Toppersnotes
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CSIR-NET

Council of Scientific & Industrial Research

CHEMICAL SCIENCE

VOLUME - III

PHYSICAL **CHEMISTRY**

SIERRA
INNOVATIONS

Index

Dual nature of particle or e⁻ given by De-broglie

Quantum Mech

Dual nature of radiatn, quanta photon given by Einstein.

→ The behavioural study of matter like position, momentum, KE, PE etc.

→ when it is in motion, c/o Mechanics.

→ If the study of matter is at macroscopic scale it comes under the study of Classical Mech.

& if it is at microscopic scale then comes under study of Quantum Mech.

Mechanics

→ Quantum Mech

→ Classical Mech

Quantum Mech

- It is theory that describes dynamics of matter at microscopic scale.
- Invisible World.
- Theory is based on the assumptions c/o Postulates of Quantum Mech. These postulates are unproven but accepted, & no-longer questioned.

eg Schrodinger eqn
De-broglie eqn

Classical Mech

- study of matter at macroscopic scale.
- Visible World.
- Can be exp. proved in labs.
- Well-established theories i,e well packaged theories based on principles like Newton's Mech, Maxwell's electrodyanamics.

Maths Involved in Quantum Mech :-

Differentiation $\longrightarrow$ $\sin\theta \longrightarrow \cos\theta$
$\cos\theta \longrightarrow -\sin\theta$

① $\frac{d}{dx} c = 0$ $\quad$ ($c \rightarrow$ const)

② $\frac{d}{dx} x^n = n x^{n-1}$

③ $\frac{d}{dx}(u \pm v) = \frac{du}{dx} \pm \frac{d}{dx} v$

④ $\frac{d}{dx}(uv) = u\frac{dv}{dx} + v\frac{du}{dx}$

⑤ $\frac{d}{dx}(uvz) = uv\frac{dz}{dx} + uz\frac{dv}{dx} + vz\frac{du}{dx}$

⑥ $\frac{d}{dx} e^{\pm ikx^n} = \pm ikn x^{n-1} e^{\pm ikx^n}$

⑦ $\frac{d}{dx} \sin(\overset{\theta}{ikx^n}) = ikn x^{n-1} \cos ikx^n$

⑧ $\frac{d}{dx} \cos(\overset{\theta}{ikx^n}) = ikn x^{n-1} (-\sin ikx^n)$

⑨ $\frac{d^2}{dx^2}(u+v) = \frac{d^2 u}{dx^2} + \frac{d^2}{dx^2} v$

$$\frac{d^2}{dx^2}(UV) \neq u\frac{d^2 v}{dx^2} + v\frac{d^2 u}{dx^2}$$

bcz $\frac{d^n}{dx^n}$ means 'n' times differentiatn of the functn.

Q. Give result of following differentn?

① $\frac{d}{dx} x^4$

$\frac{d}{dx}\, 4x^{4-1} \Rightarrow 4x^3$

② $\frac{d^2}{dx^2} kx^4$

$= \cancel{\frac{d}{dx}\left(\frac{d}{dx} kx^2\right)}$

$= \frac{d}{dx}(2kx)$ $\quad = 2k\frac{dx}{dx}$

$= 2k$

$\frac{d}{dx}\frac{d}{dx} kx^4$

$k\frac{d}{dx}\left(\frac{d}{dx}x^4\right)$

$k\frac{d}{dx}(4x^3)$

$4k\frac{d}{dx}(x^3)$

$4k\cancel{\frac{d}{dx}}(3x^2)$

$\boxed{12kx^2}$ Ans.

