



Lectures of
Quantum mechanics of Chemistry

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Lecture No. 2:
General properties of Eigen Functions

Introduction:

The properties of chemical system, some of quantized and the other are not. If a property is quanta, what possible results will be measure of such a property yield? These questions can answer mathematically. According to conditions

Q//What the main conditions the of chemical systems to be properties are quantize?

- The allowed values of any property are limited to the Eigenvalues of the operator that's represent this property.
- If the corresponding Eigenvalues are discrete, this property is quantized; otherwise, it is not.

The "Eigenvalues" and "Eigen functions" of an operator? ("Eigen" came from the German word "Eigentum" that does not seem to have a precise English translation. It means something like "characteristic" or "distinct," or more precisely:

Eigen function is the function that's produced or give us the same function if they operate by the linear mathematical operator and the attached constant value is Eigenvalue.

1-Eigen values and Eigen functions:

In general, an operator acting on an arbitrary state function will change it to another state function. These state functions are called the "Eigenfunctions" of this operator. Application of such an operator on each of its Eigenfunctions leads to a characteristic number, which is an integer number (no imaginary part), associated with this Eigen function. The characteristic number corresponding to each Eigen function of the operator is called the "Eigenvalue" corresponding to this Eigen function. For example, the Eigenvalue equation with discrete Eigenvalues:

$$\hat{A}(\chi_i) f(\chi_i) = p f(\chi_i)$$

Eq.1 gives the effect of an operator $\hat{A}(\chi_i)$ on its Eigen function $f(\chi_i)$ corresponding to the Eigenvalue p . For continuous Eigenvalues: where χ_i is a continuous variable. For some operators, some of the Eigenvalues are discrete while the others are continuous.

Examples: -

$$\frac{\partial^2}{\partial x^2}(\sin ax) = \frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} \sin ax \right) = \left(\frac{\partial}{\partial x} a \cos ax \right) = -a^2 \sin ax$$

Therefore, $\sin ax$ is Eigen function and $-a^2$ is Eigenvalue.

2-Postulates of Quantum mechanics:

Postulates are rules governing the behavior of Eigen function as follows:-

- 1- The probability of electron foundation anywhere has a single value along the axis of dimension.
- 2- A mathematical operator (linear operator) must represent any physical quantity for a chemical system.

- 3- The wave function $\Psi(q, t)$ is the Schrödinger equation depend on the time since it determines the past and future state of the system if the present state is known.

$$\hat{H} \Psi(q, t) = \hbar/2\pi i \cdot \partial/\partial t \cdot \Psi(q, t).$$

- 4- If a single measurement has been done on the system according to mathematical operator \hat{H} , the only mathematics value (Eigen value) is the associated value to the function $\hat{H} \Psi = \alpha \Psi$.

- 5- If both of Ψ_1 and Ψ_2 are Eigen functions for the Eigenvalues a_1 and a_2 respectively for the mathematic operator \hat{H} , they found other solutions are borne from a linear combination of Ψ_1 and Ψ_2 , its Ψ as following

$\Psi = C_1 \Psi_1 + C_2 \Psi_2$ since C_1 and C_2 are constant quantities for the system state to give finite probability to measurable a_1 and a_2 respectively.

3- Hermetic character of mathematical operators

Prove the hermetic character of mathematic operators.

If they \hat{A} is a hermetic operator for Ψ , and α is Eigenvalue. According to the fourth postulate of quantum mechanics: $\hat{A} \Psi = \alpha \Psi$ -----1

By taking the conjugated complex of eq. 1

$$\hat{A}^* \Psi^* = \alpha^* \Psi^* \text{-----2}$$

At this time multiply eq.1 by Ψ^* and eq.2 by Ψ and integration both equations respected to the element of volume $d\tau$ to get on:

$$\Psi^* \hat{A} \Psi = \Psi^* \alpha \Psi \text{-----3}$$

$$\Psi \hat{A}^* \Psi^* = \Psi \alpha^* \Psi^* \text{-----4}$$

$$\int \Psi^* \hat{A} \Psi d\tau = \alpha \int \Psi^* \Psi d\tau \text{-----5}$$

$$\int \Psi \hat{A}^* \Psi^* d\tau = \alpha^* \int \Psi \Psi^* d\tau \text{-----6}$$

Due that \hat{A} is hermetic operator therefore $\int \Psi^* \hat{A} \Psi d\tau = \int \Psi \hat{A}^* \Psi^* d\tau$

So that:

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

At this time that's mean $\alpha^* = \alpha$ and α^* is not a complex value but it is true value because it's equal to original value α .

