Particle in a Box Model

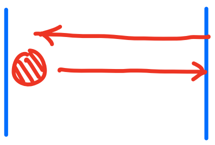
Small particles have wave-like properties and can thus be described by Wave Equations.

De Broglie Hypothesis.

From the Wave equations, We can find the energy. ⟶ Energy of Standing Waves.

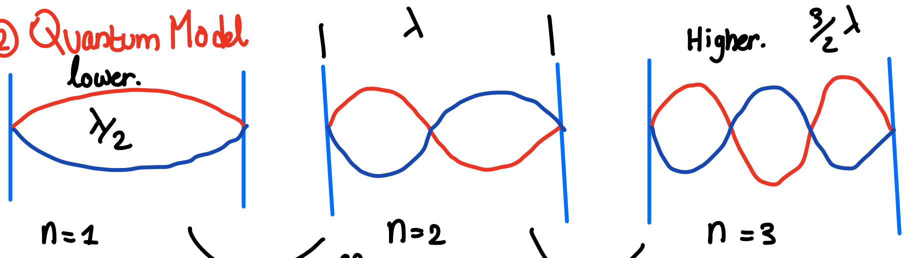
Models

① Newtonian Model



To/fro motion

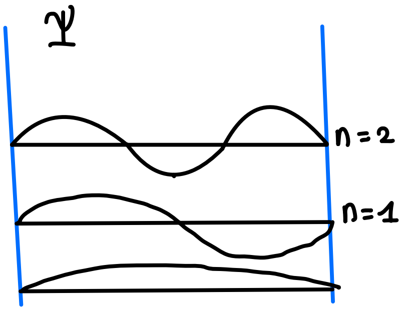
② Quantum Model



Different Energy levels.

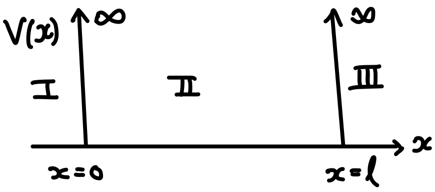
More wavelength => Higher Energy

When confined in a box, the electrons are allowed only certain energy levels



Ψ^2 corresponds to the probability of finding a particle within a certain space.

Particle in a 1D box. : Solve time independant S·E for a particle in a 1D box.



Classical Mechanics applies only to Macroscopic particles. [Originally, when Clausius derived entropy, it was only a mathematical object which appeared to satisfy certain conditions.] To better understand entropy, we need to look at "microscopic mechanics". Quantum Mechanics.

"Quanta" – Small.

Schrö dinger Equation. (Time independent)

$H\Psi = E\Psi$ ← Wave function.

Hamiltonian $(T+V)$

Energy Eigen Value

$$\boxed{E\Psi = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = (E-\infty)\Psi$$
$$\searrow -\infty$$

Neglecting E in comparison to ∞,

$$\frac{d^2\Psi}{dx^2} = \infty\Psi \Rightarrow \Psi = \frac{1}{\infty}\frac{d^2\Psi}{dx^2} \Rightarrow \Psi_I, \Psi_{III} = 0 \text{ (Outside box)}$$

For region II, x between 0 & l, $V=0$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = (E-0)\Psi_{II}$$

$$\frac{d^2\Psi}{dx^2} = -\frac{2m}{\hbar^2}E\Psi_{II}$$

$$\boxed{\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}E\Psi_{II} = 0}$$

Solving ODE,

$$\Psi_{II} = C_1 e^{i(2mE)^{1/2}x/\hbar} + C_2 e^{-i(2mE)^{1/2}x/\hbar}$$

let $\theta = \frac{(2mE)^{1/2}x}{\hbar} \Rightarrow \Psi_{II} = C_1e^{i\theta} + C_2e^{-i\theta}$

$e^{i\theta} = \cos\theta + i\sin\theta \quad e^{-i\theta} = \cos\theta - i\sin\theta$

$$\Rightarrow C_1\cos\theta + iC_1\sin\theta + C_2\cos\theta - iC_2\sin\theta$$
$$= (C_1+C_2)\cos\theta + (iC_1 - iC_2)\sin\theta$$

$= A\cos\theta + B\sin\theta$ (A & B are new Constants)

$$\psi_{II} = A\cos[\hbar^{-1}(2mE)^{1/2}x] + B\sin[\hbar^{-1}(2mE)^{1/2}x]$$

Find A & B by applying boundry conditions.