③ $\frac{d}{dx} e^{ikx^2}$

$\frac{d}{dx}\, ik\,2x^1\, e^{ikx^2}$

Ans $\frac{d}{dx}\, 2ikx\, e^{ikx^2}$

किसी 1 का कोई power 0 = 1
$(x^0 = 1)$

$$= -ik \frac{d}{dx} \underbrace{x}_{u}\underbrace{e^{-ikx}}_{v} + \frac{d}{dx} e^{-ikx}$$

$$= -ik\left(-ikx\, e^{-ikx} + e^{-ikx} - ik\, e^{-ikx}\right)$$

(4) $\frac{d^2}{dx^2} x e^{-ikx}$

$$\frac{d}{dx}\left(\frac{d}{dx} \underbrace{x}_{u} \underbrace{e^{-ikx}}_{v}\right)$$

$$\frac{d}{dx}\; x \frac{d}{dx} e^{-ikx} + e^{-ikx} \frac{dx}{dx}$$

$$\frac{d}{dx}\left(-ikx\, e^{-ikx} + e^{-ikx}\right)$$

$$= -ik\left(-ikx + 1 + 1\right) e^{-ikx}$$

$$= -ik\left(-ikx + 2\right) e^{-ikx}$$

(5) $\frac{d^2}{dx^2} \sin kx$

$$\frac{d}{dx}\left(\frac{d}{dx} \sin kx\right)$$

$$\frac{d}{dx}\, k \cos kx$$

$$k\left(\frac{d}{dx} \cos (kx)\right)$$

$$= -k^2 \sin kx$$

(6) $\frac{d}{dx}\left(4x^2 + e^{kx^2}\right)$

$$\frac{d}{dx} 4x^2 + \frac{d}{dx} e^{kx^2}$$

$$8x + 2kx\, e^{kx^2}$$

⑦ $\frac{d^2}{dx^2}(\sin kx + \cos kx)$

$\frac{d^2}{dx^2}\sin kx + \frac{d^2}{dx^2}\cos kx$

$-k^2 \sin kx - k^2 \cos kx$

Ans: $\boxed{-k^2(\sin kx + \cos kx)}$

⑧ $\left(\frac{d}{dx} + 4x\right)e^{-kx^3}$

$\frac{d}{dx}e^{-kx^3} + 4x\,e^{-kx^3}$ const. कोई operator nae है|

$-3kx^2 e^{-kx^3} + 4x\,e^{-kx^3}$

$\boxed{(-3kx^2 + 4x)\,e^{-kx^3}}$

11.10

⑨ $\left(\frac{d^2}{dx^2} + 2x\right)e^{-kx}$

$\frac{d^2}{dx^2}e^{-kx} + 2x\,e^{-kx}$ $= +k^2 e^{-kx} + 2x\,e^{-kx}$

$= (k^2 + 2x)\,e^{-kx}$

$\frac{d}{dx}\cdot\left(\frac{d}{dx}e^{-kx}\right) + 2x\,e^{-kx}$

$\frac{d}{dx}\left(-k\,e^{-kx}\right) + 2x\,e^{-kx}$

$-k\left(\frac{d}{dx}e^{-kx}\right) + 2x\,e^{-kx}$

Differentiation

$\sin\theta \rightarrow \cos\theta$

$\cos\theta \rightarrow -\sin\theta$

$\boxed{\begin{array}{l} \sin\theta \rightarrow -\cos\theta \\ \cos\theta \rightarrow \sin\theta \end{array}}$

Integration :-

$$\int_{x_1}^{x_2} dx = [x]_{x_1}^{x_2} = x_2 - x_1 = \Delta x \qquad \int dx = x$$

