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Atomic Structure

→ According to classical mechanics atomic and molecular problems are associated with electronic concept

→ But later on it was believed that wave motion is also related to molecular and atomic ~~motion~~ problems.

→ It was Erwin Schrodinger who develop the wave mechanical model of atom in 1926. Acc to Bohr an atom is having a nucleous and electrons are surrounding this nucleous, Erwin describe wave model according to which electron is described as a three dimensional wave in electric field of the nucleus. This approach is called probability approach.

→ The probability of finding an electron around the nucleus can be calculated using 'Schrodinger Wave Equation'

→ So ultimately an electron is like "wave", so it should obey all the equations which all other are obeying (wave motion). He explains the wave character of an Electron via De broglie equation which is

$$\boxed{\lambda = \frac{h}{mv}}$$ It is classical equation

But according to Quantum Mechanics equation is like

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{—(1)}$$

This is <u>Schrodinger Wave Equation</u>

where E = Total energy of electron (K.E + P.E)

V = Potential energy or the work done against the attractive force when electron moves away from the nucleous.

m = Mass of electron

h = Planck's Constant

ψ (Psi) wave function $\rightarrow$ Amplitude of electromagnetic wave

Equation ① can also be written as

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

$$\nabla^2 = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$$

Laplacian operator

Derivation

De broglie equation represents idea of dual behaviour of matter ($\bar{e}$)

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Total Energy = Kinetic + Potential

$$= \frac{1}{2}mv^2 + V \quad \text{—— (1)}$$

where m = mass of e^- and v = velocity of electron

From eq. (1)

$$E = \frac{1}{2}mv^2 + V$$

multiply and divide $\frac{1}{2}mv^2$ with m we get

$$E = \frac{1}{2}\frac{m.mv^2}{m} + V$$

$$E = \frac{1}{2}\frac{(mv)^2}{m} + V \quad \text{—— (2)}$$

From De broglie equation

$$\lambda = \frac{h}{mv} \qquad \boxed{mv = \frac{h}{\lambda}} \quad \text{—— (3)}$$

Putting the value of mv from eq. (3) to equation (2)

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$$E = \frac{1}{2}\left(\frac{h}{\lambda}\right)^2 \times \frac{1}{m} + V$$

$$E = \frac{1}{2}\,\frac{h^2}{\lambda^2 \times m} + V$$

$$E = \frac{h^2}{2\lambda^2 \times m} + V$$

$$\frac{E-V}{1} = \frac{h^2}{2\lambda^2 \times m}$$

$$\boxed{\frac{2m(E-V)}{h^2} = \frac{1}{\lambda^2}} \quad — (4)$$

Matter is Considered as wave so wave motion of a vibrating string is

$$\psi = A \sin \frac{2\pi x}{\lambda} \quad — (5)$$

ψ = wave function x = Displacement
λ = wave length A = amplitude of wave

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Differentiating equation (5) with respect to x we get

$$\frac{d\psi}{dx} = A\left(\cos\frac{2\pi x}{\lambda}\right) \times \left(\frac{2\pi}{\lambda}\right)$$

$$= A \times \frac{2\pi}{\lambda} \cdot \cos\frac{2\pi x}{\lambda} \quad \text{--- (6)}$$

Again Differentiating this equation (6) we get

$$\frac{d^2\psi}{dx^2} = A \times \frac{2\pi}{\lambda}\left(-\sin\frac{2\pi}{\lambda}x\right) \cdot \frac{2\pi}{\lambda}$$

$$= -\frac{4\pi^2}{\lambda^2}\left(A\sin\frac{2\pi}{\lambda}x\right)$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\left(\psi\right) \quad \text{--- (7)}$$

$\hookrightarrow$ From eq (5)

$$\boxed{\frac{1}{\lambda^2} = \frac{2m(E-V)}{h^2}}$$

Putting this value of $\frac{1}{\lambda^2}$ in equation (7) we get

$$\frac{d^2\psi}{dx^2} = -4\pi^2 \times \frac{2m(E-V)}{h^2}(\psi)$$

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

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

This Equation is in one direction But when it moves ($\bar{e}$) in three Cartesian Co-ordinates we have. (x, y, z)

