Day 6

Eigen Function and Eigen Value

If the effect of operating on some function f(x) with the operator $\hat{\mathbf{A}}$ is simply to multiply f(x) by a certain constant K then we can say that f(x) is an Eigen function of $\hat{\mathbf{A}}$ **with eigenvalue K**.

$$\mathbf{Af(x) = Kf(x)}$$

$$\mathbf{d/dx(e^{2x})=2e^{2x}}$$

Hence e^{2x} is an ***Eigen-function*** of the operator d/dx with ***Eigen value*** of 2.

- Sin3x is not an Eigen function of **d/dx**. But what if **d^2/dx^2**?
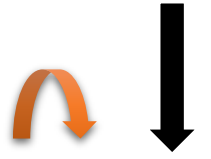- e^{ax^2} is not an Eigen function of d/dx,

As, $d/dx(e^{ax^2})= (2ax)e^{ax^2}$

2x is not constant

- If we write $2a(xe^{ax^2})$, then 2a is constant but xe^{ax^2} is not the same function.

Eigen Function and Eigen Value in simple words…

An operator A if operates upon a wave-function Ψ in such a way that $A\Psi=\beta\Psi$
Where, β is real quantity and for selected value of Ψ is found to be physically significant the later is said to be Eigen function and β is Eigen value.

Lets consider:

$$d^2/dx^2(\Psi) = -\lambda\Psi$$

'In order to understand this we need to Get help from Mathematics!'

Degenerated Eigen Function

- $\hat{A}\Psi_1 = \alpha\Psi_1$

- $\hat{A}\Psi_2 = \alpha\Psi_2$

- **If for two selected value of α, Ψ_1 and Ψ_2 are real then these are Eigen function.**

- **This means two wave functions have equal *energy-degenerated* Eigen function.**

- **The linear combination of two degenerated Eigen Function is also an Eigen function of the same operator with same Eigen value.**

$$\Psi_+ = c_1\Psi_1 + c_2\Psi_2$$

$$\hat{A}\Psi_+ = c_1\hat{A}\Psi_1 + c_2\hat{A}\Psi_2 = c_1\alpha\Psi_1 + c_2\alpha\Psi_2 = = \alpha\,(c_1\Psi_1 + c_2\Psi_2) = \alpha\Psi_+$$

$$\Psi_- = c_1\Psi_1 - c_2\Psi_2?$$

Hermitian Operator

An operator $\hat{A}$ is said to be Hermitian if the following is satisfied:

$$\int \Psi_n^* \hat{A}\psi_m d\tau = \int (\hat{A}\,\Psi_n^*)\,\psi_m d\tau$$

Postulate 4

- If a system is in a state is described by a **normalized function** Ψ, then the average value of the observable corresponds to Â is given by,

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi \, dx \text{ [all over the space]}$$

Derivation of Schrodinger Equation

- Lets consider an electron inside an atom.
- Total energy (E) = Kinetic Energy + Potential energy = $(½)mv^2$ + V(pot)
- E= $p_x^2/2m$ + V(pot) **Can we apply it on microscopic world?**
- E can be converted to the quantum mechanical operator in the following way:

$$P_x = -i\hbar(d/dx) \text{ and } V(pot) = V(X)$$

- *The operator corresponding to energy E is called the Hamiltonian operator and represented by* Ĥ.
  - *Ĥ =[(1/2m)×(-iℏ(d/dx) ×(-iℏ(d/dx)]+V(x)=- ℏ²/2m(d²/dx²) + V(x)*

Time Independent Schrödinger Equation

$$[\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)]\psi=E\psi$$

- The value 'E' are the Eigen values and Ψ is the Eigen function.
- The operator is called Hamiltonian operator.

Remember:
This type of equation may have infinite number of solution of which only a few are physically significant and hence acceptable. Such functions are called as Eigen function and corresponds to an atomic orbital.
3D Volume & space around a nucleus where the probability of finding a electron is maximum is called as orbital.

In classical theory, square of amplitude is proportional to intensity.

Similarly, square of Ψ at any point gives the probability of the system at that point.

Wave-function-Summary

There exists a function Ψ(x, y, z, t) of the co-ordinates and time, which we call a wave-function and describe as a probability amplitude.

