D.N.R.COLLEGE (AUTONOMOUS): BHIMAVARM
DEPARTMENT OF PG CHEMISTRY

GENERAL CHEMISTRY –II

II SEMESTER
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UNIT-I

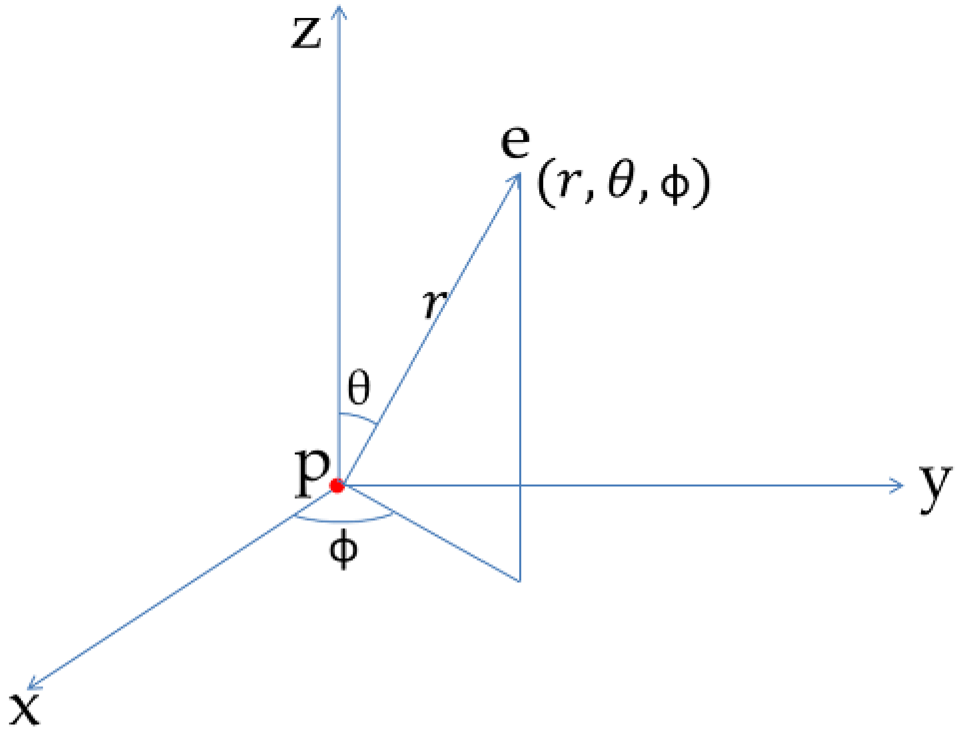
BASIC QUANTUM CHEMISTRY-I

The Schrödinger equation is a fundamental equation in quantum mechanics that describes how the quantum state of a physical system changes over time. When applied to the hydrogen atom, the Schrödinger equation provides solutions that describe the allowed energy levels and corresponding wavefunctions of the electron.

For the hydrogen atom, which consists of a single proton and a single electron, we solve the time-independent Schrödinger equation in spherical coordinates because of the spherical symmetry of the problem. The time-independent Schrödinger equation is given by:

$$\mathbf{H\hat{}\psi=E\psi}$$

where $H\hat{}$ is the Hamiltonian operator, E is the energy of the system, and ψ is the wavefunction of the electron.



The Hamiltonian for the Hydrogen Atom

In spherical coordinates (r,θ,ϕ), the Hamiltonian for the hydrogen atom is:

$$\mathbf{H\hat{} = -\hbar^2/2\mu\nabla 2 - e^2/4\pi\epsilon_0 r}$$

where:

- $\hbar$ is the reduced Planck's constant.

- μ is the reduced mass of the electron-proton system, which for hydrogen can be approximated as the electron mass m.
- e is the elementary charge.
- ϵ_0 is the permittivity of free space.
- r is the radial distance from the nucleus
- ∇^2 is the Laplacian operator in spherical coordinates.

Schrodinger Wave equation for Hydrogen atom

Hydrogen atom contains 1 $e^{\ominus}$ and 1 proton. So simplest form of all atomic systems becomes a hydrogen atom.

According to schrodinger wave equation (in simplest form)

$$H\psi = E\psi \longrightarrow (1)$$

$$\hat{H} = \hat{T} + \hat{V} \qquad [\because \text{Total Energy} = K.E + P.E]$$

where.

$\hat{H} \longrightarrow$ Total energy of Hamiltion operator

$\hat{T} \longrightarrow$ Kinetic Energy

$\hat{V} \longrightarrow$ potential Energy

According to quantum postulates

$$K.E = \hat{T} = \frac{-h^2}{8\pi^2 m}\nabla^2 \longrightarrow (2)$$

[Here K.E from setting up of operators

Schrodinger wave equation

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

here $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ [T.E = K.E + P.E

$\because E = T + V$

$E - V = T$]

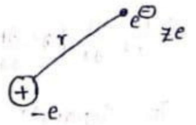
$\nabla^2 \longrightarrow$ Laplacian operator

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

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

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

$$\therefore K.E = \hat{T} = \frac{-h^2}{8\pi^2 m}\nabla^2]$$



$$P.E = \hat{V} = \frac{(-e)(ze)}{r} = \frac{-ze^2}{r}$$

Atomic number of Hydrogen (H) z = 1

$$P.E = \hat{V} = \frac{-e^2}{r} \text{———} (3)$$

where,

z → atomic Number

r → distance

e → charge on atom

potential Energy can be written on the basis of no of interactions. In hydrogen atom there are one $e^{\ominus}$ & one proton so there will be only one interaction $(Z=1)$

Substitute eq ② & eq ③ in eq ①

$$\hat{H}\psi = E\psi$$

$$\left(\frac{-h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r}\right)\psi(x,y,z) = E\psi(x,y,z)$$

This is the Schrodinger wave equation w.r.to Cartesian Coordinates.

Spherical polar coordinates (r,θ,ϕ) are more convesion to explain the shapes of the orbitals of hydrogen atom.

Schrodinger wave equation in terms of Spherical polar coordinates can be written as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)\psi = 0 \quad \text{——— (4)}$$

Total Wave function is Separated into the functions of three parts (r,θ,ϕ)

$$\psi(r,\theta,\phi) = R(r)\,T(\theta)\,Z(\phi)$$

$$\psi = RTZ$$

Sub $\psi = RTZ$ in eq (4)

$$④ \Rightarrow \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}(RTZ)\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}(RTZ)\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}(RTZ) + \frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)(RTZ) = 0$$

$$\frac{TZ}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{RZ}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right) + \frac{RT}{r^2\sin^2\theta}\frac{\partial^2 Z}{\partial\phi^2} + \frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)(RTZ)$$

To Separate Z-part, Multiply above eq. with $\frac{r^2\sin^2\theta}{RTZ}$

$$\frac{\cancel{r^2}\sin^2\theta}{R\cancel{T}\cancel{Z}}\cdot\frac{\cancel{TZ}}{\cancel{r^2}}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{r^2\sin^2\theta}{\cancel{R}T\cancel{Z}}\frac{\cancel{RZ}}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right) + \frac{r^2\sin^2\theta}{RTZ}\frac{RT}{r^2\sin^2\theta}\frac{\partial^2 Z}{\partial\phi^2} + \frac{r^2\sin^2\theta}{RT\cancel{Z}}\frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)(R\cancel{T}Z) = 0$$

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{T}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)+\frac{1}{Z}\frac{\partial^2 Z}{\partial\phi^2}+r^2\sin^2\theta\frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)=0$$

Let Z-part

Let us consider $\frac{1}{Z}\cdot\frac{\partial^2 Z}{\partial\phi^2}=-m^2$

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{T}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)-m^2+\frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)r^2\sin^2\theta=0$$

divide the above equation with $\sin^2\theta$

$$\underbrace{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)}_{\text{R-part}}+\underbrace{\frac{1}{T\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)}_{\text{T-part}}-\underbrace{\frac{m^2}{\sin^2\theta}}_{\text{T-part}}+\underbrace{\frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)r^2}_{\text{R-part}}=0$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)r^2+\frac{1}{T\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)-\frac{m^2}{\sin^2\theta}=0$$

Let R-part

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)r^2=\beta$$

Let T-part

$$\frac{1}{T\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)-\frac{m^2}{\sin^2\theta}=-\beta$$

Solutions for three component equation

1. Solution for Z-part

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial\phi^2}=-m^2$$

$$\frac{\partial^2 Z}{\partial\phi^2}=-m^2 Z$$

$$\frac{\partial^2 Z}{\partial\phi^2}+m^2 Z=0$$

(m: Magnetic quantum Number = 0, ±1, ±2)

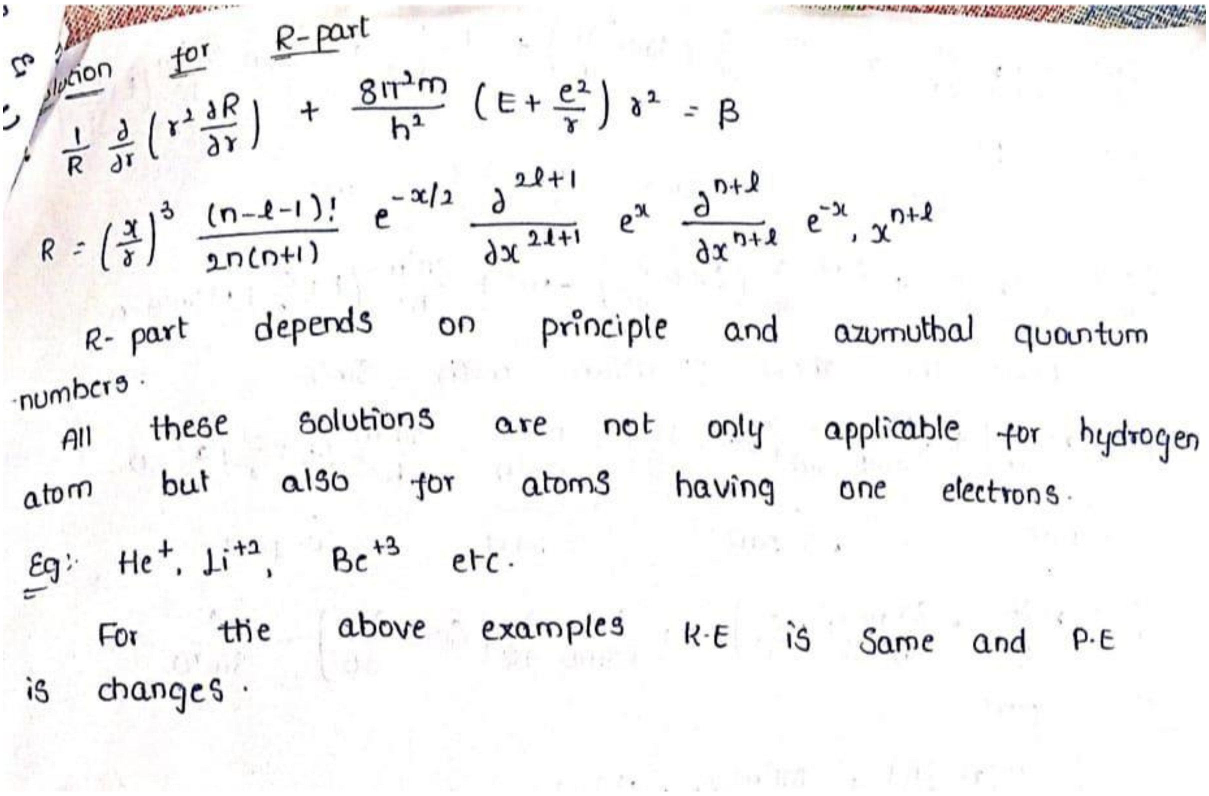
$$\Rightarrow Z=\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

2. Solution for T-part

$$\frac{1}{T\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)-\frac{m^2}{\sin^2\theta}=-\beta$$

$$\Rightarrow T=\sqrt{\left(\frac{2l+1}{2}\right)\frac{(l-|M|!)}{(l+|M|!)}}\,(1-x)^{|M|/2}\frac{\partial^{|M|}}{\partial x^{|M|}}\frac{1}{2l\,l!}\frac{\partial^{l}}{\partial x^{l}}(x^2-l)$$

T-part depends on Azumuthal quantum number (l) and Magnetic quantum number (m).



lution for R-part

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right) r^2 = \beta$$

$$R = \left(\frac{x}{r}\right)^3 \frac{(n-l-1)!}{2n(n+1)} e^{-x/2} \frac{\partial^{2l+1}}{\partial x^{2l+1}} e^{x} \frac{\partial^{n+l}}{\partial x^{n+l}} e^{-x}, x^{n+l}$$

R- part depends on principle and azumuthal quantum numbers.

All these solutions are not only applicable for hydrogen atom but also for atoms having one electrons.

Eg: He^+, Li^{+2}, Be^{+3} etc.

For the above examples K.E is Same and P.E is changes.

VARIATION PRINCIPLE

The variation principle, also known as the variational principle, is a fundamental concept in quantum mechanics used to approximate the ground state energy and wavefunction of a quantum system. It is particularly useful when the exact solution of the Schrödinger equation is not feasible.

Basic Concept of the Variation Principle

The variational principle states that for any trial wavefunction ψ_{trial} that is normalized (i.e., $\psi_{trial}=1$, the expectation value of the Hamiltonian $\hat{H}$using this trial wavefunction provides an upper bound to the true ground state energy E_0:

$$E_0 \leq \langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle$$

-: Variation theorem :-

Statement :- If $\hat{H}$ is the Hamitonion of the discrete system then the trail energy of the system is always grater then the energy of the system.

$$\boxed{E \geq E_0} \longrightarrow ①$$

where E = Trail energy
E_0 = True energy.

the above eqn is the mathametical formula of variation theorem.

From Schrodinger wave eqn

$$\hat{H}\psi = E\psi \longrightarrow ②$$

multiply with ψ^* on b.s

$$\psi^* \hat{H}\psi = \psi^* E\psi$$

Integrating on b.s

$$\int \psi^* \hat{H} \psi \, d\tau = \int \psi^* E \psi \, d\tau$$

$$E_0 = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

If ψ is normalised then $\int \psi^* \psi \, d\tau = 1$

$$E = \int \psi^* \hat{H} \psi \, d\tau$$

The wave function (ψ) which is replaced by-ano trail function (ϕ)

$$E = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau}$$

Conclusion:- ψ is replaced by ϕ.
the trail energy is always grater than ground state energy of system.

Applications:-

- calculate the ground state energy of one-d harmonic oscillator by using variation theorem (or) principle.

⇒ let us consider a particle of mass "m" which oscillates with reference to a fixed position point.

