Science

Quantum Mechanics

Physics (Hons), Sem- IV

— By Principal

Eigenvalue equations, eigen functions, eigenvalues and stationary states :

The time-independent Schrödinger equation in three dimension is given by

$$\nabla^2\psi(r) + \frac{2m}{\hbar^2}[E-V]\psi(r) = 0 \quad \text{---(1)}$$

where, the wave function $\Psi(\vec{r},t) = \psi(r)\, e^{-iEt/\hbar}$; $\psi(r)$ is the spatial part of the wave function. $V \equiv V(\vec{r})$ does not depend on t. Thus, in one dimension the time-independent Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$$

or

$$\boxed{\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E-V(x)]\psi(x) = 0} \quad \text{---(2)}$$

Each solution of (1) & (2) corresponds to a definite energy. If we write $\psi = \psi_n$ as the solution of (1) or (2) for $E = E_n$, then

$$\Psi_n(x,t) = \psi_n(x)\, e^{-iE_n t/\hbar}$$

gives us a state with a well defined energy. The wave function $\Psi(x,t)$ therefore belongs to a definite energy E. Obviously, the probability density $|\Psi(x,t)|^2$ for this state is independent of time. Such states are known as stationary states.

Now for the stationary states of a system, the spatial part of the wave function $\psi(x)$ obeys the time-independent wave equation (2). This equation belongs to a class known as eigenvalue equations. The equation of the type (2) can be solved only for a special set of values of E consistent with the boundary conditions. These energy values are known as energy eigenvalues and the corresponding wave functions as energy eigenfunctions.

In general if we consider an operator $\hat{\alpha}$ which operating on a function $\phi(x)$ multiplies the latter by a constant a, then $\phi(x)$ is called an eigenfunction of $\hat{\alpha}$ belonging to the eigen value a. To each operator $\hat{\alpha}$, there belongs a set of eigenvalues a_n and a set of eigenfunctions ϕ_n defined by the equation $\hat{\alpha}\phi_n(x) = a_n\phi_n(x)$ ---- (3)

The eigenfunctions are thus a special set of function which when operated upon by the operator $\hat{A}$ remains unchanged being simply multiplied by the corresponding eigenvalues.

To be an eigenfunction, $\phi(x)$ must be well-behaved which means that it must satisfy the following requirements:

(a) $\phi(x)$ must be single-valued everywhere;
(b) $\phi(x)$ must be square-integrable so that the integral of its modulus-squared is finite;
(c) $\phi(x)$ must be continuous everywhere;
(d) the derivative $\frac{d\phi}{dx}$ should be continuous everywhere (except probably at some isolated points);
(e) $\phi(x)$ must remain finite or vanish as $x \to \pm\infty$.

The above conditions are imposed out of consideration for the physical nature of the system. For example in the case of a particle obeying Schrödinger equation (2), the condition of single-valuedness follows from the probability interpretation of the wave function $\psi(x)$. Since the probability density of finding the particle at x is $|\psi(x)|^2$ which must necessarily have one value at a point, $\psi(x)$ must be single valued.

Again the total probability of finding the particle anywhere on the x-axis is finite, given by $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$

Hence $\psi(x)$ must be square-integrable. The continuity of $\psi(x)$ and its derivative can be proved easily.

The finiteness of $\psi(x)$ everywhere is also a consequence of the probability interpretation, since the probability-density of finding the particle at any point (including $x = \pm\infty$) must remain finite.

One of the basic assumptions of quantum mechanics is that the wave equation satisfied by the wave function Ψ must be linear so that the principle of superposition of states may be valid. The stationary state solutions of the time-independent Schrödinger equation may thus be superposed to give a general solution. These stationary state solutions represent the energy eigenfunctions belonging to different possible energy eigenvalues consistent with the boundary conditions of a given problem. It can be shown that they form a complete orthogonal set, apart from being well behaved.

The requirement of well-behaviour of the eigenfunction may in some cases impose restrictions on the admissible solutions of the eigenvalue equations. This can be seen from the following simple examples.

Example: Let $\hat{\alpha}\phi = a\phi$ where $\hat{\alpha} = \frac{d^2}{dx^2}$

Sol^n: Case I: when $a < 0$

Let $a = -k^2$; Hence $\frac{d^2\phi}{dx^2} + k^2\phi = 0$ ---(4)

Sol^n of (4) is $\phi(x) = Ae^{ikx} + Be^{-ikx}$ ---(5).

or $\phi(x) = C\cos kx + D\sin kx$ ---(6)

Here $\phi(x)$ is well-behaved in the entire range $-\infty < x < \infty$.

Case II: If $a > 0$

Writing $a = k^2$ we get $\frac{d^2\phi}{dx^2} - k^2\phi = 0$ or $\phi = Ae^{kx} + Be^{-kx}$ ---(7)

For $x > 0$, $e^{kx} \to \infty$ as $x \to +\infty$. Hence for the range $0 < x < \infty$, we must put $A = 0$ to get a well-behaved solution which is then given by, $\phi(x) = Be^{-kx}$ ---(8) for $0 < x < \infty$

For $x < 0$; $e^{-kx} \to \infty$ as $x \to -\infty$, we must have $B = 0$ to get the well-behaved sol^n which is then given by

$\phi(x) = Ae^{kx}$ ---(9) for $-\infty < x < 0$

Expansion of an arbitrary function in terms of eigenfunctions

In quantum mechanics if $\hat{\alpha}$ is an operator representing a real dynamical variable α such that the eigenvalue equation

$$\hat{\alpha}\, u_n(x) = a_n u_n(x) \quad ---(11)$$

is satisfied then the above equation is interpreted by saying that the result of measurement of the real dynamical variable α in the eigenstate $u_n(x)$ is certainly a_n. Here $u_n(x)$ is the eigenfunction of $\hat{\alpha}$ belonging to the eigenvalue a_n.

In general the solution of an eigenvalue equation of the type (11) yields a whole set of solutions with different eigenvalues. The totality of the possible solutions of the eigenvalue equations usually

constitute a complete set of eigenfunctions with different eigenvalues.

Suppose we have obtained such a complete set of eigenfunctions $u_n(x)$ of the operator $\hat{\alpha}$ representing the dynamical variable α belonging to the eigenvalues a_n (with $n=0, 1, 2, 3, \ldots$). Then the principle of superposition permits us to expand any arbitrary square-integrable state function $\psi(x)$ obeying the same boundary conditions as $u_n(x)$ in terms of the eigenfunctions:

$$\psi(x) = \sum_n c_n u_n(x) \quad \text{---(12)}$$

The numbers c_n are the amplitudes of the different states $u_n(x)$. In other words, the modulus-squared $|c_n|^2$ measures the probability with which the eigenstate $u_n(x)$ is represented in the state $\psi(x)$. The coefficients c_n can be determined utilizing the orthogonality property of the eigenfunctions.