This wave-function is a complex function.
Ψ(x, y, z, t)=u(x, y, z, t)+iv(x, y, z, t)

The complex conjugate of Ψ can be designated by Ψ*(x, y, z, t)= u(x, y, z, t)-iv(x, y, z, t)
Ψ Ψ* is a purely real function and is the probability density.

The product ΨΨ*dx dy dz is equal to ΨΨ*dτ.

The product ΨΨ*is the probability at time 't' that the system will be in the volume element 'dτ' at position x, y, z.

Ψ alone has no physical significance but the product ΨΨ*is related to probability density.
ΨΨ* is such that the probability of finding the system in a volume element dτ over all position is unity.

$$\int \Psi\Psi^*d\tau=1$$

However, we can also have:
$$\int \Psi\Psi^* d\tau = N$$

N is the normalization constant.
$$(1/N)\int \Psi\Psi^* d\tau = 1$$

$\int (1/N^{1/2} \, \Psi) (1/N^{1/2} \, \Psi^*) d\tau = 1$

$1/N^{1/2}$ is known as normalization constant and $1/N^{1/2} \, \Psi$ is the normalized wave-function.

The solution of Schrodinger equation often yields more than one wave-function and each satisfy Schrodinger equation with its own Eigen value.

If two such wave function satisfy the expression:

$$\int \Psi_i \Psi_j \, d\tau = 0$$

(Reflects the two functions are orthogonal to each other)

**Orthonormal Set:** $\int \Psi_i \Psi_j \, d\tau = \delta_{ij}$

$\delta_{ij} = 0 \; if, i \neq j$
$\delta_{ij} = 1 \; if. i = j$

δ_{ij} is called as Kronecker delta

Objective of L6

1. Schrodinger eqn.
2. To introduce a simple model problem in quantum mechanics known as particle in **1D box with infinite (∞)** potential boundary.
3. To demonstrate the **solution of Schrodinger eqn**. using the above model using differential eqn. with certain boundary condition.
4. To demonstrate the **Quantization of energy** due to imposition of boundary condition and finding the **probability** from the square of the wave function.
5. Particle in **2D Box.**

Particle in 1D box

V_X= infinite V_X= infinite

V_X=0

X=0   X=L
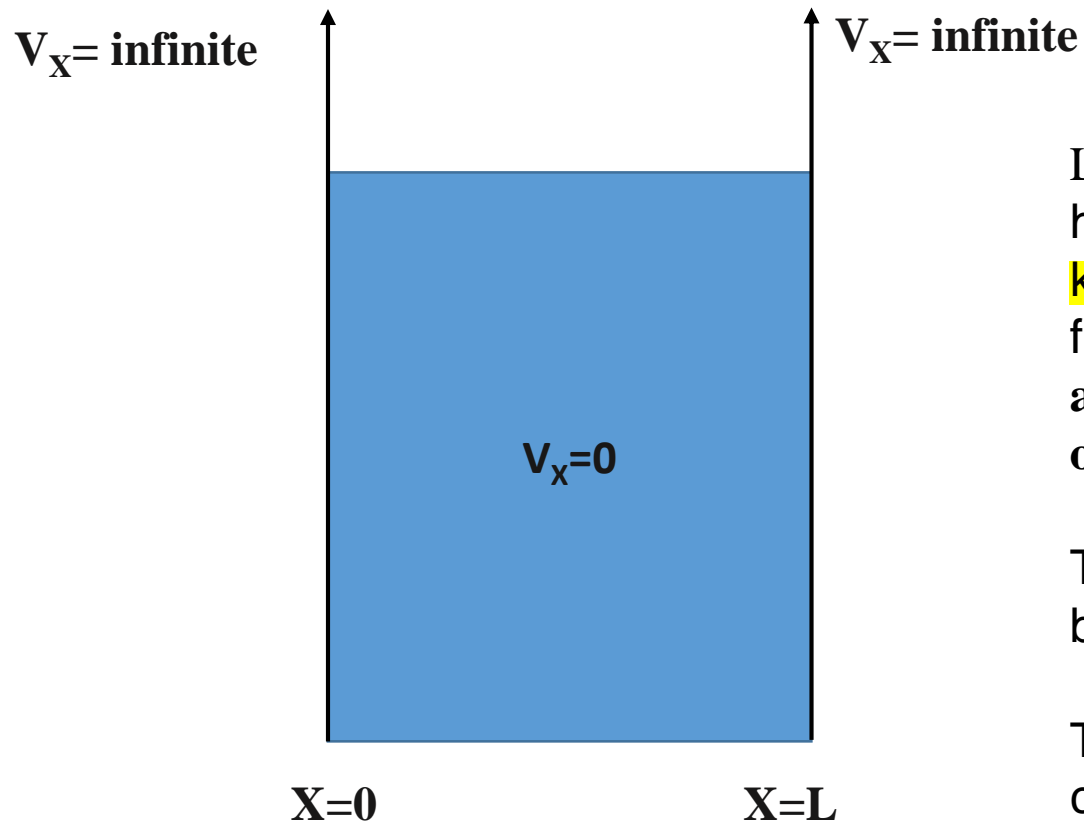
Lets confine a particle (**of mass m**) to a finite region in which it has no potential energy (V_x=0). Its energy is only due to its kinetic energy. It experiences no potentials due to any external force, i.e., its potential energy is zero inside the region. **At X=0 and L, there are two absolutely rigid impenetrable potential wall of infinite heights. [Boundary conditions]**

