

$$= \langle \psi(0) | \hat{A} | \psi(0) \rangle \quad \text{(independent of time).}$$

Let us now calculate the position probability density of a particle in a stationary state. Eq. (13), expressed in the coordinate representation can be written as

$$\langle x | \psi(t) \rangle = e^{-iE_n t/\hbar} \langle x | E_n \rangle$$

or

$$\psi(x,t) = e^{-iE_n t/\hbar} \phi_n(x) \quad \cdots\cdots\cdots (13)$$

where $\phi_n(x)$ is the eigenfunction of $\hat{H}$ with eigenvalue $E_n$ defined as $\phi_n(x) \equiv \langle x | E_n \rangle$. Thus the wave function $\psi(x,t)$ of the particle at time $t$ is the eigenfunction $\phi_n(x)$

multiplied by the time-dependent phase factor $e^{-iE_nt/\hbar}$. The position probability density at time $t$ is

$$
\begin{aligned}
\rho(x,t) &= \psi^*(x,t)\,\psi(x,t) \\
&= |\psi(x,t)|^2 \\
&= |\phi_n(x)|^2 \\
&= \rho(x,t=0).
\end{aligned}
$$

Thus, we see that the position probability density of a particle in a stationary state is independent of time.

In a stationary state, no measurable quantity of the system changes with time, i.e., the measurable quantities are stationary. This is the reason why such states are called stationary.