Recap :-

Particle in a 3-D box model (boundary condition)

$+$ $\Downarrow$

$K_x, K_y, K_z = K_x\hat{i} + K_y\hat{j} + k_z\hat{k}$

Free electron theory of metals [Periodic boundary condition]

$\Downarrow$

$K_x, K_y, K_z = (n_x, n_y, n_z)$

only evens will be solution for this model [integral multiple of 2π]

* K-space =>

$\Delta k_x = \dfrac{2\pi}{L}$

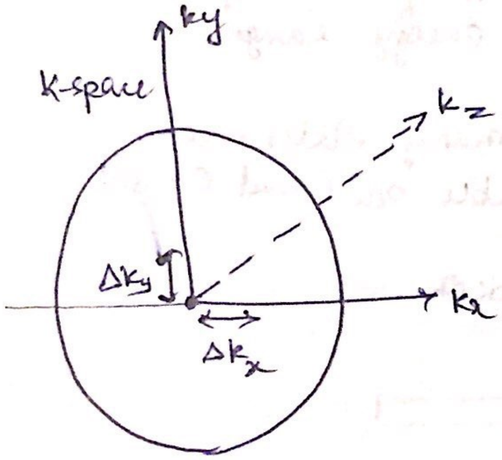
$\Delta K_y = \Delta K_z$

For a large L, $\Delta K_x, \Delta K_y, \Delta K_z \to 0$.

(essentially you will have a continuous space in reciprocal space)

* $\boxed{E_f} = \dfrac{\hbar^2}{2m}\left[3\pi^2\rho\right]^{2/3}$

$\Rightarrow$ Fermi energy $= \dfrac{\hbar^2 K_f^2}{2m}$



Each K-particle can occupy 2 electrons.

$\Delta K_x = \Delta k_y = \dfrac{2\pi}{L}$

# of K-parts inside the fermi-sphere ≡>

$$= \frac{\frac{4\pi}{3} k_f^3}{\left(2\pi/L\right)^3}$$

where $\rho = \dfrac{N}{V}$ is free electron density of the metal.

No. of free electrons (N) $\Rightarrow \dfrac{N}{3\pi^2}$

$\Rightarrow K_f = \left[3\pi^2 \dfrac{N}{V}\right]^{1/3}$

$= \left[3\pi^2\rho\right]^{1/3}$

$N = \dfrac{V}{6\pi^2} k_f^3 = \dfrac{2 \times V \times \frac{4\pi}{3} k_F^3}{8\pi^3} \Rightarrow k_F^3 = \dfrac{3\pi^2 N}{V}$

$k_F = \left[\dfrac{3\pi^2 N}{V}\right]^{1/3}$

Highest Linear Momentum →

$$\hat{P} = -i\hbar \hat{\nabla}$$

$m \rightarrow$ mass of $e^{\ominus}$.

$$\left[\hat{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right]$$

$$\hat{P}\,\psi_k(\vec{r}) = \hbar\vec{k}\,\psi(\vec{r})$$

Linear velocity, $\vec{v} = \frac{\hbar\vec{k}}{m}$

$e^{\ominus} \rightarrow$ velocity at the fermi surface, $v_F = \frac{\hbar k_F}{m}$

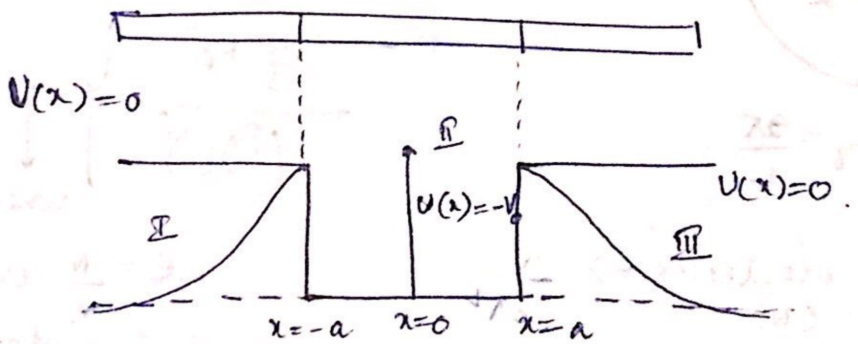
$$\Rightarrow v_F = \frac{\hbar}{m}\left[3\pi^2\frac{N}{V}\right]^{1/3} = \frac{\hbar}{m}\left[3\pi^2 e\right]^{1/3}$$

Density of states for a metal;

$D[E] = \frac{dN}{dE} \longrightarrow$ no. of states per unit energy range

$D(E).dE \longrightarrow$ how many states are available b/w E and $E+dE$.

* Particle in a well of finite depth :-



$U(x) = -V_0$, if $-a < x < a$ (inside region II)

$= \frac{\hbar^2}{2m}K_f^2$

$= 0$, otherwise

Total Energy, $E =$ Kinetic energy + Potential Energy

$\downarrow$ +ve $\qquad \downarrow$ $-V_0$.

Case ① $\quad E > 0$;

Case ② $\quad E < 0$;

Case ③ $\quad E = 0$.

Case ② : $E < 0$.

Region-I :-

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} = E\psi(x) \quad [\because U(x) = 0]$$

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

Let ϵ be a positive parameter; such that $E = -\epsilon$

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

Let $k_1^2 = \frac{2m\epsilon}{\hbar^2}$; k_1 — should be positive

$$\Rightarrow \frac{d^2\psi(x)}{dx^2} = k_1^2\psi(x)$$

General Solution, $\psi_I(x) = c_1 e^{k_1 x} + c_2 e^{-k_1 x}$

c_1 and c_2 are arbitrary constants.

Boundary Condition $\Rightarrow$ $x \to -\infty$, $\psi_I(x) \to 0$

($\because$ Since $E < 0$, the particle is bound in the well)

$$\Rightarrow \boxed{c_2 = 0}$$

$$\psi_I(x) = c_1 e^{k_1 x}$$

$$\frac{d\psi_I(x)}{dx} = c_1 k_1 e^{k_1 x}$$

Similarly
region-III;

$$\psi_{III}(x) = A_1 e^{k_1 x} + A_2 e^{-k_1 x}$$

Boundary condition for region III $\Rightarrow$

$$x \to \infty \;,\; \psi_{III}(x) \to 0$$

$$\Rightarrow A_1 = 0.$$

$$\psi_{III}(x) = A_2 e^{-k_1 x}$$

$$\frac{d\psi_{III}(x)}{dx} = -A_2 k_1 e^{-k_1 x}.$$

Region-II :-

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\,\psi(x) = E.\psi(x)$$

$$\Rightarrow \frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + (V_0 \mp E)\,\psi(x) = 0$$

$$\boxed{\because E = -E}$$

Let $k_2^2 = \frac{2m}{\hbar^2}(V_0 \mp E)$

k_2-positive

$$\frac{d^2\psi(x)}{dx^2} + k_2^2\,\psi(x) = 0.$$

$$\Rightarrow \psi_{II}(x) = B_1 \cos k_2 x + B_2 \sin k_2 x$$

$$\frac{d\psi_{II}(x)}{dx} = -B_1 k_2 \sin k_2 x + B_2 k_2 \cos k_2 x$$

Exploit the continuity property of wave function

- single valued
- continuous.

