Day 5

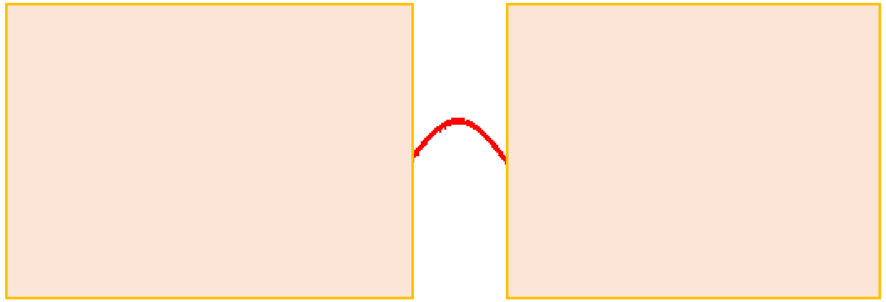
Concept of Wave Function

Schrodinger Wave Theory-Wave Mechanics (1926)

Schrodinger proposed wave theory based on the assumption that: behavior of electrons in an atom can be described as an equation analogues to a vibrating string, fixed at both end.

The equation used for wave-motion:

$$\frac{\partial^2\Psi}{\partial x^2} = 1/u^2 \frac{\partial^2\Psi}{\partial t^2}$$



Ψ is the amplitude, ‘u’ is the speed of propagation. If ‘u’ does not depends on time, Ψ can be written as a product of two function (x and t):

$\Psi = \Psi(x)\exp(i2\pi\nu t)$ **[ν = vibration frequency]**

$$\frac{\partial^2 \Psi(x)\exp(i2\pi\nu t)}{\partial x^2} = 1/u^2 \frac{\partial^2 \Psi(x)\exp(i2\pi\nu t)}{\partial t^2}$$

$$\frac{\exp(i2\pi\nu t)\partial^2 \Psi(x)}{\partial x^2} = \frac{1}{u^2}\Psi(x)(i2\pi\nu t)^2 \exp(i2\pi\nu t)$$

$$\frac{\partial^2 \Psi(x)}{\partial x^2} = -\frac{4\pi^2\nu^2}{u^2}\Psi(x)$$

ν = vibration frequency

u= speed

λ=wavelength

Since, u = ν × λ

$$\frac{\partial^2 \Psi(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}\Psi(x) \quad \text{[independent of time] (1)}$$

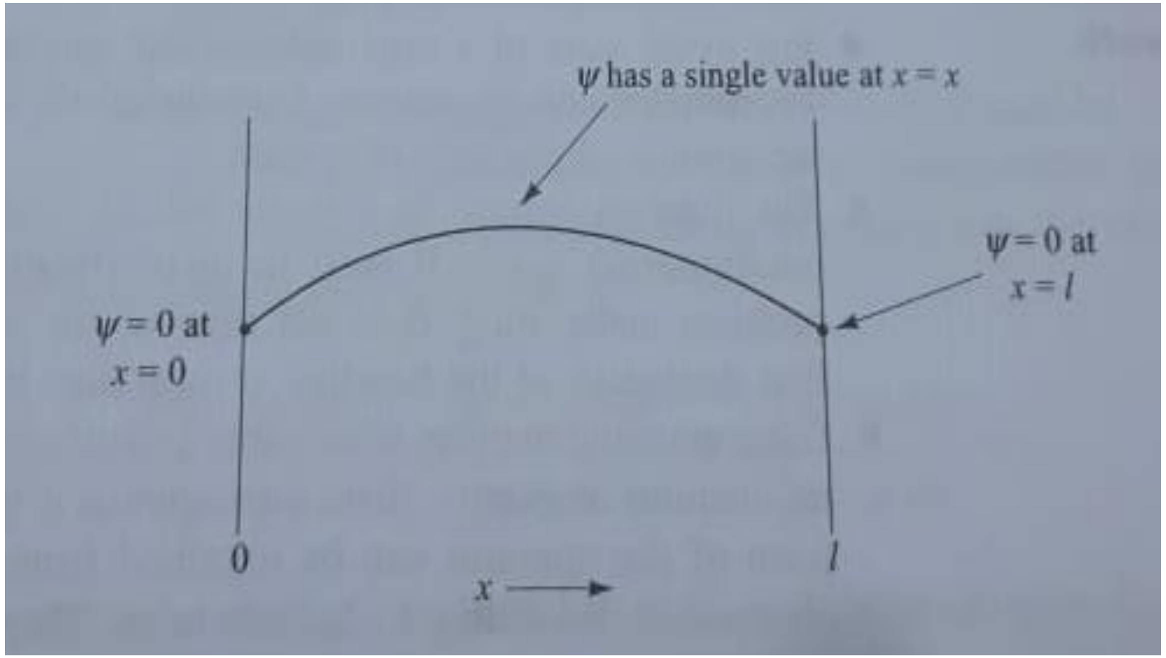
Eqn. 1 is independent of time and thus gives only the vibration of the amplitude function w.r.t $'x'$.

