Sem-II

PEPAR- VII

UNIT - I

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-: OPERATORS :-

The concept of operators is very important in quantum chemistry.

An operator is a symbol that endicates that a particular operation is to be performed on what follows the operator.

If the operator $\hat{U}$ is to be applied several times in succession, then it is written $\hat{U}\hat{U}\hat{U}f(x)$ $= \hat{U}^3 f(x)$.

eg → If $\hat{U} = d/dx$ & $f(x) = x^5$

then,
$$U^4(x^5) = \frac{d^4(x^5)}{dx^4} = 120x$$

If $\hat{U}$, $\hat{V}$ & $\hat{W}$ are three operators, then $\hat{U}\hat{V}\hat{W}f(x)$ means as follows:
first operates on $f(x)$ with $\hat{W}$, then operate on result with $\hat{V}$, finally operate on that resulting function with $\hat{U}$.

An operator is a symbolic instruction for carrying out certain mathematical operations such as multiplication, differentiation, intigration etc. on an operand that follows the operator.

An operand is usually a mathematical function. Acting on a function, an operator generates a new function.

operator	operand	=	new function
x	y	=	xy
d/dx	x^2	=	$2x$

We shall generally represent an operator by placing a Caret (^) symbol, over a Capital English letter.

* **Commutation of Operators :-**

If two numbers (symbol) are a & b Then -

$$a \times b = b \times a$$

However, If $\hat{A}$ & $\hat{B}$ are two operators, then their product may or may not be equal.

i.e.

$$\hat{A} \times \hat{B} = \hat{B} \times \hat{A}$$

or

$$\hat{A} \times \hat{B} \neq \hat{B} \times \hat{A}$$

When, $\hat{A} \times \hat{B} = \hat{B} \times \hat{A}$ Then this is called Commution of operator (Commutative operators).

If $\hat{A} \times \hat{B} = \hat{B} \times \hat{A}$

then,

$$[\hat{A} \times \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 .$$

operators can be Complex. They can also be vector.

Q. show that the commutator $\left[x, \frac{d}{dx}\right] = -1$

Soln.

$$\left[x, \frac{d}{dx}\right] = x\frac{d}{dx} - \frac{d}{dx}x$$

let $\psi(x)$ be the operand, then operating on $\psi(x)$ by the R.H.S expression, we have -

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

$$= -\psi$$

$$\simeq \left(x\frac{d}{dx} - \frac{d}{dx}x \right)\psi = -\psi.$$

$$\simeq \left(x\frac{d}{dx} - \frac{d}{dx}x \right) = -1$$

$$\simeq \left[x \frac{d}{dx} \right] = -1.$$

Linear operators :-

An operator $\hat{A}$ is said to be linear when it satisfies the following relations -

$$\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

where, c_1 & c_2 are two real or complex constants and $f_1(x)$ & $f_2(x)$ are functions of x.

Q. Show that —

1). $[\hat{A}\ \hat{B}] = -[\hat{B}\ \hat{A}]$

Soln $[\hat{A}\ \hat{B}] = [\hat{A}\hat{B} - \hat{B}\hat{A}]$

$= -[\hat{B}\hat{A} - \hat{A}\hat{B}]$

$= -[\hat{B}\ \hat{A}]$

ii) $[\hat{A}^2 \hat{B}] = \hat{A}[\hat{A}\hat{B}] + [\hat{A}\hat{B}]\hat{A}$

Solⁿ from R.H.S.

$$\hat{A}[\hat{A}\hat{B}] + [\hat{A}\hat{B}]\hat{A} = \hat{A}[\hat{A}\hat{B} - \hat{B}\hat{A}] + [\hat{A}\hat{B} - \hat{B}\hat{A}]\hat{A}$$

$$= \hat{A}^2\hat{B} - \cancel{\hat{A}\hat{B}\hat{A}} + \cancel{\hat{A}\hat{B}\hat{A}} - \hat{B}\hat{A}^2$$

$$= \hat{A}^2\hat{B} - \hat{B}\hat{A}^2$$

$$= [\hat{A}^2\hat{B}]$$ L.H.S.

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