ψ should be single-valued $\Rightarrow$ so;

$$\psi_I(x=-a) = \psi_{II}(x=-a) \quad \text{--- (1)}$$

$$\frac{d\psi_I}{dx}(x=-a) = \frac{d\psi_{II}}{dx}(x=-a) \quad \text{--- (2)}$$

(1) $\Rightarrow$ $$c_1 e^{-k_1 a} = B_1 \cos k_2 a - B_2 \sin k_2 a \quad \text{--- (3)}$$

(2) $\Rightarrow$ $$c_1 k_1 e^{-k_1 a} = B_1 k_2 \sin(k_2 a) + B_2 k_2 \cos(k_2 a) \quad \text{--- (4)}$$

For the boundary at $x = +a$;

$$\psi_{II}(x=a) = \psi_{III}(x=a)$$

$$B_1 \cos(k_2 a) + B_2 \sin k_2 a = A_2 e^{-k_1 a} \quad \text{--- (5)}$$

$$\frac{d\psi_{II}}{dx}(x=a) = \frac{d\psi_{III}}{dx}(x=a)$$

$$-B_1 k_2 \sin k_2 a + B_2 k_2 \cos k_2 a = -A_2 k_1 e^{-k_1 a} \quad \text{--- (6)}$$

(3) + (5) $\Rightarrow$

$$2B_1 \cos(k_2 a) = (C_1 + A_2) e^{-k_1 a} \quad \text{--- (7)}$$

(3) $-$ (5) $\Rightarrow$

$$-2B_2 \sin k_2 a = (C_1 - A_2) e^{-k_1 a} \quad \text{--- (8)}$$

$\parallel^{ly}$

(4) + (6) $\Rightarrow$

$$2B_2 k_2 \cos k_2 a = (C_1 - A_2) k_1 e^{-k_1 a} \quad \text{--- (9)}$$

(4) $-$ (6) $\Rightarrow$

$$2B_1 k_2 \sin k_2 a = (C_1 + A_2) k_1 e^{-k_1 a} \quad \text{--- (10)}$$

<u>Note</u>: $c_1 \neq 0$; $A_2 \neq 0$.

(9)/(8) $\Rightarrow$ $$k_1 = -k_2 \cot(k_2 a) \quad \text{--- (11)}$$

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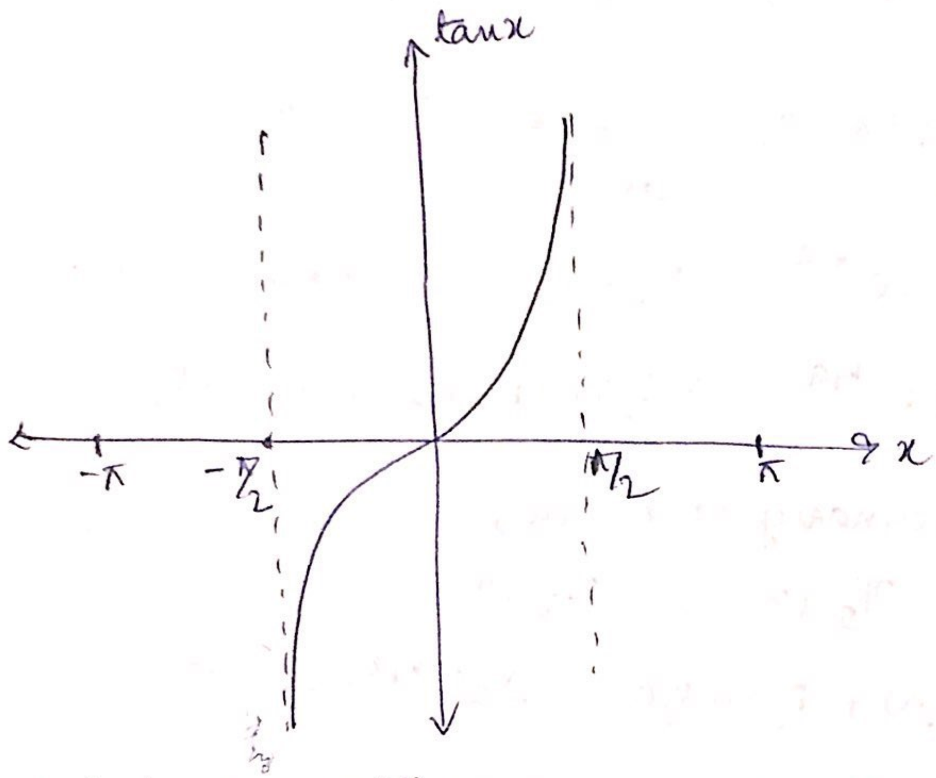
$\frac{(10)}{(9)} \Rightarrow \quad k_1 = k_2 \tan(k_2 a) \quad — (12)$

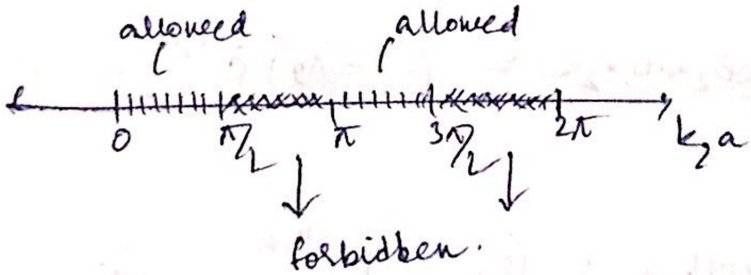


Since k_1, k_2 are positive;

$(12) \Rightarrow \quad \tan(k_2 a) > 0$

$$2n\,\pi/2 \leq k_2 a \leq (2n+1)\pi/2 \quad , \text{ where } n = 0, 1, 2, \ldots$$

$$k_2^2 = \frac{2m}{\hbar^2}[V_0 - E]$$



·Recall:-

$$k_1^2 = \frac{2mE}{\hbar^2} \quad , \quad k_2^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

$$k_1^2 + k_2^2 = \frac{2mV_0}{\hbar^2}.$$

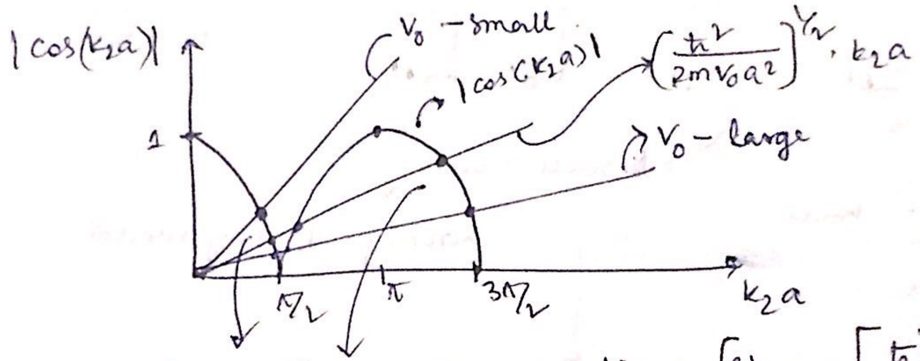
$$k_2^2 = \frac{2mV_0}{\hbar^2} - k_2^2 \tan^2(k_2 a) \qquad \left[\because\ k_1^2 + k_2^2 = \frac{2mV_0}{\hbar^2}\right]$$

$$k_2^2\left[1 + \tan^2(k_2 a)\right] = \frac{2mV_0}{\hbar^2}$$

$$\sec^2 k_2 a = \frac{2mV_0}{\hbar^2 \times k_2^2}$$

$$\cos^2 k_2 a = \frac{\hbar^2}{2mV_0} \times k_2^2 \times \frac{a^2}{a^2}$$

$$\Rightarrow \quad |\cos k_2 a| = \left[\frac{\hbar^2}{2mV_0 a^2}\right]^{1/2} \cdot k_2 a$$



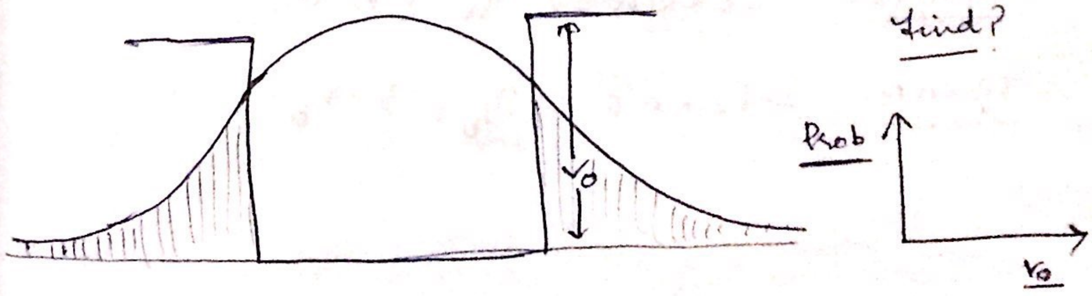
intersection points $\rightarrow$ solutions $\left[\text{Slope} = \left[\frac{\hbar^2}{2\pi m V_0 a^2}\right]^{1/2}\right]$

$k_2 a \rightarrow$ quantized

$\Rightarrow$ Energy is quantized

* Increase the barrier, multiple intersections.
$\uparrow (V_0)$

Assignment - III :-



If $V_0 \rightarrow \infty \Rightarrow$ particle in a 1-D box of infinite barrier

For K_1; it is a sin wave.

