Foundation of Quantum Mechanics
(Particle in a box)
SEM IV
(Department of Chemistry)
Biswajit Halder

Quantisation of motion

If a stretched string is rigidly clamped at both ends then it will have fixed length. We can only set up standing wave on it. This standing wave can only have definite and discrete frequencies (fundamental mode and overtones). So quantisation of motion arises due to confining of the wave at definite region of space. This concept is applied to all kind of waves including matter wave. For matter wave, dealing with energy (E) is easier then frequency because of Schrodinger equation.

Confinement Principle

An electron of an atom held within the atom by columbic interaction between electron and nucleus and it can exist only in a set of discrete energy states. This electron is not a free electron. On the other hand an electron moving in positive x direction and subject to no net force is a free particle that can have any reasonable value. According to confinement principle, Confinement of a wave leads to quantisation – that is, to the existence of discrete states and discrete energies.(Halliday, Resnick and Walker – Fundamentals of Physics, 6th edition . (page 980).

Particle in one dimensional box

A particle of mass m is confined in region along x direction between x = 0 and x = a. suppose, the particle experience no potential energy, V(x) = 0 inside this region.This is called the problem of a free particle in one dimensional box. This simple model has a crude application to the π electron in linear conjugated hydrocarbon. Schrodinger equation for this problem is

$$(d^2/dx^2)\psi(x) + (2mE/\hbar^2)\,\psi(x) = 0 \qquad 0 \le x \le a$$

So the probability of finding the particle outside the region is zero. Ψ(x) is continuous inside this box of length a. Therefore $\psi(0) = \psi(a) = 0$ is the boundary for this problem.

*Now the discrete wave patterns(in which the string can oscillate) are those for which the length **a** of the string is equal to integral **multiple of half wave length**. Where n indicates state of the oscillating string. For particle wave n is called quantum number.*

$$a = (n\lambda/2)$$

The general solution of Schrodinger equation for this problem is

$$\psi(x) = A\cos kx + B\sin kx$$

$$\text{where } k = (2mE)^{1/2}/\hbar$$

Applying boundary condition

$$\psi(0)= 0 \text{ implies } A = 0.$$

The second boundary condition gives

$$\psi(a) = B \sin kx = 0$$

$$\text{So} ka = n\pi \text{ where } n = 1,2,3, \ldots\ldots$$

Putting $k = n\pi/a$ we find that $E_n = (h^2/8ma)\, n^2 n = 1,2,3, \ldots\ldots$

(derivation see McQuarrie page 49 – 53).

So energy of the particle is quantised.(Sothe introduction of integral arises in the same natural way as in vibrating string for which the number of nodes is integral). The quantum state for lower possible energy state E_1 is called ground state. It can be changed to an excited state only if an external source provides the energy that is required for this transition. If confined electron is to absorb a photon, the energy hν of the photon must be equal to the energy difference ΔE between initial energy level to next higher energy level.

$$\Delta E = h\nu = E_{n+1} - E_n$$

(*Though absorption and emission can applied to the electron traps. But in reality it cannot be applied to one dimensional case because photo absorption and emission require conservation of angular momentum.*)

Zero point energy

E_1 is the ground energy state for particle in one dimensional box. Electron will occupy this state unless no energy is supplied to excite the electron in its next higher energy state. If ground state energy was zero it would have $|\Psi|^2 = 0$. So there cannot be any electron inside the one dimensional box. So it is an important conclusion that any confined system cannot exist in state with zero energy. They always have a certain minimum energy ($E = h^2/8ma$ here) called *zero point energy*.

Probability of an electron detected at a point inside the one dimensional box

We cannot see an electron inside a one dimensional box and finding the electron inside at any position of the confined space is also not logical as we cannot materialiseelectron because electron is a matter wave. So we can only find probability of detecting electron at any position inside the box. It is related with the probability density $\Psi^2(x)$(as$\Psi(x)$ is real quantity here. Probability density is probability per unit length along x direction . The probability p(x) that an electron can be detected at position x within the wall is
(probability density at position x)(width dx centered on position x).

$$\text{Therefore } p(x) = |\Psi(x)|^2\, dx$$

So probability of finding the electron at any finite section within the box can be detected as

$$\text{So} \qquad \int_{x1}^{x2} |\Psi|^2\, dx$$

$$\text{Or } \int_{x1}^{x2} p(x) = \int_{x1}^{x2} A^2 \sin^2 (n\pi x/a)\, dx$$

(Presentation of wave function and probability density see McQuarrie page 86)

Normalisation of the Wave function

According to the Born approximation $p(x) = \Psi_n^*(x)\Psi_n(x)\, dx$ is the probability that a particle is locate between x and x + dx. Particle is confined in space between x=0 and x=a so the probability of the particle lies between x=0 and x=a must be unity.

$$\int_0^a \Psi_n^*(x)\Psi_n(x)\, dx = \int_0^a A^2 \sin^2 (n\pi x/a)\, dx = 1$$

The wave function that satisfy this equation is said to be normalised.

$$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin^2 (n\pi x/a)$$

$$A = \sqrt{\frac{2}{a}} \text{ is called normalisation constant.}$$

(Complete derivation see McQuarrie page 88)

Particle under a potential field v(x)

Schrodinger equation for particle under potential field describe by v(x)

$$(d^2/dx^2)\psi(x) + (E-V(x))(2m/\hbar^2)\, \psi(x) = 0 \qquad 0 \le x \le a$$

Momentum of the particle wave $p = \sqrt{(E-V)2m}$. again $\lambda = h/p = (h / \sqrt{(E-V)2m})$

Expectation value

Suppose we have some number $x_j$is associated with some outcome j .then we define average value or expectation value of x to be $< x> = \Sigma_{j=1}^{n} x_j f\ (x_{j)}.$ f(xj) is probability of realising the number $x_{j.}$ Probability distribution of a measurable quantity. So $< x^2> = \Sigma_{j=1}^{n} x_j^2 f\ (x_{j)}$ this is called second moment. Now suppose individual observation of $x_j$differs from < x> then $< (x- <x>)^2>$ = square of standard deviation that is most observation likely to be observed in this spreading.then the outcomes of event is probabilistic.For the continuous distribution

$$< x> = \int_{-\alpha}^{+\alpha} xf(x)dx$$

$$<x^2>= \int_{-\alpha}^{+\alpha} x^2 f(x)dx$$

$$\sigma_x^2= \int_{-\alpha}^{+\alpha}(x- <x>)^2 f(x)dx$$

(mathematical problem McQuarrie. Page 92 to 100.)