We assume function is continuous.

If ψ is to be continuous at the point $x=0$, then ψ_1 and ψ_2 must approach the same value at $x=0$.

$$\lim_{x\to 0}\psi_1 = \lim_{x\to 0}\psi_2$$

$$0 = \lim_{x\to 0}\left[[A\cos[\hbar^{-1}(2mE)^{1/2}x] + B\sin[\hbar^{-1}(2mE)^{1/2}x]\right]$$

$$0 = A$$

How?!

$\Rightarrow$ With $A=0$ Eqn becomes

$$\psi_{II} = B\sin\left[\left(\frac{2\pi}{h}\right)(2mE)^{1/2}x\right]$$

x can be equal to l.

Applying continuity condition at $x=l$, we get (0 at l and l is a soln)

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

Sin = 0 at $0 \pm\pi, \pm 2\pi, \dots, \pm n\pi$

$$\Rightarrow \frac{2\pi}{h}(2mE)^{1/2}l = \pm n\pi$$

$n=0$ Corresponds to $E=0$ ... $n=0$ is not allowed.

$$\Rightarrow E = \frac{n^2h^2}{8ml^2} \quad n = 1, 2, 3, \dots$$

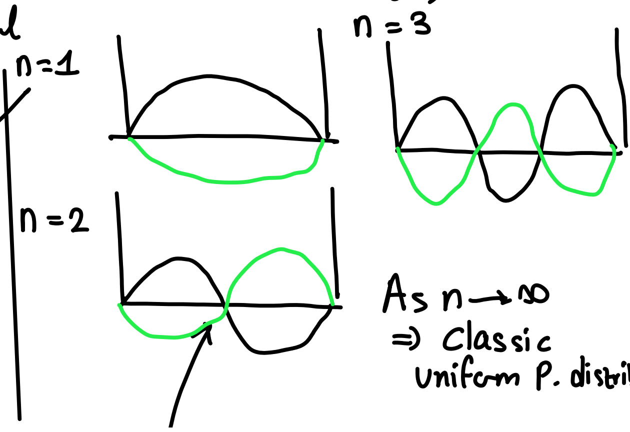
These Satisfy cont. at $x=l$

Length of the box

Each harmonics

$$\psi_i = \left(\frac{2}{l}\right)^{1/2}\sin\left(\frac{n_i\pi x}{l}\right)$$

Expressed in terms of E-levels.



As $n\to\infty$
$\Rightarrow$ Classic Uniform P. distribution.

Q number.

Argument of the term

More maths

$$\psi_{II} = \left(\frac{2}{l}\right)^{1/2}\sin\left(\frac{n\pi x}{l}\right) \quad n = 1, 2, 3, \dots$$

(Stationary State Wave eqn)

Tunneling.

Eigenvalues

Operators...

How can P = 0 here.
↳ The particle "jumps" in the box

Two identical particles in a box.

In the classical case, the particles can be labelled but in Q.M, we can only predict the prob. that the particle is in region dx, about x_1 and same for x_2. This affects both the allowed energies and the wave function.

Classical Energy in box is: $\frac{P_1^2}{2m} + \frac{P_2^2}{2m} = E$

Energy is sum of independant energies: $E = \varepsilon_1 + \varepsilon_2$

Why not independant?
↳ The particles affect each other.

The wave function will depend on the positions x_1 and x_2: $\Psi(x_1, x_2)$
↳ for the particles. ↳ Wavefunction for one particle or the system of 2?
↳ // We are looking at total Energy.

We have 4 B.C.

