The Postulates of Quantum Mechanics. The formulation of quantum mechanics or wave mechanics for the wave mechanical treatment of the structure of atom rests upon a few postulates which, for a system moving in one dimension, say, along the x-coordinate, are given below.

First Postulate. The physical state of a system at time t is described by the wave function $\psi(x, t)$.

Second Postulate. The wave function $\psi(x, t)$ and its first and second derivatives $\partial\psi(x,t)/\partial x$ and $\partial^2\psi(x,t)/\partial x^2$ are continuous, finite and single valued for all values of x. Also, the wave function $\psi(x, t)$ is *normalized, i.e.*,

$$\int_{-\infty}^{\infty} \psi^*(x,t)\,\psi(x,t)dx = 1 \qquad \ldots(48)$$

where ψ^* is the *complex conjugate* of ψ formed by replacing i with $-i$ wherever it occurs in the function ψ ($i = \sqrt{-1}$).

Third Postulate. A physically observable quantity can be represented by a *Hermitian operator*. An operator $\hat{A}$ is said to be Hermitian if it satisfies the following condition :

$$\int \psi_i^* \hat{A}\psi_j\,dx = \int \psi_j\,(\hat{A}\psi_i)^*\,dx \qquad \ldots(49)$$

where ψ_i and ψ_j are the wave functions representing the physical states of the quantum system, such as a particle, an atom or a molecule.

Fourth Postulate. The allowed values of an observable A are the eigenvalues, a_i, in the operator equation

$$\hat{A}\,\psi_i = a_i\psi_i \qquad \ldots(50)$$

Eq. 50 is known as an **eigenvalue equation**. Here $\hat{A}$ is the operator for the observable (physical quantity) and ψ_i is an eigenfunction of $\hat{A}$ with eigenvalue a_i. In other words, measurement of the observable A yields the eigenvalue a_i.

Fifth Postulate. The average value (or, the expectation value), $< A >$, of an observable A, corresponding to the operator $\hat{A}$, is obtained from the relation

$$< A > = \int_{-\infty}^{\infty} \psi^*\,\hat{A}\,\psi\,dx \qquad \ldots(51)$$

where the function ψ is assumed to be normalized in accordance with Eq. 48. Thus, the average value of, say, the x-coordinate is given by

$$< x > = \int_{-\infty}^{\infty} \psi^*\,\hat{x}\,\psi\,dx \qquad \ldots(52)$$

Sixth Postulate. The quantum mechanical operators corresponding to the observables are constructed by writing the classical expressions in terms of the variables and converting the expressions to the operators, as shown in Table 1.

TABLE 1

Wave Mechanical Operators for Evaluating Various Classical Variables

Classical variable	Quantum mechanical operator	Operator	Operation
x	$\hat{x}$	x	Multiplication by x
p_x	$\hat{p}_x$	$-i\hbar \dfrac{\partial}{\partial x}$	Taking derivative with respect to x and multiplying by $-i\hbar$
x^2	$\hat{x}^2$	x^2	Multiplication by x^2
p_x^2	$\hat{p}_x^2$	$-\hbar^2 \dfrac{\partial^2}{\partial x^2}$	Taking second derivative with respect to x and multiplying by $-\hbar^2$
t	$\hat{t}$	$\hat{t}$	Multiplying by t
E	$\hat{E}$	$i\hbar \dfrac{\partial}{\partial t}$	Taking derivative with respect to t and multiplying by $i\hbar$

Seventh Postulate. The wave function $\psi(x, t)$ is a solution of the time-dependent equation

$$\hat{H}\,\psi(x,t) = i\hbar\,\frac{\partial\psi(x,t)}{\partial t} \qquad \ldots(53)$$

where $\hat{H}$ is the Hamiltonian operator of the system.

The Schrödinger Wave Equation

Erwin Schrödinger, in 1926, gave a wave equation to describe the behaviour of electron waves in atoms and molecules. In Schrödinger's wave model of an atom, the discrete energy levels or orbits proposed by Bohr are replaced by mathematical functions, ψ, which are related to the probability of finding electrons at various places around the nucleus.

Consider a simple wave motion as that of the vibration of a stretched string. Let y be the amplitude of this vibration at any point whose coordinate is x at time t. The equation for such a wave motion may be expressed as

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{u^2} \times \frac{\partial^2 y}{\partial t^2} \qquad \ldots(54)$$

where u is the velocity with which the wave is propagating. There are two variables, x and t, in the above differential equation, *i.e.*, the amplitude y depends upon two variables x and t.