The term $\frac{\partial^2}{\partial x^2}$ is an operator which on operating over Ψ gives back the function Ψ multiplied by $\frac{4\pi^2}{\lambda^2}$, which is an ***Eigen value?***.

In order that the function Ψ is an acceptable solution, it should have the following:

Must be 0 at each end of the string and amplitude=0

Must be single valued in between.



$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}=-\frac{4\pi^2}{\lambda^2}\Psi$$ –(for 3D)

$\nabla^2\Psi+\frac{4\pi^2}{\lambda^2}\Psi=0$ [∇ is called as Laplacian operator]

This eqn. can be applied to all sub atomic particles in atom and in order to do that Schrodinger replaced λ by h/P [λ = de Broglie's wavelength; P=momentum]

$$\nabla^2\Psi+\frac{4P^2\pi^2}{h^2}\Psi=0$$

For electron,

E=Kinetic Energy + Potential Energy

= $(1/2)mv^2+V = P^2/2m + V = E$

$$P^2=2m(E-V)$$

Thus,

$$\nabla^2 \Psi + \frac{8\pi^2 m(E-V)}{h^2}\Psi = 0$$

This is the Schrodinger equation describes the behavior of e- in atom.

$$\nabla^2 \Psi = -\frac{8\pi^2 m\boxed{(E-V)}}{h^2}\Psi$$

Postulates:

1. For every state of a time independent physical system, a function 'Ψ' of the coordinates can be written, which describes the state of the system. All possible information can be derived from Ψ

- **Ψ- must be single values, continuous and finite throughout the space.**

  - must be quadratically integrable. First derivative must be continuous.

  - should be normalized so that $\int \Psi\Psi^* d\tau = 1$

2. To every observable in classical mechanics there corresponds a linear operator in quantum mechanics.

- ✓ **Momentum operator (P_x): $-i\hbar(d/dx)$**
- ✓ **Kinetic energy operator (: $-\hbar^2/2m\ (d^2/dx^2)$**
- ✓ **Potential energy operator: V(X)**
- ✓ **Position operator: x**

- **Ψ- must be single values, continuous and finite throughout the space.**

e^{-x} (0 to infinite); $\sin^{-1}x$ (-1 to +1)

Infinite means electron is located at one space-impossible!

- must be quadratically integrable.

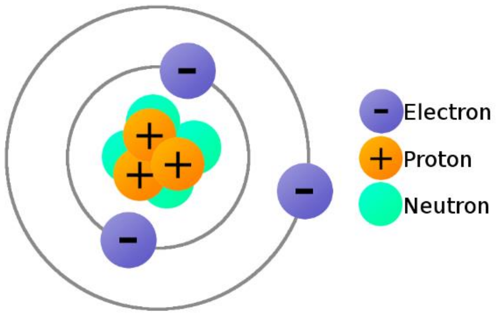
- first derivative bust be continuous.