Determination of the expansion coefficients

The expansion coefficients c_n in (12) can be evaluated by writing the general solution for $t=0$;

$$\psi(x, 0) = \psi(x) = \sum_n c_n u_n(x) \quad \text{---(13)}$$

Multiplying both sides of eq^n (13) by $u_m^*(x)$ and integrating we get, using the orthogonality property of the eigenfunctions $u_n(x)$

$$\int \psi(x)\, u_m^*(x)\, dx = \sum_n c_n \int u_m^*(x)\, u_n(x)\, dx$$

$$= c_m \int u_m^* u_m\, dx = c_m \int |u_m|^2\, dx$$

Since, the only non-vanishing term on the r.h.s is that for $m=n$. Thus, $c_m = \int \psi(x)\, u_m^*(x)\, dx \Big/ \int |u_m(x)|^2 dx$ ----- (14)

~~Since $u_m(x)$ is normalized~~

If the functions $u_m(x)$ are normalized, so that the eigenfunctions constitute an orthonormal set, then

$$\int |u_m(x)|^2 dx = 1$$

and $$\boxed{c_m = \int \psi(x)\, u_m^*(x)\, dx} \quad \text{---(15)}$$

Probability of Stationary States

The physical interpretation of the coefficients C_n is that $|C_n|^2$ gives the probability P_n of the occurrence of the stationary state $u_n(x)$ in the state wavefunction $\psi(x)$.

According to the probability interpretation of the wavefunction, $\int_{-\infty}^{\infty} |\psi(x)|^2 dx$ is a measure of the total probability (at $t=0$) of finding the particle in any one of the complete set of stationary states $u_n(x)$ while $\int_{-\infty}^{\infty} |C_n u_n(x)|^2 dx$ gives the probability of occurrence of the state $u_n(x)$ in the set of stationary states $u_n(x)$.

Then from definition, we get

$$P_n = \int_{-\infty}^{\infty} |C_n u_n(x)|^2 dx \Big/ \int_{-\infty}^{\infty} |\psi(x)|^2 dx \quad \cdots (16)$$

Now, $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\, dx$

$$= \int_{-\infty}^{\infty} \Big[\sum_n C_n^* u_n^*(x)\Big]\Big[\sum_m C_m u_m(x)\Big] dx$$

$$= \int_{-\infty}^{\infty} \Big[\sum_n C_n^* u_n^*(x)\Big]\Big[C_1 u_1(x) + C_2 u_2(x) + \cdots + C_n u_n(x) + \cdots\Big] dx$$

$$= \sum_n |C_n|^2 \int_{-\infty}^{+\infty} u_n^*(x)\, u_n(x)\, dx + \sum_n \sum_m{}' C_n^* C_m \int_{-\infty}^{\infty} u_n^*(x)\, u_m(x)\, dx$$

where the first term is for $m=n$ and in the second term $\sum_m{}'$ denotes summation over all terms except $m=n$. No for $m \neq n$, $\int_{-\infty}^{\infty} u_n^*(x)\, u_m(x)\, dx = 0$ because of the orthogonality of the eigenfunctions $u_n(x)$. Further since the eigenfunctions are normalized $\int_{-\infty}^{\infty} |u_n(x)|^2 dx = 1$.

Hence we have $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \sum_n |C_n|^2 \quad \cdots (17)$

which is a constant. So we have from eq^n (17) the probability of the state $u_n(x)$,

$$P_n = \frac{|C_n|^2}{\sum_n |C_n|^2} \qquad \int_{-\infty}^{\infty} |u_n(x)|^2 dx = \frac{|C_n|^2}{\sum_n |C_n|^2} \quad \cdots (18)$$

The total probability of any of the states occurring is thus

$$\sum_n P_n = \sum_n |C_n|^2 \Big/ \sum_n |C_n|^2 = 1$$

This result is consistent with the basic requirement of the probability theory. If $\psi(x)$ is normalized, then

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \sum_n |C_n|^2 = 1$$

So the probability of the occurrence of the state $u_n(x)$ becomes from (18)

$$P_n = \int_{-\infty}^{\infty} |C_n u_n(x)|^2 dx = |C_n|^2 \quad \text{---------- (19)}$$

If for example, there are only two eigenstates $u_1(x)$ and $u_2(x)$, then we can write $\psi(x) = C_1 u_1(x) + C_2 u_2(x)$

Assuming the functions $u_1(x)$, $u_2(x)$ and $\psi(x)$ to be normalized, we interpret $|C_1|^2$ as the probability with which the eigenstate $u_1(x)$ is represented in the state $\psi(x)$. Similarly $|C_2|^2$ is the probability for the eigenstates $u_2(x)$ in $\psi(x)$.

It may be noted that in most problems of interest in quantum mechanics, the operators belong to a class known as Hermitian operators. The eigenvalues of Hermitian operators are real and the eigenfunctions are orthogonal.

Reality of energy eigenvalues:

Let us consider the stationary state $\Psi_n(\vec{r},t)$ of a ~~system~~ particle which is an eigenstate of its Hamiltonian Operator to the energy eigenvalue E_n. Then we can write

$$\Psi_n(\vec{r},t) = \psi_n(\vec{r})\, e^{-iEt/\hbar}$$

The probability density of finding the particle at a point in space is given by $\rho(\vec{r},t) = \Psi_n^* \Psi_n = \psi_n^*(\vec{r})\, \psi_n \exp[-i(E_n - E_n^*)t/\hbar]$

The probability current density i.e. the flow of probability of the wave packet associated to the ~~moving~~ motion of the particle through a unit area around the point under consideration held normally to the direction of the flow is

$$J(\vec{r},t) = \frac{i\hbar}{2m}\left(\Psi_n \vec{\nabla} \Psi_n^* - \Psi_n^* \vec{\nabla} \Psi\right)$$

or $\vec{J}(\vec{r},t) = \frac{i\hbar}{2m}\left[\psi_n(\vec{r})\vec{\nabla}\psi_n^*(\vec{r}) - \psi_n^*(\vec{r})\vec{\nabla}\psi_n(\vec{r})\right]\exp\left[-i(E_n - E_n^*)t/\hbar\right]$

$= \vec{J}_1(\vec{r})\exp\left[-i(E_n - E_n^*)t/\hbar\right]$ ---- (20)

In the above expression $\vec{J}_1(\vec{r})$ represents the space dependent part of the current density so that

$$\vec{\nabla}\cdot\vec{J} = \exp\left[-i(E_n - E_n^*)t/\hbar\right]\vec{\nabla}_1\cdot\vec{J}_1(\vec{r}) \quad \text{---(21)}$$

The equation of continuity $\frac{\partial\rho}{\partial t} = -\vec{\nabla}\cdot\vec{J}$ gives on integration

$$\frac{\partial}{\partial t}\int_\tau \rho\, d\tau = -\int_\tau \vec{\nabla}\cdot\vec{J}\, d\tau = -\oint_S \vec{J}\cdot d\vec{s} \quad \text{---(22)}$$ [where the volume τ is bounded by the surface S]