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

ψ is related to ~~electron~~ its Energy
(wavefunction of electron)

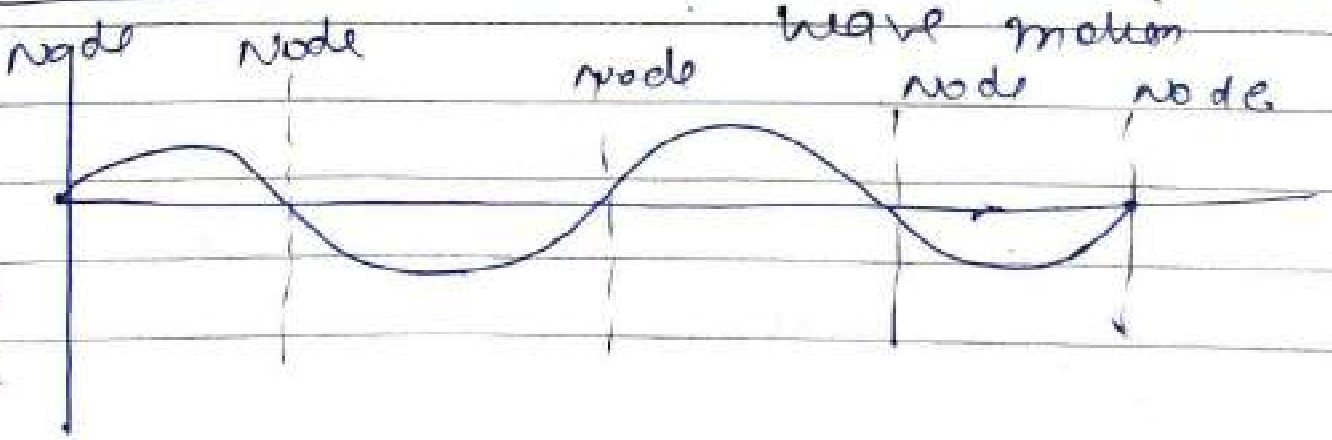
Eigen values :- The values of the total energy (E) for which the wave equation can have significant solution are called Eigen values.

Eigen functions :- The various value of ψ which can be derived from the wave equation corresponding to different values of energy (eigen values)

Condition of ψ

1) It must be single valued and finite
2) It must be continuous
3) It must become zero at infinity

when ψ=0 called node

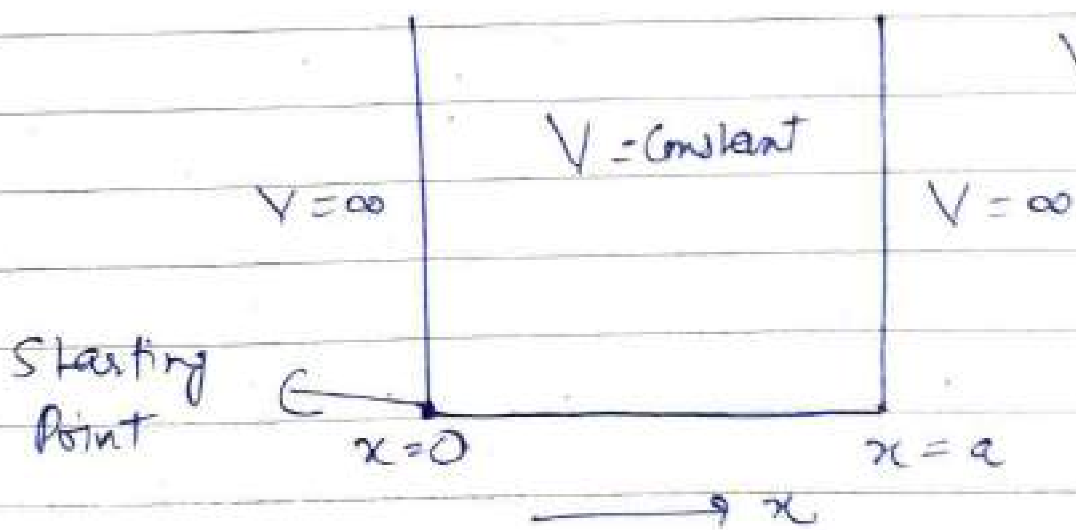


Particle in One Dimensional Box

Schrodinger wave equation is applicable for the translational motion of a particle (electron, atom or molecule) in space.