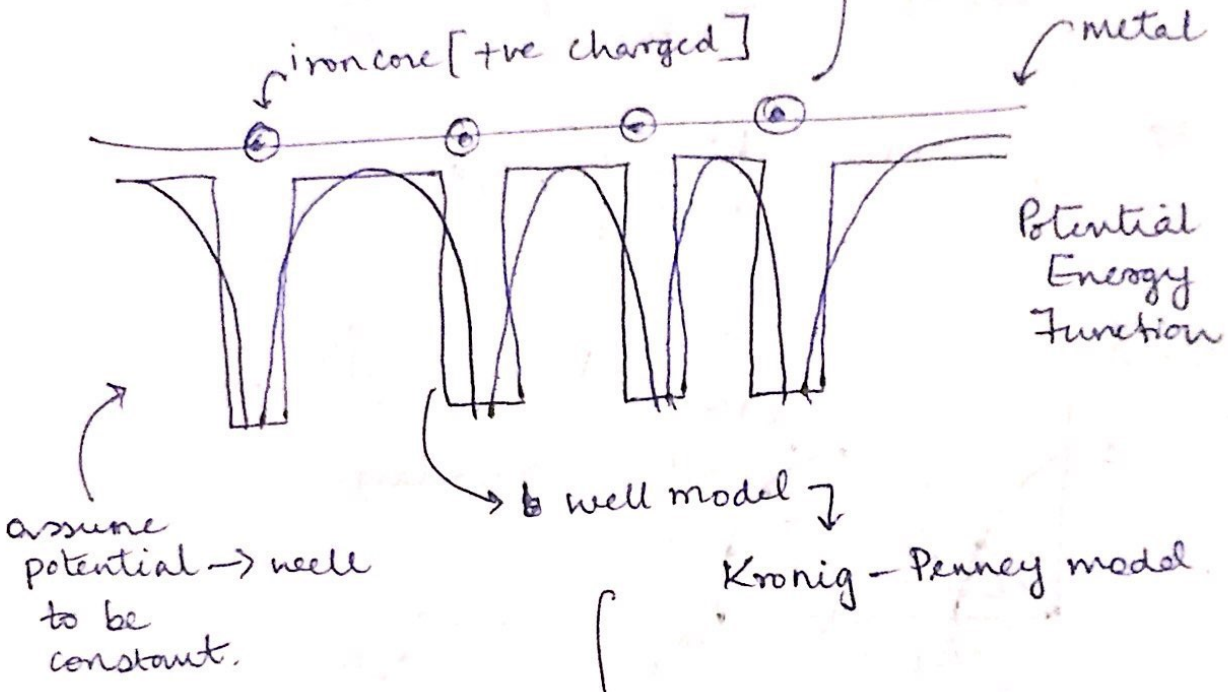
Kronig-Penney model →

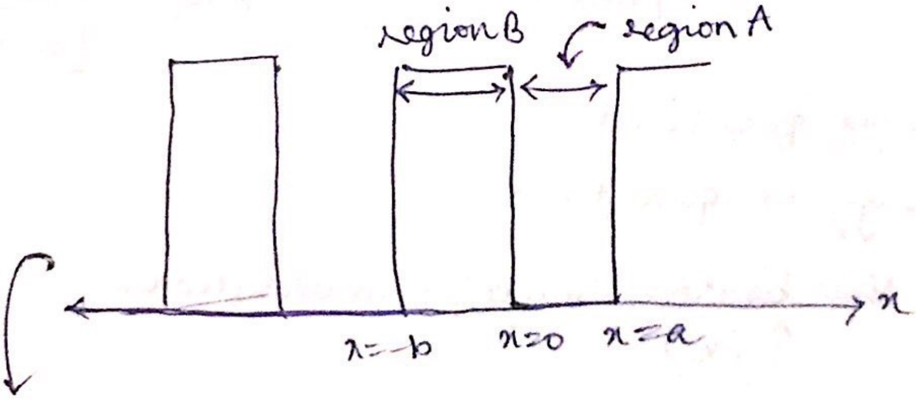
→ Particle in a finite well to a crystalline lattice

→ Consider 1D Lattice.

$$E = \frac{1}{4\pi\epsilon_0}\frac{q_1 q_2}{r}$$

lattice site





Periodicity = (a+b)

<u>region A:</u> $0<x<a \Rightarrow \psi_a$; $V=0$

<u>region B:</u> $-b<x<0 \Rightarrow \psi_b$; $V=V_b$

For region A :

$$\frac{d^2 \psi_a(x)}{dx^2} + \alpha^2 \psi_a(x) = 0 \quad , \text{where } \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

For region B :

$$\frac{d^2 \psi_b(x)}{dx^2} + \beta^2 \psi_b(x) = 0 \; ; \text{ where } \beta = \sqrt{\frac{2m}{\hbar^2}[E-V_0]}$$

General Solutions :-

$$\psi_a(x) = A_a \sin\alpha x + B_a \cos\alpha x$$

$$\frac{d\psi_a(x)}{dx} = A_a \alpha \cos\alpha x - B_a \alpha \sin\alpha x .$$

based on $\beta \rightarrow$ it can be either decaying or increasing.

$e^{i\beta x}$ $\hookrightarrow$ imaginary if $\underline{[E-V_0] < 0}$.

$e^{i\beta} = e^{i^2 k} = e^{-(ve)}$
$\downarrow$
decaying.

$$\psi_b(x) = A_b \sin\beta x + B_b \cos\beta x .$$

$\downarrow$
hyperbolic function (sin (imaginary quantity))

$$\frac{d\psi_b(x)}{dx} = A_b \beta \cos\beta x - B_b \beta \sin\beta x .$$

boundary conditions. $\rightarrow$

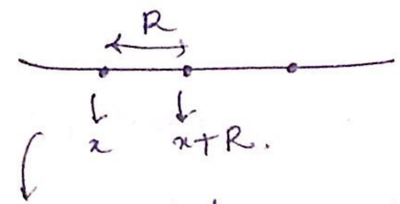
$$\psi_a(x=0) = \psi_b(x=0) \quad \text{—— } ①$$

$$\frac{d\psi_a(x=0)}{dx} = \frac{d\psi_b(x=0)}{dx} \quad \text{—— } ②$$

$\downarrow$
crystalline Lattice

Bloch's Theorem :-

$$\psi(x+R) = e^{ikR}\,\psi(x)$$



Lattice points separated by R,

Using Bloch's Theorem :-

$$\psi_a(x=a) = e^{ik(a+b)}\,\psi_b(x=-b) \quad \text{--- (3)}$$

$$\frac{d\psi_a(x=a)}{dx} = e^{ik(a+b)}\,\frac{d\psi_b}{dx}(x=-b) \quad \text{--- (4)}$$

from (1) $\Rightarrow$ $\quad B_a = B_b$ --- (5)

from (2) $\Rightarrow$ $\quad \alpha A_a = \beta A_b$ --- (6)

from (3) $\Rightarrow$

$$A_a \sin\alpha a + B_a \cos\alpha a = e^{ik(a+b)}\left[-A_b \sin\beta b + B_b \cos\beta b\right] \quad \text{--- (7)}$$

from (4) $\Rightarrow$

$$\alpha A_a \cos\alpha a - \alpha B_a \sin\alpha a = e^{ik(a+b)}\left[\beta A_b \cos\beta b - \beta B_b \sin\beta b\right] \quad \text{--- (8).}$$

