

Hamiltonian Operator (\hat{H})

The Operator Corresponding to the total energy of the quantum-mechanical system. The total energy of a system is the sum of kinetic energy and potential energy.

In term of Operator it is defined as Hamiltonian Operator. Denoted by a symbol ' \hat{H} '.

The total energy of a single particle having mass m is defined as E .

$$\text{Hence, } E = K.E + P.E$$

$$= \frac{p^2}{2m} + V(x, y, z)$$

$$= \frac{1}{2m} (P_x^2 + P_y^2 + P_z^2) + V(x, y, z) \quad \text{--- (1)}$$

The Operator for total energy will be

$$\hat{H} = \frac{1}{2m} (\hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2) + \hat{V}(x, y, z) \quad \text{--- (2)}$$

$$\text{Here, } \hat{P}_x^2 = \left(\frac{h}{2\pi i} \frac{\partial}{\partial x} \right) \left(\frac{h}{2\pi i} \frac{\partial}{\partial x} \right)$$

$$= \frac{h^2}{4\pi^2 i^2} \cdot \frac{\partial^2}{\partial x^2}$$

$$= -\frac{h^2}{4\pi^2} \cdot \frac{\partial^2}{\partial x^2} \quad (\because i^2 = -1)$$

$$\hat{P}_x^2 = -\hbar^2 \frac{\partial^2}{\partial x^2} \quad (\because \hbar = \frac{h}{2\pi})$$

$$\text{Similarly } \hat{P}_y^2 = -\hbar^2 \frac{\partial^2}{\partial y^2}$$

$$+ \hat{P}_z^2 = -\hbar^2 \frac{\partial^2}{\partial z^2}$$

On substituting the value of \hat{P}_x^2 , \hat{P}_y^2 and \hat{P}_z^2 in equation (2) we have.

$$\hat{H} = \frac{1}{2m} \left[\left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) + \left(-\hbar^2 \frac{\partial^2}{\partial y^2} \right) + \left(-\hbar^2 \frac{\partial^2}{\partial z^2} \right) \right] + \hat{V}(x, y, z)$$

$$\hat{H} = \frac{1}{2m} \hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \hat{V}(x, y, z)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(x, y, z)$$

Where ∇^2 is an Operator called Laplacian Operator.

Theorems of Operators

1. Theorem No - 1

Two eigenfunctions of a Hermitian Operator with different eigen values are orthogonal.

Proof: - Let \hat{A} is a Hermitian Operator and its eigen value equations are given below.

$$\hat{A} \psi_1 = \lambda_1 \psi_1 \quad \text{--- (1)}$$

$$\hat{A} \psi_2 = \lambda_2 \psi_2 \quad \text{--- (2)}$$

Where ψ_1 and ψ_2 are eigenfunctions of Operator \hat{A} with the corresponding eigen values λ_1 and λ_2 respectively.

On taking the Complex Conjugate of eqⁿ (1), where λ_1 is real.

$$\hat{A}^* \psi_1^* = \lambda_1 \psi_1^* \quad \text{--- (3)}$$

Multiplying eqⁿ (3) on the left by ψ_2 and integrating we have

$$\int \psi_2 \hat{A}^* \psi_1^* dz = \lambda_1 \int \psi_2 \psi_1^* dz \quad \text{--- (4)}$$

Again Multiplying eqⁿ (2) on the left by ψ_1^* and integrating we have

$$\int \psi_1^* \hat{A} \psi_2 dz = \lambda_2 \int \psi_1^* \psi_2 dz \quad \text{--- (5)}$$

Since \hat{A} is a Hermitian Operator, the left hand side of eqⁿ (4) and (5) are equal so that

$$\lambda_1 \int \psi_2 \psi_1^* dz = \lambda_2 \int \psi_1^* \psi_2 dz$$

$$\text{or } \lambda_1 \int \psi_1^* \psi_2 dz - \lambda_2 \int \psi_1^* \psi_2 dz = 0$$

$$\text{or } (\lambda_1 - \lambda_2) \int \psi_1^* \psi_2 dz = 0 \quad \text{--- (6)}$$

Since $\lambda_1 \neq \lambda_2$ i.e. $(\lambda_1 - \lambda_2) \neq 0$

$$\text{so, } \int \psi_1^* \psi_2 dz = 0$$

Thus these two eigenfunctions are orthogonal

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Theorems of Operators

Theorem No-2 —

If two operators commute, they have the same set of eigenfunctions.