→ Electron in one Dimensional box is like flow of electron in a wire.

Consider a particle which moves along x-axis between $x = 0$ and $x = a$ inside a box. The particle jumps between the walls of the box, but it does not loose energy when collides with the walls, so that Energy should be constant



V = Potential energy

x = displacement

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→ Potential energy is infinite on both sides of the Box
→ Potential energy is Constant at the Centre (or inside) of the box

→ As a particle Cannot have infinite or Unlimited energy it means it cannot Exist outside the box. So $\boxed{\psi \text{ is zero}}$ for $x \leq 0$ and $x \geq a$
→ At the centre (or inside Box)

$$\boxed{V=0}$$

Inside Box Schrodinger's wave equation for one dimensional motion.

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{—} (1)$$

(A) Outside the box $\quad V = \infty$

By Putting the value of ($V=\infty$) in eq (1)

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-\infty)\psi = 0 \quad \text{—} (2)$$

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$E \longrightarrow 0$. (as P.E is infinite)

so equation (2) becomes

$$\frac{d^2\varphi}{dx^2} + \frac{8\pi^2 m}{h^2}(-\infty)\varphi = 0$$

$$\frac{d^2\varphi}{dx^2} - \infty\varphi = 0$$

$$\frac{d^2\varphi}{dx^2} = \infty\varphi$$

$$\varphi = \frac{1}{\infty}\frac{d^2\varphi}{dx^2} = 0$$

So outside the box $\boxed{\varphi = 0}$ It means particle can not go outside the box.

(B) Inside the box $V = 0$ So eq (1) becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-0)\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \quad \text{—— (3)}$$

Acc to Quantum Mechanics for a given state of system E is constant

So equation (3) becomes

$$\frac{d^2\psi}{dx^2} + K^2\psi = 0 \quad \text{where}$$

$$K^2 = \frac{8\pi^2 m}{h^2}E \quad \text{—— (A)}$$

K^2 is independent of x and constant

Now Generally

$$\psi = A\sin Kx + B\cos Kx \quad \text{—— (4)}$$

For different values of A, B and K
ψ have many values

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Applying boundary conditions
$\psi = 0$ at $x = 0$ and $x = a$

(1) $\psi = 0$ when $x = 0$ equation (4) becomes
$0 = A\sin(0) + B\cos(0)$
$B = 0$

Now eq. (4) becomes
$\psi = A\sin Kx$ when $B = 0$ —— (5)

(2) $\psi = 0$ when $x = a$ eq (5) becomes
$0 = A\sin Ka$
$\sin Ka = 0$ —— (6)

This equation holds good only when values of Ka are integral multiples of π.
$Ka = n\pi$ —— (7)

n = integer $n = 0, 1, 2, 3$
$\psi = 0$ (For any value b/w 0 and a with in the box as $n = 0$, which make $K = 0$]

Hence equation (7) becomes
$$K = \frac{n\pi}{a} \quad \text{—— (8)}$$

Putting the value of k from ⑧ to ⑤

$$\psi = A \sin\left(\frac{n\pi}{a}x\right) \quad \text{———} (9)$$

Expression for Eigen function and hence for Eigen values equation (A) becomes

$$E = \frac{k^2 h^2}{8\pi^2 m} = \frac{\left(\frac{n\pi}{a}\right)^2 \times h^2}{8\pi^2 m}$$

$$E = \frac{n^2 h^2}{8ma^2} \qquad n = 1, 2, 3, 4 \ldots$$

$$\text{———} (10)$$

Hence eq (9) and (10) are the solutions of the Schrodinger equation for a particle in a box.