⇒ The force acting on the above system can be directly proportional to the displacement ~~of~~ in opposite direction.

$$f \propto -x$$
$$f = -kx$$

The potential energy of the system can be obtained by overall integral of force acting on the system.

$$V = -\int f\,dx \qquad \left[\int x^n dx = \frac{x^{n+1}}{n+1}\right]$$
$$V = -\int -kx\,dx$$
$$V = k\int x^1\,dx$$
$$V = k\frac{x^2}{2} \longrightarrow ③$$

let us consider K.E of the system is ~~to be~~

$$KE = \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} \longrightarrow ④$$

Hamiltanion operator is

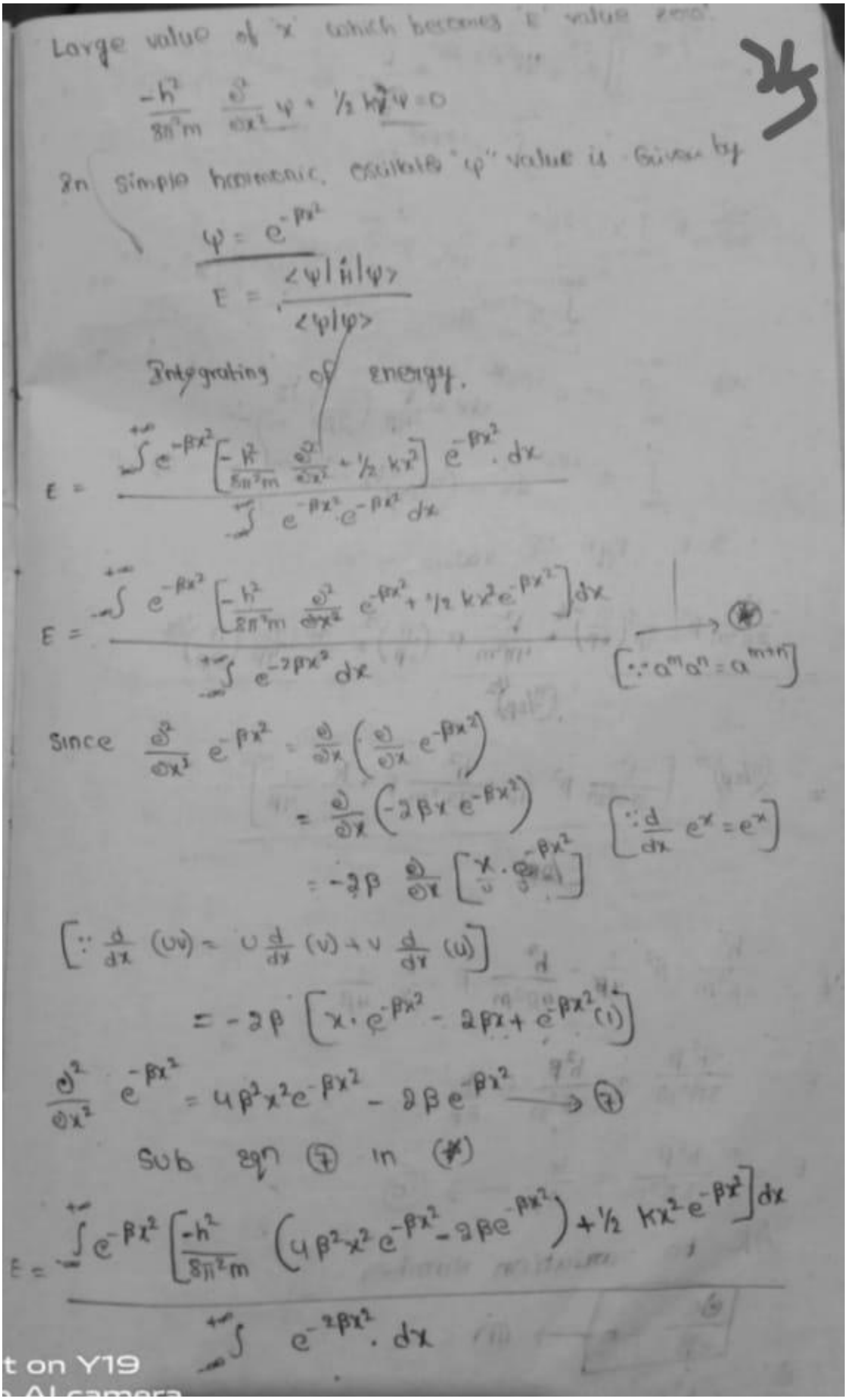
$$\hat{H} = KE + PE$$

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 \longrightarrow ⑤$$

$$H\psi = E\psi \longrightarrow ⑥$$

Sub eqn ⑤ in ⑥

$$\frac{-h^2}{2m}\frac{\partial^2}{\partial x^2}\psi + \frac{1}{2}kx^2\psi = E\psi$$



Large value of 'x' which becomes 'E' value zero.

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}\psi + \frac{1}{2}kx^2\psi = 0$$

In simple harmonic oscillator "ψ" value is Given by

$$\psi = e^{-\beta x^2}$$

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

Integrating of energy.

$$E = \frac{\int_{-\infty}^{+\infty} e^{-\beta x^2}\left[\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right]e^{-\beta x^2}\cdot dx}{\int_{-\infty}^{+\infty} e^{-\beta x^2}\cdot e^{-\beta x^2}\,dx}$$

$$E = \frac{\int_{-\infty}^{+\infty} e^{-\beta x^2}\left[\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}e^{-\beta x^2} + \frac{1}{2}kx^2 e^{-\beta x^2}\right]dx}{\int_{-\infty}^{+\infty} e^{-2\beta x^2}\,dx} \longrightarrow (*)$$

$$\left[\because a^m a^n = a^{m+n}\right]$$

$$\text{Since } \frac{\partial^2}{\partial x^2}e^{-\beta x^2} = \frac{\partial}{\partial x}\left(\frac{\partial}{\partial x}e^{-\beta x^2}\right)$$

$$= \frac{\partial}{\partial x}\left(-2\beta x\, e^{-\beta x^2}\right) \qquad \left[\because \frac{d}{dx}e^x = e^x\right]$$

$$= -2\beta\frac{\partial}{\partial x}\left[\underset{u}{x}\cdot \underset{v}{e^{-\beta x^2}}\right]$$

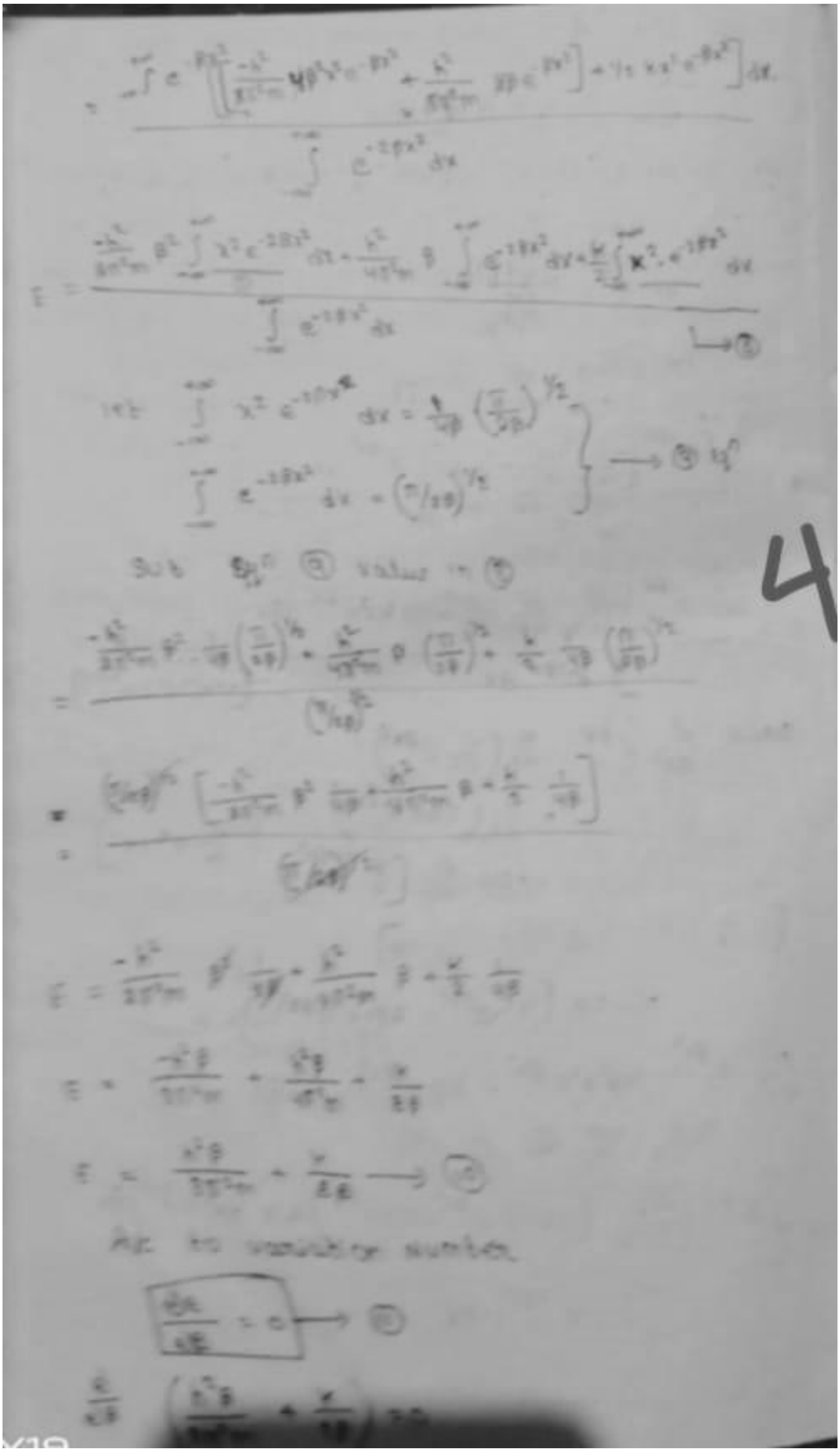
$$\left[\because \frac{d}{dx}(uv) = u\frac{d}{dx}(v) + v\frac{d}{dx}(u)\right]$$

$$= -2\beta\left[x\cdot e^{-\beta x^2} - 2\beta x + e^{-\beta x^2}(1)\right]$$

$$\frac{\partial^2}{\partial x^2}e^{-\beta x^2} = 4\beta^2 x^2 e^{-\beta x^2} - 2\beta e^{-\beta x^2} \longrightarrow ⑦$$

Sub eqn ⑦ in (*)

$$E = \frac{\int_{-\infty}^{+\infty} e^{-\beta x^2}\left[\frac{-h^2}{8\pi^2 m}\left(4\beta^2 x^2 e^{-\beta x^2} - 2\beta e^{-\beta x^2}\right) + \frac{1}{2}kx^2 e^{-\beta x^2}\right]dx}{\int_{-\infty}^{+\infty} e^{-2\beta x^2}\cdot dx}$$



$$= \frac{\int_{-\infty}^{+\infty} e^{-\beta x^2}\left[\left[\frac{-h^2}{8\pi^2 m}4\beta^2 x^2 e^{-\beta x^2} + \frac{h^2}{8\pi^2 m}2\beta e^{-\beta x^2}\right] + \frac{1}{2}kx^2 e^{-\beta x^2}\right]dx}{\int_{-\infty}^{+\infty} e^{-2\beta x^2}dx}$$

$$E = \frac{\frac{-h^2}{2\pi^2 m}\beta^2 \int_{-\infty}^{+\infty} x^2 e^{-2\beta x^2}dx + \frac{h^2}{4\pi^2 m}\beta \int_{-\infty}^{+\infty} e^{-2\beta x^2}dx + \frac{k}{2}\int_{-\infty}^{+\infty} x^2 e^{-2\beta x^2}dx}{\int_{-\infty}^{+\infty} e^{-2\beta x^2}dx} \longrightarrow ②$$

WKT
$$\left.\begin{aligned} \int_{-\infty}^{+\infty} x^2 e^{-2\beta x^2}dx &= \frac{1}{4\beta}\left(\frac{\pi}{2\beta}\right)^{1/2} \\ \int_{-\infty}^{+\infty} e^{-2\beta x^2}dx &= \left(\pi/2\beta\right)^{1/2} \end{aligned}\right\} \longrightarrow ③ \; \& \; ④$$

Sub eq^n ③ value in ②

$$= \frac{\frac{-h^2}{2\pi^2 m}\beta^2 \cdot \frac{1}{4\beta}\left(\frac{\pi}{2\beta}\right)^{1/2} + \frac{h^2}{4\pi^2 m}\beta\left(\frac{\pi}{2\beta}\right)^{1/2} + \frac{k}{2}\cdot\frac{1}{4\beta}\left(\frac{\pi}{2\beta}\right)^{1/2}}{\left(\pi/2\beta\right)^{1/2}}$$

$$= \frac{\cancel{\left(\pi/2\beta\right)^{1/2}}\left[\frac{-h^2}{2\pi^2 m}\beta^2\frac{1}{4\beta} + \frac{h^2}{4\pi^2 m}\beta + \frac{k}{2}\,\frac{1}{4\beta}\right]}{\cancel{\left(\pi/2\beta\right)^{1/2}}}$$

$$E = \frac{-h^2}{2\pi^2 m}\beta^2\,\frac{1}{4\beta} + \frac{h^2}{4\pi^2 m}\beta + \frac{k}{2}\,\frac{1}{4\beta}$$

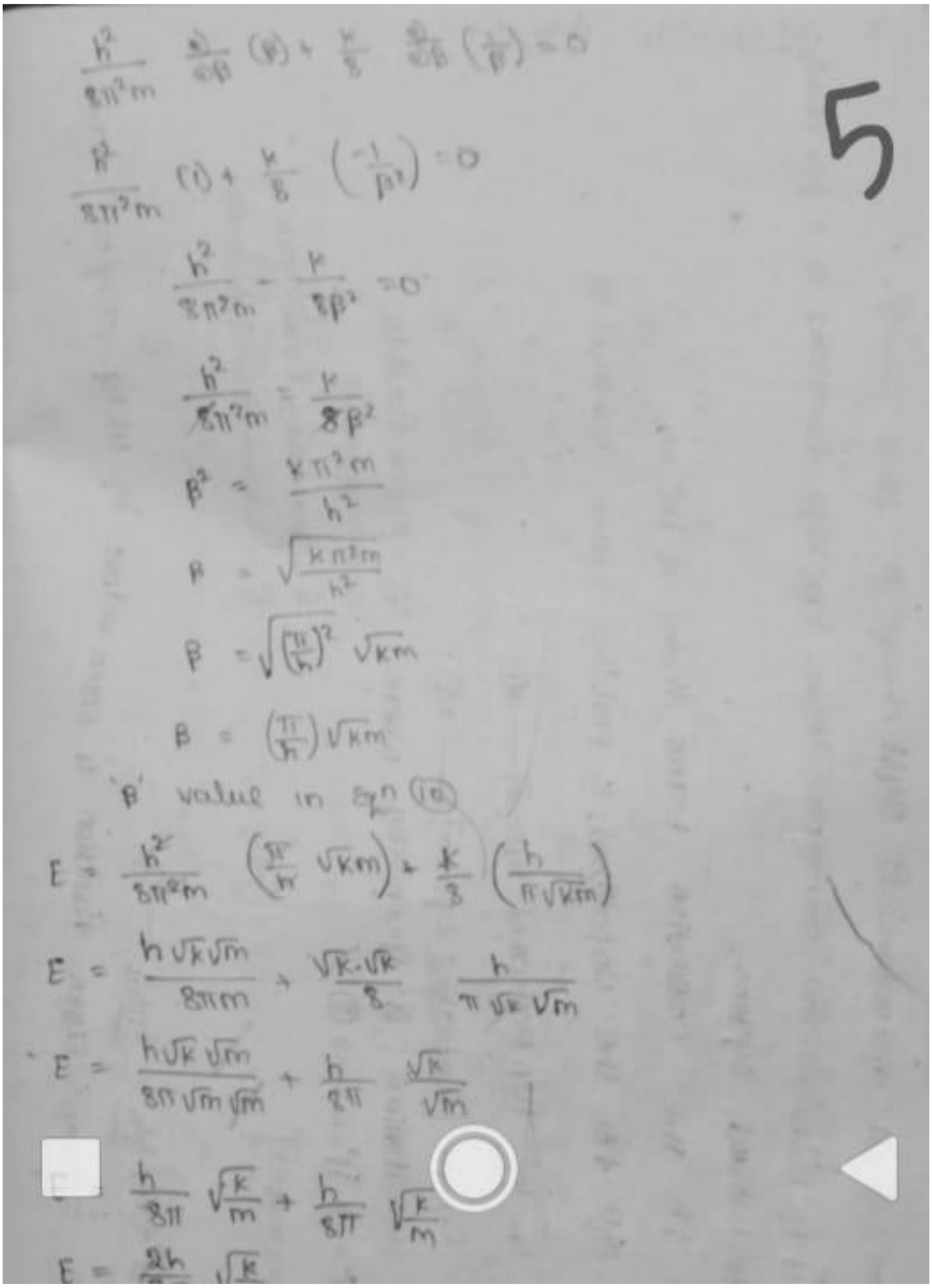
$$E = \frac{-h^2\beta}{8\pi^2 m} + \frac{h^2\beta}{4\pi^2 m} + \frac{k}{8\beta}$$

$$E = \frac{h^2\beta}{8\pi^2 m} + \frac{k}{8\beta} \longrightarrow ⑤$$

Ac. to variation method

$$\boxed{\frac{dE}{d\beta} = 0} \longrightarrow ⑥$$

$$\frac{d}{d\beta}\left(\frac{h^2\beta}{8\pi^2 m} + \frac{k}{8\beta}\right) = 0$$



