Wave function

Every microscopic particle or system particles are associated with a quantity called wave function whose variation makes up de Broglie waves or matter waves. It describes quantum state of the particle. The wave function $\psi(x,t)$ determines the entire space-time behaviour of system.

Properties of wavefunction

1. Contains all measurable information about the particle.
2. ψ must be single valued everywhere in space
3. ψ must be finite everywhere in space.
4. ψ and its first derivatives wrt its variables must be continuous everywhere.
5. For bound states, ψ must vanish at infinity
6. ψ must be normalizable, i.e. ψ must go to zero as $x \to \pm\infty$, $y \to \pm\infty$ and $z \to \pm\infty$ in order that $\int |\psi|^2 dV$ over all space be a finite quantity.

Physical Significance of wave function

1) It signifies the probability of finding the particle at the point (x, y, z) and at time t.
2) The wave function can interfere with itself (e^- diffraction)
3) The wave function ψ is a complex quantity and has no direct physical significance by itself. The product $(\psi^* \psi)$ is a real quantity where ψ^* is the complex conjugate of ψ.
4) Probability density — It is the probability of finding the particle per unit volume. It is given by $\psi\psi^*$ or $|\psi|^2$. So, $|\psi(x,t)|^2 = \psi^*(x,t)\psi(x,t)\, dV$ is proportional to probability of finding the particle in interval V and $V+dV$ at time t. The total probability

of finding the particle anywhere in space is

$$P = \int_{-\infty}^{\infty} |\psi(x,t)|^2 dV$$

Max Born's Interpretation of wave function

The space time behaviour of an atomic system is determined by the laws of probability. The probability of finding the e⁻ at a point in space is determined by the square of amplitude of wave function.

Max Born's conditions imposed on wave function are —

1. Wave function must be single valued. This means that for any given value of x and t, $\psi(x,t)$ must have a unique value. This guarantees that there is only single value of probability of system being in given state.

2. Wave function must be square integrable. In other words, the integral of $|\psi|^2$ over all space must be finite. One consequence of this proposal is that ψ must tend to 0 for infinite distances.

3. The wave function must be continuous everywhere. That is, there are no sudden jumps in the probability density when moving through space.

4. All first order derivatives of the wave function must be continuous. Following the same reasoning as (3), a discontinuous first derivative would imply an infinite second derivative, and since the energy of system is found using second derivative, a discontinuous first derivative would imply an infinite energy, which again is not physically realistic.

Normalization of wave function

As ψ itself is complex and has no physical significance but ψ^2 has significance. The integral of ψ^2 taken over all space must be equal to one i.e.

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dV = 1$$

such a wave function is called normalised wave function.
The process of integration over all space to give unity is called normalization.
If $\psi(x,t)$ is multiplied by a const C such that
$\psi_N(x,t) = C\psi(x,t)$ where $\psi_N(x,t)$ satisfy the relation →

$$\int_{-\infty}^{\infty} |\psi_N(x,t)|^2 dV = \boxed{|C|^2 \int_{-\infty}^{\infty} |\psi(x,t)|^2 dV = 1}$$

then $\psi_N(x,t)$ is called normalized wave function.

here $\boxed{|C|^2 = \dfrac{1}{\int_{-\infty}^{\infty} |\psi(x,t)|^2 dV}}$ where C is called normalization const.

Thus a wave function is normalizable if $\int_{-\infty}^{\infty} |\psi(x,t)|^2 dV$ remains finite over all space.

Operators in Quantum Mechanics

An operator is a mathematical rule operating on one function transforming it into another function.
eg - an operator like $\frac{d}{dx}$ operated on x^2 results $3x^2$.

An operator when applied to a wave function gives corresponding observable quantity multiplied by the wave function.

Momentum operator

* wave function is $\psi = A e^{\frac{i}{\hbar}(p_x x - Et)}$

Differentiating wrt x, $\frac{\partial \psi}{\partial x} = A e^{\frac{i}{\hbar}(p_x x - Et)} \left(\frac{i p_x}{\hbar}\right)$

$$\frac{\partial \psi}{\partial x} = \frac{i p_x}{\hbar} \psi$$

$$\Rightarrow p_x \psi = \frac{\hbar}{i} \frac{\partial \psi}{\partial x} \Rightarrow \boxed{p_x \psi = -i\hbar \frac{\partial \psi}{\partial x}}$$

so $\boxed{p_x = -i\hbar \frac{\partial}{\partial x}}$ is momentum operator when operated on ψ gives result.

The observable quantity here is linear momentum p_x multiplied by wave function ψ.