In equation (9) value of a is determined by using normalisation of wave function

$$\int_0^a \psi\psi^* d\tau = 1 \quad \text{——— (11)} \qquad \psi = \psi^*$$

Putting the value of ψ from equation (9) in to (11)

$$\int_0^a A^2 \sin^2\left(\frac{n\pi}{a}x\right) dx = 1$$

$$A^2 \int_0^a \sin^2\left(\frac{n\pi}{a}.x\right) dx = 1$$

$$A^2 \times \frac{a}{2} = 1 \qquad A = \sqrt{\frac{2}{a}}$$

Hence $\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$

Applications of a particle in a box

① Calculation of Energy of Conjugated molecules -

There are two types of molecular orbital when light interacts with a particle

→ HOMO (Highest occupied molecular orbital) Excited state

→ LUMO (Lowest Unoccupied molecular orbital)

LUMO - Represented by $(n+1)$ in case of Conjugated molecules

HOMO - Represented by n

The energy difference (ΔE) b/w Homo and LUMO is calculated by using the particle in a box such as Polyalkene and butadiene

π electron in Conjugated Compound Can be related to particle in a box

The length of the box may be taken as the end to end distance of the molecule. Either side of a box is considered as $\frac{1}{2}$ the C–C Bond length

By knowing mass of electron and length of 1-D box (L) the electronic energy level in polyenes (Polyethene) can be determined using an equation

$$E = \frac{n^2 h^2}{8 m a^2}$$

For LUMO $\rightarrow$ $E_{n+1} = \frac{(n+1)^2 h^2}{8 m_e L^2}$

$a = L$

For HOMO $\rightarrow$ $E_n = \frac{n^2 h^2}{8 m_e^2 L^2}$

The π electrons of polyene are distributed over these levels following the Pauli's Exclusion and Aufbau Principles.

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

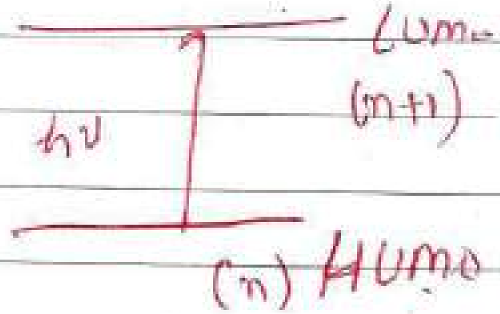
$$= \frac{(n+1)^2 h^2}{8 m_e L^2} - \frac{n^2 L^2}{8 m_e L^2}$$

$$= \left[(n+1)^2 - n^2\right] \left(\frac{h^2}{8 m_e L^2}\right)$$

$$= \left(\cancel{n^2} + 1 + 2n - \cancel{n^2}\right) \frac{h^2}{8 m_e L^2}$$

$$\Delta E = (2n+1) \frac{h^2}{8 m_e L^2}$$

Now for butadiene



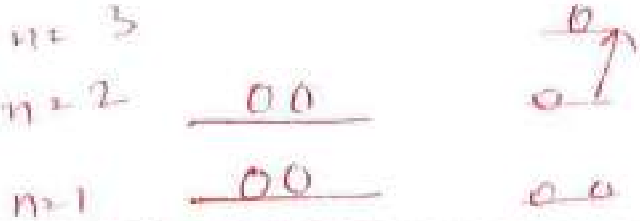
$$H_2C = \overset{H}{C} - \overset{H}{C} = CH_2$$

$$\xleftrightarrow{\quad L \quad}$$

L = 1 (Single bond) + 2 (double bond) + 154 pm

$$L = 154 + 2(135) + 154$$

$$= 578 \text{ pm} = 5.78 \times 10^{-12} \text{ m}$$



$$n = \frac{\text{no. of electrons}}{2} = \frac{4}{2} = 2$$

$$\Delta E = (2n+1)\frac{h^2}{8 m_e L^2}$$

$$\Delta E = \left(2(2)+1\right)\frac{6.626 \times 10^{-34}\,Js}{8(5.78 \times 10^{-10}m)^2 \times (9.11 \times 10^{-31}kg)}$$

