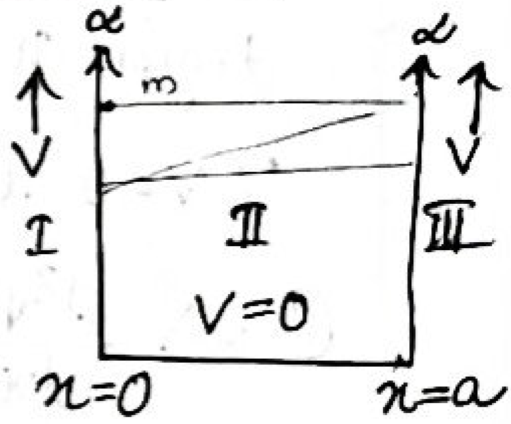
Particle In a 1D-box

Consider a particle of mass 'm' moving along the x-dirⁿ only, confined b/w $x=0$ & $x=a$; the P.E, V is 0 - inside the box & but rises abruptly to infinity at the walls.



The. Schrodinger. eqⁿ for 1D is,

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

ⓐ Outside the box

Region I $(x<0)$ & III $(x>a)$.

$\therefore$ $V = \alpha$ in I & III

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

$\frac{8\pi^2 m}{h^2}$

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

b) Inside the box

Region II $(0<x<a)$

$\because V=0$ in Region II.

$$(1) \Rightarrow \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi = 0 \quad \text{--- (3)}$$

This eq^n has the sol^n, $A\sin kx + B\cos kx$

$$\psi = A\sin\left[\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} x\right] + B\cos\left[\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} x\right] \quad \text{--- (4)}$$

A & B $\Rightarrow$ Constants.

WKT, the particle is confined in the walls, the acceptable wave fu^{n}s must satisfy the boundary conditions.

$\Rightarrow \psi = 0$ at $x = 0$

$$\overset{(4)\Rightarrow}{\Rightarrow} 0 = A\sin 0 + B\cos 0$$

$$0 = A\times 0 + B\times 1 \Rightarrow B = 0.$$

$$(4) \Rightarrow \psi = A\sin\left[\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} x\right] \quad \text{--- (5)}$$

Now apply, 2nd boundary cond^n,

$\psi = 0$ at $x = a$.

$$\overset{(4)\Rightarrow}{\Rightarrow} 0 = A\sin\left[\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} a\right] + 0$$

[$\because$ A cannot be zero.]

either A or sin ka = 0

but A never be 0.

$\Rightarrow \sin ka = 0$

$ka = 0, 180, 360$

$ka = n\pi$

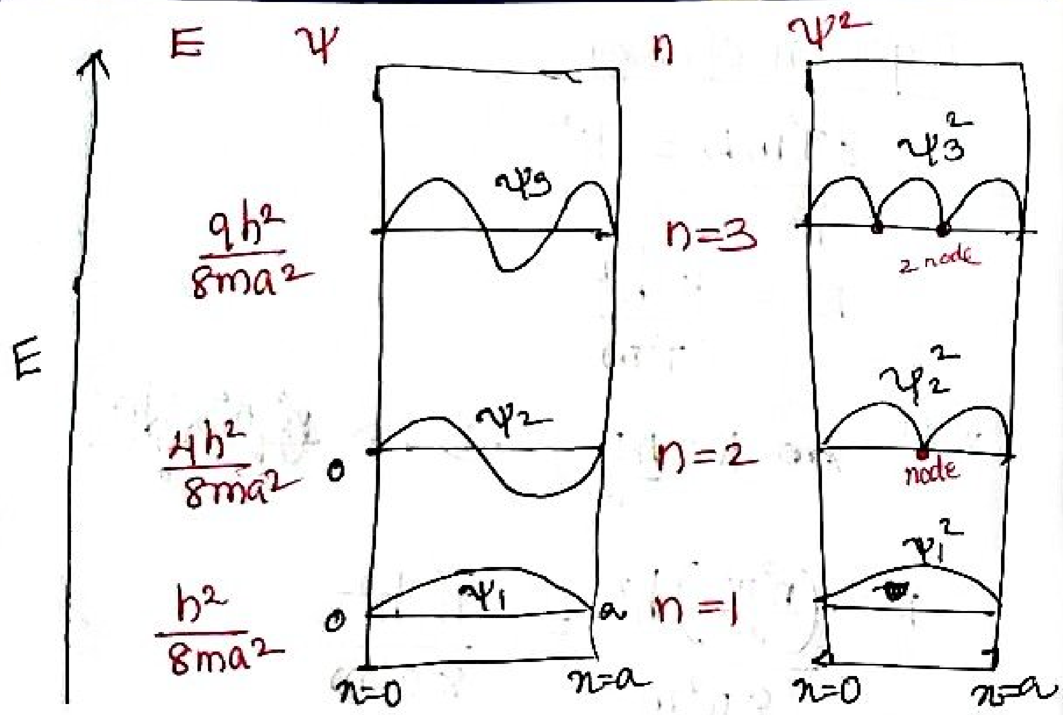
$k = \frac{n\pi}{a}$

$$\sin\left[\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2} a\right] = 0$$