Substituting for ρ and $\vec{J}$, we get from (22)

$$-\frac{i}{\hbar}(E_n - E_n^*)\exp\left[-i(E_n - E_n^*)t/\hbar\right]\int_\tau \psi_m^*(\vec{r})\psi_n(\vec{r})\, d\tau$$

$$= \exp\left[-i(E_n - E_n^*)t/\hbar\right]\oint_S \vec{J}_1(\vec{r})\cdot d\vec{s} \quad \text{---(23)}$$

If the integration is carried out over the surface of an infinitely large sphere, the surface integral vanishes because of the well-behaved properties of the wave functions:

$$\oint_S \vec{J}_1\cdot d\vec{s} = \frac{i\hbar}{2m}\oint_S \left[\psi_m(\vec{r})\vec{\nabla}\psi_n^*(\vec{r}) - \psi_n^*(\vec{r})\vec{\nabla}\psi_m(\vec{r})\right]\cdot d\vec{s} = 0$$

So we get from (23)

$$-\frac{i}{\hbar}(E_n - E_n^*)\exp\left[-i(E_n - E_n^*)t/\hbar\right]\int_\tau \psi_m^*(\vec{r})\psi_n(\vec{r})\, d\tau = 0 \quad \text{---(24)}$$

Since the integral in the above expression is not zero, we must have $\boxed{E_n = E_n^*}$

which shows that the energy eigenvalue E_n is real.

Average in quantum mechanics : Expectation values

According to Born the wavefunction ψ has probabilistic interpretation, therefore it is essential to calculate the average or expectation value of any dynamical quantity defined by the wavefunction. In physics such dynamical quantities are space-coordinates, momenta and energy of the system.

The average or expectation value of a dynamical quantity is the mathematical expectation for the results of a single measurements on each of a large number of identical systems or the expected average of a large number of independent measurements on the same system.

Let us consider the measurement of the dynamical variable α represented by the quantum mechanical operator $\hat{\alpha}$. We want to find the average of α in a state given by the wave function $\psi(x) = \sum_n C_n u_n(x)$ ----(25)

where $\psi(x)$ is obtained by the superposition of the complete set of normalized eigenfunctions $u_n(x)$. These satisfy the relation $\hat{\alpha} u_n(x) = a_n u_n(x)$, i.e. $u_n(x)$ is the eigenfunction of the operator $\hat{\alpha}$ belonging to the eigenvalue a_n. This means that the measurement of $\hat{\alpha}$ in the state $u_n(x)$ is ~~defined~~ definitely a_n. So by definition, the average of the quantity α is

$$\langle \alpha \rangle = \sum_n a_n P_n = \sum_n a_n |C_n|^2 / \sum_n |C_n|^2 \quad \text{---(26)}$$

Since the system can exist in different states $u_n(x)$ [From eqn. 18] with different possible values of a_n. Here, P_n is the probability of finding the value a_n as a result of measurement of α. Eqn. (15) gives

$$C_n = \int_{-\infty}^{\infty} \psi(x)\, u_n^*(x)\, dx \quad \text{---(27)}$$

$$C_n^* = \int_{-\infty}^{\infty} \psi^*(x)\, u_n(x)\, dx \quad \text{---(28)}$$

Hence $\sum_n a_n |C_n|^2 = \sum_n a_n C_n^* C_n = \sum_n a_n C_n \int_{-\infty}^{+\infty} \psi^*(x)\, u_n(x)\, dx$

Since the integral and the summation are interchangeable and since $\hat{\alpha}$ operates on $u_n(x)$ only we can write

$$\sum_n a_n |C_n|^2 = \int_{-\infty}^{\infty} dx\, \psi^*(x) \left[\sum_n C_n a_n u_n(x) \right]$$

$$= \int_{-\infty}^{\infty} dx\, \psi^*(x) \left[\sum_n C_n \hat{\alpha} u_n(x) \right]$$

$$= \int_{-\infty}^{\infty} dx\, \psi^*(x)\, \hat{\alpha} \left[\sum_n C_n u_n(x) \right] = \int_{-\infty}^{\infty} dx\, \psi^*(x)\, \hat{\alpha}\, \psi(x)$$

---(29)

Further from eqn (17)

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \sum_n |C_n|^2 \quad \text{---(30)}$$

So we have

$$\langle \alpha \rangle = \frac{\int_{-\infty}^{\infty} \psi^*(x)\, \hat{\alpha}\, \psi(x)\, dx}{\int_{-\infty}^{\infty} \psi^*(x)\, \psi(x)\, dx} \quad \text{---- (31)}$$

If $\psi(x)$ is normalized, the denominator in the above equation is equal to 1. So, we get in this case

$$\boxed{\langle \alpha \rangle = \int_{-\infty}^{\infty} \psi^*(x)\, \hat{\alpha}\, \psi(x)\, dx} \quad \text{------ (32)}$$

We can then enunciate the following rule for calculating the expectation values of dynamical variables in quantum mechanics:

Place the operator representing the dynamical variable to act on the wave function $\psi(x)$ and multiply the result by $\psi^*(x)$ and integrate over the spatial coordinates. Here $\psi(x)$ assumed normalized.

For three-dimensional motion, the expectation value is given by $\boxed{\langle \alpha \rangle = \int_{-\infty}^{\infty} \psi^*(\vec{r})\, \hat{\alpha}\, \psi}$ $\langle \alpha \rangle = \frac{\int_{-\infty}^{\infty} \psi^*(\vec{r})\, \hat{\alpha}\, \psi(\vec{r})\, d\tau}{\int_{-\infty}^{\infty} \psi^*(\vec{r})\, \psi(\vec{r})\, d\tau}$

To be more specific,

$$\boxed{\langle \alpha \rangle = \frac{\int_{\text{all space}} \psi^*(\vec{r})\, \hat{\alpha}\, \psi(\vec{r})\, d\tau}{\int_{\text{all space}} \psi^*(\vec{r})\, \psi(\vec{r})\, d\tau}} \quad \text{---- (33)}$$

If $\psi(\vec{r})$ is normalized, we get

$$\boxed{\langle \alpha \rangle = \int_{\text{all space}} \psi^*(\vec{r})\, \hat{\alpha}\, \psi(\vec{r})\, d\tau} \quad \text{---- (34)}$$

Example:

Problem 1: Find the expectation values of space coordinate x and momentum p_x for one-dimensional motion of a particle in a state given by the wave function $\psi(x)$.

Ans $\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x)\, \hat{x}\, \psi(x)\, dx = \int_{-\infty}^{\infty} x\, |\psi(x)|^2\, dx$

Since $\hat{x} = x$ is a multiplying operator

$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(-i\hbar \frac{\partial}{\partial x}\right) \psi(x)\, dx$

It may be noted that the same expression for the expectation value is obtained if $\psi(x)$ is replaced by $\psi(x,t)$.