Eliminate A_b and B_b $\Rightarrow$

$$B_b = B_a$$

$$A_b = \frac{\alpha}{\beta} A_a$$

(7) $\Rightarrow$

$$A_a \overbrace{\left[\sin\alpha a + \frac{\alpha}{\beta} e^{ik(a+b)} \sin\beta b\right]}^{\mathrm{I}} + B_a \underbrace{\left[\cos\alpha a - e^{ik(a+b)} \cos\beta b\right]}_{\mathrm{II}} = 0$$

(8) $\Rightarrow$

$$A_a\left[\alpha\cos\alpha a - \alpha e^{ik(a+b)}\cos\beta b\right] + B_a\left[-\alpha\sin\alpha a + \beta e^{ik(a+b)}\sin\beta b\right] = 0.$$

III IV

To solve for Aa and Ba $\Rightarrow$ $\begin{vmatrix} \text{I} & \text{II} \\ \text{III} & \text{IV} \end{vmatrix} = 0.$

$\Rightarrow$ I × IV − II × III = 0.

on solving this;

$$\left(\sin\alpha a + \frac{\alpha}{\beta}e^{ik(a+b)}\sin\beta b\right)\left(-\alpha\sin\alpha + \beta e^{ik(a+\beta)}\sin\beta b\right)$$

$$= \left(\alpha\cos\alpha a - \alpha e^{ik(a+b)}\cos\beta b\right)\left(\cos\alpha a - e^{ik(a+b)}\cos\beta b\right)$$

$$-\frac{\alpha^2+\beta^2}{2\alpha\beta}\sin\alpha a\sin\beta b + \cos\alpha a\cos\beta b = \cos k(a+b)$$

<u>Note</u>: β could be real or imaginary,

if $E > V_0 \Rightarrow \beta$ is real $\Rightarrow \beta = \beta_+$

if $E < V_0 \Rightarrow \beta$ is imaginary $\Rightarrow \beta = i\beta_-$

<u>Define</u> :- $\alpha_0 \equiv \sqrt{\frac{2mV_0}{\hbar^2}}$: $\xi = \frac{E}{V_0}$.

$\Rightarrow \alpha = \alpha_0\sqrt{\xi}$

$\Rightarrow \beta_- = \alpha_0\sqrt{1-\xi}$

$\beta_+ = \alpha_0\sqrt{\xi-1}$

when $\xi < 1$:-

$$\xi < 1 \Rightarrow E < V_0.$$

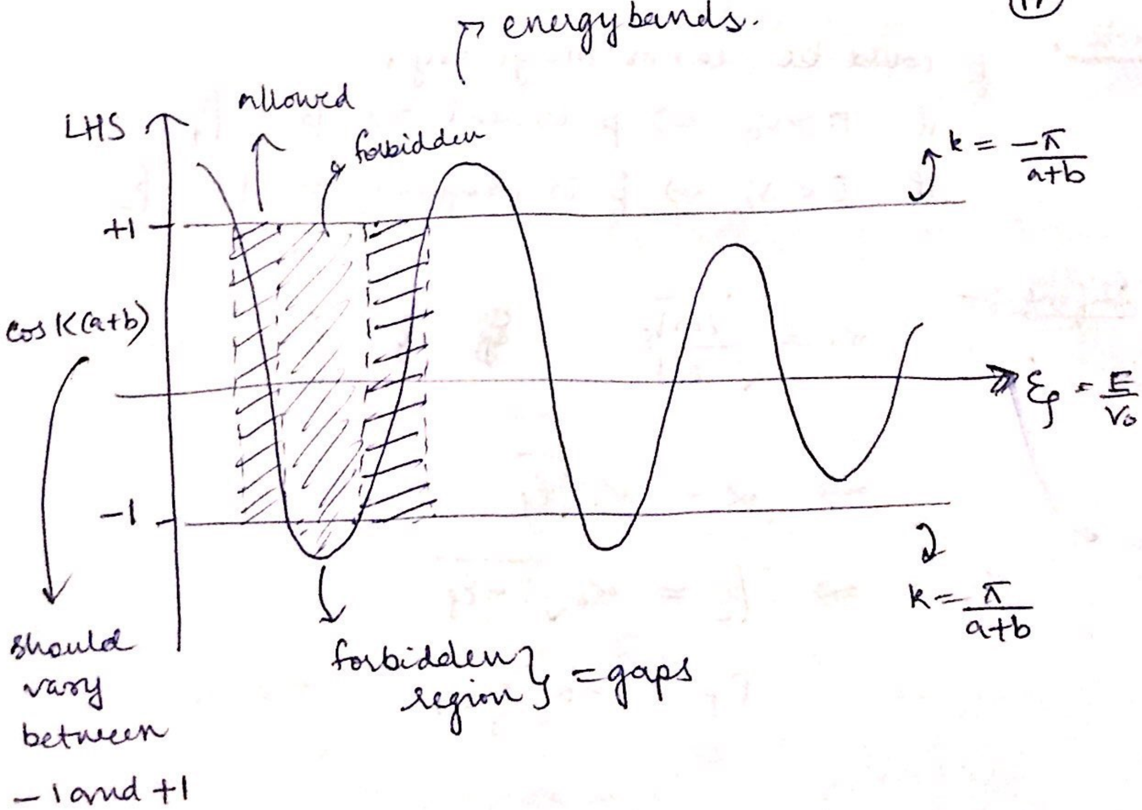
$$\frac{1-2\xi}{2\sqrt{\xi(1-\xi)}} \sin\left(\alpha_0 a\sqrt{\xi}\right) \sinh\left(\alpha_0 b\sqrt{1-\xi}\right)$$

$$+ \cos\left(\alpha_0 a\sqrt{\xi}\right) \cosh\left(\alpha_0 b\sqrt{1-\xi}\right) = \cos(k(a+b)) \quad (10)$$

when $\xi > 1$:-

$$\frac{1-2\xi}{2\sqrt{\xi(1-\xi)}} \sin\left(\alpha_0 a\sqrt{\xi}\right) \sin\left(\alpha_0 b\sqrt{\xi-1}\right) +$$

$$\cos\left(\alpha_0 a\sqrt{\xi}\right) \cos\left(\alpha_0 b\sqrt{1-\xi}\right) = \cos(k(a+b)) \quad (11)$$