In order to solve the above differential equation, it is necessary to separate the two variables. Thus, y may be expressed as

$$y = f(x)\, g(t) \qquad \ldots(55)$$

where $f(x)$ is a function of the coordinate x only and $g(t)$ is a function of the time t only. For stationary waves, such as occur in a stretched string, the function $g(t)$ is represented by the expression

$$g(t) = A \sin(2\pi\nu t) \qquad \ldots(56)$$

where ν is the vibrational frequency and A is a constant known as the maximum amplitude. Hence, for stationary waves, the equation for y may be written as

$$y = f(x)\, A \sin(2\pi\nu t) \qquad \ldots(57)$$

Hence,

$$\frac{\partial^2 y}{\partial t^2} = -f(x)\, 4\pi^2\nu^2 A \sin(2\pi\nu t) \qquad \ldots(58)$$

$$= -4\pi^2\nu^2 f(x)\, g(t) \qquad \ldots(59)$$

Similarly, it follows from Eq. 57 that

$$\frac{\partial^2 y}{dx^2} = \frac{\partial^2 f(x)}{\partial x^2} g(t) \qquad \ldots(60)$$

Combining Eqs. 54, 59 and 60, we have

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2 \nu^2}{u^2} f(x) \qquad \ldots(61)$$

As is well known, the frequency of the vibrations ν is related to the velocity u by the expression $u = \nu\lambda$, where λ is the corresponding wave length. Hence, from Eq. 61, we have

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} f(x) \qquad \ldots(62)$$

Eq. 62 is valid for the wave motion in one dimension only. We may now extend it to three dimensions represented by the coordinates x, y and z. Evidently, $f(x)$ will then be replaced by the amplitude function for the three coordinates, say, $\psi(x, y, z)$. For the sake of simplicity, it may be put merely as ψ. Hence, Eq. 62 takes the form

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi \qquad \ldots(63)$$

Following de Broglie's ideas, Schrödinger, the Austrian physicist, applied the above treatment to material waves associated with all particles including electrons, atoms and molecules.

Incorporating de Broglie's relationship, *viz.*, $\lambda = h/mu$, in Eq. 63, we have

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2 m^2 u^2}{h^2} \psi \qquad \ldots(64)$$

where m is the mass and u is the velocity of the particle.

The kinetic energy of the particle given by $\frac{1}{2}mu^2$, is equal to the total energy E *minus* the potential energy V of the particle, *i.e.*,

$$K.E. = \tfrac{1}{2}mu^2 = E - V \quad \text{or} \quad mu^2 = 2(E - V) \qquad \ldots(65)$$

Combining this result with Eq. 64, we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m(E - V)}{h^2} \psi = 0 \qquad \ldots(66)$$

Eq. 66 is the well known **Schrödinger wave equation** proposed by him in 1926. It is the most celebrated equation in wave mechanics. It is customarily written in the following form :

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right] = E\,\psi \qquad \ldots(67)$$

or

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi = E\psi \qquad (\hbar = h/2\pi) \qquad \ldots(68)$$

where ∇^2 (read as 'del squared') is the **Laplacian operator,** defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \ldots(69)$$

Defining the **Hamiltonian operator** $\hat{H}$ as

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V \qquad \text{...(70)}$$

Eq. 68 becomes

$$\hat{H}\psi = E\psi \qquad \text{...(71)}$$

E. Schrödinger (1887-1961) shared the 1933 Physics Nobel Prize with P.A.M. Dirac (1902-1984) for the discovery of new productive forms of atomic theory.

The Schrödinger equation can have several solutions, not all of which correspond to any physical or chemical reality. Such solutions or wave functions are, therefore, not acceptable. The acceptable wave functions must satisfy the following conditions :

1. The wave function ψ is *single-valued, i.e.*, for each value of the variables x, y, z, there is only one value of ψ. Suppose one of the variables is an angle θ. Then, single-valuedness of ψ requires that

$$\psi(\theta) = \psi(\theta + 2n\pi) \text{ where } n \text{ is an integer.}$$

2. The wave function ψ and its first derivative with respect to its variables must be *continuous*, *i.e.*, there must not be any sudden change in ψ when its variables are changed.

3. For bound states, ψ must vanish at infinity. If ψ is a complex function, then $\psi^*\psi$ must vanish at infinity (ψ^* is the complex conjugate of ψ).

Satisfying the above conditions, the Schrödinger equation yields *significant solutions for certain definite values of the total energy E*. These values are called eigenvalues. Eq. 71 is, thus, an eigenvalue equation and we can write it as

$$\hat{H}\psi_n = E_n\psi_n \qquad (n = 1, 2, 3,......) \qquad \text{...(72)}$$

where n is the quantum number. We express Eq. 72 by saying that ψ_n are the eigenfunctions and E_n are the eigenvalues. For an atom, these eigenvalues correspond to discrete sets of energy values postulated by Bohr.