$$= 9.02 \times 10^{-19}\ J$$

$$\Delta \tilde{E} = \frac{\Delta E}{hc} = \frac{9.02 \times 10^{-19}\ J}{6.626 \times 10^{-34} \times 3 \times 10^{8}}$$

$$= 4.54 \times 10^{4}\ cm^{-1}$$

(2) Analysis of Nanoparticles

Nanotechnology means study of atoms and molecules in nano range to produce devices

When bulk material are reduced to nanometer size, they find applications.
For Example
As Gold is chemically inert but when it is at nanoscale, gold nanoparticles serve as chemical catalysts.
opaque becomes transparent
The properties of nano-particles show strong dependency on particle size. Size changes from bulk form to nano form. Size below 100 nm.
Reduction of Size can change the chemical reactivity because size is function of structure and occupation of outermost electronic levels. Physical properties such as electrical, thermal, optical, mechanical and magnetic which are also depends on the arrangement of outermost electrons are also altered.

Wave Mechanical Model for Hydrogen Atom.

Hydrogen atoms and hydrogen atom like species eg He^{+}, Li^{+2}, Be^{+3} etc resemble with one another having one electron in their nuclei, but they differ in their nuclear charges.

Wave Equation for the motion of a single particle is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{--- (1)}$$

Reduced mass μ for hydrogen like atom is

$$\mu = \frac{m_e \times m_n}{m_e + m_n}$$ replaces the mass

$m_e = 0$ $\quad \mu = \frac{m_e \times m_n}{m_n}$ $\quad \mu = m_e$

where m_e and m_n are mass of electron and nucleons. $\quad m_e < m_n$

so $\quad \mu \simeq m_e$

A hydrogen like atom can have two kinds of motion

(1) Rotation around the nucleus
(2) Translational motion

Nucleus never moves only the electrons around the nucleus are moving.
so the Electronic Energy = G

Hence equation (1) becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 \mu}{h^2}(E-V)\psi = 0 \quad (2)$$

This equation is similar to single particle of mass μ moving in a field of PE (V). Same case for hydrogen like ~~atom~~ atom where electron is moving under the central field of nucleus.

Acc to Coulomb's law, force of attraction b/w these particle is

$$F = \frac{Ze \times (-e)}{r^2} = \frac{-Ze^2}{r^2}$$

$+Ze$ is charge on nucleus

$-e$ on electron

$r =$ distance b/w two

(V) Potential energy b/w the particles

where $F = \frac{-Ze^2}{r^2}$

$$V = \int_r^{\infty} F\,dr = \int_r^{\infty} \frac{-Ze^2}{r^2}\,dr$$

$V =$ is the P.E which is work done necessary to take e^- to infinity from its equilibrium distance r w.r.t nucleus.

$$V = \int_r^{\infty} -\frac{Ze^2}{r^2}\, dr$$

$$V = -Ze^2 \int_r^{\infty} \frac{1}{r^2}\, dr$$

$$V = -Ze^2 \int_r^{\infty} r^{-2}\, dr$$

$$V = -Ze^2 \left[\frac{r^{-2+1}}{-2+1}\right]_r^{\infty}$$

$$V = -Ze^2 \left[\frac{r^{-1}}{-1}\right]_r^{\infty}$$

$$V = -Ze^2 \left[-\frac{1}{r}\right]_r^{\infty}$$

$$V = Ze^2 \left[\frac{1}{\infty} - \frac{1}{r}\right]$$

$$\boxed{V = -\frac{Ze^2}{r}} \qquad (8)$$

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Putting this value in equation (3)

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 \mu}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0.$$

Schrodinger wave equation in terms of Polar Co-ordinates: