QUANTUM CHEMISTRY

Dr. A. DAYALAN, *Former Professor & Head*, Dept. of Chemistry,

LOYOLA COLLEGE (*Autonomous*), Chennai-34

QC-1.3. OPERATORS

1) OPERATORS:

OPERATORS: Mathematical notation signifying the nature of mathematics on a function (Arithmetic operators + , - , x & ÷)

2) LINEAR OPERATORS

$\mathbf{A(\psi_1 + \psi_2) = A\psi_1 + A\psi_2}$

Examples: Linear: d/dx & integral

Non-linear operators : ln ,sq root, $(\ )^2$

3) ALGEBRA OF OPERATORS

The operators will obey the following rules depending on their nature

AB = BA	*Commutative law*
A(B+C) = AB + AC	*Distributive law*
A(BC) = (AB)C	*Associative law*
$\psi(A\psi) = (A\psi)\psi$	*A operates on ψ only*
But, $\psi A\psi \neq A\psi\psi$	*A operates on $\psi\psi$*

Similarly,

$\psi_1(A\psi_2) = (A\psi_2)\psi_2$; A operates on ψ_2 only

$\psi_1 A\psi_2 \neq A\psi_1\psi_2$; A operates on $\psi_2$on LHS and $\psi_1\psi_2$ on RHS

Illustrate with $\psi_1 = x$; $\Psi_2 = \sin x$ as example

***Problem*:**Find operators equivalent to the following:

- $(A + B)(A-B) = A^2–AB + BA-B^2 = A^2- B^2$; if A & B commute
- $(A-B)(A+B) = A^2+AB - BA-B^2 = A^2- B^2$; if A & B commute
- $(A-B)(A+B) = A^2+AB - BA-B^2 = A^2- B^2$; if A & B commute
- $(A-B)(A+B)\psi = (A^2+AB - BA-B^2)\ \psi$

  $(A-B)(A+B)\psi = (A-B)(A\psi+B\psi)$;

  This first operation should not be completed before (A-B) operates to give the final result. The operator operates in an inclusive manner.
- $(A + B)^2 = A^2+AB + BA+B^2 = A^2+2AB+B^2$; if A & B commute
- $(A-B)^2 = A^2-AB – BA- B^2 = A^2-2AB+B^2$; if A & B commute
- $(A + B)^3$ = Determine

Mention the resultant operator in each of the following cases:

- (x + d/dx)(x- d/dx)
- (x- d/dx)(x+ d/dx)
- x(d/dx)
- (d/dx)x
- $(x + d/dx)^2$
- $(x- d/dx)^2$; $(x + d/dx)^3$
- x & d/dx do not commute.

SIMPLE & COMBINATIONAL OPERATORS

Evaluate the following by usual algebraic method (*astwo independent operations*) and by the method of operator algebra based on equivalent operator.

The function in all the cases below is $\mathbf{x^3}$

(A) x.(x + d/dx) $\mathbf{x^3}$: *Identical results*

(B) (x + d/dx).x $\mathbf{x^3}$: *Different results*

(C) x(d/dx) $\mathbf{x^3}$: ?

(D) (d/dx)x $\mathbf{x^3}$:?

(E) (x + d/dx)(x- d/dx)$\mathbf{x^3}$: *Different results*

(F) (x + d/dx)(x- d/dx)x$\mathbf{x^3}$: *Different results*

4) COMMUTATORS

[A, B] = AB-BA

[A, B] = AB-BA = 0 if A & B commute

- x & d/dx do not commute; The result of x(d/dx)ψ will not be equal to the result of (d/dx)xψ
- Position & momentum operators do not commute

  $[p_x,x] = p_x x - x p_x \neq 0$; *Illustration of uncertainty principle*

5) OPERATOR FOR DIFERENT PHYSICAL QUANTITIES

a) **Position: x**

b) **Differential Operators**

$$\frac{\partial}{\partial x}, \qquad \frac{\partial^2}{\partial x^2}, \qquad \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

c) Operator for linear momentum:

The classical expression for wave can be formulated as follows:

$f(x) = A(\cos 2\pi\nu t \pm i \sin 2\pi\nu t)$

Where, ν = frequency

But, according to wave mechanics frequency, $\nu = \frac{c}{\lambda} = \frac{x/t}{\lambda}$

Hence, $\nu t = x/\lambda$

$f(x) = \psi = A(\cos(2\pi x/\lambda) \pm i \sin(2\pi x/\lambda) = A \exp(\pm 2\pi i x/\lambda)$

Differentiating w.r.t x

$$\frac{d\psi}{dx} = \pm \frac{2\pi i}{\lambda} A \exp\left(\pm \frac{2\pi}{\lambda} ix\right) = \pm \frac{2\pi i}{\lambda} \psi$$

$\lambda = \frac{h}{p_x}$ de Broglie relation

$$\therefore \frac{d\psi}{dx} = \pm \frac{2\pi i}{h} p_x \psi$$

$$p_x \psi = \pm \frac{h}{2\pi i} \frac{d\psi}{dx}$$

$$\therefore p_x = \pm \frac{h}{2\pi i} \frac{\partial}{\partial x} = \pm \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$$p_x = \frac{h}{2\pi i} \frac{\partial}{\partial x} \quad ; \quad p_x^{*} = - \frac{h}{2\pi i} \frac{\partial}{\partial x}$$

Similarly p_y & p_z can be defined

Note x and p_z do not commute.

d) Operator for kinetic energy (KE),T:

$$KE = \frac{1}{2}mv^2 = \frac{1}{2m}p^2 = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

$$= -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

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

e) Operators for potential energy,V: The expression itself depending**on the system**

***Example*: mgh, ½ kx^2…etc**

6) HERMITIAN OPERATORS :

In general, $\int\psi_1^*(A\psi_2)dx = \int\psi_2(A\psi_1)^*dx = \int(A\psi_1)^*\psi_2 dx$

For given function, $\int\psi^*(A\psi)dx = \int\psi(A\psi)^*dx = \int(A\psi)^*\psi dx$

Hermitian operators have real Eigen values.