4. The eigenfunctions are said to form an **orthonormal set** if

$$\int \psi_n^*\psi_m \, d\tau = \left[\begin{matrix} 0, & n \neq m \\ 1, & n = m \end{matrix}\right. = \delta_{nm} \text{ (called the \textbf{Kronecker delta})} \qquad \text{...(73)}$$

They are **orthogonal** when $\int \psi_n^*\psi_m \, d\tau = 0$ ...(74)

and **normalised** when $\int \psi_n^*\psi_m \, d\tau = 1$ ...(75)

It is possible to identify regions of space around the nucleus where there is *high probability* of locating an electron associated with a specific energy. This space is called an atomic orbital. An **atomic orbital**, thus, represents a definite region in three-dimensional space around the nucleus where there is high probability of finding an electron of a specific energy E.

Statistical interpretation of ψ. It was Max Born (1882–1970), the German physicist, who gave statistical interpretation of the function ψ, calling it the **probability amplitude function**. Born won the 1954 Physics Nobel Prize for this interpretation. If $\psi(x)$ is the wave function of a particle, then, the probability of finding the particle within the range from x to $x+dx$ is given by

$$P(x)dx = \psi^*\psi \, dx = |\psi|^2 dx \qquad \text{...(76)}$$

where ψ^* denotes the complex conjugate of ψ. Note that $P(x)dx$ is the probability and $P(x)$ is the probability density.

We know that in the case of light waves, the intensity of the electromagnetic field is proportional to the square of the amplitude of the wave at that point. Likewise, in the case of a particle, the probability of its being found between the region x and $(x+dx)$ is proportional to the square of the wave function, *i.e.*, the square of the probability amplitude function at that point. Since the total probability of locating the particle must be unity, we have

$$\int_{-\infty}^{\infty} P(x)\,dx = \int_{-\infty}^{\infty} \psi^* \psi\, dx = \int_{-\infty}^{\infty} |\psi|^2\, dx = 1 \qquad \ldots(77)$$

For motion in three dimensions,

$$\int P(\vec{r})\, d^3r = \int |\psi(\vec{r})|^2\, d^3r = 1 \qquad \ldots(78)$$

where the integration is carried over the three-dimensional volume element $d^3r = dx\,dy\,dz$.

It may be noted that in Bohr's theory, the electron associated with a definite energy is considered to be located at a definite distance from the nucleus. In wave mechanics, the equation for calculating the *exact energy* of the electron has been derived but there is a considerable uncertainty with regard to its exact location. This is in conformity with the Heisenberg uncertainty principle.

Operators in Quantum Mechanics

The concept of operators is very important in wave mechanics. We have already listed a few operators in the sixth postulate of quantum mechanics. Here we shall briefly deal with the algebra of operators. If $\hat{A}$ and $\hat{B}$ are two operators and f is a function upon which they operate, then

$$(\hat{A} + \hat{B})f = \hat{A}f + \hat{B}f \qquad \ldots(79)$$

and

$$(\hat{A} - \hat{B})f = \hat{A}f - \hat{B}f \qquad \ldots(80)$$

Thus, we can generate new operators $\hat{A} + \hat{B}$ and $\hat{A} - \hat{B}$ by adding and subtracting $\hat{A}$ and $\hat{B}$. Also,

$$\hat{A} + \hat{B} = \hat{B} + \hat{A} \qquad \ldots(81)$$

$$\hat{A} - \hat{B} = -\hat{B} + \hat{A} \qquad \ldots(82)$$

The multiplication of operators can be carried out by doing successive operations with two or more operators on a function. If $\hat{A}$ and $\hat{B}$ are two operators and f is their *operand,* then we can obtain the quantity $\hat{A}\hat{B}f$ as follows : We first operate on f with $\hat{B}$ to obtain f', that is, $\hat{B}f = f'$. Then, f' is operated upon by $\hat{A}$ to obtain f'', that is, $\hat{A}f' = f''$. Thus, we have

$$\hat{A}\hat{B}f = f'' \qquad \ldots(83)$$

It should be remembered that the order of application of operators is always from right to left as they are written. Application of the same operator several times in succession is written with a power. Thus, we have

$$\hat{A}\hat{A}f = \hat{A}^2 f \qquad \ldots(84)$$

Commutation of Operators. The algebra of operators should be distinguished from the algebra of ordinary numbers. If a and b are two numbers, then we know that

$$a \times b = b \times a \qquad \ldots(85)$$

However, if $\hat{A}$ and $\hat{B}$ are two operators, then their product $\hat{A}\hat{B}$ may or may not be equal to $\hat{B}\hat{A}$. If $\hat{A}\hat{B} = \hat{B}\hat{A}$, then the **commutator** of the two operators is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \qquad \ldots(86)$$