$\Psi(0, x_2) = 0$
$\Psi(x_1, 0) = 0$
$\Psi(L, x_2) = 0$
$\Psi(x_1, L) = 0$

P(particle present at extremities (nodes) = 0)

Allowed values of ε_1 & ε_2. $\quad \varepsilon_{n_1} = \frac{\hbar^2\pi^2}{2mL^2} n_1^2 \quad \varepsilon_{n_2} = \frac{\hbar^2\pi^2}{2mL^2} n_2^2$

⇒ Allowed values of the total energy

$$= E_{n_1 n_2} = \frac{\hbar^2\pi^2}{2mL^2}(n_1^2 + n_2^2)$$

Each particle get an independant integer for enumerating the energy levels n_1 & n_2.
(The particles 1 & 2 are in their respective E. level n_1 & n_2)

Like for a single particle in a 2D box, we might expect the wave function to be a product.

$$\Psi_{n_1 n_2}(x_1, x_2) = \Psi_{n_1}(x_1)\Psi_{n_2}(x_2)$$

Property of Sys. at x_1 = P(A at x_1) × P(B at x_1)
↓ consists of A & B ↑ AND.

$$\left(\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)\right) \text{ — for 1 particle.}$$

n_1 : E level for particle 1
x_1 : Posn of particle 1

Problems | If the particles are identical, how do we know which to assign E-level n_1; could be either particle 1 or 2. Total Energy would not change.

The Product above specifies assigning n_1 to particle 1 and so on...

The second problem is that the product says $\psi_{n_1 n_2}(x,x) \neq 0$. Particles can sit onto each other!

Eigen / Hamil.
Gas in a 1D box
Boltzmann-Distribution
Fermi-Dirac Dist..
Entropy...
φ...

1^{st} Problem

We include the 2 possible product form.

ie. $\psi_{n_1}(x_1)\psi_{n_2}(x_2) \quad \psi_{n_2}(x_1)\psi_{n_1}(x_2)$

We can put them together to get

$$\psi_{n_1 n_2}(x_1,x_2) = \underbrace{\frac{1}{\sqrt{2}}}_{\text{Normalizing Factor.}}\left[\psi_{n_1}(x_1)\psi_{n_2}(x_2) \pm \psi_{n_2}(x_1)\psi_{n_1}(x_2)\right]$$

first form : $\psi_{n_1 n_2}(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(x_1)\psi_{n_2}(x_2) + \psi_{n_2}(x_1)\psi_{n_1}(x_2)\right]$

Second form : $\psi_{n_1 n_2}(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_2}(x_1)\psi_{n_1}(x_2)\right]$

The 2 particles cannot be in same space. ← For $\psi_{n_1 n_2}(x,x)$ we have $\frac{1}{\sqrt{2}}\left[\psi_{n_1}(x)\psi_{n_2}(x) - \psi_{n_2}(x)\psi_{n_1}(x)\right] \to 0$

$Pr(\text{Same space}) = 0$

also $\psi_{nn}(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\psi_n(x_1)\psi_n(x_2) - \psi_n(x_1)\psi_n(x_2)\right] \to 0$

↳ The 2 particles cannot be at same E-level.

(Pauli Exclusion Principle)

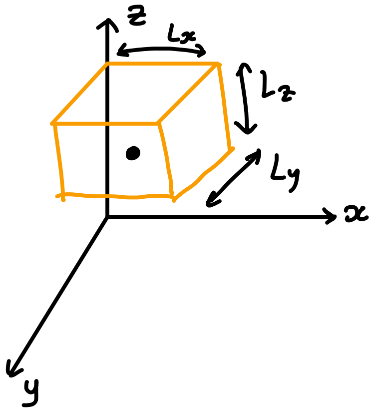
↳ 2 fermions, e^-, p, n, nuclei, atoms
cannot be in same quantum state
orbital defined by : $\underbrace{n, m_l, l}_{\text{same for } e^- \text{ in one orbital}}, s$ ← spin flip.

Particle in a 3D box.

Expansion of the 1D box problem to 3D!