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$$\frac{h^2}{8\pi^2 m}\frac{\partial}{\partial\beta}(\beta) + \frac{k}{8}\frac{\partial}{\partial\beta}\left(\frac{1}{\beta}\right) = 0$$

$$\frac{h^2}{8\pi^2 m}(1) + \frac{k}{8}\left(\frac{-1}{\beta^2}\right) = 0$$

$$\frac{h^2}{8\pi^2 m} - \frac{k}{8\beta^2} = 0$$

$$\frac{h^2}{\cancel{8}\pi^2 m} = \frac{k}{\cancel{8}\beta^2}$$

$$\beta^2 = \frac{k\pi^2 m}{h^2}$$

$$\beta = \sqrt{\frac{k\pi^2 m}{h^2}}$$

$$\beta = \sqrt{\left(\frac{\pi}{h}\right)^2}\sqrt{km}$$

$$\beta = \left(\frac{\pi}{h}\right)\sqrt{km}$$

'β' value in eqn ⑩

$$E = \frac{h^2}{8\pi^2 m}\left(\frac{\pi}{h}\sqrt{km}\right) + \frac{k}{8}\left(\frac{h}{\pi\sqrt{km}}\right)$$

$$E = \frac{h\sqrt{k}\sqrt{m}}{8\pi m} + \frac{\sqrt{k}\cdot\sqrt{k}}{8}\ \frac{h}{\pi\sqrt{k}\sqrt{m}}$$

$$E = \frac{h\sqrt{k}\sqrt{m}}{8\pi\sqrt{m}\sqrt{m}} + \frac{h}{8\pi}\frac{\sqrt{k}}{\sqrt{m}}$$

$$\frac{h}{8\pi}\sqrt{\frac{k}{m}} + \frac{h}{8\pi}\sqrt{\frac{k}{m}}$$

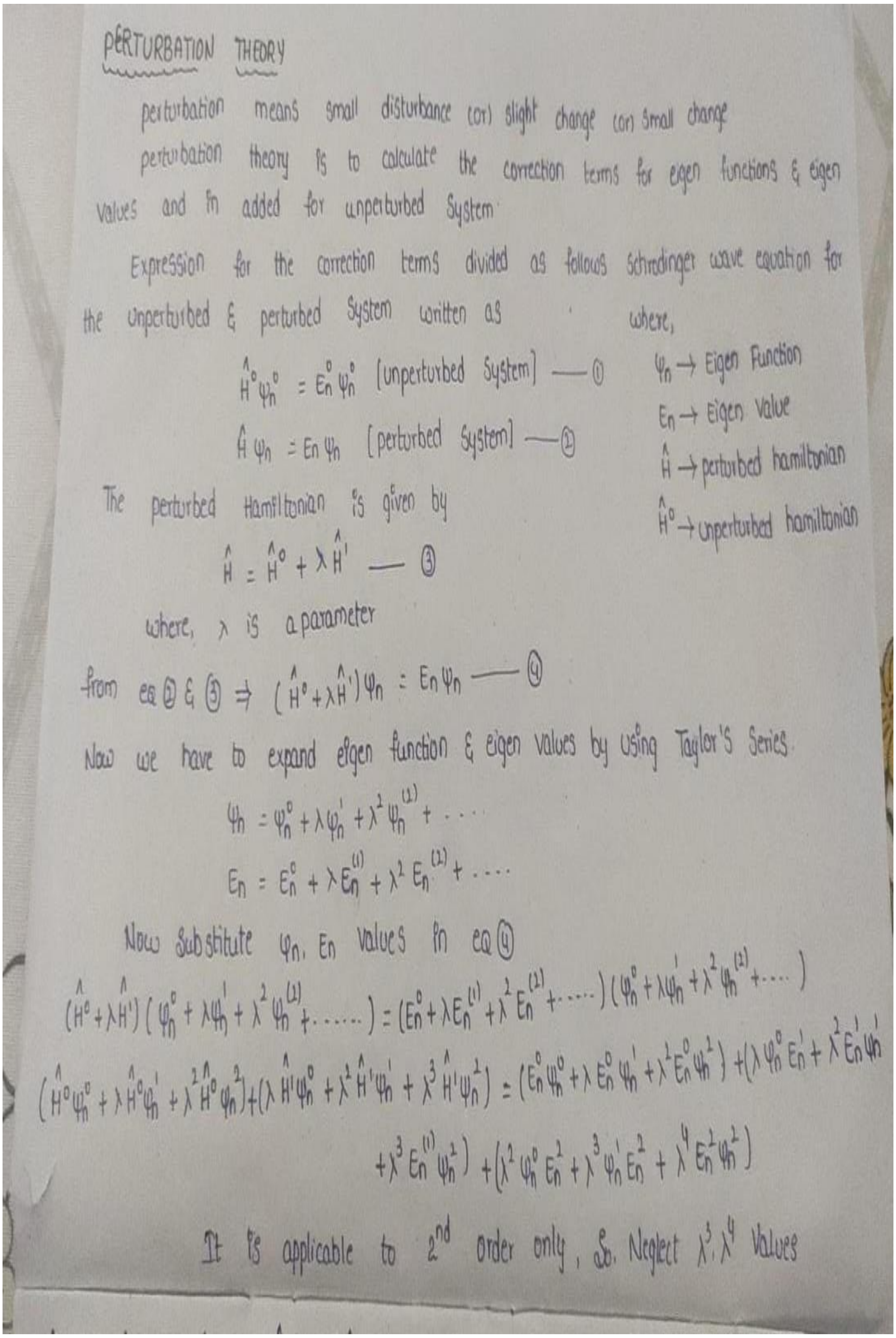
$$E = 2h\ \sqrt{k}$$

PERTURBATION THEORY:

Perturbation theory is a mathematical approach used in quantum mechanics to find an approximate solution to a complex problem by starting from the exact solution of a simpler, related problem. It is particularly useful when the Hamiltonian of a system can be divided into a solvable part and a small perturbation.

Types of Perturbation Theory

1. **Time-Independent Perturbation Theory:**
    - Used for systems where the perturbation does not depend on time.
    - Applicable to both non- degenerate and degenerate cases.



PERTURBATION THEORY

perturbation means small disturbance (or) slight change (or) Small change

perturbation theory is to calculate the correction terms for eigen functions & eigen values and in added for unperturbed System

Expression for the correction terms divided as follows Schrodinger wave equation for the Unperturbed & perturbed System written as

$$\hat{H}^0 \psi_n^0 = E_n^0 \psi_n^0 \text{ [unperturbed System]} \text{ — } ①$$

$$\hat{H} \psi_n = E_n \psi_n \text{ [perturbed System]} \text{ — } ②$$

where,

$\psi_n \rightarrow$ Eigen Function

$E_n \rightarrow$ Eigen Value

$\hat{H} \rightarrow$ perturbed hamiltonian

$\hat{H}^0 \rightarrow$ unperturbed hamiltonian

The perturbed Hamiltonian is given by

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}' \text{ — } ③$$

where, λ is a parameter

from eq ② & ③ $\Rightarrow (\hat{H}^0 + \lambda \hat{H}') \psi_n = E_n \psi_n$ — ④

Now we have to expand eigen function & eigen values by using Taylor's Series.

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^{(2)} + \cdots$$

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

Now Substitute ψ_n, E_n values in eq ④

$$(\hat{H}^0 + \lambda \hat{H}')(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^{(2)} + \cdots) = (E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^{(2)} + \cdots)$$

$$(\hat{H}^0 \psi_n^0 + \lambda \hat{H}^0 \psi_n^1 + \lambda^2 \hat{H}^0 \psi_n^2) + (\lambda \hat{H}' \psi_n^0 + \lambda^2 \hat{H}' \psi_n^1 + \lambda^3 \hat{H}' \psi_n^2) = (E_n^0 \psi_n^0 + \lambda E_n^0 \psi_n^1 + \lambda^2 E_n^0 \psi_n^2) + (\lambda \psi_n^0 E_n^1 + \lambda^2 E_n^1 \psi_n^1$$
$$+ \lambda^3 E_n^{(1)} \psi_n^2) + (\lambda^2 \psi_n^0 E_n^2 + \lambda^3 \psi_n^1 E_n^2 + \lambda^4 E_n^2 \psi_n^2)$$

It is applicable to 2nd order only, So. Neglect λ^3, λ^4 Values

$$\hat{H}^0\psi_n^0 + \lambda\hat{H}^0\psi_n^1 + \lambda^2\hat{H}^0\psi_n^2 + \lambda\hat{H}'\psi_n^0 + \lambda^2\hat{H}'\psi_n^1 = E_n^0\psi_n^0 + \lambda E_n^0\psi_n^1 + \lambda^2 E_n^0\psi_n^2 + \lambda\psi_n^0 E_n^1 + \lambda^2 E_n^1\psi_n^1 + \lambda^2\psi_n^0 E_n^2$$

$$\hat{H}^0\psi_n^0 + \lambda\hat{H}^0\psi_n^1 + \lambda^2\hat{H}^0\psi_n^2 + \lambda\hat{H}'\psi_n^0 + \lambda^2\hat{H}'\psi_n^1 - E_n^0\psi_n^0 - \lambda E_n^0\psi_n^1 - \lambda^2 E_n^0\psi_n^2 - \lambda\psi_n^0 E_n^1 - \lambda^2 E_n^1\psi_n^1 - \lambda^2\psi_n^0 E_n^2$$

$$(\hat{H}^0 - \hat{E}_n^0)\psi_n^0 + \lambda(\hat{H}^0\psi_n^1 + \hat{H}'\psi_n^0 - E_n^0\psi_n^1 - \psi_n^0 E_n^1) + \lambda^2(\hat{H}^0\psi_n^2 + \hat{H}'\psi_n^1 - E_n^0\psi_n^2 - E_n^1\psi_n^1 - \psi_n^0 E_n^2) = 0$$

The above equation represent the coefficient of each power is λ

Individually i.e $\lambda^0 = \hat{H}^0\psi_n^0 = E_n^0\psi_n^0 \longrightarrow$ ⑤

$\lambda^1 = \hat{H}^0\psi_n^1 + \hat{H}'\psi_n^0 = E_n^0\psi_n^1 + \psi_n^0 E_n^1 \longrightarrow$ ⑥

$\lambda^2 = \hat{H}^0\psi_n^2 + \hat{H}'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0 \longrightarrow$ ⑦

EQ ⑤ is the Schrodinger wave, equation for unperturbed System

EQ⑥ & eq⑦ will be proved for 1st order & 2nd order correction to be perturbed terms obtained as follows.

1st order : → correction to energy
→ correction of wave function

1. correction of Energy

Multiply eq ⑥ by ψ_n^{0*} & Integrates

According to Simple harmonic oscillator (SHO) perturbed part is odd, So the energy correction will be Zero

$$\int \psi_n^{0*}\hat{H}^0\psi_n^1\,d\tau + \int \psi_n^{0*}\hat{H}'\psi_n^0\,d\tau - \int \psi_n^{0*}E_n^0\psi_n^{(1)}\,d\tau - \int \psi_n^{0*}E_n^1\psi_n^0\,d\tau = 0$$

we are Taking only first order terms

$$\int \psi_n^{0*}\hat{H}'\psi_n^0\,d\tau - \int \psi_n^{0*}E_n^1\psi_n^0\,d\tau = 0$$

$$\int \psi_n^{0*}\hat{H}'\psi_n^0\,d\tau = \int \psi_n^{0*}E_n^1\psi_n^0\,d\tau$$

$$E_n^{(1)} = \frac{\int \psi_n^{0*} \hat{H}' \psi_n^0 \, d\tau}{\int \psi_n^{0*} \psi_n^0 \, d\tau}$$

$$E_n^1 = \int \psi^{0*} \hat{H}' \psi_n^0 \, d\tau \longrightarrow ⑧$$

$$E_n^1 = H'$$

where, $E_n^1 \rightarrow$ 1st order correction of energy

$\hat{H}' \rightarrow$ perturbation operator

$\psi_n^0 \rightarrow$ unperturbed System

2. Correction of wave Function

To determine the correction in wave function ψ_n^0

Hence $\psi_n' = a_{1n}\psi_1^0 + a_{2n}\psi_2^0 + a_{3n}\psi_3^0 + \cdots$

$$\psi_n' = \sum_{m \neq n} a_{mn} \psi_m^0 \longrightarrow ⑨$$

Eq ⑨ in eq ⑥ we get

$$(\hat{H}' - E_n')\psi_n^0 + (\hat{H}^0 - E_n^0)\psi_n' = 0$$

$$(\hat{H}' - E_n')\psi_n^0 + (\hat{H}^0 - E_n^0)\sum a_{mn}\psi_m^0 = 0 \longrightarrow ⑩$$

Multiply eq ⑩ with another function ψ_l^0 & Integrating

$$\int \psi_l^0 \hat{H}' \psi_n^0 \, d\tau - \int \psi_l^0 E_n' \psi_n^0 \, d\tau + \sum a_{mn}\left[\int \psi_l^0 \hat{H}^0 \psi_m^0 \, d\tau - \int \psi_l \psi_m^0 E_n^0 \, d\tau\right] = 0 — ⑪$$