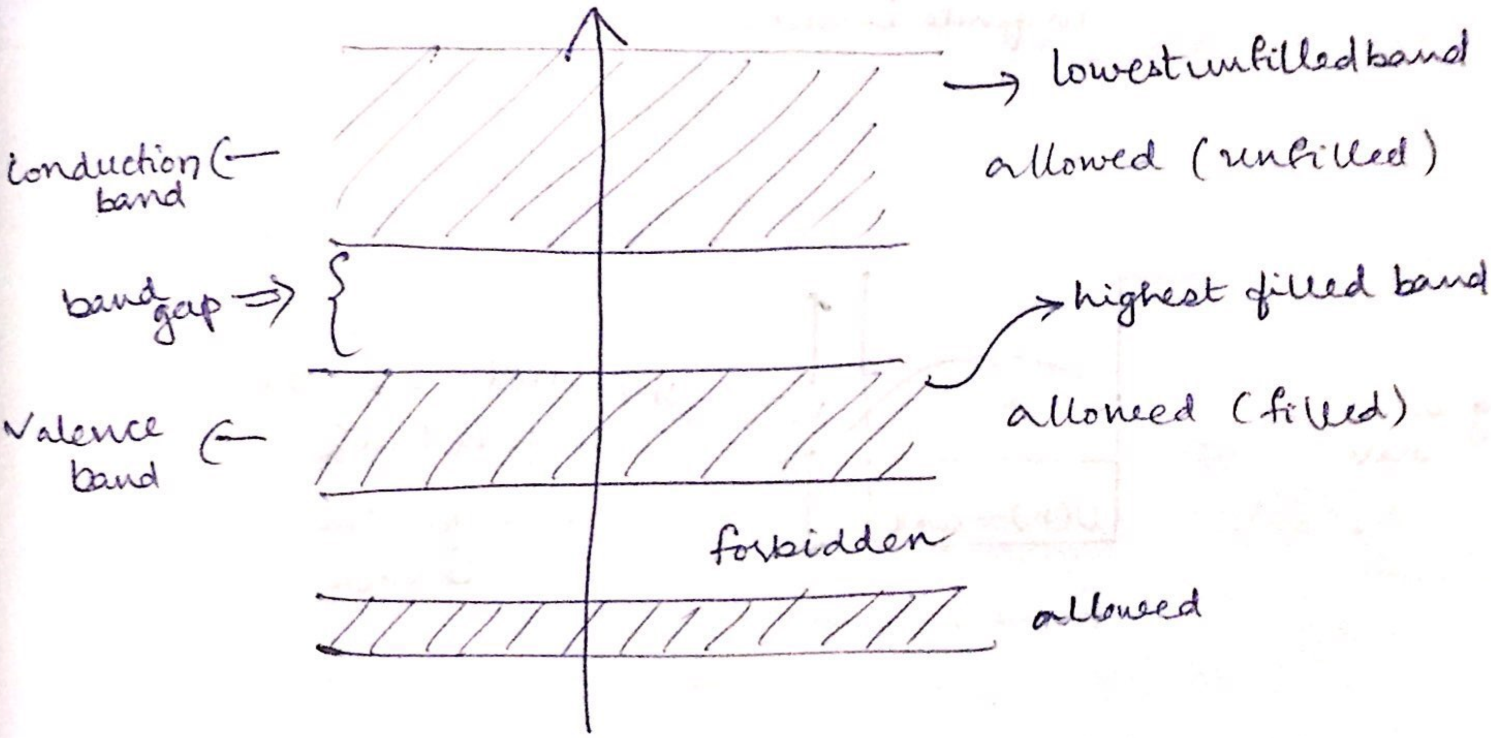
Highest occupied energy band (filled) ≡ Valence band

Lowest occupied energy band (unfilled) ≡ Conduction band

Difference: Band gap.

forbidden regions :- LHS exceeds RHS

bandwidth increases → as you go to higher energy states.



For metals, valence and conduction gap almost overlap.

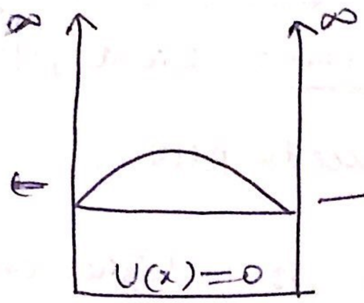
insulators, high band gap.

$\frac{dN}{dE} \Rightarrow D(E)$ density of the states

$D(E)\,dE \rightarrow$ # of free electrons with energy between E and $E + dE$

Quantum Harmonic Oscillator (1-D)

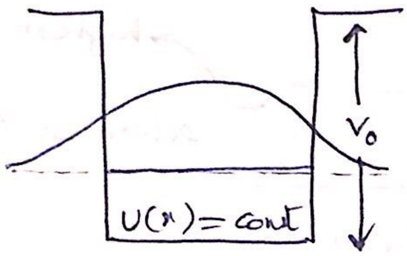
ground state



particle couldnot penetrate outside the box.

infinite barriers

ground state

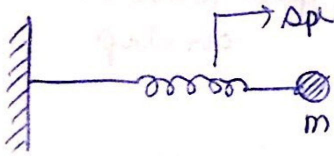


particle was able to penetrate through the barrier.

finite barriers

$U(x) = \frac{1}{2}kx^2$

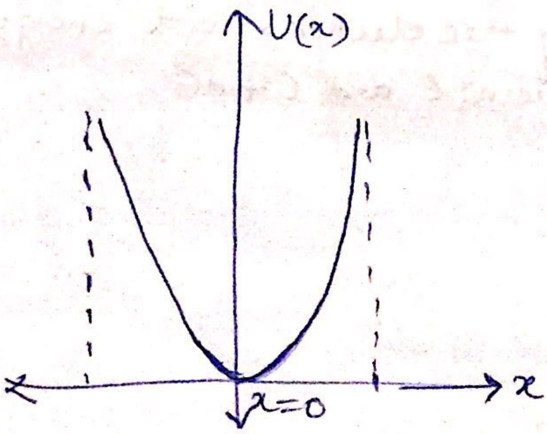
spring constant, k



$, \omega = \sqrt{\frac{k}{m}}$

frequency of oscillation.

$U(x) = \frac{1}{2}m\omega^2 x^2$



Schrodinger equation →

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + \frac{1}{2}m\omega^2x^2\psi(x) = E\cdot\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} + \left(\frac{2m}{\hbar^2}\left(E - \frac{1}{2}m\omega^2x^2\right)\right)\psi(x) = 0. \quad \text{—— (1)}$$

$$\frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2}x^2$$

$$\frac{2m\omega E}{\hbar\cdot\hbar\omega} - y^2$$

$$\frac{m\omega}{\hbar}\frac{2E}{\hbar\omega} - y^2$$

$$t^2\frac{2E}{\hbar\omega} - t^2x^2$$

Variable transformation —

$$y = tx \; ; \text{ where } t = \sqrt{\frac{m\omega}{\hbar}}$$

$$\frac{d\psi(x)}{dx} = \frac{d\psi}{dy}\cdot\frac{dy}{dx}$$

$$\frac{d\psi(x)}{dx} = t\frac{d\psi}{dy}.$$

$$\frac{d^2\psi(x)}{dx^2} = t^2\frac{d^2\psi}{dy^2}$$

$$\frac{d}{dx}\left(\frac{d\psi(x)}{dx}\right) = t^2\frac{d^2\psi}{dy^2}$$

rewrite (1) in terms of y

$$\frac{d^2\psi(y)}{dy^2} + (\lambda - y^2)\psi(y) = 0. \quad \text{—— (2)}$$

$$\lambda = \frac{2E}{\hbar\omega}, \quad y = \sqrt{\frac{m\omega}{\hbar}}\,x.$$

General transformation

$$\psi(y) = H(y)\cdot e^{-y^2/2}$$

↳ Gaussian

↓

Some function of y.

(Hermite polynomial function).

substitute this in (2) ⇒

$$\Rightarrow \frac{d^2H(y)}{dy^2} - 2y\frac{dH(y)}{dy} + (\lambda-1)H(y) = 0 \quad \text{—} (4)$$

Solution – Hermite Polynomial

Hermite differential equation

Consider, $H(y) = \sum_{n=0}^{\infty} a_n y^n$ —— (5)

coefficients.

Calculate $\Rightarrow \frac{d^2H(y)}{dy^2}, \frac{dH(y)}{dy}$

Using these, rewrite equation (4) $\Rightarrow$

$$\sum_{n=0}^{\infty} a_n\left[n(n-1)y^{n-2} - 2ny^{n} + [\lambda-1]y^n\right] = 0. \quad \text{—} (6)$$

This equation should be valid for all values of y.

$\Rightarrow$ coefficients of various powers of y must be equal to zero.

