Postulates of Quantum Theory

- The state of a system is defined by a function (usually denoted Ψ and called the wavefunction or state function) that contains all the information that can be known about the system.

- Every physical observable is represented by a linear operator called the "Hermitian" operator.

- Measurement of a physical observable will give a result that is one of the eigenvalues of the corresponding operator for that observable.

Postulate I

$\Psi(x, y, z) \equiv \text{stationary state}$

Often, Ψ is complex: $\Psi = Z(a, b)$

where: $a = \text{Real}(Z)$ & $b = \text{Imag}(Z)$

For example:

$Z \equiv a + ib$ in which

Complex Conjugate $\equiv Z^* = a - ib$

i = complex number unit vector

$$i^2 = -1\,; \quad i^3 = -i\,; \quad i^4 = 1\,; \quad \frac{1}{i} = -i\,.$$

$$Z \cdot Z^* = |Z|^2 = a^2 + b^2$$

Properties of Valid Wave Functions

Boundary conditions

1) In order to avoid infinite probabilities, the wave function must be finite everywhere.
2) In order to avoid multiple values of the probability, the wave function must be single valued.
3) For finite potentials, the wave function and its derivative must be continuous. This is required because the second-order derivative term in the wave equation must be single valued. (There are exceptions to this rule when V is infinite.)
4) In order to normalize the wave functions, they must approach zero as x approaches infinity.

- Solutions that do not satisfy these properties do not generally correspond to physically realizable circumstances.

$\Psi^* \cdot \Psi \equiv$ Probability Distribution Function

Criteria of Ψ

- must be single-valued over all space
- must be finite & continuous over all space
- $|\Psi|^2$ must have a finite integral over all space

Normalization of Ψ

$$\int_{\text{all space}} \Psi^* \cdot \Psi \cdot d\tau = 1$$

(1D-cartesian): $d\tau = dx$

(3D-cartesian): $d\tau = dx \cdot dy \cdot dz$

(3D-spherical): $d\tau = r^2 \cdot dr \cdot \sin\theta \cdot d\theta \cdot d\phi$

Probability of finding particle within a certain region of space (1D - x only):

$$\text{Prob}(x_1 \le x \le x_2) = \frac{\int_{x_1}^{x_2} |\psi|^2 dx}{\int_{-\infty}^{\infty} |\psi|^2 dx} \xrightarrow{\text{if normalized}} \int_{x_1}^{x_2} |\psi|^2 dx$$

Postulate II

Variable	CM	QM
Position	x , y , z	$\hat{x}$, $\hat{y}$, $\hat{z}$
Momentum	mv	$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} = \frac{\hbar}{i} \frac{\partial}{\partial x}$
		$\hat{p}_y = -i\hbar \frac{\partial}{\partial y} = \frac{\hbar}{i} \frac{\partial}{\partial y}$
		$\hat{p}_z = -i\hbar \frac{\partial}{\partial z} = \frac{\hbar}{i} \frac{\partial}{\partial z}$
Potential Energy	V	$\hat{V}(x, y, z) = V(x, y, z)$

Variable	**CM**	**QM**
Kinetic Energy	$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$	$\hat{T} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] = -\frac{\hbar^2}{2m}\left[\nabla^2\right]$
Total Energy	T + V	$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z)$

$\hat{H} \equiv$ Hamiltonian

Starting Point in all Quantum Mechanical Problems.

Expectation values

- The **expectation value** is the expected result of the average of many measurements of a given quantity. The expectation value of x is denoted by $\langle x \rangle$
- Any measurable quantity for which we can calculate the expectation value is called a **physical observable**. The expectation values of physical observables (for example, position, linear momentum, angular momentum, and energy) must be real, because the experimental results of measurements are real.
- The average value of x is

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_2 x_2 + N_2 x_2 + \ldots}{N_1 + N_2 + N_3 + N_4 + \ldots} = \frac{\sum_i N_i x_i}{\sum_i N_i}$$

Continuous Expectation values

- We can change from discrete to continuous variables by using the probability $P(x,t)$ of observing the particle at a particular x.

$$\bar{x} = \frac{\int_{-\infty}^{\infty} xP(x)\,dx}{\int_{-\infty}^{\infty} P(x)\,dx}$$

- Using the wave function, the expectation value is:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x\Psi^*(x,t)\Psi(x,t)\,dx}{\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx}$$

- The expectation value of any function $g(x)$ for a normalized wave function:

$$\langle g(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)g(x)\Psi(x,t)\,dx$$

The uncertainty

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

Δx, is often called the *uncertainty* in position

In general for any quantity it given by

$$\Delta Q = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2}$$

The Schrodinger Wave Equation

- The Schrödinger wave equation in its time-dependent form for a particle of energy *E* moving in a potential *V* in one dimension is

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

- The extension into three dimensions is

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

where $i=\sqrt{-1}$ is an imaginary number.

Time-Independent Schrodinger Wave Equation

- The potential in many cases will not depend explicitly on time.
- The dependence on time and position can then be separated in the Schrödinger wave equation. Let ,

$$\Psi(x,t) = \psi(x) f(t)$$

which yields:

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

Now divide by the wave function:

$$i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x)$$

- The left side of the above Equation depends only on time, and the right side depends only on spatial coordinates. Hence each side must be equal to a constant. The time dependent side is

$$i\hbar\frac{1}{f}\frac{df}{dt} = B$$

- We integrate both sides and find: $i\hbar \int \frac{df}{f} = \int B\,dt \qquad i\hbar \ln f = Bt + C$

where C is an integration constant that we may choose to be 0. Therefore

$$\ln f = \frac{Bt}{i\hbar}$$

This determines f to be $f(t) = e^{Bt/i\hbar} = e^{-iBt/\hbar}$

$$B = E$$

- This is known as the **time-independent Schrödinger wave equation**, and it is a fundamental equation in quantum mechanics.

Stationary State

- The wave function can be written as:

$$\Psi(x,t) = \psi(x)e^{-i\omega t}$$

$$\omega = \frac{E}{\hbar}$$

- The probability density becomes:

$$\Psi^*\Psi = \psi^2(x)(e^{i\omega t}e^{-i\omega t})$$

$$\Psi^*\Psi = \psi^2(x)$$

- The probability distributions are constant in time. This is a standing wave phenomena that is called the stationary state.