① $$\int x^n dx = \frac{x^{n+1}}{n+1} \qquad \boxed{n \neq -1}$$

② $$\int \frac{1}{x} dx = \ln x$$

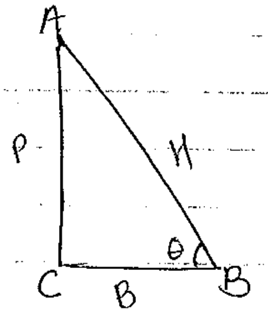
③ $$\int e^{ax} dx = \frac{e^{ax}}{a}$$

④ $$\int \sin ax \, dx = \frac{-\cos ax}{a}$$

⑤ $$\int \cos ax \, dx = \frac{\sin ax}{a}$$

⑥ $$\int (u+v) dx = \int u \, dx + \int v \, dx$$

Trignometric Relations



~~LAL~~
~~KKA~~

	sinθ	cosθ	tanθ
	P	B	P
	H	H	B

$$\sin\theta = \frac{AC}{AB}$$

$$\cos\theta = \frac{CB}{AB}$$

$$\tan\theta = \frac{AC}{BC}$$

$$\boxed{\tan\theta = \frac{\sin\theta}{\cos\theta}}$$

Angle θ	0	45° $\left(\frac{\pi}{4}\right)$	90° $\left(\frac{\pi}{2}\right)$	135° $\left(\frac{3\pi}{4}\right)$	180° (π)
sin θ	0	$\frac{1}{\sqrt{2}}$	1	$\frac{1}{\sqrt{2}}$	0
cos θ	1	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}$	−1

$$\boxed{\sin\left(\frac{\pi}{2}-\theta\right) = \cos\theta}$$

	0°	30°	45°	60°	90°
sin	0	$\frac{1}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{\sqrt{3}}{2}$	1
cos	1	$\frac{\sqrt{3}}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$	0

$$\boxed{\sin(\pi-\theta) = \sin\theta}$$

$$\boxed{\cos\left(\frac{\pi}{2}-\theta\right) = \sin\theta}$$

$$\boxed{\cos(\pi-\theta) = -\cos\theta}$$

$$\boxed{\sin x \cos x = \frac{\sin 2x}{2}}$$

$$\boxed{\sin^2 x = \frac{1-\cos 2x}{2}}$$

$$\boxed{\cos^2 x = \frac{1+\cos 2x}{2}}$$

$$\boxed{\cos^2 x - \sin^2 \theta = \cos 2x}$$

$$\boxed{\begin{gathered} ax^2+bx+c=0 \\ = \frac{-b \pm \sqrt{b^2-4ac}}{2a} \end{gathered}}$$

Q. Give result of Integratn :

① $\int \sin 4bx \, dx$ (a)

$$= -\frac{\cos 4bx}{4b}$$

② $\int \sin^2 bx \, dx$

$$= \int \frac{1-\cos 2bx}{2} \, dx$$

$$= \frac{1}{2} \int (1-\cos 2bx) \, dx$$

$$= \frac{1}{2} \left\{ \int dx - \int \cos 2bx \, dx \right\}$$ (a)

$$= \frac{1}{2} \left(x - \frac{\sin 2bx}{2b} \right)$$

$$= \frac{1}{2}[x] - \frac{1}{4b}[\sin 2bx]$$

③ $\int \cos^2 bx \, dx$

$$= \int \frac{1+\cos 2bx}{2} \, dx$$

$$= \frac{1}{2} \int (1+\cos 2bx) \, dx$$

$$= \frac{1}{2} \left[\int dx + \int \cos 2bx \, dx \right]$$

$$= \frac{1}{2} \left[x + \frac{\sin 2bx}{2b} \right]$$

$$= \frac{1}{2}[x] + \frac{1}{4b}[\sin 2bx]$$

④ $\int \sin bx \cos bx \, dx$

$$= \int \frac{\sin 2bx}{2} \, dx$$

$$= \frac{1}{2} \int \sin 2bx \, dx$$

$$= -\frac{1}{2} \left[\frac{\cos 2bx}{2b} \right]$$

$$= -\frac{1}{4b} [\cos 2bx]$$

Operator & Function

→ Functn is a rule that relates 2 or more variables.

$\boxed{H = f(T, P)}$ i.e (Enthalpy is a functn of T & P)
(functn) (variables)

→ An operator is a mathematical procedure or a mathem-atical instructor that operates a functn & gives another functn or a constant entity.