Thus the particle is trapped inside a box with no possibility of being located anywhere outside the box.

The particle can move only along one coordinate and call it x coordinate.

Since, the particle has only kinetic energy, hence inside the **box energy (E) is** only **kinetic energy (potential energy=0)** and hence:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

$$E = (1/2m)\, P_x^2 = [(1/2m) \times (-i\hbar(d/dx))\,(-i\hbar(d/dx)] = -\hbar^2/2m(d^2/dx^2) \qquad [\hbar = h/2\pi]$$

So the 1D Schrödinger equation for this particle can be written by using the operator form for the momentum as:

$$\frac{-\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E\psi$$

$$-\frac{d^2 \psi(x)}{dx^2} = \frac{2m}{\hbar^2} E\psi$$

Rearranging the above: $\dfrac{d^2}{dx^2}\Psi(x) + k^2\Psi(x) = 0$ \qquad **[Where, $K^2 = \dfrac{2mE}{\hbar^2}$]**

(Eqn 1)

General solution of equation 1:

$$\Psi(x) = A\cos(kx) + B\sin(kx)$$ **[A and B are constants]**

Applying boundary condition:

$$\Psi(x=0) = 0 \quad \Rightarrow \quad A\cos(0) + B\sin(0) = 0; \quad \therefore A = 0$$

$$\Psi(x=L) = 0 \quad \Rightarrow \quad B\sin(kL) = 0; \quad \therefore kL = n\pi; \quad n = 1,2,3,\ldots$$