Using the concept of expectation value we can easily prove that the expectation value of energy eigenvalue of the energy eigenstate $\psi_n(\vec{r},t)$ is constant in time.

Using eqn. (31) we can calculate the expectation value of energy for an energy eigenstate $\psi_n(\vec{r},t)$. Since E_n is real we have

$$\langle E \rangle = \int_{\text{allspace}} \psi_n^*(\vec{r},t)\, \hat{E}\, \psi_n(\vec{r},t)\, d\tau$$

$$= \int \psi_n^*(\vec{r}) \exp(iE_nt/\hbar) \left(i\hbar \frac{\partial}{\partial t}\right) \psi_n(\vec{r}) \exp(-iE_nt/\hbar)\, d\tau$$

$$= i\hbar \int \psi_n^*(\vec{r}) \exp(iE_nt/\hbar)(-iE_n/\hbar)\, \psi_n(\vec{r}) \exp(-iE_nt/\hbar)\, d\tau$$

$$= E_n \int \psi^*(\vec{r})\, \psi_n(\vec{r})\, d\tau = E_n \text{ ; Since } \psi_n(\vec{r}) \text{ is a normalized eigenfunction.}$$

$$\therefore \boxed{\langle E \rangle = E_n}$$

The above result shows that expectation value of energy for the stationary state n is certainly E_n which remains constant in time. This is a special case of the general result that the expectation value of any observable in quantum mechanics whose operator does not depend explicitly on time is independent of time for a stationary state.

Expectation values and Corresponding Principle; Ehrenfest's theorem:

According to Bohr's correspondence principle all laws of mechanics applicable to the motion of the subatomic particles within the atoms have to be formulated in such a way that these laws should reduce to the laws of classical mechanics in the limit of macroscopic bodies. Ehrenfest's theorem shows that the classical relationships between different dynamical variables, e.g., coordinate and momentum of a particle will also hold good between the averages or the expectation values of these quantities for the quantum mechanical wave packet associated with the particle and thus supports the correspondence principle.

Since the wave packet representing a particle has a finite extension in space, one has to take the average values of the dynamical variables over this extension to bring out the correspondence between the laws governing the motion of a particle in classical physics and that of a wave packet in quantum mechanics.

The expection value of the coordinate x for one dimensional motion is

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\, x\, \Psi(x,t)\, dx = \int_{-\infty}^{\infty} x\, |\Psi|^2 dx = \int_{-\infty}^{\infty} x\rho\, dx \quad \text{--- (31)}$$

where $\rho(x,t) = |\Psi(x,t)|^2$ is the probability density. Differentiating

with respect to time, we have

$$\frac{d}{dt}\langle x\rangle = \frac{d}{dt}\int_{-\infty}^{\infty} x\rho\,dx = \int_{-\infty}^{\infty} x\frac{\partial \rho}{\partial t}\,dx = -\int_{-\infty}^{\infty} x\frac{\partial j_x}{\partial x}\,dx \quad \text{---(36)}$$

where we have used the equation of continuity for one dimensional motion, j_x being the probability current density along x and the space coordinate x is ~~independent of~~ not differentiable with respect to time in quantum mechanics. Now j_x is given by

$$j_x = \frac{i\hbar}{2m}\left[\psi(x,t)\frac{\partial \psi^*(x,t)}{\partial x} - \psi^*(x,t)\frac{\partial \psi(x,t)}{\partial x}\right]$$

Multiplying by the mass of the particle and integrating eqn. (36) by parts, we get

$$m\frac{d}{dt}\langle x\rangle = -m\int_{-\infty}^{\infty} x\frac{\partial j_x}{\partial x}\,dx = -m\left[x j_x\right]_{-\infty}^{\infty} + m\int_{-\infty}^{\infty} j_x\,dx \quad \text{---(37)}$$

$$= m\int_{-\infty}^{\infty} j_x\,dx \quad \text{---(37)}$$

$\int uv\,dx = u\int v\,dx - \int\left[\frac{du}{dx}\int v\,dx\right]dx$

where the first term becomes zero at $\pm\infty$ since ψ and hence j_x goes to zero as $x \to \pm\infty$. Substituting j_x and integrating by parts we get

$$m\frac{d}{dt}\langle x\rangle = m\frac{i\hbar}{2m}\left[\int_{-\infty}^{\infty}\psi\frac{\partial \psi^*}{\partial x}\,dx - \int_{-\infty}^{\infty}\psi^*\frac{\partial \psi}{\partial x}\,dx\right]$$

$$= \frac{i\hbar}{2}\left\{\left[\psi\psi^*\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\psi^*\frac{\partial \psi}{\partial x}\,dx - \int_{-\infty}^{\infty}\psi^*\frac{\partial \psi}{\partial x}\,dx\right\}$$

$$= -i\hbar\int_{-\infty}^{\infty}\psi^*\frac{\partial \psi}{\partial x}\,dx = \int_{-\infty}^{\infty}\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,dx = \int_{-\infty}^{\infty}\psi^*\hat{p}_x\psi\,dx \quad \text{---(38)}$$

where we have used the operator representation of the x-component of the momentum. The r.h.s. by definition, is the expectation value of p_x. So we get,

$$\boxed{m\frac{d}{dt}\langle x\rangle = \langle p_x\rangle} \quad \text{---(39)}$$

Eqn. (39) is identical with the relationship between the coordinate and the momentum of a particle in classical physics. We thus see that the same relation also holds between the expectation values of the corresponding observables in quantum mechanics which is in conformity with the

correspondence principle.

The above result can easily be generalized in the case of three dimensional motion.

Now, $\frac{d}{dt}\langle p_x\rangle = \frac{d}{dt}\int_{-\infty}^{\infty}\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,dx$

$= \int_{-\infty}^{\infty}\left[-i\hbar\frac{\partial\psi^*}{\partial t}\frac{\partial\psi}{\partial x} - i\hbar\psi^*\frac{\partial}{\partial t}\frac{\partial\psi}{\partial x}\right]dx$

$= \int_{-\infty}^{\infty}\left[\left(-i\hbar\frac{\partial}{\partial t}\right)\psi^*\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial}{\partial x}\left(i\hbar\frac{\partial}{\partial t}\right)\psi\right]dx$

$= \int_{-\infty}^{\infty}\left[E\psi^*\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial}{\partial x}(E\psi)\right]dx$

$= \int_{-\infty}^{\infty}\left[E\psi^*\frac{\partial\psi}{\partial x} - \psi^*\frac{\partial E}{\partial x}\psi - E\psi^*\frac{\partial\psi}{\partial x}\right]dx$

$= -\int_{-\infty}^{\infty}\psi^*\frac{\partial E}{\partial x}\psi\,dx = -\int_{-\infty}^{\infty}\psi^*\frac{\partial V}{\partial x}\psi\,dx$

$\therefore \boxed{\frac{d}{dt}\langle p_x\rangle = -\left\langle\frac{\partial V}{\partial x}\right\rangle}$ ---(40)

or $\boxed{m\frac{d}{dt}\langle v_x\rangle = -\left\langle\frac{\partial V}{\partial x}\right\rangle}$ ---(41)

$\psi(x,t) = \psi(x)e^{-iEt/\hbar}$

$\psi^*(x,t) = \psi^*(x)e^{iEt/\hbar}$

$-i\hbar\frac{\partial\psi^*}{\partial t} = \psi^*(x)(-i\hbar)\left(\frac{iE}{\hbar}\right)e^{iEt/\hbar}$

$= E\psi^*$

$E = T + V$
K.E. P.E.