(operator) (functn) = New functn or Const. entity.

eg: $\hat{A} f = g$

$\left(\hat{A} = \frac{d}{dx} \quad , f = kx^2\right)$

$\hat{A} f = \frac{d}{dx} kx^2 = 2kx$

→ Quantum mechanical operator is directional i.e they have specific directions.

eg: $\hat{A}\,\psi$ (but) $\psi\,\hat{A}$

operate करेगा operate nae krega

most Quantum mech operators operate left to right but not all.

then $\underset{\text{operator}}{\frac{d}{dx}}\, \underset{\text{functn}}{x^3} = 3x^2$ const entity

$x^3 \frac{d}{dx}$ = No meaning

GATE

Q. What is the expression of following operator?

$$\left(\frac{d}{dx}+x\right)^2$$

(a) $\frac{d^2}{dx^2}+x^2+2x$

(b) $\frac{d^2}{dx^2}+x^2+2x\frac{d}{dx}$

(c) $\frac{d^2}{dx^2}+x^2+2\frac{d}{dx}x$

(d) Both (b) & (c) possible.

(e) $\frac{d^2}{dx^2}+2x\frac{d}{dx}+x^2+1$ ✓

Solⁿ बिना function के operator का मतलब नहीं.

$$\therefore \left(\frac{d}{dx}+x\right)^2\psi \Rightarrow \left(\frac{d}{dx}+x\right)\left(\frac{d}{dx}+x\right)\psi$$

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

$$=\frac{d^2\psi}{dx^2}+\frac{d}{dx}\overset{uv}{x\psi}+x\frac{d}{dx}\psi+x^2\psi$$

$$=\frac{d^2}{dx^2}\psi+\boxed{x\frac{d\psi}{dx}+\psi\cancel{\frac{dx}{dx}}}+x\frac{d\psi}{dx}+x^2\psi$$

$$=\frac{d^2}{dx^2}\psi+2x\frac{d}{dx}\psi+x^2\psi+\psi$$

$$\left(\frac{d^2}{dx^2}+x^2+2x\frac{d}{dx}+1\right)\psi$$

Ans

$$\frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1 = (\psi)^2$$

Q. What is the expression of $\left(x\frac{d}{dx}\right)^2$

$$\left(x\frac{d}{dx}\right)\left(x\cdot\frac{d}{dx}\right)\psi$$

$$= \left(x\frac{d}{dx}\right)\left(\underbrace{x}_{u}\underbrace{\frac{d\psi}{dx}}_{v}\right)$$

$$= x\left\{x\frac{d^2}{dx^2}\psi + \frac{d\psi}{dx}\cancel{\frac{dx}{dx}}\right\}$$

$$= x^2\frac{d^2}{dx^2}\psi + x\frac{d\psi}{dx}$$

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

$$(\;\;)\psi = x^2\frac{d^2}{dx^2} + x\frac{d}{dx} \text{ Ans.}$$

Q. $\left(\frac{d}{dx}x\right)^2 \Rightarrow \left(\frac{d}{dx}\cdot x\right)\left(\frac{d}{dx}x\right)\psi$

$$\left(\frac{d}{dx}x\right)\left(\frac{d}{dx}\underbrace{x}_{u}\underbrace{\psi}_{v}\right)$$

$$\left(\frac{d}{dx}x\right)\left(x\frac{d\psi}{dx} + \psi\cancel{\frac{dx}{dx}}\right)$$

(operation के बाद काट सकते हैं $\frac{dx}{dx}$ पहले नहीं)

$$\left(\frac{d}{dx}x\right)\left(x\frac{d}{dx}\psi + \psi\right)$$

$$x^2\frac{d^2}{dx^2}\psi + \frac{d}{dx}x\psi$$

$$\left(\frac{d}{dx}x\right)\left(x\frac{d}{dx}\psi\right) + \psi$$

$$\frac{d}{dx}\left(x^2\frac{d\psi}{dx}+x\psi\right)$$

$$\frac{d}{dx}\underset{u}{x^2}\underset{v}{\frac{d\psi}{dx}}+\frac{d}{dx}\underset{u}{x}\underset{v}{\psi}$$

$$x^2\frac{d}{dx}\frac{d\psi}{dx}+\frac{d\psi}{dx}\left(\frac{dx^2}{dx}\right)+x\frac{d\psi}{dx}+\psi\frac{\cancel{dx}}{\cancel{dx}}$$

ये operation के बाद आया function है; further operate नहीं होगा

$$x^2\frac{d^2\psi}{dx^2}+\frac{d\psi}{dx}(2x)+x\frac{d\psi}{dx}+\psi$$

$$x^2\frac{d^2\psi}{dx^2}+2x\frac{d\psi}{dx}+x\frac{d\psi}{dx}+\psi$$

Ans $$\left(x^2\frac{d^2}{dx^2}+2x\frac{d}{dx}+x\frac{d}{dx}+1\right)=(\quad)\psi$$

★ All Quantum Mech. operators are linear operators.