$$k^2 = \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$$

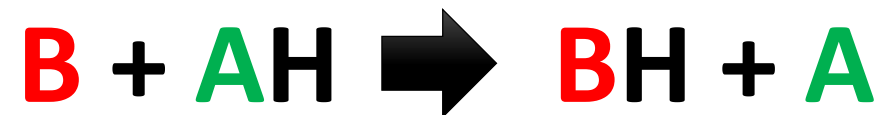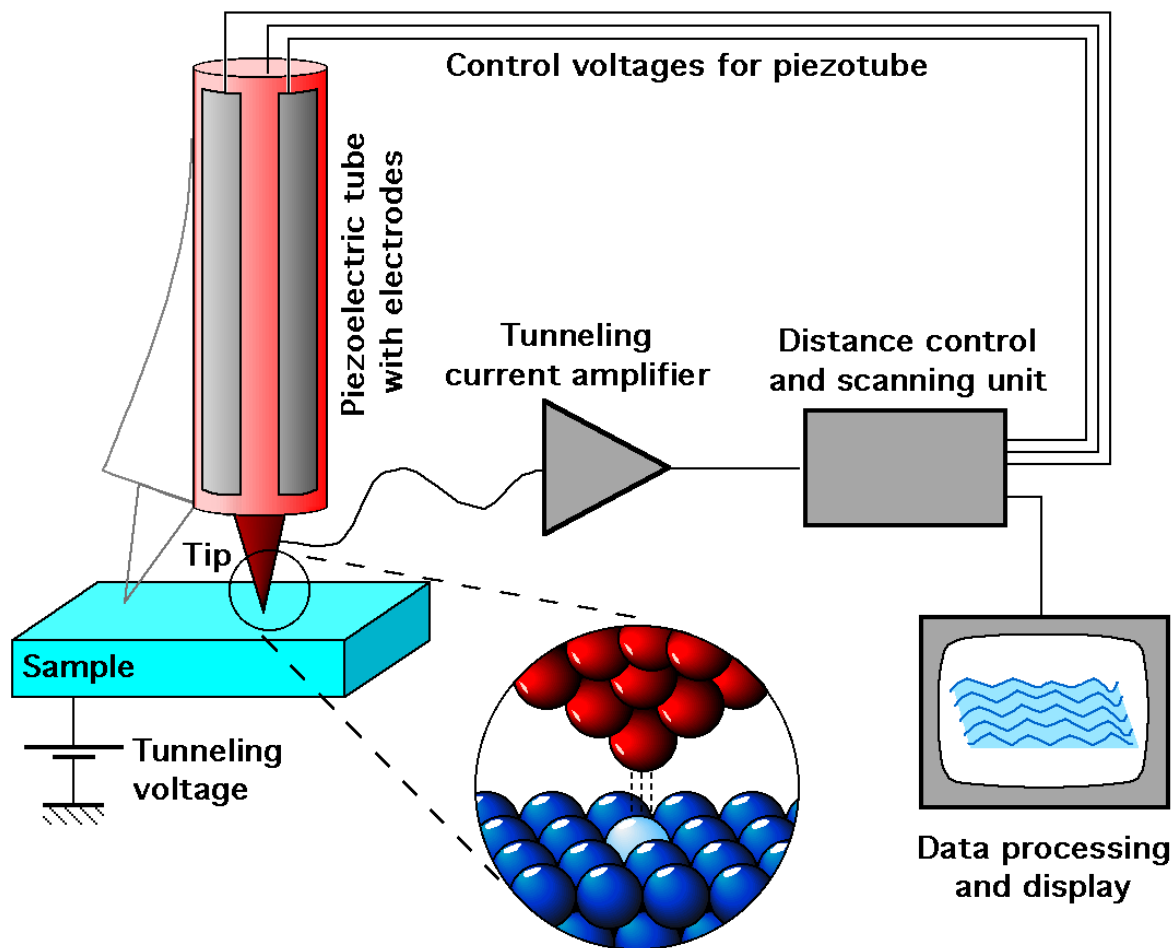$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2} = \frac{h^2 n^2}{8mL^2}$$ **Energy is quantized!**

$$\Psi_n(x) = B\sin\left(\frac{n\pi}{L}x\right)$$

Concept of tunneling

1) Case of inversion of NH_3, Proton exchange: AH+B=A+HB

2) scanning tunneling microscopy: STM

3) Emission of electrons from metal surface under electric field

4) He atom can tunnel through the radioactive disintegration of atomic nuclei.

B + AH ➡ BH + A

Proton wavelength is 1-2 A, which is comparable to the width of the energy barrier.

Q1. Can you find the normalization constant for $\Psi_n(x)$ for a particle in 1D box?

table of values of trigonometric functions

α	0° (0 rad)	30° (π/6)	45° (π/4)	60° (π/3)	90° (π/2)	180° (π)	270° (3π/2)	360° (2π)
$\sin\alpha$	0	$\dfrac{1}{2}$	$\dfrac{\sqrt{2}}{2}$	$\dfrac{\sqrt{3}}{2}$	1	0	−1	0
$\cos\alpha$	1	$\dfrac{\sqrt{3}}{2}$	$\dfrac{\sqrt{2}}{2}$	$\dfrac{1}{2}$	0	−1	0	1