4- Degenerates and Orthogonal functions:

According to the five postulates of quantum mechanics, if they acted by operator, \hat{A} on the Eigen functions Ψ_1 and Ψ_2 respectively and Ψ is not Eigen function for \hat{A} .

$$\text{If that } \Psi = C_1\Psi_1 + C_2\Psi_2 \text{-----1}$$

If they act by \hat{A} onto eq.1

$$\hat{A}\Psi = \hat{A}(C_1\Psi_1 + C_2\Psi_2) \text{-----2}$$

Or

$$\hat{A}\Psi = C_1\hat{A}\Psi_1 + C_2\hat{A}\Psi_2 \text{-----3}$$

According to the fourth postulate of quantum mechanics:

$$\hat{A}\Psi_1 = \alpha_1\Psi_1 \quad \text{and} \quad \hat{A}\Psi_2 = \alpha_2\Psi_2$$

$$\hat{A}\Psi = C_1\alpha_1\Psi_1 + C_2\alpha_2\Psi_2 \text{-----4}$$

Eq.4 became true only if that $\alpha_1 = \alpha_2$, because $\Psi = C_1\Psi_1 + C_2\Psi_2$

So that at this time can be say that both of Ψ_1 and Ψ_2 are Degenerate functions.

If the Eigenvalues of the different wave functions are equalized with each other. Can say about this function are Degenerate functions and the linear combination of Eigen degenerate functions for hermetic operator \hat{A} it can be considered Eigen function at this operator.

If that both of Ψ_1 and of Ψ_2 are Eigen function for same Hermetic quantum mechanics operator but they have different Eigenvalues.

Therefore:

$$\text{Prove that } \int \Psi_2\Psi_1^* d\tau = 0 \text{-----5}$$

At this time, it can say these functions are orthogonal. Every function of them is independent of the other function.

Can prove the orthogonal functions property by using the fourth postulate as follow:
If that

$$\hat{A}\Psi_1 = \alpha_1\Psi_1 \quad \text{-----6} \quad \text{and} \quad \hat{A}\Psi_2 = \alpha_2\Psi_2 \quad \text{-----7}$$

By taking the conjugated complex for eq.6

$$\hat{A}^*\Psi_1^* = \alpha_1^*\Psi_1^* \quad \text{-----8} \quad \text{due to that } \hat{A} \text{ is hermetic operator so that } \alpha_1 = \alpha_1^*$$

Therefore

$$\hat{A}^*\Psi_1^* = \alpha_1\Psi_1^* \quad \text{-----9}$$

By multiplying eq.9 with Ψ_2 and multiplying eq.7 with Ψ_1^* respectively to get on

$$\Psi_2\hat{A}^*\Psi_1^* = \Psi_2\alpha_1\Psi_1^* \quad \text{-----10}$$

$$\Psi_1^*\hat{A}\Psi_2 = \Psi_1^*\alpha_2\Psi_2 \quad \text{-----11}$$

By integrating eq. 10 and eq.11 respected to volume element, at last by rearrangement and teak differences between them.

$$\int \Psi_2 \hat{A}^* \Psi_1^* d\tau - \int \Psi_1^* \hat{A} \Psi_2 d\tau = (\alpha_1 - \alpha_2) \int \Psi_2 \Psi_1^* d\tau \quad \text{-----12}$$

Due to that, \hat{A} is hermetic operator; the left side of eq.12 must be equal to zero.

$$\text{So that:} \quad (\alpha_1 - \alpha_2) \int \Psi_2 \Psi_1^* d\tau = 0 \quad \text{-----13}$$

At this time, α_1 is not equal to α_2 because they are different Eigenvalues for different Eigen functions. So that, eq.13 to be right must be the term

$$\int \Psi_2 \Psi_1^* d\tau = 0 \quad \text{-----14}$$

At this time not necessary for the left side of eq.12 to be orthogonal to be the value equal to zero since Eigenvalues will be equalized ($\alpha_1 = \alpha_2$). Can be say about the wave functions are orthogonal functions. Can written $\int \Psi_i^* \Psi_j d\tau = \int_{\Omega}$

This term is call Kronecker Delta.

5-Exchange of mathematical operators:

Exchange of mathematical operators is a property of hermetic operators, therefore if **the two operators are exchanged their positions with each other's**

likes \hat{A} and \hat{S} when they act at the same wave function, at this time they have the same groups of Eigen values.

It is possible to have complete simultaneous knowledge of two specific properties of a system, say "A" and "B". Physically, for two properties to be specified simultaneously, it must be possible to measure one of the two properties without influencing the outcome of the measurement of the other property, and vice versa. This means that application of the operator $\hat{A} \hat{S}$ on any arbitrary state C should be the same as applying the operator $\hat{S} \hat{A}$ on the same state. That means the effect of the operator ($\hat{A} \hat{S} - \hat{S} \hat{A}$) on any arbitrary state of the system must be equal to zero. In this case equivalent to a null operator $(\hat{A} \hat{S} - \hat{S} \hat{A}) = 0$

Q/prove that

$$\hat{A} \hat{S} - \hat{S} \hat{A} = 0 \text{ and } \hat{A} \hat{S} = \hat{S} \hat{A} \text{-----1}$$

To prove eq.1 depending on fourth postulated

$$\hat{A} \psi = a \psi \text{-----2} \quad \text{and} \quad \hat{S} \psi = b \psi \text{-----3}$$

If that both a and b are constants that have suited for ψ for both two operators.