$\frac{\partial E}{\partial x} = \frac{\partial T}{\partial x} + \frac{\partial V}{\partial x}$

$= \frac{\partial V}{\partial x}$, since $\frac{\partial T}{\partial x} = 0$

Note: In quantum theory it is not possible even to define the derivative of x, y, z, p_x, p_y and p_z in the classical sense: since there is no such thing as a continuous particle trajectory. The approximate value of derivatives may be found by considering the time rate of change of average values of x, y, z, p_x, p_y and p_z. If the width of the wave packet can be neglected, then the values of these derivatives must be equal to the classically calculated values.

Problems:

1. Calculate the expectation value of p and p^2 for the wave function

$\psi(x) = \left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}$ in the region $0 < x < L$

and $\psi(x) = 0$ for $|x| > L$

Sol^n The expectation value of observable p in state ψ is given by, $\langle p\rangle = \int_L \psi^*\hat{p}\psi\,dx = \int\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,dx$, since here $p = \hat{p} = -i\hbar\frac{\partial}{\partial x}$

$\therefore \langle p\rangle = \int_0^L\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}\,dx$

or $\langle p \rangle = -i\hbar \frac{2}{L}\frac{\pi}{L}\int_0^L \sin\frac{\pi x}{L}\cos\frac{\pi x}{L}\,dx$

$= \frac{\pi\hbar}{iL^2}\int_0^L \sin\frac{2\pi x}{L}\,dx = -\frac{\pi\hbar}{iL^2}\cdot\frac{L}{2\pi}\left[\cos\frac{2\pi x}{L}\right]_0^L$

$= \frac{i\hbar}{2L}\left[\cos 2\pi - \cos 0\right] = 0 \quad \text{---- (i)}$

$\langle p^2 \rangle = \int \psi^* \hat{p}^2 \psi\,dx = -\int \psi^* \left(\hbar^2\frac{\partial^2}{\partial x^2}\right)\psi\,dx$

$= -\hbar^2\int_0^L \left(\frac{2}{L}\right)\sin\frac{\pi x}{L}\,\frac{\partial^2}{\partial x^2}\sin\frac{\pi x}{L}\,dx = \frac{2\hbar^2}{L}\frac{\pi^2}{L^2}\int_0^L \sin\frac{\pi x}{L}\sin\frac{\pi x}{L}\,dx$

$= \frac{\hbar^2\pi^2}{L^3}\int_0^L 2\sin\frac{\pi x}{L}\sin\frac{\pi x}{L}\,dx = \frac{\hbar^2\pi^2}{L^3}\int_0^L \left(1-\cos\frac{2\pi x}{L}\right)dx$

$= \frac{\pi^2\hbar^2}{L^3}\left[x - \frac{L}{2\pi}\sin\frac{2\pi x}{L}\right]_0^L = \frac{\pi^2\hbar^2}{L^3}\left[L - \frac{L}{2\pi}(\sin 2\pi - \sin 0)\right]$

$= \frac{\pi^2\hbar^2}{L^2} \quad \text{---- (ii)}$

② Find the expectation values of position and momentum of a particle whose normalised wave function is

$\psi(x) = N e^{-(x^2/2a^2)+ikx}$ where $N = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2}$

Sol^n $\langle x \rangle = \int_{-\infty}^{+\infty} \psi^*(x)\, x\, \psi(x)\,dx = |N|^2 \int_{-\infty}^{\infty} e^{-(x^2/2a^2)+ikx}\, x\, e^{-(x^2/2a^2)-ikx}\,dx$

$= |N|^2 \int_{-\infty}^{\infty} e^{-\frac{x^2}{a^2}}\, x\,dx$

Since the integrand is an odd function of x,

$\langle x \rangle = 0 \quad \text{---- (iii)}$

$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(x)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x)\,dx$

Now, $\frac{\partial}{\partial x}\psi(x) = \frac{\partial}{\partial x}\left(\frac{1}{\sqrt{\pi}\,a}\right)^{1/2} e^{\frac{-x^2}{2a^2}+ikx} = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2}\left(-\frac{x}{a^2}+ik\right)e^{\frac{-x^2}{2a^2}+ikx}$

We know the general formula as $\int_0^\infty x^{2n} e^{-ax^2}\,dx = \frac{1.3.5\ldots(2n-1)}{2^{n+1}\,a^n}\sqrt{\frac{\pi}{a}}$

$\therefore \langle p_x \rangle = -\frac{i\hbar}{a\sqrt{\pi}}\int_{-\infty}^{\infty}\left(-\frac{x}{a^2}+ik\right)e^{-\frac{x^2}{a^2}}\,dx = \frac{\hbar k}{a\sqrt{\pi}}\int_{-\infty}^{\infty} e^{-\frac{x^2}{a^2}}\,dx = \hbar k$

$\therefore \boxed{\langle p_x \rangle = \hbar k} \quad \text{--- (iv)}$

③ Also calculate $\langle x^2 \rangle$ & $\langle p_x^2 \rangle$ for the same wave packet as in the problem 2.