n=6

n=5

n=4

n=3

n=2

n=1
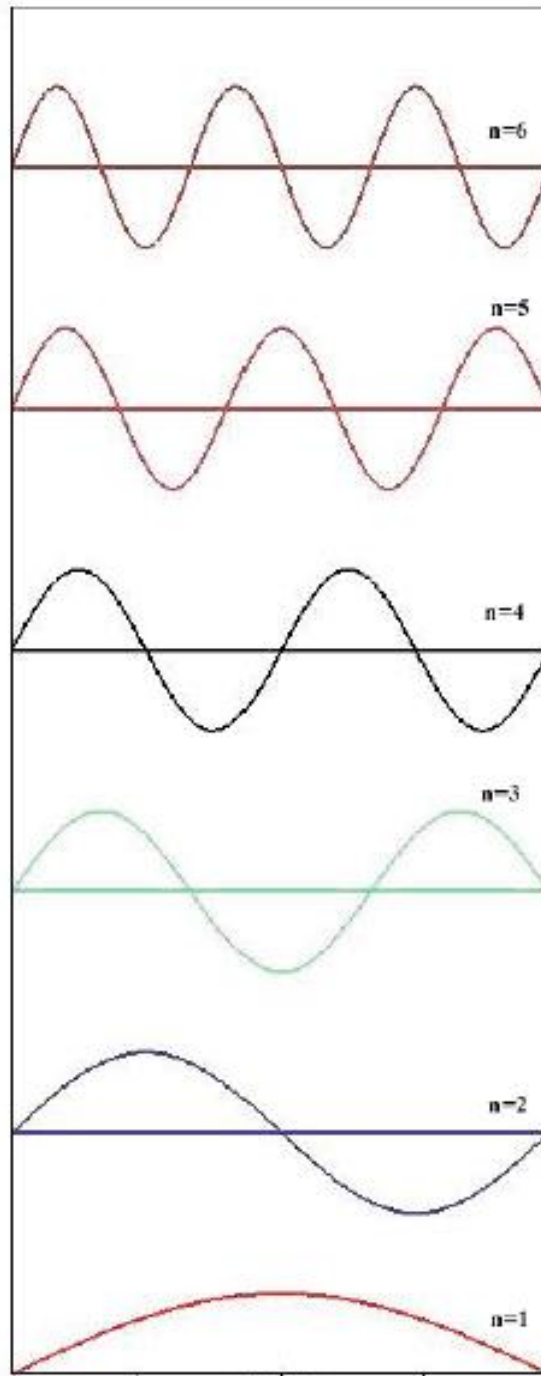
Don't think particle moves like a wave motion. However the **square of the function has a meaning**…….
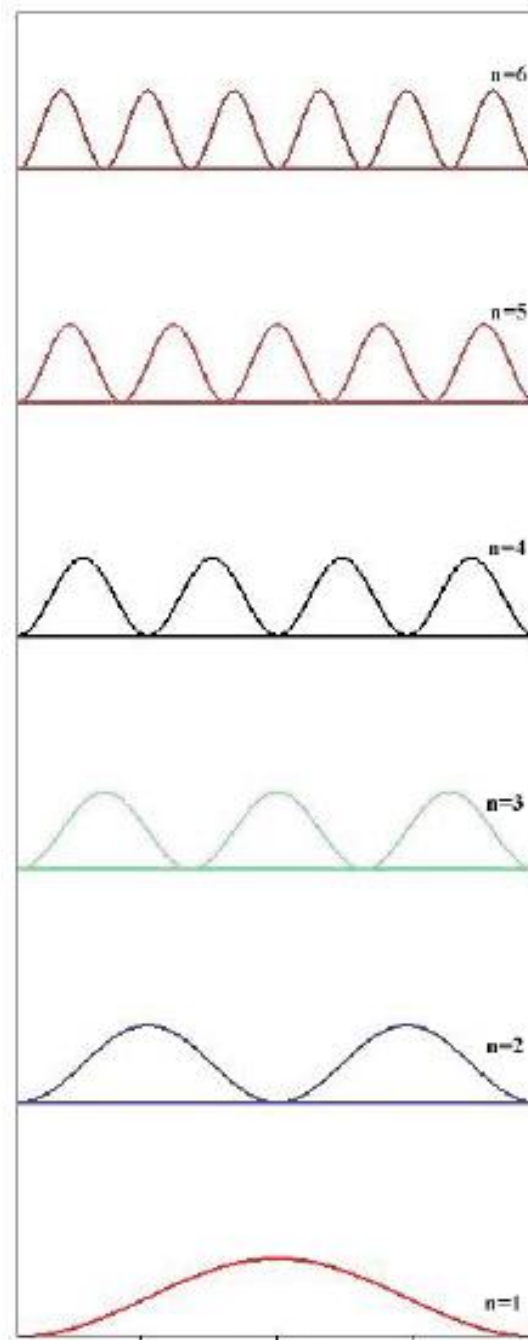
Expectation Value

- Expectation value <A> of any operator A is a statistical average o the observed values of the quantity for which the operator stands for.

- Expectation value <A> from the well behaved wave function is always greater than true Eigen value.