Consider the K^{th} power of $y \Rightarrow$

$\rightarrow$ Coefficient of y^k $(\underbrace{n-2=k \,;\, n=k}_{\text{two terms contribute}})$

$n=2+k \quad n=k$

$$\Rightarrow (k+1)(k+2)a_{k+2} - 2ka_k + (\lambda-1)a_k = 0$$

$$a_{k+2} = \left[\frac{2k-\lambda+1}{(k+1)(k+2)}\right]a_k \quad \text{—} (7)$$

recursive relation.

from $a_0 \rightarrow$ we can get all even coeffs using (7)
$a_1 \rightarrow$ we can get all odd coeffs. "

From (7) :—

$$\frac{a_{k+2}}{a_k} = \frac{2k-\lambda+1}{(k+1)(k+2)}$$

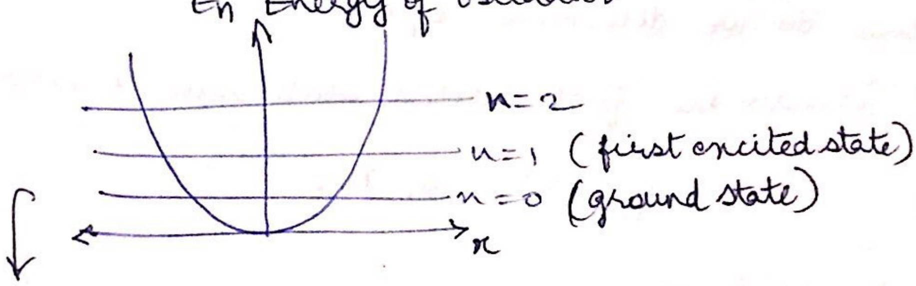
as $k \rightarrow \infty$,

$$\frac{a_{k+2}}{a_k} \simeq 0 \longrightarrow \text{converges.}$$

Truncate the infinite series, when

$$2k-\lambda+1=0$$

sub $\lambda \Rightarrow E_k = (k+\tfrac{1}{2})\hbar\omega$ Energy is quantised



quantum oscillator — takes discrete energies.

$$\psi(y) = H(y) \cdot e^{-y^2/2} \quad , \text{where } y = \left[\frac{m\omega}{\hbar}\right]^{1/2} \cdot x.$$

After normalising, $\psi(y)$:—

$$\rightarrow \quad \psi_{n=0}(x) = \left[\frac{m\omega}{\hbar\pi}\right]^{1/4} e^{-\frac{m\omega}{2\hbar} \cdot x^2}.$$

$$\alpha = \frac{m\omega}{\hbar}$$

$$\psi_n(x) = \begin{cases} e^{-\alpha x^2/2}\left[a_0 + a_2 x^2 + a_4 \dots + a_n x^n\right], & n = \text{even} \\ e^{-\alpha x^2/2}\left[a_1 x + a_3 x^3 + \dots + a_n x^n\right], & n = \text{odd} \end{cases}$$

$$a_{k+2} = \frac{2k-\lambda+1}{(k+1)(k+2)} a_k$$

~~hose~~ $\cancel{a_0} = C_0$, $a_1 = C_1$

How do we determine a_0?

→ Consider the ground state wave function

$$\psi_{n=0}(x) = a_0 . e^{-\alpha x^2/2}$$

Normalise –

$$\int_{-\infty}^{\infty} \psi^*_{n=0}(x)\, \psi_{n=0}(x)\, dx = 1$$

$$a_0^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = 1$$

$$\Rightarrow \quad a_0^2 = \sqrt{\frac{\alpha}{\pi}} \quad \Rightarrow \quad a_0 = \left[\frac{\alpha}{\pi}\right]^{1/4}, \text{ where}$$

$$\alpha = \frac{m\omega}{\hbar}$$

How do we determine a_1?

→ Consider the first excited state wave function.

$$\psi_{n=1}(x) = a_1 . x . e^{-\alpha x^2/2}$$

Normalise →

$$\int_{-\infty}^{\infty} \psi^*_{n=1}(x) . \psi_{n=1}(x)\, dx = 1$$

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}$$

↓ derivative wrt α ↓

$$-\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} = -\frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}}$$

$$a_1^2 . \int_{-\infty}^{\infty} x^2 . e^{-\alpha x^2/2} dx = 1$$

$$a_1^2 = \sqrt{\frac{4\alpha^3}{\pi}}$$

$$a_1 = \left[\frac{4\alpha^3}{\pi}\right]^{1/4}$$

$$\psi_{n=1}(x) = \left[\frac{4\alpha^3}{\pi}\right]^{1/4} . x e^{-\alpha x^2/2}$$

$$= \left[\frac{4}{\pi}\left[\frac{m\omega}{\hbar}\right]^3\right]^{1/4} . x e^{-\alpha x^2/2}$$

We can determine all the other coeffs from a_0 & a_1 ⇒

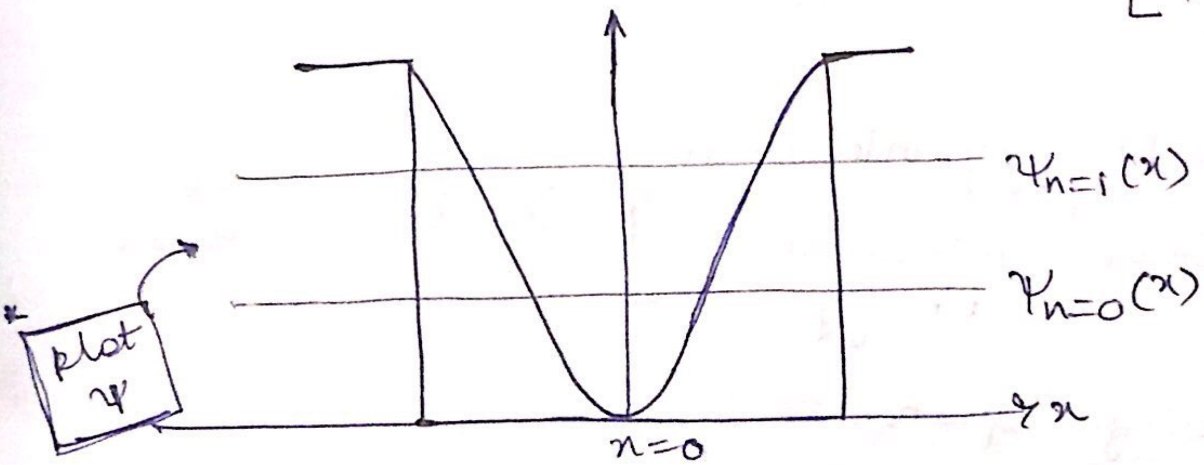
$n = 2$;

$$\psi_{n=2}(x) = e^{-\alpha x^2}\left[a_0 + a_2 x^2\right]$$

a_0 – known

a_2 – can be calculated from a_0 using the recursive relation.

Max prob:
[classical
↳ at the ends]



$$\psi_{n=0}(x) = \left[\frac{m\omega}{\hbar\pi}\right]^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}$$

$$\psi_{n=1}(x) = \left[4\left(\frac{m\omega}{\hbar}\right)^3 \cdot \frac{1}{\pi}\right]^{1/4} \cdot x \cdot e^{-\frac{\alpha x^2}{2}}.$$

when,
$n \to$ even
$\psi_n(x) \to$ even
$n \to$ odd
$\psi_n(x) \to$ odd

⇒ You can excite from one (ground) energy state to the other ⇒ Oscillator ⟺ equivalent to a bond (chemical)

Energy of light emitted on relaxing $\equiv \underbrace{\hat{H} \cdot \psi_n(x)}$

$$E = \left(n + \tfrac{1}{2}\right)\hbar\omega \quad , \text{ where } E_0 = \frac{\hbar\omega}{2}$$

$H(y) \to$ Hermite polynomial.

Quantum Mechanics of hydrogen atom ⟹

let us consider a hydrogen atom →

Potential Energy of Interaction or Interaction Potential Energy } ⟹ $\hat{U}(r) = \frac{-e^2}{4\pi\epsilon_0 r}$

→ Schrodinger equation ≡

In cartesian coordinate system,

→ $$-\frac{\hbar^2}{2m}\hat{\nabla}^2\psi(x,y,z) + U(r).\psi(x,y,z) = E.\psi(x,y,z)$$

Express $\hat{\nabla}^2$ in spherical polar coordinates and rewrite schrodinger equation, in terms of r, θ, ϕ.

$\psi(x,y,z) \rightarrow \psi(r,\theta,\phi) \rightarrow \boxed{\psi^2(r,\theta,\phi)}$

cartesian system. spherical polar coordinate system.