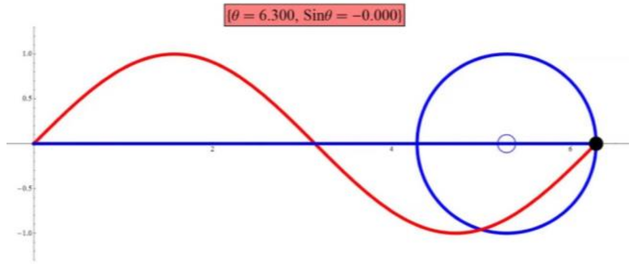
- should be normalized so that $\int \Psi\Psi^* d\tau=1$

Postulates:

1. For every state of a time independent physical system, a function 'Ψ' of the coordinates can be written, which describes the state of the system. All possible information can be derived from Ψ.

(Say an electron confined to an atom!)





Quantum Mechanical Operators

An operator is a rule that transforms a given function into another function. Lets consider $\hat{Z}$ be the operator that differentiates a function w.r.t 'x'. If a function f(x) is differentiable, the result of operating on f(x) with $\hat{Z}$ is **$\hat{Z}f(x)=f'(x)$.**

For example, **$\hat{Z}f(x^2+3e^x)=2x+3e^x$**

Similarly we can do sum and difference of two operators

$(\hat{A}+\hat{Z})f(x)=\hat{A}f(x)+\hat{Z}f(x)$ - sum

$(\hat{A} - \hat{Z})f(x)=\hat{A}f(x)-\hat{Z}f(x)$ – difference

Product of two operators: $\hat{A}\hat{Z}f(x)= \hat{A}[\hat{Z}f(x)]$; the first operator will operate over the f(x) and then the left operator will operate.

Ira N Levine, Quantum Chemistry

$3\hat{Z}f(x)=3[\hat{Z}f(x)]=3f'(x)$;
No difference in the final result will be observed if we do: $\hat{Z}3f(x)$.

However if we assume operators d/dx and x, then

$$x(d/dx)[f(x)]\neq(d/dx)xf(x)$$

Using any two operators **Â** and **Ŝ,** it is possible to construct a new operator **ÂŜ** – **ŜÂ**, called commutator of the two operators **Â** and **Ŝ** written as **[Â, Ŝ]** and **[Â, Ŝ] = ÂŜ- ŜÂ**

If **ÂŜ**= **ŜÂ** the [**Â,** Ŝ]=0 and we say **Â** and **Ŝ** commute

1. Find [x, P_x]
2. show that d/dx and x do not commute!

Linear Operator

- **An operator A is linear operator, if and only if it has the following property:**
- **$\hat{A}[f(x)+g(x)]=\hat{A}f(x)+\hat{A}g(x)$; f and g are arbitrary function**
- **$\hat{A}[cf(x)]=c\hat{A}f(x)$; c is an arbitrary constant.**
- **d/dx, x^2, d^2/dx^2 are linear. While 'root over', $()^2$ –squares the function, Cos is not a linear operator.**
- **$\sqrt{(A+B)}\neq\sqrt{(A)}+\sqrt{(B)}$**
- **$(A+B)^2\neq A^2+B^2$**

Postulate 3

- In any measurement of the observable (energy/momentum) associated with an operator $\hat{\mathbf{A}}$, the only values that will ever be observed are **eigenvalues a_n**, which satisfy the **eigenvalue** equation:

$$\hat{\mathbf{A}}\mathbf{\Psi}_n = \mathbf{a}_n\mathbf{\Psi}_n$$

(We will see that various physical parameters can be derived from direct physical consideration and then solving the above equation)

Eigen Function and Eigen Value

If the effect of operating on some function f(x) with the operator **Â** is simply to multiply f(x) by a certain constant K then we can say that f(x) is an Eigen function of **Â** 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 $\mathbf{d^2/dx^2}$?
- e^{ax2} is not an Eigen function of d/dx,

As, $d/dx(e^{ax2})= (2ax)e^{ax2}$

2x is not constant

- If we write $2a(xe^{ax2})$, then 2a is constant but xe^{ax2} 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!’