STUDY MATERIAL

VIVEKANANDA COLLEGE
THAKURPUKUR

NAAC ACCREDITED GRADE—'A'

Subject: <u>Chemistry</u>

Topic: <u>Operators in Wave Mechanics</u>

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<u>Physical Chemistry 3</u>

Course Title: Foundation of Quantum Mechanics

Representation of Physical Observables: Operators

In the second postulate of wave mechanics, it was stated that each measurable quantity of a system (physical observable) is represented by a Hermitian operator.

An operator is a mathematical entity that tells us how to change the function or number that follows it. Summation, multiplication, differentiation *etc* are common operators that we use. Linear operators are those which satisfy the following property:

Suppose Â is a linear operator operating on functions Ψ and Φ

Then it will satisfy the equation

$$\hat{A}\,(C_1\,\Psi + C_2\,\Phi) = C_1\,\hat{A}\,\Psi + C_2\,\hat{A}\,\Phi$$

where C_1 and C_2 are two constants.

To qualify as a suitable quantum mechanical operator, it has to be a Hermitian operator (a subset of linear operators).

Basic operators are defined for the space coordinates, conjugate momentum coordinates and total energy. Quantum mechanical operators for all the other measurable properties can be constructed using these basic operators.

Hermitian Operators

Hermitian operator are those linear operators which satisfy the following condition: If ψ_i and ψ_j (where $i \neq j$) are any two well-behaved wave functions, and $\hat{A}$ is a linear operator, then

$$\int \psi_i^* \hat{A} \psi_j \, d\tau = \int \psi_j \left(\hat{A}^* \psi_i^* \right) d\tau \quad \text{..........(1)}$$

The integrals are over the whole space. This is called the turn-over rule. Note that on the left hand side of the equation, the operator operates on ψ_j. But on the right hand side of the equation, the complex conjugate of the operator operates on the complex conjugate of ψ_i. The resulting function is then multiplied with ψ_j and integrated over whole space.

If we consider $i=j$, the above condition reduces to

$$\int \psi^* \hat{A} \psi \, d\tau = \int \psi \left(\hat{A}^* \psi^* \right) d\tau \quad \text{...........(2)}$$

Why should a quantum mechanical operator have to be Hermitian? The conditions stated through equations 1 and 2 ensure that the eigenvalues of well-behaved wave functions are real quantities and also that the eigenfunctions of an operator are orthogonal to each other.

Eigenvalues are real for Hermitian Operators

The postulate 3 of QM states that in any measurement of an observable, represented by an operator $\hat{A}$, the only values observed will be the eigenvalues. So, these eigenvalues have to be real quantities, although the wave function and the operator can be complex (in general).

Let us consider the eigenvalue equation

$\hat{A}\psi = \alpha\psi$ **.........(3)**

Multiplying the equation from the left with complex conjugate of the wave function and integrating over the whole space, we get

$\int \psi^* \hat{A}\psi \, d\tau = \alpha \int \psi^*\psi \, d\tau$ **...........(4)**

Now we take the complex conjugate of equation 3, $\hat{A}^*\psi^* = \alpha^*\psi^*$

Multiplying this equation from the right with the wave function and integrating over the whole space, we get

$\int \psi \left(\hat{A}^*\psi^*\right) d\tau = \int \psi(\alpha^*\psi^*) \, d\tau = \alpha^* \int \psi\psi^* \, d\tau = \alpha^* \int \psi^*\psi \, d\tau$ **...(5)**

As the operator is Hermitian, LHS of equations 4 and 5 are equal, so are the RHS. So we get, $(\alpha - \alpha^*) \int \psi^*\psi \, d\tau = 0$ **.........(6)**

For a normalized wavefunction the integral on the RHS of equation 6 is unity. Therefore, the eigenvalue α must be real, as $(\alpha - \alpha^*)$ must be 0.

Eigenfunctions are orthogonal for Hermitian Operators

For any quantum mechanical operator $\hat{A}$, we have a complete set of eigenfunctions ψ_i which may be tagged to their specific eigenvalues E_i. For these eigenfunctions to be orthogonal to each other, any two eigenfunctions, say, ψ_i and ψ_j (where $i \neq j$) should satisfy the condition:

$\int \psi_i^* \psi_j d\tau = 0$ (The integral is over all space relevant to the system).

Consider the two equations, where α_i and α_j are distinct eigenvalues,

$\hat{A}\psi_i = \alpha_i \psi_i$ ……(7) and $\hat{A}\psi_j = \alpha_j \psi_j$……..(8)

From the complex conjugate of eqn 7 we can get

$$\int \psi_j (\hat{A}^* \psi_i^*)\, d\tau = \int \psi_j ({\alpha_i}^* \psi_i^*)\, d\tau = \alpha_i \int \psi_j \psi_i^*\, d\tau \quad \text{……….(9)}$$

From eqn 8 we can get

$$\int \psi_i^* \hat{A} \psi_j\, d\tau = \alpha_j \int \psi_i^* \psi_j\, d\tau = \alpha_j \int \psi_j \psi_i^*\, d\tau \quad \text{……….(10)}$$

As $\hat{A}$ is Hermitian, that is, $\int \psi_i^* \hat{A} \psi_j\, d\tau = \int \psi_j (\hat{A}^* \psi_i^*)\, d\tau$, RHS of (9) and (10) are equal. So we have $(\alpha_j - \alpha_i) \int \psi_j \psi_i^*\, d\tau = 0$

As $(\alpha_j - \alpha_i) \neq 0$, $\int \psi_j \psi_i^*\, d\tau = \int \psi_i^* \psi_j\, d\tau = 0$

Non-degenerate eigenfunctions of Hermitian operators are orthogonal.