$$\text{or} \left[\frac{8\pi^2 mE}{h^2}\right]^{1/2} a = n\pi \quad \text{--- (6)} \qquad n = 0, 1, 2, 3 \ldots$$

$$(6) \xrightarrow{\frac{8\pi^2 mE}{h^2} a^2 = n^2\pi^2} \boxed{E_n = \frac{n^2 \cancel{\pi^2} h^2}{8\cancel{\pi^2} m a^2} = \frac{n^2 h^2}{8ma^2}} \quad \text{--- (7)}$$

$$\& \quad \boxed{\psi_n = A\sin\frac{n\pi x}{a}} \quad \text{--- (8)}$$



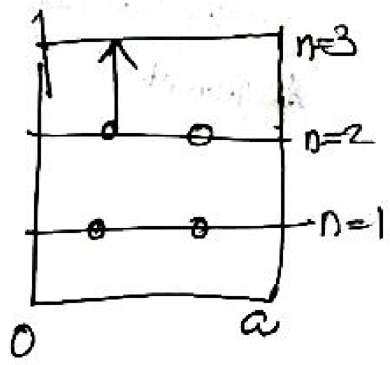
- node
  > the probability to to find ē is 0 (ie $\psi^2=0$)
- Zero point energy
  > Possible lowest energy (ie, $h^2/8ma^2$).

Applicⁿ of 1D box

1,3-butadiene

$CH_2=CH-CH=CH_2 \longrightarrow CH_2 \cdots CH \cdots CH \cdots CH_2$

4 π ē are free to move, but confined to the length of the molecule.



> ē occupy lowest 2 energy levels

> LUMO ⇒ n=3

HOMO ⇒ n=2

$$\Delta E = h\nu = E_3 - E_2$$

$$= \frac{(3^2-2^2)h^2}{8ma^2} \qquad E = \frac{n^2h^2}{8ma^2}$$

$$= \frac{5h^2}{8ma^2} = 9.615\times10^{-19}\,J \qquad 9-4=5$$

$$[a = 0.56\text{ nm}, m = 9.1\times10^{-31}\text{ kg}]$$

$\overset{\Delta E}{h\nu} = hc/\lambda$

$$\text{or } \lambda = \frac{hc}{h\nu} = \frac{hc}{\Delta E} = \frac{6.626\times10^{-34}\,JS\times3\times10^8}{9.615\times10^{-19}}$$

$\lambda = 206.7$ nm

hexa triene $CH_2=CH-CH=CH-CH=CH_2$

H.W

~~Orbit & orbital~~

~~Assignment~~

Assignment

1) Orbit & orbital.

2) Electronic Configuration of atoms.

$\lambda = 206.7\ nm$

hexa triene $CH_2=CH-CH=CH-CH=CH_2$

H.W

~~orbit & orbital~~

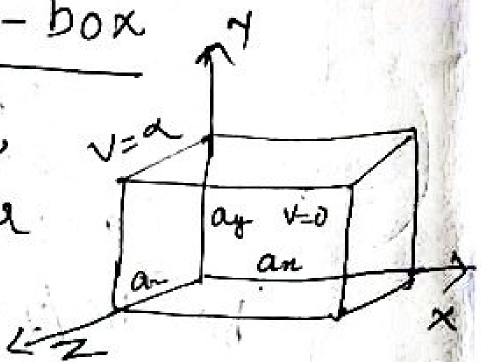
~~Assignments~~

Assignment

1) Orbit & orbital.

2) Electronic Configuration of atoms.

Particle in a 3D-box



Consider a particle of mass 'm', Confined to a 3D-rectangular box having sides a_x, a_y, a_z. Potential energy is zero (V=0) inside the box & is infinity at & outside walls.

The Time independent Schrodinger eqn for the system within the box (V=0) is,

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

To solve this eqn, we use variable separation method. Let us assume that the wave fun is a product of 3 independent wave functions $X(x), Y(y)$ & $Z(z)$, each being dependent only on its own co-ordinate.

$$\Rightarrow \psi = X(x)\cdot Y(y)\cdot Z(z)$$

For simplicity, $\psi = XYZ$

Since, X, Y & Z respectively depends upon x, y & z only

$$\Rightarrow \frac{\partial^2\psi}{\partial x^2}=YZ\frac{d^2X}{dx^2}\ ;\ \frac{\partial^2\psi}{\partial y^2}=XZ\frac{d^2Y}{dy^2}\ ;\ \frac{\partial^2\psi}{\partial z^2}=XY\frac{d^2Z}{dz^2}$$

$$(1)\Rightarrow YZ\frac{d^2X}{dx^2}+XZ\frac{d^2Y}{dy^2}+XY\frac{d^2Z}{dz^2}+\frac{8\pi^2 m E}{h^2}(XYZ)=0 \quad \text{--- (2)}$$

$$\therefore E = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2}+\frac{n_y^2}{a^2}+\frac{n_z^2}{a^2}\right]$$

$$= \frac{h^2}{8ma^2}\left[n_x^2+n_y^2+n_z^2\right]$$

- If $n_x = n_y = n_z = 1$, then the corresponding wave function is $\Psi_{(111)}$, then

$$E_{111} = \frac{h^2}{8ma^2}\left[1^2+1^2+1^2\right] = \frac{3h^2}{8ma^2}$$ [non degenerate]