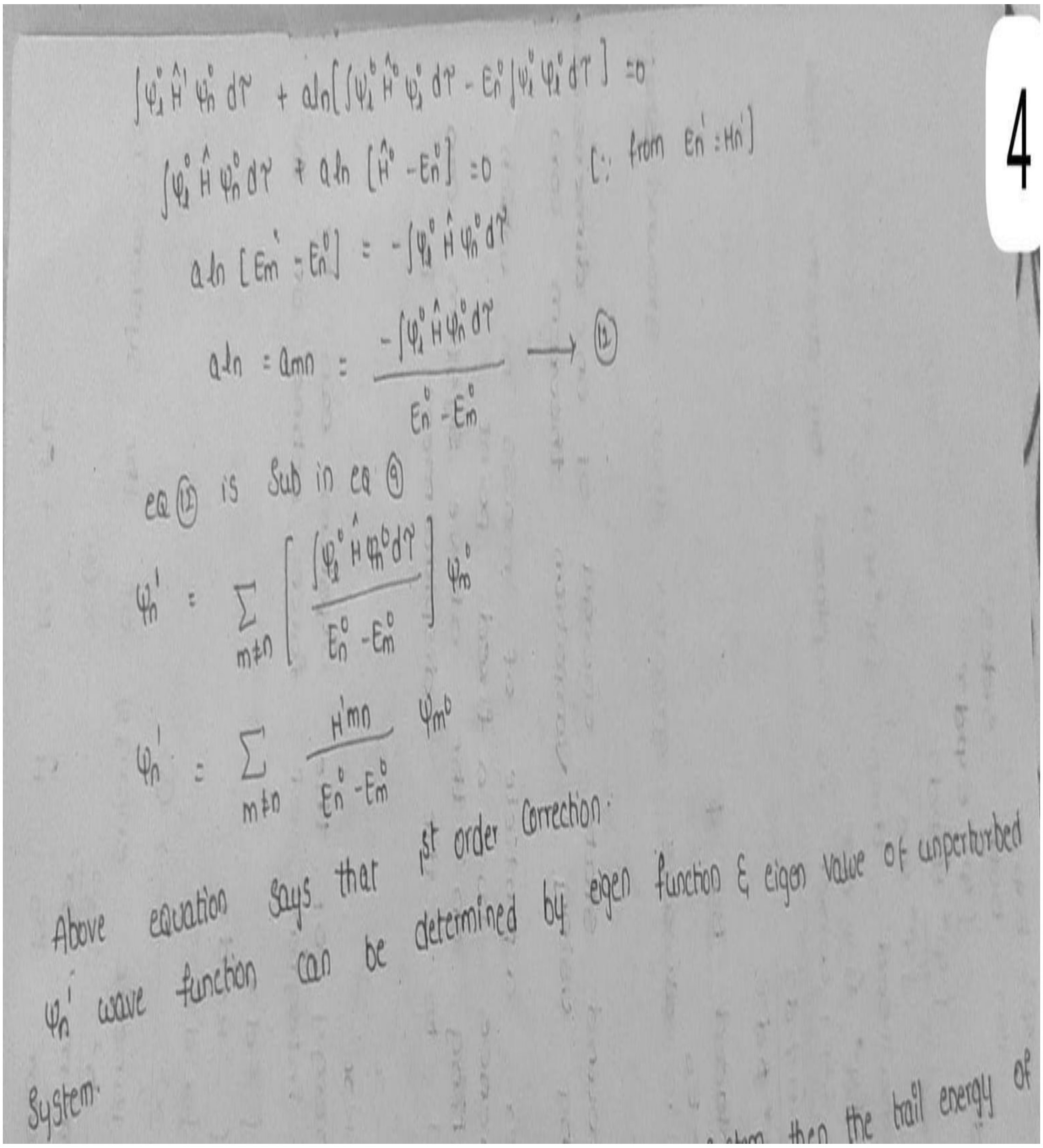
Now we can make use of parts

i) $\hat{H}\psi_m^0 = E_n^0 \psi_m^0$ [∵ $\hat{H}\psi = \hat{E}\psi$]

ii) Eigen function $\psi_l^0, \psi_m^0, \psi_n^0$ are orthonormal for $l = n$

eq ⑪ reduced to ⑧

$l \neq n$ all terms in the Summation Vanish except those $m = l$



4

$$\int \varphi_l^0 \hat{H}' \varphi_n^0 \, d\tau + a_{ln}\left[\int \varphi_l^0 \hat{H}^0 \varphi_l^0 \, d\tau - E_n^0 \int \varphi_l^0 \varphi_l^0 \, d\tau\right] = 0$$

$$\int \varphi_l^0 \hat{H} \varphi_n^0 \, d\tau + a_{ln}\left[\hat{H}^0 - E_n^0\right] = 0 \qquad [\because \text{from } E_n' = H_n']$$

$$a_{ln}\left[E_m' - E_n^0\right] = -\int \varphi_l^0 \hat{H} \varphi_n^0 \, d\tau$$

$$a_{ln} = a_{mn} = \frac{-\int \varphi_l^0 \hat{H} \varphi_n^0 \, d\tau}{E_n^0 - E_m^0} \longrightarrow ⑫$$

eq ⑫ is Sub in eq ⑨

$$\varphi_n' = \sum_{m \neq n}\left[\frac{\int \varphi_l^0 \hat{H} \varphi_n^0 \, d\tau}{E_n^0 - E_m^0}\right]\varphi_m^0$$

$$\varphi_n' = \sum_{m \neq n} \frac{H'_{mn}}{E_n^0 - E_m^0} \varphi_m^0$$

Above equation says that 1st order Correction φ_n' wave function can be determined by eigen function & eigen value of unperturbed System.

then the trail energy of

SHAPES OF ORBITALS:

In basic quantum chemistry, orbitals are regions in space where there is a high probability of finding an electron. The shapes and sizes of these orbitals are determined by the solutions to the Schrödinger equation for the hydrogen atom, but the concepts apply to other atoms as well. The primary orbitals are designated as sss, ppp, ddd, and fff orbitals, each with distinctive shapes and properties. Here is a summary of these orbitals and their shapes:

s Orbitals

- **Shape**: Spherical
- **Number of Orbitals per Energy Level**: 1
- **Nodes**: Spherical nodes where the probability of finding an electron is zero, increasing with the principal quantum number nnn.

The sorbital is the simplest, with a spherical shape centered around the nucleus. As nnn increases, the size of the sss orbital increases, and the number of radial nodes (spherical shells with zero probability) also increases.

For example:

- The 1s orbital has no nodes.
- The 2s orbital has one radial node.

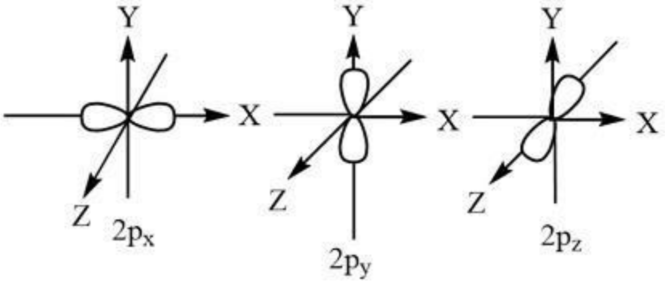
p Orbitals

- **Shape**: Dumbbell-shaped
- **Number of Orbitals per Energy Level**: 3 (denoted as pxp_xpx, pyp_ypy, and pzp_zpz)
- **Nodes**: One planar node passing through the nucleus.

The p orbitals have a dumbbell shape and are oriented along the x, y, and z axes. They have one angular node (a plane where the probability of finding an electron is zero) that passes through the nucleus.

For example:

- The 2p orbitals have one nodal plane.

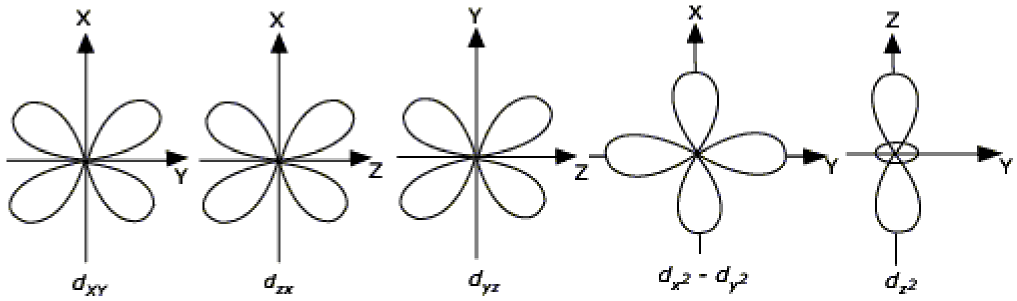


d Orbitals

- **Shape**: Complex, typically cloverleaf-shaped, and one with a doughnut shape
- **Number of Orbitals per Energy Level**: 5 (denoted as dxy, dyz, dzx, dx2−y2, and dz2
- **Nodes**: Two angular nodes.

The d orbitals are more complex:

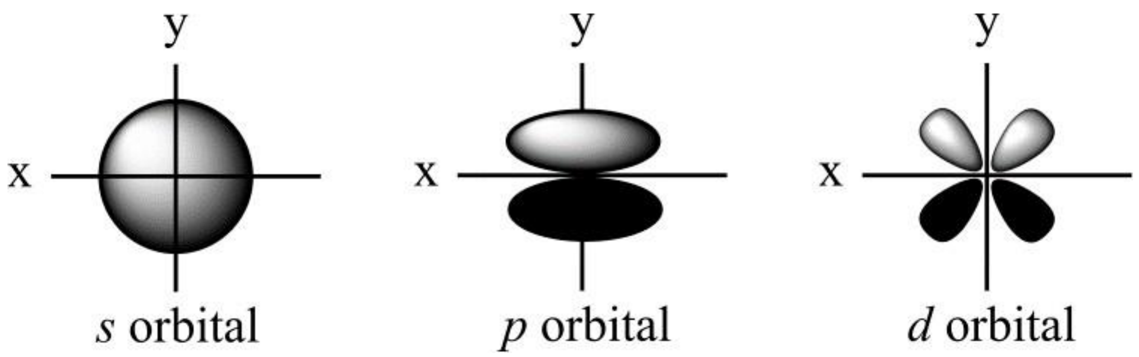
- dxy,dyz, and dzx have four lobes lying in the respective planes.
- dx2−y2 has four lobes lying along the x and y axes.
- dz2 has two lobes along the z-axis with a doughnut-shaped ring around the nucleus in the xy-plane.

- 

f Orbitals

- **Shape**: Even more complex shapes with multiple lobes
- **Number of Orbitals per Energy Level**: 7
- **Nodes**: Three angular nodes.

The f orbitals are rarely encountered in basic chemistry, as they are relevant for elements in the lanthanide and actinide series. They have very complex shapes with multiple lobes and nodes.



s orbital *p* orbital *d* orbital

Understanding the shapes of orbitals is crucial in quantum chemistry, as these shapes determine how atoms interact and bond with each other. The sss, ppp, ddd, and fff orbitals each have unique characteristics that influence the chemical properties of elements.

HARTREE-FOCK (HF) METHOD:

The Hartree-Fock (HF) method is a fundamental computational technique in quantum chemistry used to approximate the wavefunctions and energies of many-electron systems. The Hartree-Fock method is based on the assumption that the exact many-electron wavefunction can be approximated by a single Slater determinant (or a single Hartree product in the Hartree method), which is a mathematical construct that ensures the antisymmetry of the wavefunction with respect to the exchange of any two electrons (Pauli exclusion principle).

Key Concepts in Hartree-Fock Method

1. **Hartree Product and Slater Determinant:**

   - The Hartree product is a simple product of single-electron wavefunctions (orbitals). However, it does not account for the antisymmetry requirement.
   - The Slater determinant is a more sophisticated construct that ensures the wavefunction changes sign when any two electrons are exchanged, thus incorporating the Pauli exclusion principle.
2. **Fock Operator:**
   - The Hartree-Fock method introduces the Fock operator (F^), an effective one-electron Hamiltonian that includes the average effect of electron-electron repulsion.
3. **Self-Consistent Field (SCF) Procedure:**
   - The HF method uses an iterative process called the SCF procedure to solve for the optimal set of molecular orbitals.
   - The process involves guessing an initial set of orbitals, constructing the Fock matrix, solving the Fock equations to obtain new orbitals, and repeating the process until convergence is achieved.

Hartree-Fock Equations

The HF equations are derived from the variational principle, which states that the best single-determinant wavefunction is the one that minimizes the total energy of the system. The resulting equations are:

$$F^\wedge\psi i=\epsilon i\psi i$$

where:

- F^ is the Fock operator.
- ψi are the molecular orbitals.
- ϵi are the orbital energies.

Limitations and Extensions

- **Electron Correlation:** The HF method neglects electron correlation (the instantaneous interaction between electrons). To include electron correlation, post-Hartree-Fock methods such as Configuration Interaction (CI), Møller-Plesset perturbation theory (MP2), and Coupled Cluster (CC) are used.
- **Computational Cost:** The HF method scales approximately as N4 with the number of basis functions N, making it computationally demanding for large systems.

Example: Hartree-Fock Calculation for Hydrogen Molecule (H2)

1. **Initial Guess:**
   - Use atomic orbitals of hydrogen atoms as the initial guess.
2. **Construct Fock Matrix:**
   - Calculate the integrals involving overlap, kinetic energy, nuclear attraction, and electron repulsion.
3. **Solve Fock Equations:**
   - Diagonalize the Fock matrix to obtain new molecular orbitals.

4. **Form Density Matrix:**
    - Construct the density matrix using the occupied molecular orbitals.
5. **Iterate:**
    - Use the new density matrix to construct a new Fock matrix and repeat until convergence.

UNIT-II

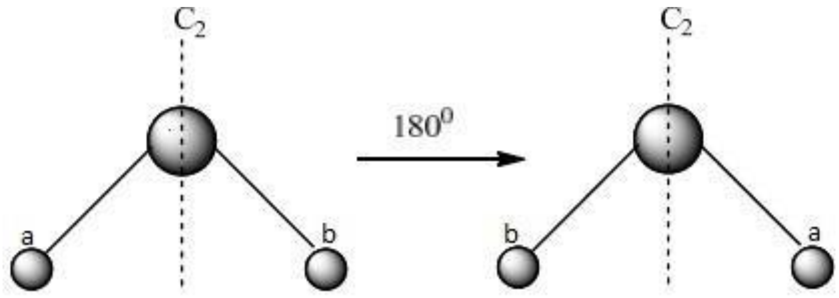
MOLECULAR SYMMETRY AND GROUP THEORY IN CHEMISTRY

Molecular symmetry is a fundamental concept in chemistry that helps to understand the properties and behavior of molecules. It involves the study of the symmetry elements and operations that describe the symmetry of a molecule. These notes provide an overview of molecular symmetry, including symmetry elements, operations, and their significance.

Symmetry Elements

Symmetry elements are geometric entities about which symmetry operations are performed. The main symmetry elements are:

1. **Identity (E)**:
   - Every molecule has at least the identity element.
   - It represents doing nothing to the molecule.
2. **Axis of Rotation (Cn_)**:
   - A rotation about an axis by 360∘/n leaves the molecule unchanged.
   - n is the order of the axis.
   - Example:C2 axis involves a 180° rotation.



C_2 axis of rotation in water molecule

Examples:

1. Ammonia (NH_3)

- **Symmetry Elements**:
  - Ammonia has a C3C_3C3 axis of rotation.
- **Description**:
  - The molecule can be rotated by 120° (or 240°) around an axis passing through the nitrogen atom and perpendicular to the plane of the hydrogen atoms.
  - After such a rotation, the molecule appears indistinguishable from its original orientation.

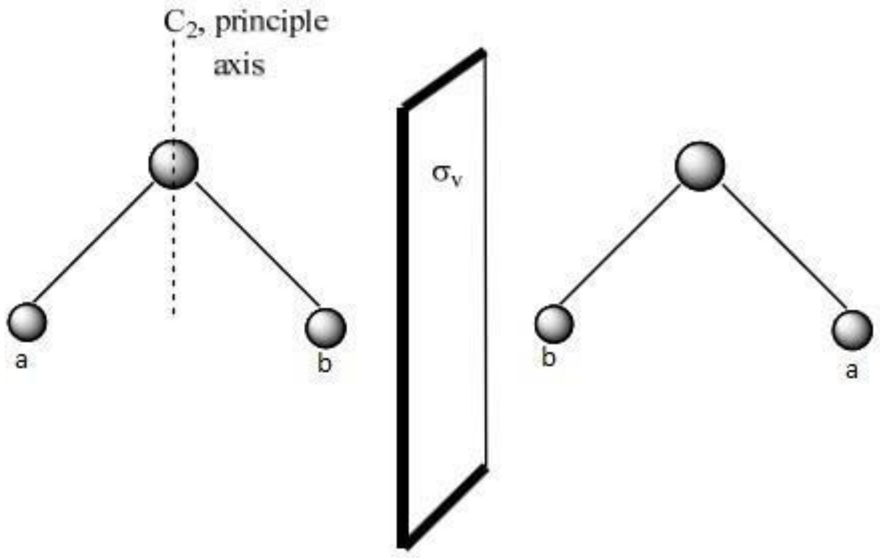
2. Benzene (C_6H_6)

- **Symmetry Elements**:
  - Benzene has a C6 axis of rotation.
- **Description**:
  - The benzene molecule can be rotated by 60° (or multiples of 60°) around an axis passing through the center of the ring and perpendicular to the plane of the ring.
  - After each 60° rotation, the molecule appears unchanged.