Polar

$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

$0 < r < \infty$
$0 \le \theta < \pi$
$0 \le \phi < 2\pi$

ψ^2 of finding $e^\ominus$

→ Prob ↑ decreases as we go away from the nucleus, radially. [in any direction]

* ground state: 1s → spherical orbital [atomic orbital]

$\psi^2(r,\theta,\phi) \longrightarrow$ prob of finding an $e^\ominus$ at a given (r,θ,ϕ)

$$-\frac{\hbar^2}{2m}\left[\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right]\psi(r,\theta,\phi)\right] - \frac{\hbar^2}{2m}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\phi}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi)$$

$$= E.\Psi(r,\theta,\phi) \quad \text{——} \textcircled{1}$$

$$\Psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{radial part}} . \underbrace{Y(\theta,\phi)}_{\text{angular part}}$$

Substitute this in ① and $\div$ by $\frac{R(r).Y(\theta,\phi)}{r^2}$ on both the sides $\Rightarrow$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{r^2}{R(r)}\left[\frac{\partial}{\partial r}\left[r^2\frac{dR}{dr}\right]\right] - \frac{\hbar^2}{2m}\frac{r^2}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) - \frac{e^2 r^2}{4\pi\varepsilon_0 r} = Er^2$$

$\vec{L}^2$

Rotational Kinetic energy $\Rightarrow$ $\frac{L^2}{2I}$ — L^2: square of angular momentum [angular momm. square] ; I: moment of inertia

$$\vec{L}^2 = \left[\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2}\right]$$

From a particle on a sphere problem $\Rightarrow$

$\hat{L}^2 Y(\theta,\phi) \Rightarrow$ introduced angular momentum quantum number (l) and magnetic quantum number (m)

By solving the radial part and the anguler part,

n, l, m — 3 degrees of freedom.

- $n = 0, 1, 2, \ldots \infty$ [principal quantum number]
- $l = 0, 1, 2, \ldots, n-1$ [angular quantum number]
- $m = 0, \pm 1, \pm 2, \ldots \pm l$ [magnetic quantum number]

(just the names are enough)

For the radial part :— Power series solution $\downarrow$ Laguare Polynomial

For the angular part :— Power series solution $\downarrow$ Associated Legendre polynomial.

$$\psi_{n,l,m}(r,\theta,\phi) = R_n^l(r) \cdot Y_l^m(\theta,\phi)$$

radial part is dependent on n and l.

ψ_{nlm}	n	l	m	
$\psi_{100}(r,\theta,\phi)$	1	0	0	$\longrightarrow$ 1s orbital
$\psi_{200}(r,\theta,\phi)$	2	0	0	$\Longrightarrow$ 2s
	2	1	0	2p orbitals $\{2p_x, 2p_y, 2p_z\}$
	2	1	1	
	2	1	-1	

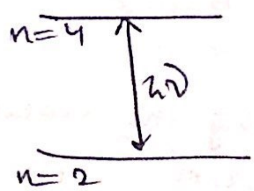
Problems in Quantum Mechanics $\rightarrow$

① An electron in a one-dimensional infinite particle well defined by ; $V(x) = 0$ for $-a \leq x \leq a$ and $V(x) = \infty$ otherwise, goes from the $n=4$ to $n=2$ level. the frequency of the excited photon is 3.43×10^{14} Hz. Find the width of the box. $m_e = 9.1 \times 10^{-31}$ kg

$\longrightarrow$ $P = \frac{nh}{2L}$, $E = \frac{p^2}{2m}$

$E_n = \frac{n^2 h^2}{8mL^2}$, $n = 1, 2, .$

$E_4 - E_2$



$\Delta E = h\nu$

$E_4 - E_2 = h\nu$

$$\frac{h^2}{8mL^2}[16-4] = 3.43 \times 10^{14} . h$$

$$L^2 = \frac{\frac{h^2 . 12}{8m}}{3.43 \times 10^{14} . h} = \frac{12h}{8m \times 3.43 \times 10^{14}}$$

$$= \frac{12 \times 6.63 \times 10^{-34}}{8 \times 9 \times 10^{-31} \times 3.43 \times 10^{14}}$$

$$= 0.322 \times 10^{-17}$$

$$L = 17 \times 10^{-10} = 1.7\,nm$$

(2) Consider a one-dimensional harmonic oscillator in the ground state. Calculate the expectation / average values of the following operators

(a) $\langle \hat{x} \rangle$

(b) $\langle \hat{p} \rangle$

(c) $\langle \hat{x}^2 \rangle$

(d) $\langle \hat{p}^2 \rangle$

(e) $\langle (\Delta x)^2 \rangle = \langle (x - \langle x \rangle)^2 \rangle$
$= \langle x^2 \rangle - (\langle x \rangle)^2$

(f) $\langle (\Delta p)^2 \rangle = \langle (p - \langle p \rangle)^2 \rangle$
$= \langle p^2 \rangle - (\langle p \rangle)^2$

(g) $\sqrt{\langle (\Delta x)^2 \rangle} \sqrt{\langle (\Delta p)^2 \rangle}$

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* . x \psi \, dx \qquad \psi_{n=0}(x) = \left[\frac{\alpha}{\pi}\right]^{1/4} . e^{-\alpha x^2/2}$$

$$= \int_{-\infty}^{\infty} \sqrt{\frac{\alpha}{\pi}} . x . e^{-\alpha x^2} dx$$

odd function

$$= 0$$

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} . \psi \, dx$$

$$= \int_{-\infty}^{\infty} \sqrt{\frac{\alpha}{\pi}} . e^{-\frac{\alpha x^2}{2}} . \left[i\hbar \frac{\partial}{\partial x} \left[e^{-\alpha x^2/2} \right] \right] dx$$

$$= i\hbar \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\frac{\alpha x^2}{2}} . (-\alpha x) . e^{-\alpha x^2/2} dx$$

$$= i\hbar \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha x^2} . (-\alpha x) dx = 0$$

odd function

$$\langle \hat{x}^2 \rangle = \int_{-\infty}^{\infty} \psi^* x^2 \psi dx \qquad \int e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}$$

wrt α

$$= \int_{-\infty}^{\infty} \sqrt{\frac{\alpha}{\pi}} . x^2 e^{-\alpha x^2} dx \qquad -\int x^2 e^{-\alpha x^2} = -\frac{1}{2} \sqrt{\frac{\pi}{\alpha^3}}$$

$$= \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} x^2 . e^{-\alpha x^2} dx = \sqrt{\frac{\alpha}{\pi}} \left[\frac{\pi}{4\alpha^3}\right]^{1/2} = \frac{1}{2\alpha}.$$

$$\langle \hat{p}^2 \rangle = \int_{-\infty}^{\infty} \psi^* (p.p) \psi \, dx$$

$$= \int_{-\infty}^{\infty} \sqrt{\frac{\alpha}{\pi}} \left[e^{-\frac{\alpha x^2}{2}} . -\hbar^2 \frac{\partial^2}{\partial x^2} e^{-\alpha x^2/2} \right] dx$$

$$= \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} \cdot \left(-\hbar^2 \frac{\partial^2}{\partial x^2} e^{-\alpha x^2/2}\right) dx$$

$$= -\hbar^2 \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha x^2} \cdot (-\alpha x)(-\alpha x) dx$$

$$= -\alpha^2 \hbar^2 \sqrt{\frac{\alpha}{\pi}} \underbrace{\int_{-\infty}^{\infty} e^{-\alpha x^2} \cdot x^2 dx}_{\sqrt{\frac{\pi}{4\alpha^3}}}$$

$$= \frac{-\alpha^2 \hbar^2}{2\alpha} = \frac{-\alpha \hbar^2}{2}.$$

$$\langle (\Delta x)^2 \rangle = \langle x^2 \rangle - (\langle x \rangle)^2 = \langle x^2 \rangle = \frac{1}{2\alpha}.$$

$$\langle (\Delta p)^2 \rangle = \langle p^2 \rangle - (\langle p \rangle)^2 = \langle p^2 \rangle = -\frac{\alpha \hbar^2}{2}.$$

$$\sqrt{\langle \Delta x^2 \rangle} \sqrt{|\langle (\Delta p)^2 \rangle|} = \sqrt{\frac{1}{2\alpha} \frac{\alpha \hbar^2}{2}} = \frac{\hbar}{2} = \frac{h}{4\pi}.$$

↓

Uncertainity principle.