Let

$$A\psi = a\psi \quad \text{------------- (1)}$$

Multiply both sides by ψ^* and integrate

$$\int \psi^* A \psi \, d\tau = a \int \psi^* \psi \, d\tau = a \quad \text{---- (2)}$$

" $\because$ ψ is normalised "

Take complex conjugate

$$A^* \psi^* = a^* \psi^* \quad \text{------ (3)}$$

Multiply by ψ both sides and integrate

$$\int \psi A^* \psi^* \, d\tau = a^* \int \psi \psi^* \, d\tau = a^* \quad \text{---- (4)}$$

The LHS of Equations - 2 and 4 are equal according to the definition of Hermitian operator

$$\therefore a = a^*$$

i.e., a is real.

The proof can be more general as follows:

In general,for A to be anhermitian operator against two different function **ψ_1&ψ_2, the requirement is "$\int\psi_1^*(A\psi_2)dx = \int\psi_2(A\psi_1)^*dx = \int(A\psi_1)^*\psi_2 dx$" .**

Let

$$A\psi_2 = a\,\psi_2 \text{ ------------------ } (1)$$

Multiply by ψ^* and integrate

$$\int \psi_1^* A \psi_2 \, d\tau = a \int \psi_1^* \psi_2 \, d\tau \text{ ------ } (2)$$

Let

$$A^*\psi_1^* = a^* \psi_1^* \text{ ---------- } (3)$$

Multiply by ψ_2 and integrate

$$\int \psi_2 A^* \psi_1^* \, d\tau = a^* \int \psi_1^* \psi_2 \, d\tau \text{ ------ } (4)$$

The LHS of equations - 2 & 4 are equal according to the definition of hermitian operator

Hence, b

$$a \int \psi_1^* \psi_2 \, d\tau = a^* \int \psi_1^* \psi_2 \, d\tau \text{ ----- } (5)$$

a

The integrals in equation-5 is either unity if $\psi_1 = \psi_2$ or zero if $\psi_1 \neq \psi_2$

Therefore, $a = a^*$

Examples of Hermitian operators: Position, Linear momentum operator, d^n/ dx^n ,operator for KE , operator for PE , operator for total energy (Hamiltonian)

Eigen values of Hermitian operators are measurable as they are real.

Problem: Prove that linear momentum operator is hermitian

The requirement for A to be Hermitian is :

In general, $\int \psi_1^*(A\psi_2)dx = \int \psi_2(A\psi_1)^*dx = \int (A\psi_1)^*\psi_2 dx$

For given function, **$\int\psi^*(A\psi)dx = \int\psi(A\psi)^*dx = \int(A\psi)^*\psi dx$**

"$\int\psi^*A\psi dx = \int\psi^*p_x\psi dx$"*for a single function*

"$\int\psi_1^*(p_x\psi_2)dx = \int\psi_2(p_x\psi_1)^*dx = \int(p_x\psi_1)^*\psi_2 dx$"*for two different functions*.

$$\int_a^b \psi_1^*\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)\psi_2\,dx = \frac{h}{2\pi i}\int_a^b \psi_1^*\,d\psi_2$$

$$= \frac{h}{2\pi i}\left[\psi_1^*\psi_2 - \int_a^b \psi_2\,d\psi_1^*\right]$$

$\psi_1\psi_2^* = 0$, "according to the requirement of boundary conditions."

Hence, the integral becomes,

$$\int_a^b \psi_2\left(-\frac{h}{2\pi i}\right)d\psi_1^* = \int_a^b \psi_2\left(-\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)\psi_1^*\,dx$$

$$= \int_a^b \psi_2\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\psi_1\right)^* dx$$

Hence, the linear momentum operator $\frac{h}{2\pi i}\frac{\partial}{\partial x}$ is Hermitian.

7) LAPLACIAN OPERATOR, ▼^{2}:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

8) HAMILTONIAN OPERATOR,H (operator for total energy).

Hamiltonian operator, H

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

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

9) EIGEN FUNCTIONS AND EIGEN VALUES

Aψ = aψ(Eigen equation)

A = Eigen operator

a = Eigen value

ψ = Eigen function

Eigen Function	**Eigen Operator**	**Eigen Value**
ASin(ax)	d^2/ dx^2	$-a^2$
ACos(ax)	d^2/ dx^2	$-a^2$
Aexp(ax)	d/ dx	a
Aexp(ax)	d^2/ dx^2	a^2
$\psi_n = (2/l)^{1/2}$Sin $(n\pi/ l)x$	d^2/ dx^2	?

Eigen values of Hermitian operators are measurable as they are real.