3. Methane (CH_4)

- **Symmetry Elements**:
  - Methane has multiple C3 axes of rotation.
- **Description**:
  - Each C3 axis passes through the central carbon atom and one of the hydrogen atoms.
  - Rotations of 120° around any of these C3 axes leave the molecule unchanged.

3. **Plane of Symmetry (σ)**:
   - A reflection through a plane leaves the molecule unchanged.
   - Types:
     - σh: Horizontal plane (perpendicular to the principal axis).
     - σv: Vertical plane (contains the principal axis).
     - σd: Dihedral plane (bisects the angle between two C2 axes).



σ_v plane of symmetry

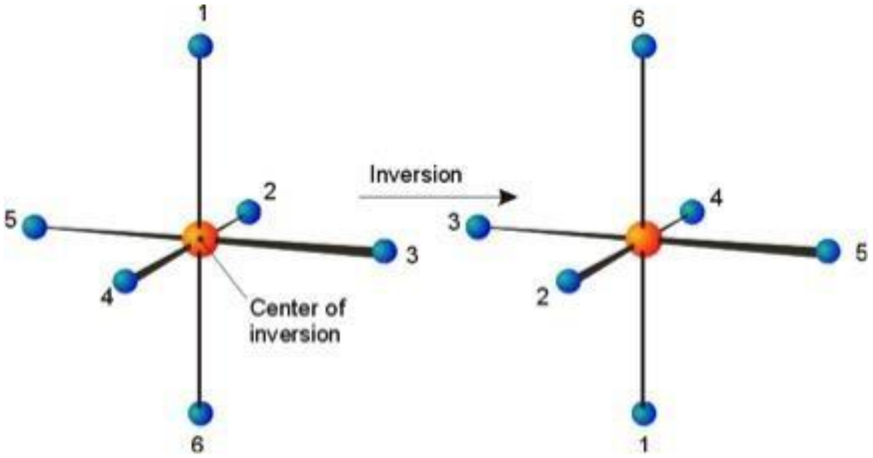
Example:

Consider a water molecule (H_2O):

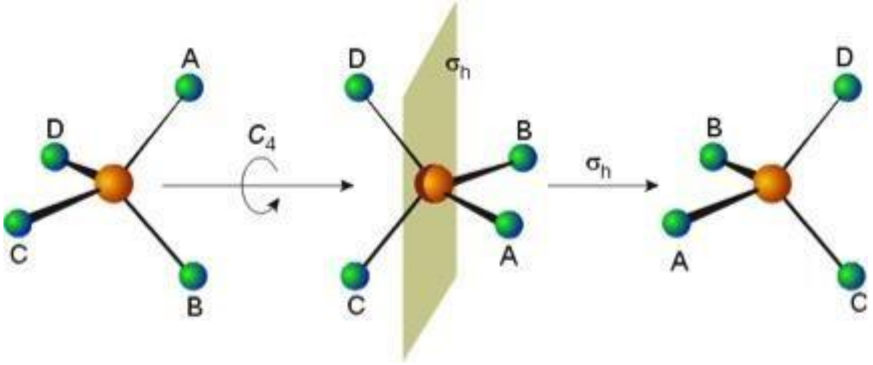
- The water molecule has a bent structure with an angle of approximately 104.5 degrees between the hydrogen atoms.
- The molecule has two planes of symmetry:
  - One plane that bisects the molecule through the oxygen atom and both hydrogen atoms (vertical plane, σv).
  - Another vertical plane that contains the oxygen atom and bisects the angle between the hydrogen atoms (another σv plane).

4. **Center of Inversion (i)**:

   - Inversion through a point at the center of the molecule leaves the molecule unchanged.



4. **Improper Axis of Rotation (Sn)**:
   - A rotation about an axis followed by a reflection through a plane perpendicular to the axis.
   - Example: S4 involves a 90° rotation followed by reflection.



Symmetry Operations

Symmetry operations are actions that move the molecule in such a way that it appears unchanged. The main symmetry operations are:

1. **Identity (E)**:
   - Doing nothing to the molecule.
2. **Rotation (Cn)**:
   - Rotation by 360∘/n about an axis.
3. **Reflection (σ)**:
   - Reflection through a symmetry plane.
4. **Inversion (i)**:
   - Each point of the molecule is moved through a center of inversion to an opposite point.
5. **Improper Rotation (Sn)**:
   - Rotation by 360∘/n followed by reflection through a perpendicular plane.

Point Groups

Point groups classify molecules according to their symmetry elements. Each point group contains a set of symmetry operations. The common point groups include:

1. **Cn_**: Contains a principal Cn axis.
2. **Cnv**: Contains a principal Cn axis and vertical planes (σv).
3. **Cnh**: Contains a principal Cn axis and a horizontal plane (σh).
4. **Dn_nn**: Contains a principal Cn axis and C2 axes perpendicular to the principal axis.
5. **Dnh**: Contains a principal Cn axis, C2 axes, and a horizontal plane (σh).
6. **Dnd_{nd}nd**: Contains a principal Cn axis, C2 axes, and dihedral planes (σd).
7. **T, Td_**: Tetrahedral symmetry.
8. **O, Oh_**: Octahedral symmetry.
9. **I, Ih_**: Icosahedral symmetry.

Determining Point Groups

To determine the point group of a molecule:

1. **Identify the highest order rotation axis (Cn)**.
2. **Check for perpendicular C2 axes**.
3. **Check for horizontal (σh) and vertical (σv) planes**.
4. **Look for center of inversion (i)**.
5. **Identify any improper rotation axes (Sn)**.

Applications of Molecular Symmetry

1. **Spectroscopy**:
   - Symmetry helps predict the activity of molecular vibrations in IR and Raman spectroscopy.
   - Determines the selection rules for electronic transitions.
2. **Molecular Orbitals**:
   - Symmetry simplifies the construction of molecular orbital diagrams.
   - Helps in determining the allowed interactions between orbitals.
3. **Chemical Reactions**:
   - Symmetry considerations can predict the feasibility and stereochemistry of reactions.
   - Woodward-Hoffmann rules in pericyclic reactions are based on symmetry properties.
4. **Crystallography**:
   - Symmetry is essential in understanding crystal structures and space groups.

Example: Water Molecule (H2O)

1. **Symmetry Elements**:
   - C2 axis: Passes through the oxygen atom and bisects the H-O-H angle.

    - Two vertical planes (σ_v): Each plane contains the C2 axis and one H atom.
2. **Point Group**:
    - Water belongs to the C2v point group.

MULTIPLICATION TABLES

In the context of point groups and molecular symmetry, "multiplication tables" refer to the tables that describe the combination of symmetry operations within a point group. These tables show how applying one symmetry operation followed by another results in a third operation. Understanding these tables is crucial for group theory, which is extensively used in chemistry to analyze molecular symmetry, vibrational modes, and molecular orbitals.

Key Concepts

1. **Point Group**: A set of symmetry operations that leave at least one point fixed and describe the symmetry of a molecule.
2. **Symmetry Operations**: Actions such as rotations, reflections, inversions, and improper rotations that map a molecule onto itself.
3. **Group Theory**: A mathematical framework that uses groups to study symmetry. Each point group forms a group in the mathematical sense.

Symmetry Operations and Their Notation

- **E**: Identity operation (doing nothing).
- **Cn_**: Rotation by 360∘/n about an axis.
- **σ**: Reflection in a plane.
- **i**: Inversion through a point.
- **Sn_**: Improper rotation (rotation followed by reflection).

Example: Multiplication Table for the C2v Point Group

The C2v point group is common in molecules like water (H2O). It consists of the following symmetry operations:

1. **E**: Identity.
2. **C2**: 180° rotation about the z-axis.
3. **σxz_**: Reflection in the xz-plane.
4. **σyz_**: Reflection in the yz-plane.

5. The multiplication table for C2v shows the result of performing one symmetry operation followed by another:

C2v	**E**	**C2**	**σxz**	**σyz**
E	**E**	**C2**	**σxz**	**σyz**
C2	**C2**	**E**	**σyz**	**σ**
σxz	**σxz**	**σyz**	**E**	**C2**
σyz	**σyz**	**σxz**	**C2**	**E**

Constructing the Multiplication Table

1. **Identity (E)**: Multiplying by the identity leaves any operation unchanged.
   - Example: $E \times C_2 = C_2$
2. **Rotations (C_2)**:
   - $C_2 \times C_2 = E$(since a 180° rotation followed by another 180° rotation is equivalent to doing nothing).
3. **Reflections (σ)**:
   - Reflecting twice across the same plane brings the molecule back to its original state: $\sigma_{xz} \times \sigma_{xz} = E$.
   - Reflecting across two perpendicular planes is equivalent to a rotation: $\sigma_{xz} \times \sigma_{yz} = C_2$.

Axioms:

C2v

1. **Closure property**: The product of any two elements in a group must be equal to the element of the same group.

Ex: 1. $C_2 . \sigma_{xz} = \sigma_{yz}$

2. $\sigma_{xz} . \sigma_{yz} = C_2$
3. $C_2 . \sigma_{yz} = \sigma_{xz}$

This explains closure property in C2v with all other members in the group.

2. **Identity law**: $E.C_2 = C_2$

$E. \sigma_{xz} = \sigma_{xz}$

$E. \sigma_{yz} = \sigma_{yz}$

$E.E = E$

3. Associative Law:

Case1: $(ab)c = a(bc)$

$(\sigma_{xz} \sigma_{yz})C_2 = \sigma_{xz}(\sigma_{yz} C_2)$

$C_2.C_2 = \sigma_{xz} \sigma_{xz}$

$E = E$ (Abelian)

Case2: $(\sigma_{yz}. \sigma_{xz})C_2 = (\sigma_{yz})(\sigma_{xz}.C_2)$

$C_2.C_2 = \sigma_{yz} \sigma_{yz}$

E= E (Abelian)

Reciprocal law (E=E) $B=x^{-1}Ax(x=C2,A=E)$

$= C2^{-1}EC2$

$= C2^{-1}C2E$

=E.E=E

Every member have a reciprocal in the group .

Commutative law (ab=ba)

σxz σyz= σyz σxz

C2=C2 (Abelian)

So,C2v is Abelian

Example: Multiplication Table for the C3vPoint Group

The C3v point group is common in molecules like ammonia (NH3). It consists of the following symmetry operations:

1. **E**: Identity.
2. **C3**: 120° rotation.
3. **$C3^2$**: 240° rotation (or -120° rotation).

The multiplication table for **C3V** is:

C3v	**E**	**$C3^1$**	**$C3^2$**	**σv1**	**σv2**	**σv3**
E	**E**	**$C3^1$**	**$C3^2$**	**σv1**	**σv2**	**σv3**
$C3^1$	**$C3^1$**	**$C3^2$**	**E**	**σv2**	**σv3**	**σv1**
$C3^2$	**$C3^2$**	**E**	**$C3^2$**	**σv3**	**σv1**	**σv2**
σv1	**σv1**	**σv3**	**σv2**	**E**	**$C3^2$**	**$C3^1$**
σv2	**σv2**	**σv1**	**σv3**	**$C3^1$**	**E**	**$C3^2$**
σv3	**σv3**	**σv2**	**σv1**	**$C3^2$**	**$C3^1$**	**E**

UNIT-III

TREATMENT OF ANALYTICAL DATA

Errors in scientific measurements and experiments can arise from various sources and can impact the accuracy and reliability of results. Understanding the types of errors helps in identifying their sources, minimizing their effects, and improving the quality of experimental data. Here's a classification of errors commonly encountered in scientific research:

1. Systematic Errors

Definition: Systematic errors are consistent and repeatable deviations from the true value, often due to flaws in equipment, experimental design, or environmental conditions.

Types:

- **Instrumental Errors**: Result from inaccuracies or limitations in measuring instruments.
    - Example: A balance consistently reads 0.1 g heavier due to calibration issues.
- **Methodological Errors**: Arise from flaws in experimental design or execution.
    - Example: Improper mixing technique affecting reaction yields.
- **Environmental Errors**: Due to variations in experimental conditions.
    - Example: Temperature fluctuations affecting reaction rates.

Impact: Systematic errors can lead to biased results, affecting the accuracy of conclusions.

2. Random Errors (Statistical Errors)

Definition: Random errors are unpredictable fluctuations in measurement readings that occur randomly and without a pattern. They are caused by inherent variability in measurement processes.

Types:

- **Measurement Variability**: Inherent fluctuations in measurement readings.
    - Example: Variations in electronic noise affecting the precision of electronic measurements.
- **Human Errors**: Mistakes made by experimenters during data collection or analysis.
    - Example: Misreading a scale or recording incorrect data.
- **Environmental Fluctuations**: Random changes in environmental conditions affecting measurements.
    - Example: Air currents causing fluctuations in a balance reading.

Impact: Random errors typically cause imprecision and scatter in data points but do not bias results systematically when averaged over many measurements.

3. Gross Errors (Blunders)

Definition: Gross errors are large, noticeable mistakes that result in significant deviations from expected values. They are often caused by human error or equipment malfunction.

Examples:

- Mislabeling samples or switching labels.
- Using incorrect units or incorrect calculation procedures.
- Equipment malfunctions leading to extreme measurement outliers.

Impact: Gross errors can significantly skew experimental results and must be identified and corrected to ensure data reliability.

4. Accidental Errors

Definition: Accidental errors refer to unforeseen circumstances or events that affect measurements but are typically beyond experimental control.

Examples:

- Power outages during measurements.
- Physical disturbances (e.g., earthquakes, vibrations).
- Sudden chemical reactions affecting experimental conditions.

Impact: While accidental errors are unpredictable and rare, they can lead to unexpected deviations in results.

Error Minimization Strategies

1. **Calibration and Standardization**: Regularly calibrate instruments and use standard methods to reduce systematic errors.
2. **Replication and Averaging**: Perform multiple measurements and average results to minimize random errors.
3. **Quality Control**: Implement quality control measures to detect and correct errors during experimental procedures.
4. **Error Analysis**: Analyze data to identify and quantify errors, distinguishing between systematic and random components.

Understanding the classification of errors is crucial for maintaining the accuracy, precision, and reliability of scientific measurements and experimental results. By identifying the sources and types of errors, scientists can implement appropriate strategies to minimize their impact and improve the quality of data. Effective error management supports robust scientific conclusions and advances knowledge across various disciplines.

Accuracy and precision:

Accuracy and precision are critical concepts in analytical chemistry that describe the reliability and correctness of experimental measurements. Understanding the difference between these terms is essential for assessing the quality and validity of data obtained from experiments. Here’s an overview of accuracy and precision, including their definitions, importance, and methods for evaluation:

Accuracy

Definition: Accuracy refers to how close a measured value is to the true or accepted value. It indicates the absence of systematic error or bias in measurements.

Importance:

- **Validity of Results**: Accurate measurements ensure that experimental results reflect the true characteristics of the system being studied.
- **Reliability**: Accurate data supports scientific conclusions and enhances the credibility of research findings.
- **Comparability**: Accurate measurements enable comparisons between different experiments, studies, or datasets.