Soln:- $\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 |\psi(x)|^2 dx = \frac{2}{a\sqrt{\pi}} \int_0^{\infty} x^2 e^{-\frac{x^2}{a^2}} dx$

$= \frac{2}{a\sqrt{\pi}} \frac{1}{(\frac{2}{a})^2} \sqrt{\frac{\pi}{(\frac{1}{a})^2}} = \frac{2}{a\sqrt{\pi}} \frac{a^2}{4} a\sqrt{\pi} = \frac{a^2}{2}$

$\therefore \boxed{\langle x^2 \rangle = \frac{a^2}{2}}$ ---(v)

$\langle p_x^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(-i\hbar \frac{\partial}{\partial x}\right)^2 \psi(x)\, dx = -\hbar^2 \int_{-\infty}^{\infty} \psi^*(x) \frac{\partial^2 \psi(x)}{\partial x^2} dx$

$= -\hbar^2 \int_{-\infty}^{\infty} \psi^*(x) \frac{\partial^2 \psi(x)}{\partial x^2} dx$

$= -\frac{\hbar^2}{a\sqrt{\pi}} \int_{-\infty}^{\infty} \left[\frac{x^2}{a^4} - \left(k^2 + \frac{1}{a^2}\right) - \frac{2ikx}{a^2}\right] e^{-\frac{x^2}{a^2}} dx$

$= -\frac{\hbar^2}{a\sqrt{\pi}} \frac{1}{a^4} \int_{-\infty}^{\infty} x^2 e^{-\frac{x^2}{a^2}} dx + \hbar^2 \left(k^2 + \frac{1}{a^2}\right) \frac{1}{a\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{a^2}} dx$

$= -\frac{2\hbar^2}{a\sqrt{\pi}} \frac{1}{a^4} \frac{a^2}{4} a\sqrt{\pi} + \hbar^2 \left(k^2 + \frac{1}{a^2}\right)$

$\therefore \boxed{\langle p_x^2 \rangle = -\frac{\hbar^2}{2a^2} + \hbar^2 k^2 + \frac{\hbar^2}{a^2} = \hbar^2 k^2 + \frac{\hbar^2}{2a^2}}$ ---(vi)

To express uncertainty relations in x & p_x in terms of standard deviation and expectation values

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From the definition of standard deviation, the mean squared deviation of x is

$\Delta x^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle$

$= \langle x^2 \rangle - 2\langle x \rangle\langle x \rangle + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2$ ---(12)

Similarly the mean squared deviation of the momentum p_x is given by $\Delta p_x^2 = \langle (p_x - \langle p_x \rangle)^2 \rangle = \langle p_x^2 \rangle - \langle p_x \rangle^2$ ---(13)

The uncertainties in x and p_x are then

$\Delta x = |\langle x^2 \rangle - \langle x \rangle^2|^{1/2}$ ---(14)

$\Delta p_x = |\langle p_x^2 \rangle - \langle p_x \rangle^2|^{1/2}$ ---(15)

Using the expectation values x, x^2, p_x and p_x^2 for a given system it can be shown that $\Delta x \Delta p_x \geq \frac{\hbar}{2}$

Using data of problem (2) & (3) eqns (11) & (15) reduce to

$$\Delta x = \sqrt{\frac{a^2}{2} - 0} = \frac{a}{\sqrt{2}} \quad ; \quad \Delta p_x = \sqrt{\hbar^2 k^2 + \frac{\hbar^2}{2a^2} - \hbar^2 k^2} = \frac{\hbar}{\sqrt{2}a}$$

$$\therefore \boxed{\Delta x \, \Delta p_x = \frac{a}{\sqrt{2}} \times \frac{\hbar}{\sqrt{2}a} = \frac{\hbar}{2}}$$

Hermitian Property of Operators: Basic Postulates of Quantum Mechanics

We know that the expectation value of a dynamical variable gives the expected average of the results of measurement of dynamical variable. So it must be a real number since it is a physically measurable quantity. The operators representing such dynamical variables whose expectation values are real are said to be Hermitian Operators. If $\hat{\alpha}$ is the operator representation of a dynamical variable α, then the expectation value of α, assuming one dimentional motion, is given by

$$\langle \alpha \rangle = \int \psi^* \hat{\alpha} \psi \, dx \quad \cdots (46)$$

$\psi(x)$ is the normalized wave function specifying the state of the system on which measurement is performed.

The complex conjugate of the expectation value of α is

$$\langle \alpha \rangle^* = \left\{ \int \psi^* \hat{\alpha} \psi \, dx \right\}^* = \int \psi \hat{\alpha}^* \psi^* \, dx \quad \cdots (57)$$

$$\langle \alpha \rangle^* = \left[\int \psi^* \hat{\alpha} \psi \, dx \right]^*$$
$$= \int (\hat{\alpha}\psi)^* (\psi^*)^* \, dx$$
$$= \int (\hat{\alpha}^* \psi^*) \psi \, dx$$
$$= \int \psi \hat{\alpha}^* \psi^* \, dx$$

For the expectation value to be real we have, $\langle \alpha \rangle = \langle \alpha \rangle^*$

or $$\boxed{\int \psi^* \hat{\alpha} \psi \, dx = \int \psi \hat{\alpha}^* \psi^* \, dx} \quad \cdots (58)$$

Eqn (58) is the condition for the operator $\hat{\alpha}$ to be Hermitian.

In the three dimensional ~~state~~ case, the above condition becomes,

$$\boxed{\int \psi^*(\vec{r}) \hat{\alpha} \psi(\vec{r}) \, d\tau} \quad \cdots (59)$$

where $\psi(\vec{r})$ is now a function of the three coordinates x, y & z.

If $\psi_1(x)$ & $\psi_2(x)$ are two ~~normalised~~ normalizable eigen states of $\hat{\alpha}$, the general condition for $\hat{\alpha}$ to be Hermitian is

$$\boxed{\int \psi_1^* \hat{\alpha} \psi_2 \, dx = \int \psi_2 \hat{\alpha}^* \psi_1^* \, dx} \quad \text{---(60)}$$

Reality of eigenvalues of Hermitian Operators:

If $\psi(x)$ is an eigenfunction of the Hermitian operator $\hat{\alpha}$ belonging to the eigen value a, then we can write

$$\hat{\alpha}\psi(x) = a\psi(x)$$

Taking its complex conjugate we get

$$\hat{\alpha}^* \psi^*(x) = a^* \psi^*(x)$$

So we have,

$$\int \psi^* \hat{\alpha} \psi \, dx = \int \psi^* a \psi \, dx = a \int \psi^* \psi \, dx \quad \text{---(61)}$$

$$\int \psi \hat{\alpha}^* \psi^* \, dx = \int \psi \, a^* \psi^* \, dx = a^* \int \psi^* \psi \, dx \quad \text{---(62)}$$

Since $\hat{\alpha}$ is Hermitian, $a \int \psi^* \psi \, dx = a^* \int \psi^* \psi \, dx$

which gives, $\boxed{a = a^*}$

Hence, the eigen value of Hermitian operator is real.