3 lengths - L_x, L_y, L_z

No force acts on the particles inside the box!



Potential for the particle inside the box:

$$V(\vec{r}) = 0$$

$\vec{r}$ is a vector with all 3 components along the axes:

$$\vec{r} = L_x \hat{x} + L_y \hat{y} + L_z \hat{z}$$

$0 \leqslant x \leqslant L_x \qquad L_x < x < 0$

$0 \leqslant y \leqslant L_y \qquad L_y < y < 0$

$0 \leqslant z \leqslant L_z \qquad L_z < z < 0$

meaning of this?

When p. Energy is infinite, Wave function = 0.
When p.E is 0, the wave function obeys the Time independant SE.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r) = E\,\psi(r)$$

We are dealing with 3D figure. We need to add 3 axes to SE.

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\,\psi(r) \quad -(3)$$

Consider x AND y AND z

To solve this p.d.e, let wave function be a product of individual function for each indep. Variable

$$\psi(x,y,z) = X(x)\,Y(y)\,Z(z) \quad (4)$$

Each function has its own Variable
$X(x)$ is a function of Var x only.

Sub (4) in (3) and divide it by xyz product

e.g. Heat Equation

$$\frac{\partial u}{\partial t} - \alpha \frac{\partial^2 u}{\partial x^2} = 0$$

Let $u(x,t) = X(x)T(t)$
Sub u back in first eqn. & Product Rule.

$$\frac{\partial}{\partial t} X(x)T(t)$$

$$\frac{\partial X(x)T(t)}{\partial t} - \alpha \frac{\partial^2}{\partial x^2} X(x)T(t) = 0$$

$$X(x)T'(t) - \alpha X''(x)T(t) = 0$$

$$X(x)T'(t) = \alpha X''(x)T(t)$$

$$\Rightarrow \frac{T'(t)}{\alpha T(x)} = \frac{X''(x)}{X(x)}$$

RHS depends only on x and LHS only on t, both sides are equal to some constant value $-\lambda$

Eigen value of both differential operators.

TISE in 1D $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$

$\hbar = \frac{h}{2\pi} \Rightarrow h = \hbar 2\pi$

The term $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)$ can be identified with the E_K $\frac{P_x^2}{2m} = \frac{\hbar^2 K_x^2}{2m}$

$\frac{P}{h} = \frac{1}{\lambda}$ (De Broglie's Relation)

$\frac{P}{2\pi\hbar} = \frac{1}{\lambda}$

$\frac{P}{\hbar} = \frac{2\pi}{\lambda}$ Wave number (K)

$\Rightarrow P = K\hbar$

$\frac{1}{2}mv^2 \xrightarrow{\times m} \frac{1}{2}m^2v^2 \rightarrow \frac{p^2}{2} \xrightarrow{\text{div. } m} \frac{p^2}{2m}$

In 3D $E_K = \frac{P_x^2 + P_y^2 + P_z^2}{2m}$

$E_K = \frac{p^2}{2m}$

$E_K = \frac{1}{2}mv^2$

Vel. is a vector.

$\therefore$ net disp.

$= |\vec{V}| = (V_x^2 + V_y^2 + V_z^2)^{1/2}$

$= V^2 = V_x^2 + V_y^2 + V_z^2$

$\Rightarrow mv^2 = mV_x^2 + mv_y^2 + mv_z^2$

$E_K \Rightarrow \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$

xm

$mE_K = \frac{1}{2}m^2v^2 = \frac{1}{2}m^2v_x^2 + \frac{1}{2}m^2v_y^2 + \frac{1}{2}m^2v_z^2$

div. m

$= \frac{1}{2m}m^2v^2 = \frac{1}{2m}m^2v_x^2 + \frac{1}{2m}m^2v_y^2 + \frac{1}{2m}m^2v_z^2$