Evaluation:

- **Comparison to a Standard**: Measure the experimental value against a known standard or reference material.
- **Bias Assessment**: Identify and quantify systematic errors through calibration and control measurements.
- **Error Analysis**: Calculate the percent error or deviation from the true value:

$$\text{Percent Error}=\text{Measured Value}-\text{True Value}/\text{True Value}\times 100\%$$

- **Precision**

Definition: Precision refers to the degree of reproducibility or scatter in measurements. It assesses how close repeated measurements are to each other.

Importance:

- **Consistency**: Precise measurements have low variability among repeated trials.
- **Data Quality**: High precision reduces uncertainty and increases confidence in the reliability of experimental data.
- **Statistical Significance**: Precise data allow for meaningful statistical analysis and interpretation.

Evaluation:

- **Statistical Analysis**: Calculate measures of dispersion such as standard deviation or variance:
- Standard Deviation $(s)=\sqrt{\sum(x_i-\bar{x})^2/N-1}$
- where x_i are individual measurements, $\bar{x}$ is the mean, and N is the number of measurements.
- **Repeatability**: Conduct replicate measurements under the same conditions to assess variability.
- **Precision Limits**: Define acceptable precision based on experimental requirements or industry standards.

Relationship Between Accuracy and Precision

- **High Accuracy, Low Precision**: Measurements are close to the true value but vary widely among themselves.
- **Low Accuracy, High Precision**: Measurements cluster closely together but deviate from the true value.

- **High Accuracy and High Precision**: Measurements are both close to the true value and tightly clustered around the mean.

Improving Accuracy and Precision

- **Calibration**: Regularly calibrate instruments using certified reference materials (CRMs) to minimize systematic errors.
- **Standardization**: Follow standardized methods and procedures to reduce variability and improve consistency.
- **Quality Control**: Implement quality control measures to monitor and verify the accuracy and precision of measurements.
- **Error Analysis**: Identify sources of error and take corrective actions to enhance accuracy and precision.

SIGNIFICANT FIGURES

Significant figures (also known as significant digits) are a crucial concept in measurement and data reporting, particularly in science and engineering. They indicate the precision or uncertainty of a measured or calculated quantity. Here's an in-depth explanation of significant figures, their rules, and their importance in scientific calculations:

Definition

Significant Figures: These are the meaningful digits in a measured or calculated quantity that reflect the precision of the measurement.

Rules for Determining Significant Figures

1. **Non-Zero Digits**: All non-zero digits are significant.
    - Example: In 123, all three digits (1, 2, and 3) are significant.
2. **Leading Zeros**: Zeros that precede all non-zero digits are not significant.
    - Example: In 0.0032, only 3 and 2 are significant (2 significant figures).
3. **Captured Zeros**: Zeros between non-zero digits are significant.
    - Example: In 503, 3 is the only significant digit (3 significant figures).
4. **Trailing Zeros**:
    - Trailing zeros in a number containing a decimal point are significant.
        - Example: In 12.300, all digits (1, 2, 3, and the final 0) are significant (5 significant figures).
    - Trailing zeros without a decimal point are not significant.
        - Example: In 1200, the significant figures depend on context; if precise, four significant figures.
5. **Exact Numbers**: Numbers derived from definitions or counting have an infinite number of significant figures.
    - Example: Exactly 12 items, 1 meter = 100 centimeters (an exact conversion).

Significance in Calculations

Multiplication and Division:

- The result should have the same number of significant figures as the factor with the fewest significant figures.
  - Example: $2.5 \times 3.14 = 7.85$ (result has 2 significant figures, matching the least precise input).

Addition and Subtraction:

- The result should have the same number of decimal places as the term with the fewest decimal places.
  - Example: $3.24 + 5.1 = 8.34$ (result has 2 decimal places, matching the least precise input).

Importance of Significant Figures

1. **Precision Communication**: Significant figures convey the precision or uncertainty of a measurement or calculation.
2. **Error Estimation**: They indicate the potential error range in reported values.
3. **Consistency**: Ensures consistency in reporting and comparing measurements across experiments or studies.

Practical Applications

- **Scientific Research**: Ensures accuracy in reporting experimental data and results.
- **Engineering and Technology**: Critical for designing systems and ensuring measurements meet required specifications.
- **Quality Control**: Used in manufacturing to maintain product consistency and reliability.

CLASSIFICATION OF ERRORS

Errors in scientific measurements and experiments can arise from various sources and can impact the accuracy and reliability of results. Understanding the types of errors helps in identifying their sources, minimizing their effects, and improving the quality of experimental data. Here's a classification of errors commonly encountered in scientific research:

1. Systematic Errors

Definition: Systematic errors are consistent and repeatable deviations from the true value, often due to flaws in equipment, experimental design, or environmental conditions.

Types:

- **Instrumental Errors**: Result from inaccuracies or limitations in measuring instruments.
  - Example: A balance consistently reads 0.1 g heavier due to calibration issues.
- **Methodological Errors**: Arise from flaws in experimental design or execution.
  - Example: Improper mixing technique affecting reaction yields.
- **Environmental Errors**: Due to variations in experimental conditions.
  - Example: Temperature fluctuations affecting reaction rates.

Impact: Systematic errors can lead to biased results, affecting the accuracy of conclusions.

2. Random Errors (Statistical Errors)

Definition: Random errors are unpredictable fluctuations in measurement readings that occur randomly and without a pattern. They are caused by inherent variability in measurement processes.

Types:

- **Measurement Variability**: Inherent fluctuations in measurement readings.
  - Example: Variations in electronic noise affecting the precision of electronic measurements.
- **Human Errors**: Mistakes made by experimenters during data collection or analysis.
  - Example: Misreading a scale or recording incorrect data.
- **Environmental Fluctuations**: Random changes in environmental conditions affecting measurements.
  - Example: Air currents causing fluctuations in a balance reading.

Impact: Random errors typically cause imprecision and scatter in data points but do not bias results systematically when averaged over many measurements.

3. Gross Errors (Blunders)

Definition: Gross errors are large, noticeable mistakes that result in significant deviations from expected values. They are often caused by human error or equipment malfunction.

Examples:

- Mislabeling samples or switching labels.
- Using incorrect units or incorrect calculation procedures.

- Equipment malfunctions leading to extreme measurement outliers.

Impact: Gross errors can significantly skew experimental results and must be identified and corrected to ensure data reliability.

4. Accidental Errors

Definition: Accidental errors refer to unforeseen circumstances or events that affect measurements but are typically beyond experimental control.

Examples:

- Power outages during measurements.
- Physical disturbances (e.g., earthquakes, vibrations).
- Sudden chemical reactions affecting experimental conditions.

Impact: While accidental errors are unpredictable and rare, they can lead to unexpected deviations in results.

Error Minimization Strategies

1. **Calibration and Standardization**: Regularly calibrate instruments and use standard methods to reduce systematic errors.
2. **Replication and Averaging**: Perform multiple measurements and average results to minimize random errors.
3. **Quality Control**: Implement quality control measures to detect and correct errors during experimental procedures.
4. **Error Analysis**: Analyze data to identify and quantify errors, distinguishing between systematic and random components.

UNIT-IV

INTRODUCTION TO COMPUTER PROGRAMMING

Basic Structures and Functioning of a Computer with Personal Computer (PC) Focus

A computer, particularly a personal computer (PC), is a versatile electronic device designed to process data and perform a variety of tasks. The basic structure of a computer includes both hardware and software components. Here’s an overview of these components and how they function together:

1. Hardware Components

a. Central Processing Unit (CPU)

- **Function**: The CPU, often referred to as the brain of the computer, executes instructions from programs.
- **Components**:
    - **Control Unit (CU)**: Directs operations within the computer by interpreting instructions.
    - **Arithmetic Logic Unit (ALU)**: Performs arithmetic and logical operations.
    - **Registers**: Small, fast storage locations within the CPU used to store temporary data and instructions.

b. Memory (RAM)

- **Function**: Random Access Memory (RAM) temporarily stores data and instructions that the CPU needs while performing tasks. It is volatile, meaning it loses its content when power is turned off.

c. Storage

- **Types**:
  - **Hard Disk Drive (HDD)**: Uses magnetic storage to store data.
  - **Solid State Drive (SSD)**: Uses flash memory for faster data access.
- **Function**: Permanent storage for the operating system, applications, and user data.

d. Motherboard

- **Function**: The main circuit board that houses the CPU, memory, and other essential components. It also provides connectors for other peripherals.

e. Input Devices

- **Examples**: Keyboard, mouse, scanner.
- **Function**: Allow users to interact with the computer and input data.

f. Output Devices

- **Examples**: Monitor, printer, speakers.
- **Function**: Display or produce the result of computer processes.

g. Power Supply Unit (PSU)

- **Function**: Converts electrical power from an outlet into usable power for the computer's components.

h. Peripheral Devices

- **Examples**: External hard drives, USB drives, printers.
- **Function**: Extend the functionality of the computer.

2. Software Components

a. Operating System (OS)

- **Function**: Manages hardware resources and provides an interface for user interaction. Examples include Windows, macOS, and Linux.
- **Components**:
  - **Kernel**: Core part of the OS, managing system resources.
  - **Drivers**: Software that allows the OS to communicate with hardware devices.

  - **User Interface**: Allows users to interact with the computer, either through a graphical user interface (GUI) or command line interface (CLI).

b. Application Software

- **Function**: Programs that perform specific tasks for users. Examples include word processors, web browsers, and games.

c. System Software

- **Function**: Includes the OS and utility programs that manage computer resources and provide a platform for application software.

3. Functioning of a Computer

a. Boot Process

1. **Power On**: The PSU supplies power to the motherboard and other components.
2. **BIOS/UEFI**: The Basic Input/Output System or Unified Extensible Firmware Interface performs initial hardware checks and loads the bootloader from the storage device.
3. **Bootloader**: Loads the OS into RAM.
4. **OS Initialization**: The OS takes over, initializes hardware, loads necessary drivers, and starts system processes.

b. Processing Data

1. **Input**: Data is entered into the computer via input devices.
2. **Processing**: The CPU processes the data by executing program instructions stored in RAM.
3. **Storage**: Processed data is stored back in RAM, written to storage, or both.
4. **Output**: Results are sent to output devices for display or further action.

c. Running Applications

1. **Loading**: When an application is opened, it is loaded from storage into RAM.
2. **Execution**: The CPU executes the application's instructions.
3. **User Interaction**: The user interacts with the application through input devices, and the application provides feedback via output devices.

By understanding these basic structures and their functions, one can gain a clear insight into how a personal computer operates, from powering on to executing complex applications.

Arithmetic Statements in Fortran

Fortran (short for "Formula Translation") is a high-level programming language primarily used for numerical and scientific computing. Fortran supports various arithmetic operations, including addition, subtraction, multiplication, division, and exponentiation. Below are the key aspects and examples of arithmetic statements in Fortran.

1. Basic Arithmetic Operations

a. Addition (+)

- **Purpose**: Adds two numbers.
- **Example**:

fortran
Copy code

```
PROGRAM addition_example
  IMPLICIT NONE
  REAL :: a, b, result

  a = 5.0
  b = 3.0
  result = a + b
  PRINT *, 'Addition: ', result  ! Output: 8.0
END PROGRAM addition_example
```

b. Subtraction (-)

- **Purpose**: Subtracts the second number from the first.
- **Example**:

fortran
Copy code

```
PROGRAM subtraction_example
  IMPLICIT NONE
  REAL :: a, b, result

  a = 10.0
  b = 4.0
  result = a - b
  PRINT *, 'Subtraction: ', result  ! Output: 6.0
END PROGRAM subtraction_example
```

c. Multiplication (*)

- **Purpose**: Multiplies two numbers.
- **Example**:

fortran

Copy code

```
PROGRAM multiplication_example
  IMPLICIT NONE
  REAL :: a, b, result

  a = 7.0
  b = 6.0
  result = a * b
  PRINT *, 'Multiplication: ', result  ! Output: 42.0
END PROGRAM multiplication_example
```

d. Division (/)

- **Purpose**: Divides the first number by the second.
- **Example**:

fortran
Copy code

```
PROGRAM division_example
  IMPLICIT NONE
  REAL :: a, b, result

  a = 20.0
  b = 5.0
  result = a / b
  PRINT *, 'Division: ', result  ! Output: 4.0
END PROGRAM division_example
```

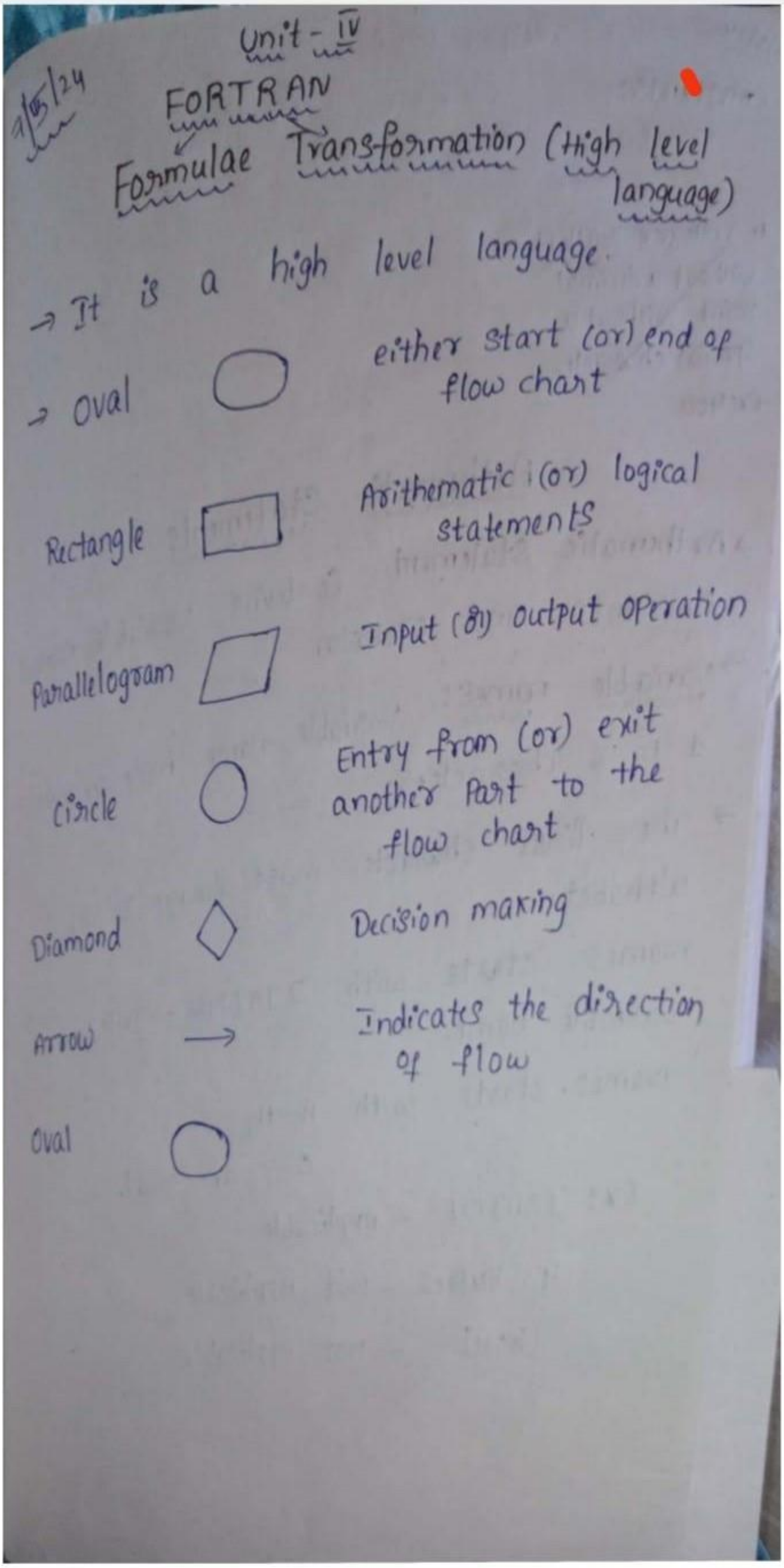
e. Exponentiation (**)

