

LITTLE FLOWER COLLEGE
DEPARTMENT OF CHEMISTRY

TOPIC : HERMITIAN OPERATOR AND
POSTULATES

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HERMITIAN OPERATORS

- Using Quantum mechanical principles we can predict theoretically the value of physical observable .
- When we measure that property we are actually getting the eigen value of the operator associated with the property.
- The eigen values can be real or imaginary
- But we cannot make an imaginary measurement.
- So we have to develop an operator which will yield only real values . Such operator are known as **Hermitian operator**.
- The eigen function of a hermitian operator are orthogonal.
- All quantum mechanical operators are hermitian operator such as x , P_x , V_x , T_x , H_x .

• Let A^{\wedge} be the linear operator representing the physical property of A and it has two eigen function

ψ^* and ψ . The average value of A is

$$\langle A \rangle = \int \psi^* A \psi d\tau$$

Since the average value of a physical quantity must be a real number, we demand that

$$\langle A \rangle = \langle A \rangle^*$$

$$\int \psi^* A \psi d\tau = \left[\int \psi^* A \psi d\tau \right]^* = \int (\psi^*)^* (A\psi)^* d\tau$$

$$\int \psi^* A \psi d\tau = \int \psi (A\psi)^* d\tau$$

The linear operator that satisfies for all well behaved functions is called a Hermitian operator.

PROPERTIES OF HERMITIAN OPERATOR

- THEOREM 1:
- Eigen values of hermitian operator are real numbers.

For Hermitian operator \hat{A}

$$\int (\hat{A}\Psi)^* \Psi d\tau = \Psi^* (\hat{A}\Psi) d\tau \rightarrow \textcircled{1}$$

From Eigen value equation

$$\hat{A}\Psi = a\Psi \rightarrow \textcircled{2}$$

Using $\textcircled{2}$ & $\textcircled{1}$

$$\int (a\Psi)^* \Psi d\tau = \int \Psi^* (a\Psi) d\tau$$

$$a^* \int \Psi^* \Psi d\tau = a \int \Psi^* \Psi d\tau$$

$$\int \Psi^* \Psi d\tau = \text{constant}$$

$$\int \Psi^* \Psi d\tau \neq 0$$

$$\text{Hence } (a^* - a) \int \Psi^* \Psi d\tau = 0$$

$$a^* - a = 0$$

$$a^* = a \quad a \text{ is real.}$$

THEOREM 2:

- The eigen function corresponding to two different eigen values for hermitian operator are orthogonal
- Let \hat{A} is hermitian operator and we have two different eigen function ψ_m, ψ_n corresponding to two different eigen values a_m, a_n , then from eigen value equation

$$\hat{A}\Psi_m = a_m\Psi_m \rightarrow \textcircled{1}$$

$$\hat{A}\Psi_n = a_n\Psi_n \rightarrow \textcircled{2}$$

From the definition of hermitian operator

$$\int (\hat{A}\Psi_n)^* \Psi_m d\tau = \int \Psi_n^* (\hat{A}\Psi_m) d\tau$$

Using $\textcircled{1}$ & $\textcircled{2}$ In this equation

$$\int (a_n\Psi_n)^* \Psi_m d\tau = \int \Psi_n^* (a_m\Psi_m) d\tau$$

$$a_n^* \int \Psi_n^* \Psi_m d\tau = a_m \int \Psi_n^* \Psi_m d\tau$$

$$a_n^* = a_m$$

$$a_n - a_m \int \Psi_n^* \Psi_m d\tau = 0$$

$$a_n \neq a_m \rightarrow a_n - a_m \neq 0$$

$$\int \Psi_n^* \Psi_m d\tau = 0$$

EIGEN VALUE POSTULATE

- This tells us about the **result of the measurement of variable** .
- The result of measurement of an observable A will always be one of the eigen value of the operator associated with the property as given by the eigen value equation. $\hat{A}\varphi_n = a_n \varphi_n$ and it need not be the state function .
- If the eigen function becomes the state function **we can make precise measurement.**

This postulate connect the theory and experiment .

- The eigen function and the eigen value of a system can be obtained by solving the equation .
- But here $a_n = a_1, a_2, a_3, \dots$. So that we get a spectrum of value ie, the theory doesn't tell about the accuracy .
- If we want to obtain concordant value we have to apply some condition .
- Here the eigen values must be real since they represent observable physical quantity.
- So the operators must be a hermitian one which yield only real eigen values

- As an example, consider the measurement of energy. The operator corresponding to the energy is the hamiltonian

Operator and its eigen equation is

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

- This is just a schrodinger equation the solution of this equation gives the ψ_n and E_n .
- For the case of a particle in a box $E_n = n^2h^2/8ma^2$
- Postulate 3 says that if we measure the energy of a particle in a box we shall find one of these energies and no other.

EXPECTATION / MEAN VALUE POSTULATES

- According to third postulate when we measure a definite value we get a spectrum of value then we have to go for an average .
- The fourth postulate states that in a series of measurement of an observable A of a system described by the state function ψ_n a distribution of eigen value will be obtained .
- The average / mean / expectation value of which is given by the expression.

Value of which is given by the expression $\langle \bar{A} \rangle = \bar{a}_n$

$$= \frac{\int \Psi_n^* \hat{A} \Psi_n d\tau}{\int \Psi_n^* \Psi_n d\tau} \rightarrow \frac{\int \Psi_n^* a_n \Psi_n d\tau}{\int \Psi_n^* \Psi_n d\tau}$$

If Ψ_n is eigen function of \hat{A} , then $\bar{a}_n = a_n \rightarrow \textcircled{1}$

ie. the expectation value | avg value is an eigen value itself

Taking square of the observable

$$\begin{aligned} \langle \hat{A}^2 \rangle &= \bar{a}_n^2 = \frac{\int_{\text{all space}} \Psi_n^* \hat{A}^2 \Psi_n d\tau}{\int_{\text{all space}} \Psi^* \Psi d\tau} \\ &= \frac{\int_{\text{all space}} \Psi_n^* \hat{A} (\hat{A} \Psi_n) d\tau}{\int_{\text{all space}} \Psi^* \Psi d\tau} \\ &= \frac{\int \Psi_n^* \hat{A} (a_n \Psi_n) d\tau}{\int \Psi^* \Psi d\tau} \end{aligned}$$

$$= \frac{a_n \int \Psi_n^* (\hat{A} \Psi_n) d\tau}{\int \Psi^* \Psi d\tau}$$

$$= \frac{a_n \int \Psi_n^* a_n \Psi_n d\tau}{\int \Psi^* \Psi d\tau}$$

$$= \frac{a_n^2 \int \Psi_n^* \Psi_n d\tau}{\int \Psi^* \Psi d\tau}$$

So, $\bar{a}_n^2 = a_n^2 \rightarrow \textcircled{2}$

From $\textcircled{1}$ & $\textcircled{2}$

$$\bar{a}_n^2 = a_n^2 = (\bar{a}_n)^2$$

$[(\bar{a}_n)^2 \rightarrow \text{avg. of the square}]$

Average of square = square of the average

- This is true only when all the measurements give rise to the same result i.e., $a_1 = a_2 = a_3 \dots = a_n$
- This condition is true when the state function ψ_n is an eigen function of the operator A . It is very difficult to generate a state function which is an eigen function too.
- For every system there is a state function ψ corresponding to the operator which is also an eigen function of H .
- So we have $H \psi = E \psi$, therefore precise measurement of energy of a system is possible.

THANK YOU