$E_K = \frac{P^2}{2m} = \frac{P_x^2}{2m} + \frac{P_y^2}{2m} + \frac{P_z^2}{2m}$

$P_{NET} = \sqrt{P_x^2 + P_y^2 + P_z^2}$

$P_{NET}^2 = P_x^2 + P_y^2 + P_z^2$

$\psi = e^{i(Kx - \omega t)}$

$\frac{d^2\psi}{dx^2} = -K^2\psi \qquad K = \frac{P}{\hbar}$

$= -\frac{P^2}{\hbar^2}\psi$

$-\hbar^2\frac{d^2\psi}{dx^2} = P^2\psi \Rightarrow \boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = P^2\psi}$

In 3D

Grad = Collection of Partial der. in all directions. (Net sum)

$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\psi(x,y,z) + \frac{\partial^2}{\partial y^2}\psi(x,y,z) + \frac{\partial^2}{\partial z^2}\psi(x,y,z)\right) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$

Inside box, $V(x,y,z) = 0$, $V(x,y,z) = \infty$ at walls.

Use Separation of Variable to Solve p.d.e (3D SE)

Let $\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$, Sub. this in 3D SE. , $V(x,y,z) = 0$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}X(x)Y(y)Z(z) + \frac{\partial^2}{\partial y^2}X(x)Y(y)Z(z) + \frac{\partial^2}{\partial z^2}X(x)Y(y)Z(z)\right) = E\,X(x)Y(y)Z(z)$$

$$= -\frac{\hbar^2}{2m}\left(Y(y)Z(z)\frac{d^2X}{dx^2} + X(x)Z(z)\frac{d^2Y}{dy^2} + X(x)Y(y)\frac{d^2Z}{dz^2}\right) = E\,X(x)Y(y)Z(z)$$

X is a function of x only. p. der disapp. as X is a function of one variable. (X, Y and Z)

$\frac{dy}{dx} = K$

$\int dy = \int K\,dx$

$y = Kx$

$x = 1 \quad y = K$

$x = 2 \quad y = 2K$

* Possible Soln

Divide both sides by $-\frac{\hbar^2}{2m}X(x)Y(y)Z(z)$

$$\Rightarrow \left(\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2}\right) = -\frac{2mE}{\hbar^2} \quad (1)$$

* For a given Soln, E is a constant.

ie. $\underset{\substack{\uparrow \\ x \text{ value of Soln}}}{\varepsilon_x} + \underset{\substack{\uparrow \\ y \text{ value of Soln}}}{\varepsilon_y} + \underset{\substack{\uparrow \\ z \text{ value of Soln}}}{\varepsilon_z} = E_{Total}$ of 1 Soln (x,y,z)

Each part contributes ε amount of Energy to E_{Tot}

$$\Rightarrow \text{If } \frac{1}{X}\frac{d^2X}{dx^2} = -\frac{2m\varepsilon_x}{\hbar^2} \quad (11)$$

$$+ \frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2m}{\hbar^2}\varepsilon_y$$

$$+ \frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{2m}{\hbar^2}\varepsilon_z$$

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{2m}{\hbar^2}\underbrace{(\varepsilon_x + \varepsilon_y + \varepsilon_z)}_{E}$$

Consider (11)

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{2m\varepsilon_x}{\hbar^2} \Rightarrow \frac{d^2X}{dx^2} = -\frac{2m\varepsilon_x}{\hbar^2}X \Rightarrow \frac{d^2X}{dx^2} + \frac{2m\varepsilon_x}{\hbar^2}X = 0$$

Like 1D Particle in a box.

$$\Rightarrow \left.\begin{array}{l} \dfrac{d^2X}{dx^2} + \dfrac{2m\varepsilon_x}{\hbar^2}X = 0 \\[2ex] \dfrac{d^2Y}{dy^2} + \dfrac{2m\varepsilon_y}{\hbar^2}Y = 0 \\[2ex] \dfrac{d^2Z}{dz^2} + \dfrac{2m\varepsilon_z}{\hbar^2} = 0 \end{array}\right\} \text{3 } \underbrace{\text{1D box problems!}}$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0 \xrightarrow{\text{Soln}} \psi = B\sin\left(\frac{2\pi}{\hbar}(2mE)^{1/2}\ell\right)$$