- **Purpose**: Raises the first number to the power of the second.
- **Example**:

fortran
Copy code

```
PROGRAM exponentiation_example
  IMPLICIT NONE
  REAL :: a, b, result

  a = 2.0
  b = 3.0
  result = a ** b
  PRINT *, 'Exponentiation: ', result  ! Output: 8.0
END PROGRAM exponentiation_example
```



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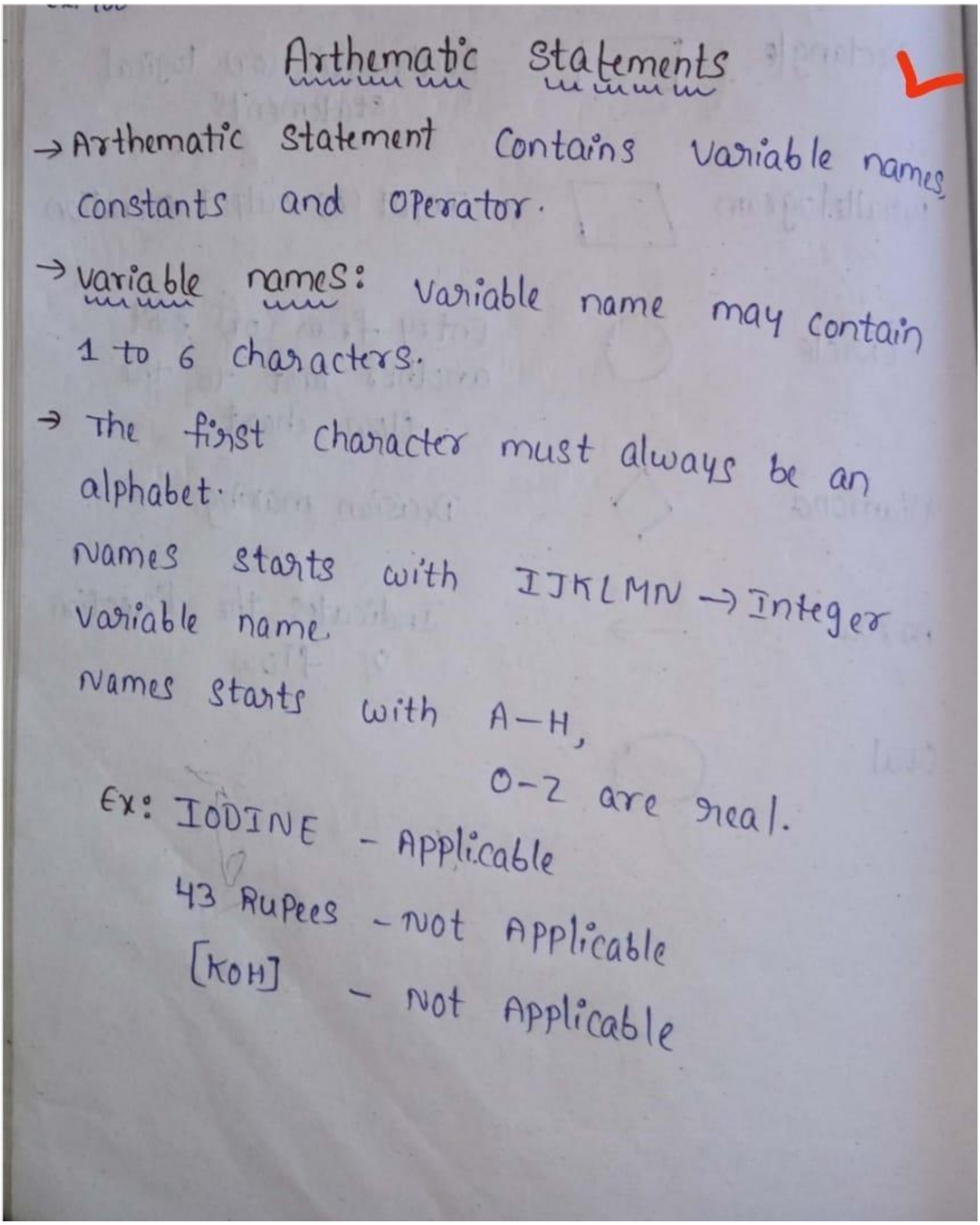
Unit - IV

FORTRAN

Formulae Transformation (High level language)

→ It is a high level language.

→ Oval	⬭	either start (or) end of flow chart
Rectangle	▭	Arithematic (or) logical statements
Parallelogram	▱	Input (or) output operation
Circle	○	Entry from (or) exit another part to the flow chart
Diamond	◇	Decision making
Arrow	→	Indicates the direction of flow
Oval	⬭	



Arthematic Statements

→ Arthematic Statement Contains Variable names, constants and Operator.

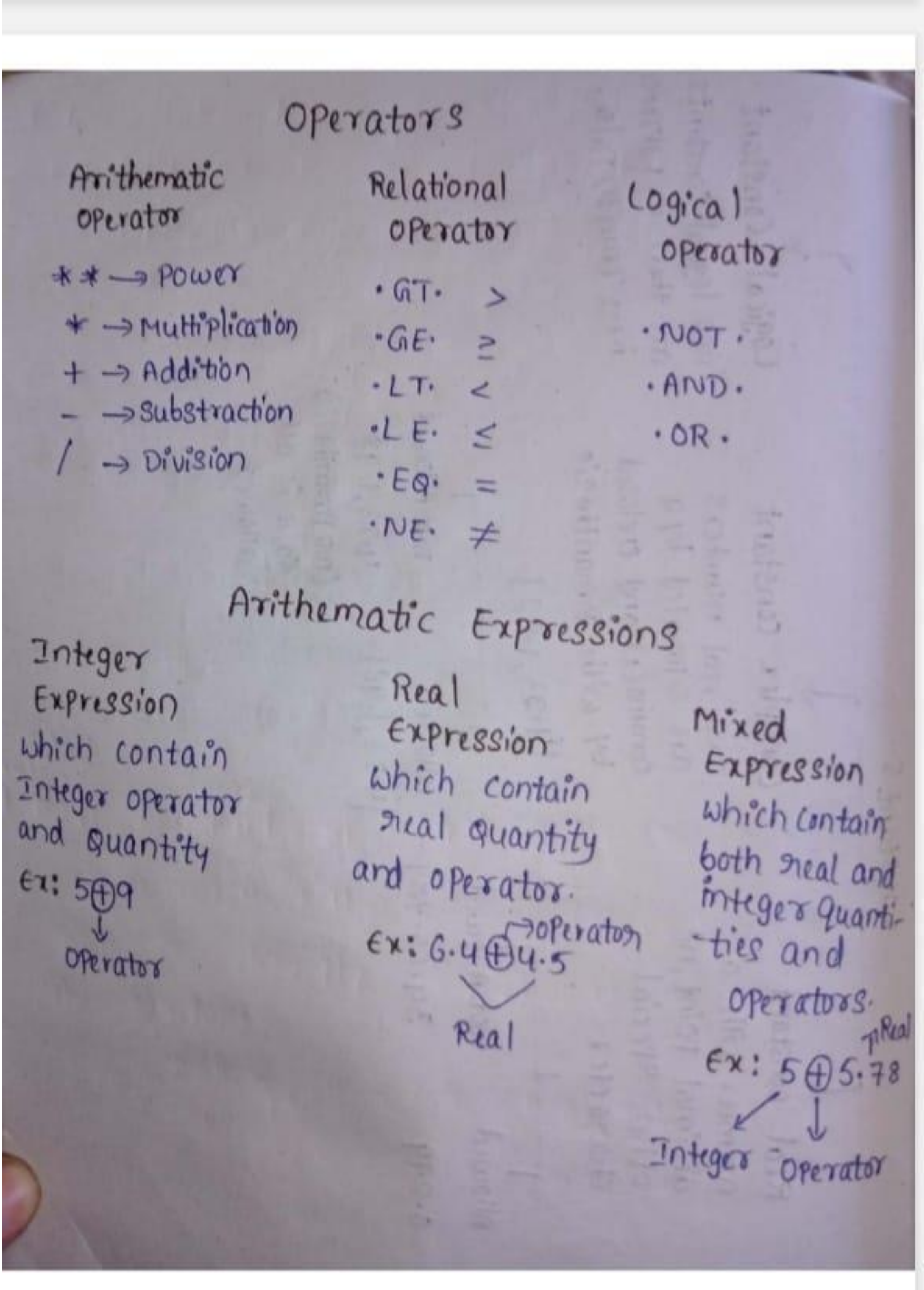
→ Variable names: Variable name may contain 1 to 6 characters.

→ The first character must always be an alphabet.

Names starts with IJKLMN → Integer variable name.

Names starts with A–H,
O–Z are real.

Ex: IODINE – Applicable
43 Rupees – Not Applicable
[KOH] – Not Applicable



Operators

Arithematic operator

- ** → Power
- * → Multiplication
- + → Addition
- − → Substraction
- / → Division

Relational operator

.GT.	>
.GE.	≥
.LT.	<
.LE.	≤
.EQ.	=
.NE.	≠

Logical operator

- .NOT.
- .AND.
- .OR.

Arithematic Expressions

Integer Expression

which contain Integer operator and Quantity

Ex: $5 \underset{\text{Operator}}{\oplus} 9$

Real Expression

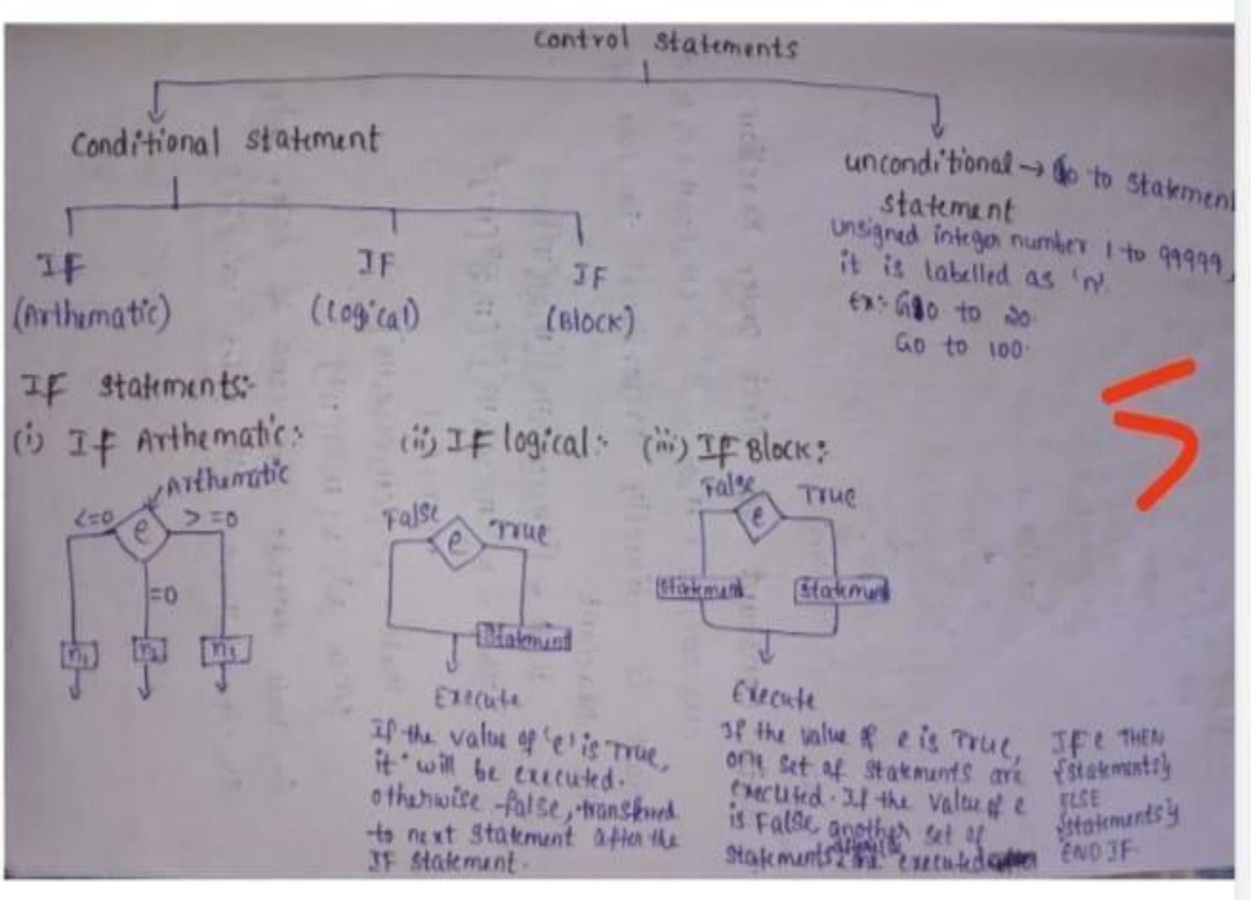
which contain real quantity and operator.

Ex: $\underbrace{6.4 \overset{\text{Operator}}{\oplus} 4.5}_{\text{Real}}$

Mixed Expression

which contain both real and integer Quantities and Operators.

Ex: $\underset{\text{Integer}}{5} \underset{\text{Operator}}{\oplus} \overset{\text{Real}}{5.78}$



unsigned integer number 1 to 99999, it is labelled as 'n'.

ex: Go to 20.

Go to 100.