⇒ An operator is said to be linear if they defined as —

$$\hat{A}(f\pm g)=\hat{A}f\pm\hat{A}g$$

sum/diff को operate करने पे result = individual operate करने के बाद sum/diff करने का result equal आए

than c/o linear operator.

eg ① $\frac{d}{dx}, \frac{d^2}{dx^2}, \frac{d^3}{dx^3} \cdots \frac{d^n}{dx^n}$ are linear operator.

② Integration $\int$

$\int (u+v)\, dx$

$\int u\, dx + \int v\, dx.$

* All quantum mech. operators are linear operator.

$$\boxed{x,\ x^2,\ P_x,\ P_x^2,\ T_x,\ V_x,\ H_x \text{ etc} \ldots}$$

$$\boxed{\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}}$$

∇ is linear operator.

(∇) Laplation operator is a linear operator.

$$\nabla^2(f+g) = \nabla^2 f + \nabla^2 g$$

$$\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}(f+g)$$

$$= \frac{d^2}{dx^2}f + \frac{d^2}{dy^2}f + \frac{d^2}{dz^2}f + \frac{d^2}{dx^2}g + \frac{d^2}{dy^2}g + \frac{d^2}{dz^2}g$$

$$= \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)f + \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)g$$

$$= \nabla^2 f + \nabla^2 g \quad \text{Proved}$$

Non-linear Operators:-

→ An operator said to be non-linear if they defined as

$$\hat{A}(f+g) \neq \hat{A}f \pm \hat{A}g$$

eg. • $\sqrt{\ }$ is a non-linear

bcz $\sqrt{(g+f)} \neq \sqrt{g} + \sqrt{f}$

• $(\ )^2$ (square) is a Non linear operator.

eg: $(f+g)^2 \neq f^2 + g^2$

• log is Non-linear operator.

eg. $\log(f+g) \neq \log f + \log g$

$(\hat{A})^n$ means operator is operated 'n' times.

eg: $\hat{A}^2\psi = \hat{A}(\hat{A}\psi)$

Q. Which of the following operators are linear?

① $\hat{A}\phi = \lambda\phi$ (λ is const)

② $\hat{C}\phi = \phi^2$

(a) $\hat{A}$ is linear whereas $\hat{C}$ is Non linear. ✓

(b) $\hat{A}$ is NL whereas $\hat{C}$ is linear.

(c) Both $\hat{A}$ & $\hat{C}$ linear

(d) Both $\hat{A}$ & $\hat{C}$ are N.L.

★Imp★
Quantum Mech. Operators :-

→ Each physical observable of classical mech. has their corresponding operator in quantum mech; i.e every variable of classical mech. has their corresponding operator in Quantum Mech.

Classical obs.	Operator in Q.M.	Operation.
① Position		
x	$\hat{x}$	Multiplied $\bar{c}$ the funcn. i.e c/o Multiplication operator
y	$\hat{y}$	
z	$\hat{z}$	
② Square of position		
x^2	$\hat{x}^2$	Multiplicator Operator
y^2	$\hat{y}^2$	
z^2	$\hat{z}^2$	
Imp ③ Linear Momentum (or) Momentum		$\left(\frac{d}{dx}\right)$
P_x	$\boxed{\hat{P}_x = -i\hbar \frac{d}{dx}}$ $\boxed{\hat{P}_x = \frac{\hbar}{i} \frac{d}{dx}}$	Taking 1st derivative wrt x then multiplying by $(-i\hbar)$

$$\boxed{\left(\hbar = \frac{h}{2\pi}\right)}$$