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E$$

$$\hbar = \frac{h}{2\pi} \Rightarrow \hbar^2 = \frac{h^2}{4\pi^2}$$

$$E_n = \frac{n^2h^2}{8m\ell^2} = \frac{n^2\hbar^2\pi^2}{2m\ell^2}$$

$$\Rightarrow \varepsilon_{nx} = \frac{n_x^2h^2}{8m\ell_x^2}$$

Stationary wave Eqn:

$$\psi = B\sin\left(\frac{2\pi}{\hbar}(2mE)^{1/2}\ell\right) \qquad E_{n_xn_yn_z} = \varepsilon_{nx} + \varepsilon_{ny} + \varepsilon_{nz} = \frac{h^2}{8m}\left(\left(\frac{n_x}{\ell_x}\right)^2 + \left(\frac{n_y}{\ell_y}\right)^2 + \left(\frac{n_z}{\ell_z}\right)^2\right)$$

ℓ is the length of the box.
ℓ in that case is the total length occupied by the wave/e^-.

Also:

$$\psi_{(x)} = \left(\frac{2}{\ell}\right)^{1/2}\sin\left(\frac{n\pi x}{\ell}\right) \quad \text{Stationary wave eqn.}$$

$$X = A_x\sin\left(\frac{2\pi}{\hbar}(2m\varepsilon_x)^{1/2}L_x\right)$$

$$\Rightarrow X_{(x)} = \left(\frac{2}{L_x}\right)^{1/2}\sin\left(\frac{n_x\pi x}{L_x}\right)$$

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

$$\boxed{\Rightarrow \psi(x,y,z) = A\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right)\sin\left(\frac{n_z\pi z}{L_z}\right)} \quad \psi_{n_xn_yn_z}$$

$$\boxed{E_{n_xn_yn_z} = \frac{h^2}{8m}\left(\left(\frac{n_x}{\ell_x}\right)^2 + \left(\frac{n_y}{\ell_y}\right)^2 + \left(\frac{n_z}{\ell_z}\right)^2\right)}$$

G.S Energy is $E_{111} = \dfrac{h^2}{8m}\left(\dfrac{1}{L_x^2} + \dfrac{1}{L_y^2} + \dfrac{1}{L_z^2}\right)$

If box is a cube $L_x = L_y = L_z = L$

$$\frac{h^2}{8m} \cdot \frac{1}{L^2} \cdot (n_x^2 + n_y^2 + n_z^2)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2}\right) = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$$

$$\therefore \text{G.S Energy} = E_{111} = \frac{3\hbar^2\pi^2}{2mL^2} = \frac{3h^2}{8mL^2}$$

$h = \hbar 2\pi$

$$\frac{3(\hbar^2 \cancel{4}\pi^2)}{\cancel{8}mL^2}$$ 2

Degeneracy.

For the next higher level, 3 states have the same Energy

Same L, cube $\frac{\hbar^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) = \psi_{121}, \underbrace{\psi_{211}, \psi_{112}}_{}$

Different states. as probability densities are different

$\Rightarrow$ Same Energy Different States.

$$|\psi_{211}| = |A|^2 \sin^2\left(\frac{2\pi x}{L}\right)\sin^2\left(\frac{\pi y}{L}\right)\sin^2\left(\frac{\pi z}{L}\right) \neq |A|^2 \sin^2\left(\frac{\pi x}{L}\right)\sin^2\left(\frac{2\pi y}{L}\right)\sin^2\left(\frac{\pi z}{L}\right) \neq |\psi_{121}|^2$$

This is called degeneracy

In the case of the cube, the next lowest E-level is threefold degenerate

$$E_{211} = E_{121} = E_{112} = \frac{3\hbar^2\pi^2}{mL^2}$$

G.S is non-degenerate. Threefold degeneracy of the first excited state is removed $L_x \neq L_y \neq L_z$

Degeneracy is intimately connected to symmetry. The greater the symmetry the higher the degeneracy of the quantum states.