5

IF statements:-

(i) If Arthematic:

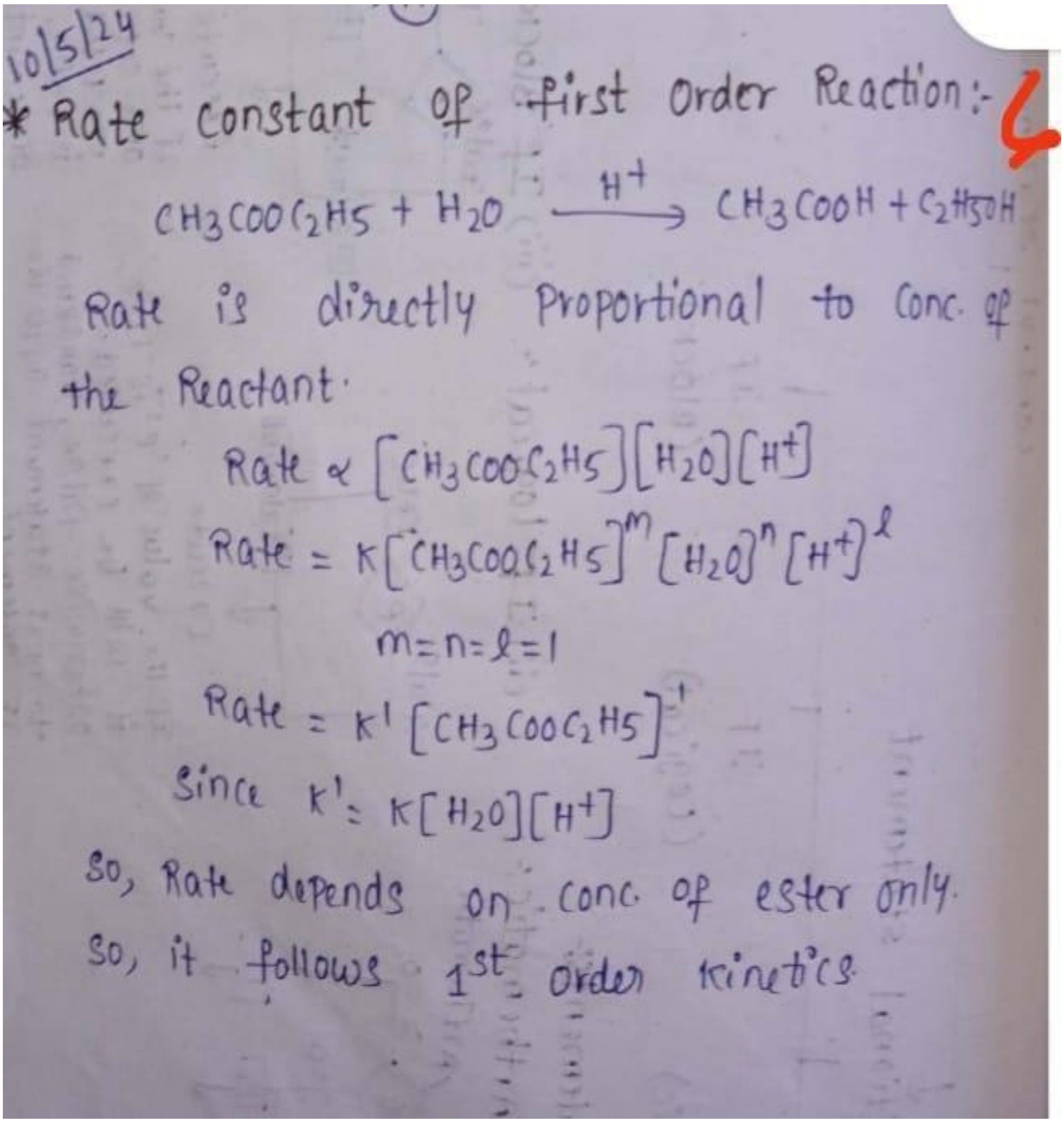
(ii) IF logical:

(iii) If Block:

If the value of 'e' is True, it will be executed. otherwise false, transfered to next statement after the IF statement.

If the value of e is True, one set of statements are executed. If the value of e is False, another set of statements are executed.

IF e THEN
{statements}
ELSE
{statements}
END IF



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* Rate constant of first Order Reaction:-

4

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Rate is directly Proportional to Conc. of the Reactant.

$$Rate \propto [CH_3COOC_2H_5][H_2O][H^+]$$

$$Rate = k[CH_3COOC_2H_5]^m[H_2O]^n[H^+]^l$$

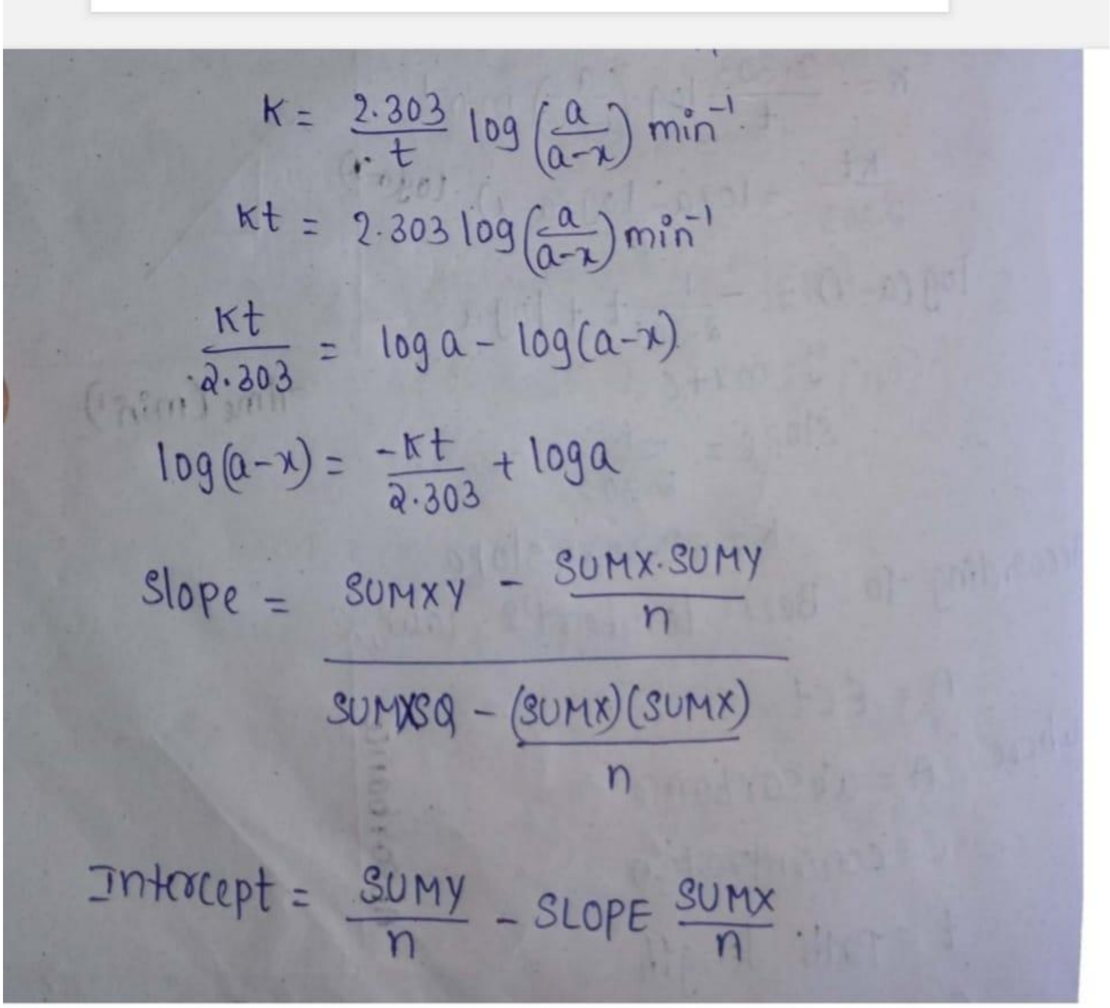
$$m = n = l = 1$$

$$Rate = k^1[CH_3COOC_2H_5]^1$$

Since $k^1 = k[H_2O][H^+]$

So, Rate depends on conc. of ester only.

So, it follows 1st order kinetics.



$$K = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)\ \text{min}^{-1}$$

$$Kt = 2.303\log\left(\frac{a}{a-x}\right)\text{min}^{-1}$$

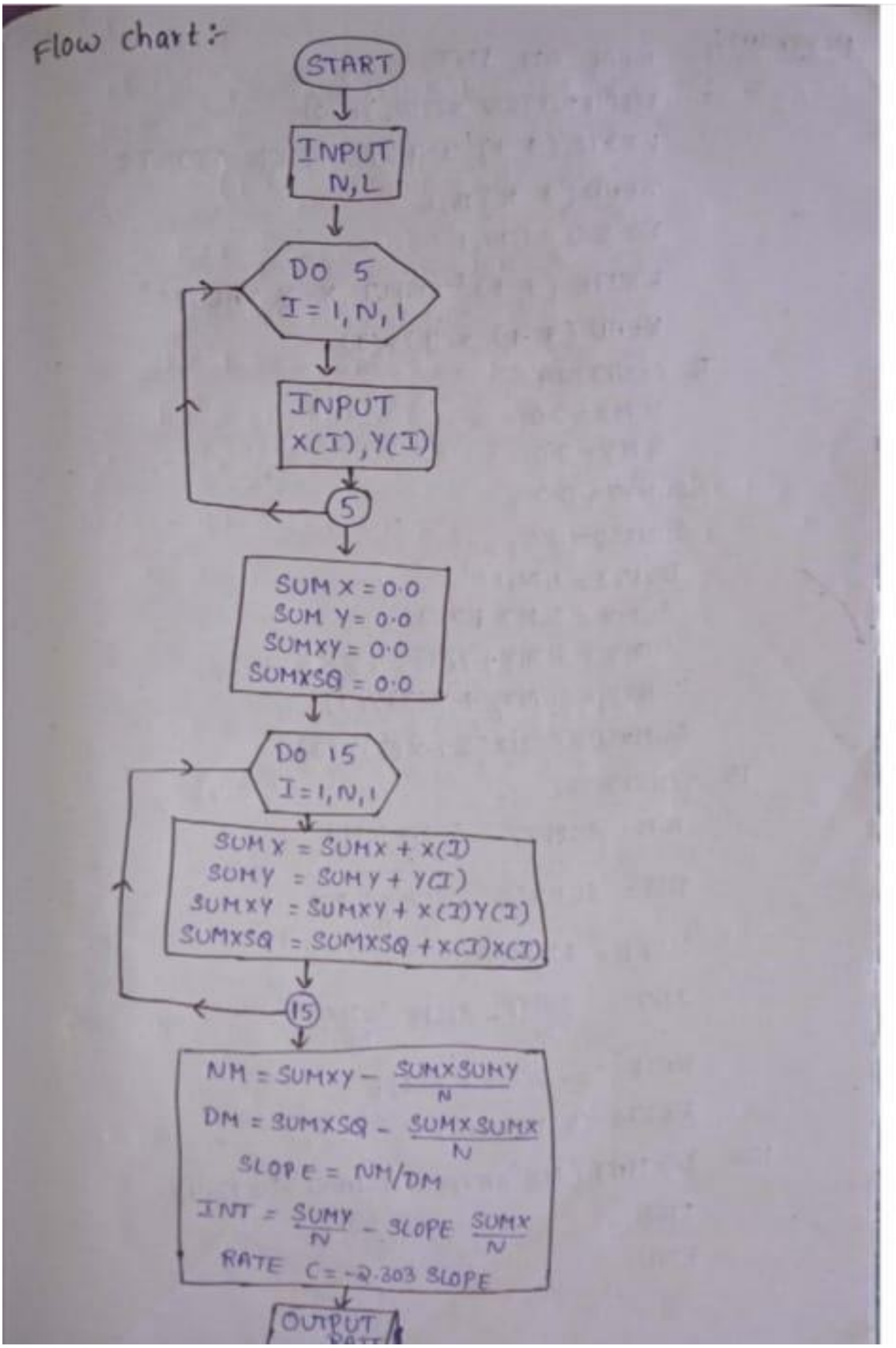
$$\frac{Kt}{2.303} = \log a - \log(a-x)$$

$$\log(a-x) = \frac{-Kt}{2.303} + \log a$$

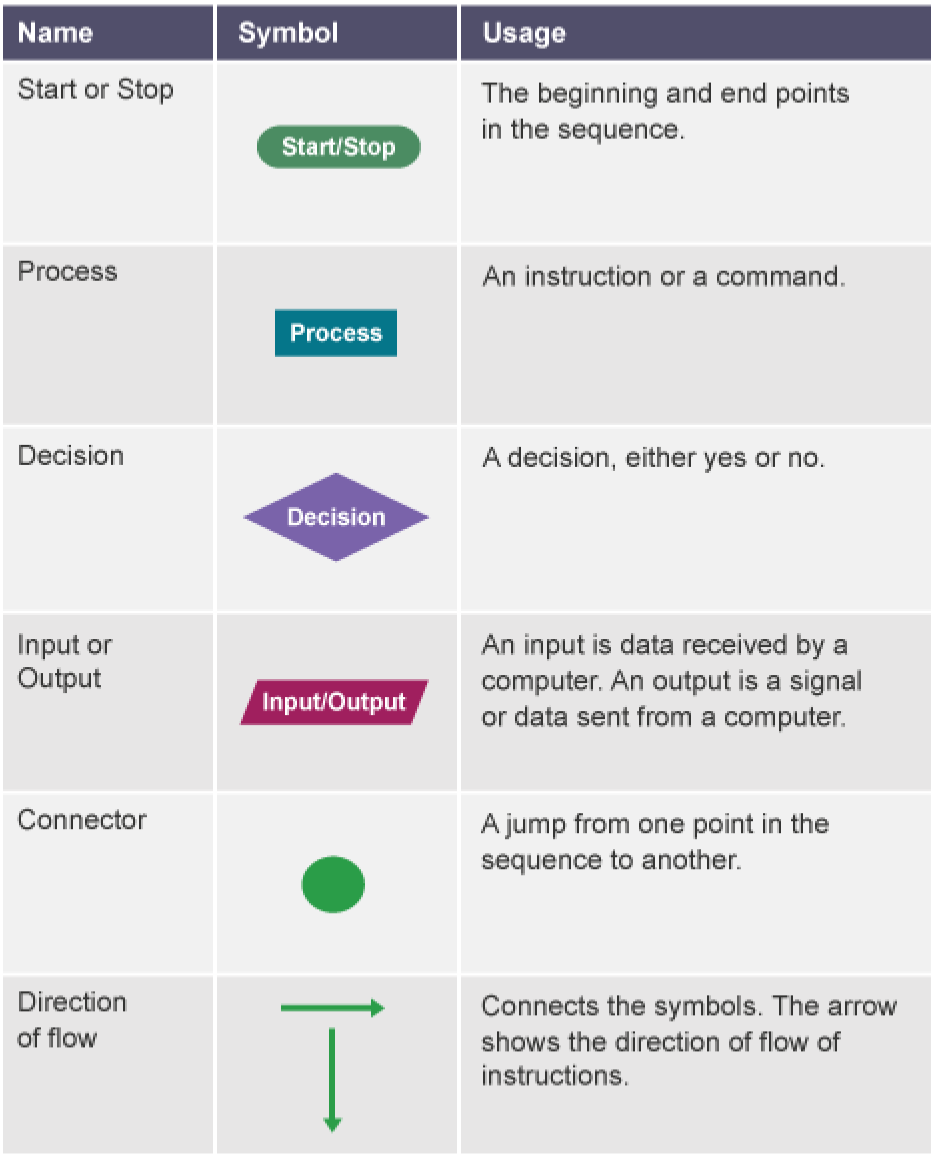
$$\text{Slope} = \frac{\text{SUMXY} - \frac{\text{SUMX}\cdot\text{SUMY}}{n}}{\text{SUMXSQ} - \frac{(\text{SUMX})(\text{SUMX})}{n}}$$

$$\text{Intercept} = \frac{\text{SUMY}}{n} - \text{SLOPE}\ \frac{\text{SUMX}}{n}.$$

Flow chart:-



START
INPUT N,L
DO 5 I = 1, N, 1
INPUT X(I), Y(I)
5
SUM X = 0.0
SUM Y = 0.0
SUMXY = 0.0
SUMXSQ = 0.0
DO 15 I = 1, N, 1
SUM X = SUMX + X(I)
SUMY = SUMY + Y(I)
SUMXY = SUMXY + X(I)Y(I)
SUMXSQ = SUMXSQ + X(I)X(I)
15
NM = SUMXY – SUMXSUMY / N
DM = SUMXSQ – SUMXSUMX / N
SLOPE = NM/DM
INT = SUMY / N – SLOPE SUMX / N
RATE C = –2.303 SLOPE
OUTPUT RATE



Name	Symbol	Usage
Start or Stop	Start/Stop	The beginning and end points in the sequence.
Process	Process	An instruction or a command.
Decision	Decision	A decision, either yes or no.
Input or Output	Input/Output	An input is data received by a computer. An output is a signal or data sent from a computer.
Connector	●	A jump from one point in the sequence to another.
Direction of flow	→ ↓	Connects the symbols. The arrow shows the direction of flow of instructions.