Proof: — Let \hat{A} be the operator whose eigenvalue equation is —

$$\text{like as, } \hat{A} \psi_i = a_i \psi_i \quad \text{————— (1)}$$

where ψ_i s are the set of eigenfunctions with a_i s as the corresponding eigenvalues.

Since \hat{A} and \hat{B} commute,

$$\text{Hence } \hat{A} \hat{B} = \hat{B} \hat{A} \quad \text{————— (2)}$$

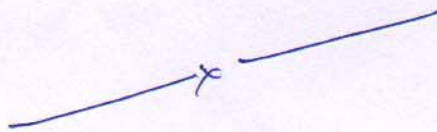
Operating on ψ_i

$$\begin{aligned} \hat{A} \hat{B} \psi_i &= \hat{B} \hat{A} \psi_i \\ &= \hat{B} (a_i \psi_i) \\ &= a_i (\hat{B} \psi_i) \end{aligned} \quad \text{————— (3)}$$

This shows that $(\hat{B} \psi_i)$ is an eigenfunction of \hat{A} with eigenvalue a_i .
This is possible only if $(\hat{B} \psi_i)$ is a multiple of ψ_i

$$\text{i.e. } \hat{B} \psi_i = b_i \psi_i \quad \text{————— (4)}$$

In other words, ψ_i is also an eigenfunction of \hat{B} .



Theorems of Operators

Theorem No. 3 : -

An arbitrary function which is not an eigenfunction of an Operator, \hat{A} can be arbitrarily expanded in a series of orthonormal functions.

i.e., It can be written as a linear superposition of the orthonormal eigenfunctions of \hat{A} .

Proof : - The proof of this theorem has not been rigorously established but it seems to be valid for Hermitian operators.

This theorem states that

$$\psi = \sum_i C_i \phi_i$$

where ψ is an arbitrary function and ϕ_i are orthonormal functions i.e. they are both orthonormal and normalized

$$\left. \begin{aligned} \int \phi_i^* \phi_j dz &= 0 \quad (\text{Orthogonal Condition}) \\ \int \phi_i^* \phi_i dz &= 1 \quad (\text{Normalization Condition}) \end{aligned} \right\}$$

The two conditions or criteria can be summed up by the relation

$$\int \phi_i \phi_j dz = \delta_{ij} = \begin{cases} 1, & i=j \\ 0, & i \neq j \end{cases}$$

where δ_{ij} is called the Kronecker delta.

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Theorems of Operator

4. Variation Theorem: -

If the ψ is an approximate wave function of a system described by the Hamiltonian, " \hat{H} ." Then the expectation value of the energy $\langle E \rangle$ is given by integral mentioned below.

$$\langle E \rangle = \int \psi^* \hat{H} \psi d\tau \equiv \langle \psi^* | \hat{H} | \psi \rangle \quad \text{--- ①}$$

The upper limit is the E_0 (ground state energy) of the system

$$\text{i.e. } E \geq E_0$$

5. Kramers Theorem: -

In absence of the external magnetic field, the electronic states of any molecule or ion having an odd number of electrons are at least doubly degenerated.

It follows that all complicated interactions by transition metal ions cannot remove the degeneracy of the state with total electron spin $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ etc. is the multiplicity ($2S+1$) of a state so that the states with $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ etc. are doublet, quartet and sextet states respectively.

The spin degeneracy of systems containing odd number of electrons is called Kramers degeneracy.

The spin-levels are split even in the absence of the magnetic field, such type of splitting is referred as zero-field splitting (ZFS).

6. Virial Theorem: -

According to virial theorem, if potential energy $V(x)$ of a quantum mechanical system moving in the X-direction is of the form

$$V(x) \propto x^S \quad \text{--- ①}$$

Where S is a constant, then the expectation (average) value of the kinetic energy, $\langle \hat{T} \rangle$ and the expectation value of the potential energy, $\langle \hat{V} \rangle$ are related by

$$\langle \hat{T} \rangle = \frac{1}{2} S \langle \hat{V} \rangle$$

It gives accuracy of the wave function obtained by the solution of Schrodinger wave eqⁿ by Hartree-Fock self-consistent ^{field} method, i.e. (SCF) Method