Orthogonality of ~~Hermitian~~ eigenfunctions of Hermitian Operator:

Let $\hat{\alpha}$ be the operator representation of the dynamical variable α. Let $u_n(x)$ and $u_m(x)$ be the two eigenfunctions of $\hat{\alpha}$ belonging to the eigenvalues a_n and a_m respectively. Then we can write,

$$\hat{\alpha} u_n = a_n u_n \quad \text{---(63)}$$

$$\hat{\alpha} u_m = a_m u_m \quad \text{---(64)}$$

Taking the complex conjugate of (64) we have

$$\hat{\alpha}^* u_m^* = a_m^* u_m^* \quad \text{---(65)}$$

From the general requirement of hermicity of $\hat{\alpha}$ and the fact that the eigenvalue of Hermitian Operator is real

~~$\int u_m^* \hat{\alpha} u_n \, dx$~~

$$\int u_m^* \hat{A} u_n \, dx = \int u_n \hat{A}^* u_m^* \, dx$$

or $\int u_m^* a_n u_n \, dx = \int u_n a_m^* u_m^* \, dx$

or $(a_n - a_m^*) \int u_m^* u_n \, dx = 0$ or $(a_n - a_m) \int u_m^* u_n \, dx = 0$ ----(66)

Since a_n & a_m are real, $a_n = a_n^*$; $a_m = a_m^*$

If $a_n \neq a_m$ in (66) $\boxed{\int u_m^* u_n \, dx = 0}$ ----(67)

Hence, u_m & u_n are orthogonal eigen functions of $\hat{A}$

Hermitian Character of the Hamiltonian operator

The Hamiltonian operator for the three dimensional motion is $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$ ----(68)

We assumed the potential $V(\vec{r})$ is real. If $\psi(\vec{r})$ is normalized wave functions of $\hat{H}$, we have

$$\int \psi^*(\vec{r}) \hat{H} \psi(\vec{r}) \, d\tau = \int \psi^* \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi \, d\tau$$

$$= -\frac{\hbar^2}{2m} \int \psi^* \nabla^2 \psi \, d\tau + \int \psi^* V \psi \, d\tau$$

Now $\int \psi^* \nabla^2 \psi \, d\tau = \int \vec{\nabla} \cdot (\psi^* \vec{\nabla} \psi) \, d\tau - \int \vec{\nabla} \psi^* \cdot \vec{\nabla} \psi \, d\tau$

$$= \oint_S (\psi^* \vec{\nabla} \psi) \cdot d\vec{s} - \int_\tau \vec{\nabla} \psi^* \cdot \vec{\nabla} \psi \, d\tau$$

The surface integral in the right hand side vanishes if it is evaluated over all spaces where ψ and ψ^* vanishes over the surface. Hence

$$\int \psi^* \nabla^2 \psi \, d\tau = -\int \vec{\nabla} \psi^* \cdot \vec{\nabla} \psi \, d\tau \quad \text{----(69)}$$

Similarly $\int \psi \nabla^2 \psi^* \, d\tau = \int \vec{\nabla} \cdot (\psi \vec{\nabla} \psi^*) \, d\tau - \int (\vec{\nabla} \psi \cdot \vec{\nabla} \psi^*) \, d\tau$

$$= \oint_S (\psi \vec{\nabla} \psi^*) \cdot d\vec{s} - \int \vec{\nabla} \psi \cdot \vec{\nabla} \psi^* \, d\tau$$

Again as before the surface integral ~~in made~~ on the right hand side of the above eqn vanishes if the integration be carried over all surfaces. Thus

$$\int \psi \nabla^2 \psi^* \, d\tau = -\int \vec{\nabla} \psi^* \cdot \vec{\nabla} \psi \quad \text{----(70)}$$

Hence from (69) & (70) we get $\boxed{\int \psi^* \nabla^2 \psi \, d\tau = \int \psi \nabla^2 \psi^* \, d\tau}$ ---(71)

Again since V is real, we have $V = V^*$ and

$$\int \psi^* V \psi \, d\tau = \int \psi V^* \psi^* \, d\tau = \int \psi V \psi^* d\tau \quad \text{---(72)}$$

Hence from (69), (71) and (72) we have

$$\int \psi^* \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi \, d\tau = \int \psi \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right]^* \psi^* d\tau$$

since ∇^2 is real. Hence

$$\boxed{\int \psi^* \hat{H} \psi \, d\tau = \int \psi \hat{H}^* \psi^* d\tau} \quad \text{---(73)}$$

So, $\hat{H}$ is Hermitian.

Prove that:

(a) The sum (or difference) of two Hermitian Operators is Hermitian

(b) The product of two Hermitian operators is Hermitian if and only if they commute.

Proof: (a) Let $\hat{\alpha}$ and $\hat{\beta}$ are two Hermitian operators. Then if $u(x)$ and $v(x)$ are two functions of x, then we have

$$\int u^* \hat{\alpha} v \, dx = \int v \hat{\alpha}^* u^* \, dx \quad \text{---(74)}$$

$$\int u^* \hat{\beta} v \, dx = \int v \hat{\beta}^* u^* dx \quad \text{---(75)}$$

Adding (74) & (75) we get

$$\int u^* (\hat{\alpha} + \hat{\beta}) v \, dx = \int v (\hat{\alpha}^* + \hat{\beta}^*) u^* \, dx$$

$$= \int v (\hat{\alpha} + \hat{\beta})^* u^* \, dx$$

$\therefore (\hat{\alpha} + \hat{\beta})$ is Hermitian.

(b): Let us consider $f(x)$ & $g(x)$ as two functions and $\hat{A} = \hat{\alpha}\hat{\beta}$.

Then $\int f^* \hat{O} g \, dx = \int f^* \hat{\alpha}\hat{\beta} g \, dx = \int f^* \hat{\alpha} (\hat{\beta} g) \, dx$

$$= \int (\hat{\beta} g) \hat{\alpha}^* f^* \, dx \quad [\text{Since } \hat{\alpha} \text{ is Hermitian}]$$

or $\int f^* \hat{O} g \, dx = \int (\hat{\beta} g) (\hat{\alpha} f)^* \, dx = \int (\hat{\alpha} f)^* \hat{\beta} g \, dx$

$$= \int g \hat{\beta}^* (\hat{\alpha} f)^* \, dx = \int g (\hat{\beta}\hat{\alpha})^* f^* \, dx$$

Hence, $\int f^* (\hat{\alpha}\hat{\beta}) g \, dx = \int g (\hat{\beta}\hat{\alpha})^* f^* \, dx \quad \text{---(76)}$

If $\hat{\alpha}\hat{\beta} = \hat{\beta}\hat{\alpha}$ i.e. $[\hat{\alpha}, \hat{\beta}] = 0$, then (76) becomes

$$\int f^* (\hat{\alpha}\hat{\beta}) g \, dx = \int g (\hat{\alpha}\hat{\beta})^* f^* dx$$

Hence $\hat{\alpha}\hat{\beta}$ will be Hermitian if $\hat{\alpha}\hat{\beta} = \hat{\beta}\hat{\alpha}$ i.e. if $\hat{\alpha}$ and $\hat{\beta}$ commute.

Equation of Motion in Quantum Mechanics:

Dynamical variables like the coordinate x and momentum p_x are usually time varying in classical mechanics. However their operator representations in quantum mechanics do not change with time. The time variation of the quantum mechanical states comes through the dependance of the wave function $\psi(x,t)$ on time. In quantum mechanics, it is the time derivatives of the expectation values of the dynamical variables which are of significance.