Energy Operator

* Wave function is $\psi = A e^{\frac{i}{\hbar}(p_x x - Et)}$

Differentiating wrt time $\frac{\partial \psi}{\partial t} = \left(-\frac{iE}{\hbar}\right) \psi$

or $\boxed{E\psi = i\hbar \frac{\partial \psi}{\partial t}}$. Here operator is $E = i\hbar \frac{\partial}{\partial t}$

The observable quantity is total energy E multiplied by wave function ψ.

Quantity	Classical definition	Quantum operator
① Position	R	r
② Linear Momentum	P	$-i\hbar\frac{\partial}{\partial x}$ or $-i\hbar\nabla$
③ Angular momentum	$r\times p$	$-i\hbar(r\times\nabla)$
④ Kinetic energy	$\frac{p^2}{2m}$	$-\frac{\hbar^2}{2m}\nabla^2$
⑤ Potential energy	V	V
⑥ Total energy (time dependent)	E	$i\hbar\frac{\partial}{\partial t}$
⑦ Hamiltonian (time independent)	$H=\frac{p^2}{2m}+V$	$-\frac{\hbar^2}{2m}\nabla^2+V$

Eigenvalues and Eigenfunctions

If an operator $\tilde{A}$ operating on a function $\psi(x)$ multiplies the latter by a constant λ, then $\psi(x)$ is called the eigenfunction of $\tilde{A}$ belonging to eigenvalue λ.

Eigenfunctions $\psi_n(x)$ are a set of functions which when operated by an operator $\tilde{A}$ remains unchanged and are multiplied by the corresponding eigenvalues λ_n.

eg - If $\tilde{A}=\frac{d^2}{dx^2}$ and $\psi(x)=\alpha e^{-2x}$

$$\Rightarrow \tilde{A}\psi(x)=\frac{d^2}{dx^2}[\alpha e^{-2x}] = 4\alpha e^{-2x} \text{ or } \boxed{\tilde{A}\psi(x)=4\psi(x)}$$

$4\rightarrow$ eigenvalue
$\psi(x)\rightarrow$ e function

when applied to a general operator Q

$$Q_{op} \psi_i = q_i \psi_i \rightarrow \text{efunction}$$

↓ operator ↓ e value

If the function ψ_i is an efunction for that operator, the eigenvalues q_i may be discrete, and in such cases we say physical variable is quantised and index i plays the role of a "quantum number" which characterizes that state.

Expectation values

To relate a quantum mechanical calculation to an observation made in lab, the "expectation value" of measurable parameter is calculated. It is defined as

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

It is interpreted as avg value of x that we would expect to obtain from a large number of measurements.

eg- the expectation value of radius of the e^- in the ground state of hydrogen atom is avg value you expect to obtain from making measurement for large number of hydrogen atoms.

The expectation value of momentum $\langle p \rangle = \int_{-\infty}^{\infty} \psi^* (-i\hbar \nabla) \psi \, dV$

" " " energy $\langle E \rangle = \int_{-\infty}^{\infty} \psi^* \left(i\hbar \frac{\partial}{\partial t}\right) \psi \, dV$

" " " position $\langle x \rangle = \int_{-\infty}^{\infty} \psi^* x \psi \, dV$

Free Particle wave function

A free particle is one which is subject to no forces of any kind. Thus, it moves in a region of constant potential. The particle motion is confined to x dirⁿ only. Let the potential be considered as zero

so $V=0$

Time independent Schrodinger's eqⁿ → $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V) = 0$

As $V=0$, ⇒ $\frac{d^2\psi}{dx^2} + \left(\frac{2m}{\hbar^2}E\right)\psi = 0$

or $\boxed{\frac{d^2\psi}{dx^2} + k^2\psi = 0}$ — ① where $k^2 = \frac{2mE}{\hbar^2}$

so $\boxed{k = \frac{\sqrt{2mE}}{\hbar}}$

solⁿ of eq ① is $\psi = Ae^{ikx} + Be^{-ikx}$

if particle moves only along $+x$ then 2nd term $=0$

so $\boxed{\psi = Ae^{ikx}}$ — ②

To normalise, consider $\int_{-\infty}^{\infty} \psi^*\psi \, dx = 1$

substituting ②, $\int_{-\infty}^{\infty} Ae^{-ikx} Ae^{ikx} dx = 1 \Rightarrow \int_{-\infty}^{\infty} A^2 dx = 1$

Or $A^2 \int_{-\infty}^{\infty} dx = 1$

$\int_{-\infty}^{\infty} dx$ is infinite ⇒ A must be zero. This difficulty arises since we are considering an ideal case of infinite length. But in reality, the particle is confined to finite length so that normalization is possible.

For a free particle, there is no restriction on energy. Generally, for bound systems like e^- trapped in an atom, the energies are discrete. But the unbound systems like free particle will give continuum energy