- If $n_x = 1$, $n_y = 2$, $n_z = 1$

$$\left.\begin{aligned} E_{(1,2,1)} &= \frac{h^2}{8ma^2}\left[1^2+2^2+1^2\right] = \frac{6h^2}{8ma^2} \\ E_{(2,1,1)} &= \frac{h^2}{8ma^2}\left[2^2+1^2+1^2\right] = \frac{6h^2}{8ma^2} \\ E_{(1,1,2)} &= \frac{h^2}{8ma^2}\left[1^2+1^2+2^2\right] = 6h^2/8ma^2 \end{aligned}\right\}\text{degenerate}$$

÷ through out by XYZ

$$\Rightarrow \frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{1}{Z}\frac{d^2Z}{dz^2}+\frac{8\pi^2 m}{h^2}\cdot E=0 \quad —③$$

E = Total energy

$\therefore E = E_x + E_y + E_z$.

$$③ \Rightarrow \frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{1}{Z}\frac{d^2Z}{dz^2}+\frac{8\pi^2 m}{h^2}E_x+\frac{8\pi^2 m}{h^2}E_y+\frac{8\pi^2 m}{h^2}E_z=0 \quad —④$$

$$④ \Rightarrow \frac{1}{X}\frac{d^2X}{dx^2}+\frac{8\pi^2 m}{h^2}E_x=0 \quad —ⓐ$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{8\pi^2 m}{h^2}E_y=0 \quad —ⓑ$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2}+\frac{8\pi^2 m}{h^2}E_z=0 \quad —ⓒ$$

ⓐ $\times$ by X $\Rightarrow \frac{d^2X}{dx^2}+\frac{8\pi^2 m}{h^2}E_x\cdot X=0$ —⑤

ⓑ $\times Y$ $\Rightarrow \frac{d^2Y}{dy^2}+\frac{8\pi^2 m}{h^2}E_y Y=0$ —⑥

ⓒ $\times Z$ $\Rightarrow d^2Z/dz^2+8\pi^2 m/h^2\, E_z\cdot Z=0$ —⑦

⑤, ⑥ & ⑦ are the same as that for a particle in 1D-box.

⇒ W.K.T, in 1D box,

$$\psi=\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$$

$$X=X(x)=\sqrt{\frac{2}{a_x}}\sin\left(\frac{n_x\pi x}{a_x}\right) \quad —⑧$$

$$Y=Y(y)=\sqrt{\frac{2}{a_y}}\sin\left(\frac{n_y\pi y}{a_y}\right) \quad —⑨$$

$$Z=Z(z)=\sqrt{\frac{2}{a_z}}\sin\left(\frac{n_z\pi z}{a_z}\right) \quad —⑩$$

∴ Total wavefuⁿ of a particle in 3D-box,

$$\psi=XYZ=\left[\sqrt{\frac{2}{a_x}}\sin\left(\frac{n_x\pi x}{a_x}\right)\right]\cdot\left[\sqrt{\frac{2}{a_y}}\sin\left(\frac{n_y\pi y}{a_y}\right)\right]\cdot\left[\sqrt{\frac{2}{a_z}}\sin\left(\frac{n_z\pi z}{a_z}\right)\right] \quad —⑪$$

$$\psi=\sqrt{\frac{8}{\phi}}\sin\left[\frac{n_x\pi x}{a_x}\right]\sin\left[\frac{n_y\pi y}{a_y}\right]\sin\left[\frac{n_z\pi z}{a_z}\right]$$

where $\phi = a_x\cdot a_y\cdot a_z$ = volume of the box.

Energy

for 1D-box, $E = \frac{n^2h^2}{8ma^2}$ —— (1)

In 3D-box, $E = E_x + E_y + E_z$

$$(1) \Rightarrow E = \frac{n_x^2 h^2}{8ma_x^2} + \frac{n_y^2 h^2}{8ma_y^2} + \frac{n_z^2 h^2}{8ma_z^2}$$

$$E = \frac{h^2}{8m}\left[\frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2}\right]$$

Degeneracy:-

* When different states have same energy, those states and the corresponding energy levels are said to be degenerate & the phenomenon is called degeneracy.

W.K.T, $E = \frac{h^2}{8m}\left[\frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2}\right]$

If we consider the cubic box,

$$a_x = a_y = a_z$$