Let us consider an operator $\hat{\alpha}$ representing a dynamical variable α. The expectation value of α is given by

$$\langle \alpha \rangle = \int \psi^*(x,t) \, \hat{\alpha} \, \psi(x,t) \, dx$$

Here we assume one dimensional motion. The time rate of change of $\langle \alpha \rangle$ is then

$$\frac{d}{dt}\langle \alpha \rangle = \frac{d}{dt} \int \psi^* \hat{\alpha} \psi \, dx$$

$$= \int \left(\frac{\partial \psi^*}{\partial t} \hat{\alpha} \psi + \psi^* \frac{\partial \hat{\alpha}}{\partial t} \psi + \psi^* \hat{\alpha} \frac{\partial \psi}{\partial t} \right) dx \quad \text{.....(77)}$$

In the above expression we have provided for the time variation of the operator $\hat{\alpha}$ through the second term when the operator $\hat{\alpha}$ contains time explicitly. In those cases (e.g. for $\hat{x}$ or $\hat{p}_x$) when this is lacking this term is zero.

Schrödinger equation gives us

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \quad \text{or} \quad \frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \psi$$

Taking the complex conjugate, we get

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

Thus, $\frac{d}{dt}\langle\alpha\rangle = \frac{i}{\hbar}\int[(\hat{H}^*\psi^*)\hat{\alpha}\psi - \psi^*\hat{\alpha}(\hat{H}\psi)]dx + \int\psi^*\frac{\partial\hat{\alpha}}{\partial t}\psi\,dx$

Since $\hat{H}$ is a Hermitian operator, we have

$$\int(\hat{H}^*\psi^*)\hat{\alpha}\psi\,dx = \int(\hat{\alpha}\psi)\hat{H}^*\psi^*dx \quad \cancel{-\int\psi^*\hat{H}\hat{\alpha}\psi\,dx}$$

$$= \int\psi^*\hat{H}\hat{\alpha}\psi\,dx$$

Using the relation $\int\psi_1^*\hat{A}\psi_2 dx = \int\psi_2\hat{A}^*\psi_1^*dx$

Hence, $\frac{d}{dt}\langle\alpha\rangle = \frac{i}{\hbar}\int\psi^*(\hat{H}\hat{\alpha} - \hat{\alpha}\hat{H})\psi\,dx + \int\psi^*\frac{\partial\hat{\alpha}}{\partial t}\psi\,dx$ ------ (78)

The above equation gives us the time rate of change of the expectation value of α if the commutator $[\hat{H},\hat{\alpha}]$ is known. In particular if $\hat{\alpha}$ does not depend on time explicitly, we get

$$\frac{d}{dt}\langle\alpha\rangle = \frac{i}{\hbar}\int\psi^*(\hat{H}\hat{\alpha} - \hat{\alpha}\hat{H})\psi\,dx \quad ---(79)$$

or $$\frac{d}{dt}\langle\alpha\rangle = \frac{i}{\hbar}\langle\hat{H}\hat{\alpha} - \hat{\alpha}\hat{H}\rangle \quad ---(80)$$

The quantity $\langle\hat{H}\hat{\alpha} - \hat{\alpha}\hat{H}\rangle$ on the right hand side is the expectation value of the commutator of $\hat{H}$ and $\hat{\alpha}$. We can symbolically write

$$\langle\dot{\alpha}\rangle = \frac{d\langle\alpha\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{H},\hat{\alpha}]\rangle \quad ---(81)$$

or $$\boxed{\dot{\alpha} = \frac{i}{\hbar}[\hat{H},\hat{\alpha}]} \quad ---(82)$$

Equation (80) is known as the equation of motion in quantum mechanics. It is a generalization of Ehrenfest's theorem. If $\hat{H}$ & $\hat{\alpha}$ commute we get $\boxed{\dot{\alpha} = \frac{d\alpha}{dt} = 0}$ ---(83)

In this case we say that the dynamical variable α is a constant of motion.

We know from classical mechanics that for a conservative system the Hamiltonian H is independent of time so that its operator representation $\hat{H}$ in quantum mechanics does not contain time explicitly. Hence from (82)

$$\dot{H} = \frac{dH}{dt} = \frac{i}{\hbar}[\hat{H},\hat{H}] = 0$$

This shows that for a conservative system, the energy is a constant of motion in quantum mechanics.

Fundamental postulates of quantum mechanics:

The fundamental postulates of quantum mechanics which we give here are five in number. These are applicable in general to a quantum mechanical system though in our discussion, we shall restrict ourselves to a single particle system for the sake of simplicity.

Postulate I: There is a wave function $\psi(\vec{r},t) = \psi(x,y,z,t)$ which completely describes the space-time behaviour of the particle, consistent with the uncertainty principle.

Postulate II: Dynamical variables relating to the motion of a particle are represented by linear and Hermitian mathematical operators in quantum mechanics.

Postulate III: The only possible results of measurement of a dynamical variable α are the eigenvalues of the operator $\hat{\alpha}$ satisfying the eigenvalue equation

$$\hat{\alpha}\psi_n = a_n\psi_n$$

where ψ_n is the eigenfunction of the operator $\hat{\alpha}$ belonging to the eigenvalue a_n. The eigenfunctions ψ_n are well-behaved, i.e. they must be single-valued and square-integrable. They also form a complete set and are orthogonal.

The eigenvalue equation satisfied by the Hamiltonian operator associated with the Hamiltonian with the Hamiltonian H of classical mechanics, known as the Schrödinger wave equation, can be written as $\hat{H}\psi_n = E_n\psi_n$ where E_n is the energy of the system.

Postulate IV: The probability $p\,d\tau$ of finding a particle in the volume element $d\tau$ is given by $p\,d\tau = \psi^*\psi\,d\tau = |\psi|^2 d\tau$ where $p = |\psi|^2$ is known as the probability density. In a finite region of space the probability of finding the particle is obtained by integrating the above equation over the volume under consideration: $\int_\tau p\,d\tau = \int_\tau |\psi|^2 d\tau$

The integral on the r.h.s. must always remain finite since the probability must be finite for any physically admissible state. ψ must be normalized by multiplying it by a suitable complex number so that $\int_\tau p\,d\tau = \int_\tau |\psi|^2 d\tau = 1$ which states that the total probability of finding the particle somewhere in space is unity.

where the integration is carried over the entire available space.

Postulate V: The expectation value of the expected average of the results of a large number of measurements of a physical quantity α of a particle is given by

$$\langle \alpha \rangle = \int_{\tau} \psi^* \hat{\alpha} \psi \, d\tau$$

where $\hat{\alpha}$ is the operator representing the dynamical variable α. Here we assume ψ to be normalized, otherwise

$$\langle \alpha \rangle = \frac{\int_{\tau} \psi^* \hat{\alpha} \psi \, d\tau}{\int_{\tau} \psi^* \psi \, d\tau}$$