③ The ground state wave function of a hydrogen atom is given as $\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} \cdot e^{-r/a_0}$

Evaluate the expectation value of r of the electron in the ground state $\Rightarrow$ ($a_0 \equiv$ constant)

$$\langle r \rangle = \int_\theta \int_\phi \int_r \psi^*_{1,0,0}(r,\theta,\phi) \cdot r \, \psi(r,\theta,\phi) \cdot r^2 \sin\theta \, dr \, d\theta \, d\phi.$$

$$\rightarrow \quad \psi_{1,0,0}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left[\frac{1}{a_0}\right]^{3/2} \cdot e^{-r/a_0}$$

$$\langle r \rangle = \int_\theta \int_\phi \int_r \psi^*(r,\theta,\phi) \cdot r \cdot \psi(r,\theta,\phi) \cdot r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 \int_\theta \int_\phi \int_r r \cdot e^{-2r/a_0} \cdot r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{1}{\pi (a_0)^3} \int_\theta \int_\phi \int_r e^{-2r/a_0} \cdot r^3 \sin\theta \, dr \, d\theta \, d\phi$$

let $r/a_0 = u$;

$$= \frac{1}{\pi} \int_\theta \int_\phi \int_r e^{-2u} \cdot \left(\frac{r}{a_0}\right)^3 . \sin\theta . dr . d\theta . d\phi$$

$0 < r < \infty$

$0 \leq \theta \leq \pi$

$0 \leq \phi \leq 2\pi$

$$= \frac{1}{\pi} \int_\theta \int_\phi \int_r e^{-2u} \cdot u^3 . \sin\theta \, du \, d\theta \, d\phi \cdot a_0$$

$$= \frac{1}{\pi} \int_0^\pi \sin\theta \, d\theta . \int_0^{2\pi} d\phi \int_0^\infty e^{-2u} \cdot u^3 \cdot a_0 \, du$$

$$= \frac{2}{\pi} . 2\pi . a_0 \int_0^\infty e^{-2u} . u^3 \, du$$

$\int uv = u \int v - \int u' \int v$

$$= 4a_0 \cdot \int_0^\infty e^{-2u} . u^3 du = \frac{3}{2} a_0 .$$

$$4a_0 . \frac{3}{2} \times \frac{1}{2} . \frac{1}{2} .$$

Expectation value $= \frac{3}{2} a_0$

$$\langle r \rangle = \int_\theta \int_\phi \int_r \psi^*(r,\theta,\phi) . r . \psi(r,\theta,\phi) \underbrace{r^2 \sin\theta \, dr \, d\theta \, d\phi}$$

$$\downarrow$$

$$dx \, dy \, dz = J \, dr \, d\theta \, d\phi$$

where $J \Rightarrow$

$$J = \underbrace{\begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix}}$$

$$J = r^2 \sin\theta .$$

Nuclear Physics →

Atomic Nucleus = protons + neutrons. (Nucleons)

held together by forces

$^{A}_{Z}X$ — A → No. of protons + neutrons; Z → number of protons

→ Assume nucleus to be a sphere.

Nucleus can emit $e^{\ominus}$, {β-particle}

radius of Nucleus ⇒ $r = r_0 A^{1/3}$, where $r_0 = 1.2 \times 10^{-15}$ m

density, volume, surface area can be calculated.

→ To determine the radius of nucleus ⇒
⇒ Scattering Techniques

Common probes → X-rays, → Laser [electromagnetic waves]

→ But we need a probe that can penetrate the $e^{\ominus}$ cloud and go hit the nucleus.
— Neutrons scattering technique
(carry no charge)

$$\rho = \frac{M}{V} = \frac{Am}{[4/3\,\pi][1.2 \times 10^{5} A^{1/3}]^3}$$

independent of nucleons

Nuclear stability ⇒

Stable :– No. of nucleons dont change with time

Unstable :– Nucleus emits radioactive rays and become a stable nucleus.
→ no. of nucleons changes
radioactive rays → α rays, β rays, γ rays

As nuclei get larger,
more neutrons are required for stability.

Nucleus + Binding Energy $\longrightarrow$ Separated nucleons

(small mass) (greater mass)

Binding Energy $= (\Delta m)\, c^2$

$\Delta m \downarrow$ Mass defect.

* Mass of Nucleus $\neq$ sum of masses of nucleons

* 1 atomic mass unit = 931.5 MeV

$1u = 931.5$ MeV

Liquid drop Model $\Rightarrow$

Nucleus $\leftrightarrow$ liquid drop.

Heat of Vaporisation $\longleftrightarrow$ binding energy per nucleon of a nucleus.

$$E_B = a_v A - a_s A^{2/3} - a_c \frac{Z(Z-1)}{A^{1/3}}$$

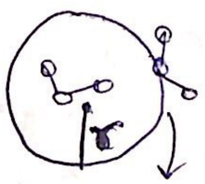
(binding energy)

$a_v A \downarrow$ Volume term

$a_s A^{2/3} \downarrow$ surface term (for surface nucleons)

$a_c \frac{Z(Z-1)}{A^{1/3}} \rightarrow$ Coulomb term.

water drop.



$SA = 4\pi r^2$

surface molecules require lesser energy than the molecules inside

$\rightarrow$ we need 2 terms
- volume
- surface

$SA = 4\pi r^2$

$r = r_0 A^{1/3}$

$= 4\pi r_0^2 A^{2/3}$

$$U_{Coulomb} = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \qquad q_1 = +e, \quad q_2 = +e$$

$$= \frac{1}{4\pi\epsilon_0}\left[e^2/r\right] \quad \text{— for each protons}$$

for z protons $\Rightarrow \dfrac{Z(Z-1)}{A^{1/3}}$.

$A^{1/3} \hookrightarrow$ [from r]

$\rightarrow$ A magnetic field separates all the three particles (α, β, γ)

Alpha decay $\Rightarrow$ ${}^{A}_{Z}P \rightarrow {}^{A-4}_{Z-2}D + {}^{4}_{2}He + Q$

Q = excess energy

${}^{4}_{2}He$ = helium nucleus (α-particle)

$$Q = \underbrace{\left[m\left({}^{A}_{Z}P\right) - m\left({}^{A-4}_{Z-2}D\right) - m\left({}^{4}_{2}He\right)\right]}_{\text{mass defect}} c^2$$

Ex.

$\Rightarrow$ ${}^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$ + Nuclear Energy

Beta decay $\Rightarrow$ ${}^{A}_{Z}P \rightarrow {}^{A}_{Z+1}D + e + n$ (neutrino)

e — β emission (originated from nucleus)

Gamma decay $\Rightarrow$ (no change in the nucleus)

$${}^{A}_{Z}P^{*} \rightarrow {}^{A}_{Z}P + \gamma$$

${}^{A}_{Z}P^{*}$ — excited energy state

Radioactive decay $\Rightarrow$

Law of radioactive disintegration $\Rightarrow$

$$\frac{dN}{N} = -\lambda dt.$$

$$\int_{N_0}^{N} \frac{dN}{N} = -\int_{0}^{t} \lambda dt$$

$$\frac{N}{N_0} = e^{-\lambda t}$$

N_0 = initial concn of nuclei.

$$\boxed{N = N_0 e^{-\lambda t}}$$

Half-life $\Rightarrow$ $N = N_0/2$.

$$T_{1/2} = \frac{\ln 2}{\lambda}$$

λ $\rightarrow$ decay constant