Foundationof Quantum Mechanics
(Concept of wave function and operator)
SEM IV
(Department of Chemistry)

The State of a system in classical mechanics is defined by specifying all forces acting and all positions and velocities of the particles. In quantum mechanics,the state of a system is defined by a mathematical function ψ, called the state function or the wave function. Ψ is a function of coordinates of all the particles and also time. For two particles system $\Psi=\Psi$ $(x_1, y_1,z_1,x_2,y_2,z_2,t)$ where x_1, y_1, z_1, and x_2, y_2, z_2 are coordinates of particles 1 and 2 respectively.

Physical meaning of the wave function Ψ

According to the Born postulation $|\Psi|^2$ is the probability density for finding the particles at given locations in space. For one particle system $|\Psi|^2$is probability of finding the particle at time t,with coordinates x_1 to x_1+dx, y_1 to y_1+dy, and z_1 to z_1+dz in a tiny volume of dimension dxdydz.

$Pr(x_1 < x < x_1+dx,\ y_1 < y < y_1+dy,\ z_1 < z < z_1+dz)$

$$= |\Psi (x_1, y_1, z_1,t) |^2 dxdydz$$

(Mathematical problems on determination of probability density.Levine, Physical Chemistry, 5 th edition, sec 17.6)

Ψ is a complex quantity so value of $|\Psi|^2 = \Psi^* \Psi$ where Ψ^* is complex conjugate of Ψ. For one particle one dimensional (say in x direction) system, the probability of finding the particle somewhere in x direction must by 1. So $\int_{-\alpha}^{+\alpha} |\Psi|^2 dx= 1$. When Ψ satisfy this equation, it is said to be normalised.

(Mathematical problem see, Levine, chap 17.6)

The time independent Schrodinger equation

For an isolated atomic or molecular system, the forces acting depend on the coordinates of the system. Therefore potential energy is only a function of space coordinates. For one particle one dimensional system, time independent Schrodinger equation is as follows

$$-(h^2 /8\pi^2 m)(\partial^2/\partial x^2)\psi(x) + V(x)\psi(x) = E\ \psi(x)$$

(for general solution of wave equation see, McQuarrie, Quantum Chemistry (2003) Chap2 , sec,2.2,2.2,2.3 and 2.4)

The solution of this equation ψ is time independent wave function. State for ψ is called stationary state when a measure of its energy is certain to give a particular energy value. The wave function ψ of a stationary state of energy E must satisfy the time independent Schrodinger equation. A wave function must meet the three condition

A. It must be single valued

(Only one value at each point in space)

B. It must be continuous

C. It must be quadraticallyintegrable.
(Integral over all space $\int \psi^2 d\tau$is finite number)
A wave function that satisfies all these three criteria is called well behave wave function.

Operator

An operator is a rule for transforming a given function into another function. Suppose Â symbolise an operator that transforms a function f(x) into g(x) then Â f(x) = g(x).
In quantum mechanics, each physical property of a system has a corresponding operator.(list of quantum mechanical operator see McQuarrie , sec 4.2) . When an operator is applied to a function gives the function back but multiplied by the constantc , Â f = c f then f is called an eigen function of Â with eigen value c .

The operators that corresponds to physical entities in quantum mechanics are linear.

$$\hat{A}(f + g) = \hat{A} f + \hat{A} g \quad \text{and} \quad \hat{A}(cf) = c \hat{A} f$$

If the system's state function ψ happens to be an eigen function of Â correspond to the property A with eigen value c, then a measurement of A is certain to give the value c as the result.

The average value of any physical property A in a system whose state function is ψ is given by $\langle A \rangle = \int \psi^* \hat{A} \psi d\tau$
Where Â is the operator for property A and integral is done over whole space.
(More details see McQuarrie , Quantum Chemistry (2007), chap 4).

Commutation relation

The product of two operators is define by operating them on a function. Suppose a and b are two operators and f(x) is a function. Ab f(x) indicates that b is operating upon f(x) , producing new function and then a is operating on that new function. consider two fundamental operators x and p, xpf(x) = x(-iħ) $\frac{d}{dx}$f(x) and pxf(x) = (-iħ) $\frac{d}{dx}x$f(x) = (-iħ)f(x) - x(-iħ) $\frac{d}{dx}$f(x) and (xp – px)f(x) = iħf(x) if f(x) is differentiable. So x and p non commutating. It is customary to use [Ab]=ab – ba and this is called commutator of a and b. if [Ab]= 0 then a and b commute with each other .commmutator operator have simultaneous eigenstates. These cannot be measured simultaneously.