If the acted-on eq.2 with \hat{S} and same thing on eq.3 with \hat{A} that's produced:

$$\hat{S} \hat{A} \psi = \hat{S} a \psi \text{-----4} \quad \text{and} \quad \hat{A} \hat{S} \psi = \hat{A} b \psi \text{-----5}$$

Due to that

$\hat{S} \psi = b \psi$ and $\hat{A} \psi = a \psi$ so that can be write the following:

$$\hat{S} a \psi = ab \psi \text{-----6} \quad \text{and} \quad \hat{A} b \psi = ab \psi \text{-----7}$$

Or

$$ab \psi = \hat{S} \hat{A} \psi \quad \text{and} \quad ab \psi = \hat{A} \hat{S} \psi$$

Therefore

$$\hat{S} \hat{A} \psi = \hat{A} \hat{S} \psi$$

6-Expansion of wave functions:

There are common applications for expansion of wave functions in the problems of quantum mechanics since the general wave function (ψ) represents the

linear combination for completely groups of orthonormal functions as in the following representation: -

$$\Psi = C_1 \Psi_1 + C_2 \Psi_2 + C_3 \Psi_3 + C_4 \Psi_4 + \dots + C_n \Psi_n \text{ ----- (1)}$$

Since the C_1, C_2, C_3, C_4, C_n are constants, and eq-1 are equivalent with the equation of direction analysis by its components along the dimensions.

To find the constants must be multiple eq-1 by Ψ_j^* if that $J=1$ into n values.

$$\Psi_j^* \Psi = C_1 \Psi_j^* \Psi_1 + C_2 \Psi_j^* \Psi_2 + C_3 \Psi_j^* \Psi_3 + C_4 \Psi_j^* \Psi_4 + \dots + C_n \Psi_j^* \Psi_n \text{(2)}$$

By integral eq-2 according to the element of volume.

$$\int \Psi_j^* \Psi d\tau = C_1 \int \Psi_j^* \Psi_1 d\tau + C_2 \int \Psi_j^* \Psi_2 d\tau + C_3 \int \Psi_j^* \Psi_3 d\tau + C_4 \int \Psi_j^* \Psi_4 d\tau + \dots + C_n \int \Psi_j^* \Psi_n d\tau \text{ ----- (3)}$$

At the right side of eq-3, j will take the same values of wave functions ($\Psi_j^* = \Psi_1^*$) and so on for each term and therefore all integrals in eq-3 equal to 1 due to normalization condition. If the values differ, all integrals are equal to zero due to orthogonal conditions.

$$\int \Psi_j^* \Psi d\tau = C_j \text{ ----- (4)}$$

Eq.4 represent the value of the expansion coefficient and can be using this equation to find the **average value of unobservable quantity**.

Q// Find the average value of unobservable quantity

If supposed that $\Psi_1, \Psi_2, \Psi_3, \Psi_4$, and Ψ_n are completely groups of orthonormal functions for the mathematical operator \hat{A} that's a suitable for observed value in this system. So that if eq-1 acted by \hat{A} this produced:

$$\hat{A} \Psi = C_1 \hat{A} \Psi_1 + C_2 \hat{A} \Psi_2 + C_3 \hat{A} \Psi_3 + C_4 \hat{A} \Psi_4 + \dots + C_n \hat{A} \Psi_n \text{ ----- (5)}$$

According to the fourth hypothesis $\hat{A} \Psi = a \Psi$ so that

$$\hat{A} \Psi = C_1 a_1 \Psi_1 + C_2 a_2 \Psi_2 + C_3 a_3 \Psi_3 + C_4 a_4 \Psi_4 + \dots + C_n a_n \Psi_n \text{ ---- (6)}$$

$\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_n$ are Eigenvalues for Eigenfunctions $\Psi_1, \Psi_2, \Psi_3, \Psi_4$, and Ψ_n respectively. By taking the conjugated complex for eq.1

$$\Psi^* = C^*_1 \Psi^*_1 + C^*_2 \Psi^*_2 + C^*_3 \Psi^*_3 + C^*_4 \Psi^*_4 + \dots + C^*_n \Psi^*_n \text{ ----- (7)}$$

By multiplying the first side of eq-6 by the first side of eq-7 and the second side by the second side for the same equations.

$$\int \Psi^* \hat{A} \Psi d\tau = C^*_1 C_1 \alpha_1 \int \Psi^*_1 \Psi_1 d\tau + C^*_2 C_2 \alpha_2 \int \Psi^*_2 \Psi_2 d\tau + C^*_3 C_3 \alpha_3 \int \Psi^*_3 \Psi_3 d\tau + C^*_4 C_4 \alpha_4 \int \Psi^*_4 \Psi_4 d\tau + C^*_n C_n \alpha_n \int \Psi^*_n \Psi_n d\tau \text{-- (8)}$$

Eq-8 is clear from the terms of $C^*_i C_j \alpha_j \int \Psi^*_i \Psi_j d\tau$ because it is equal to zero (orthogonal functions), due to all terms in right side equal to one in equation -8 , so that:-

$$\int \Psi^* \hat{A} \Psi d\tau = C^*_1 C_1 \alpha_1 + C^*_2 C_2 \alpha_2 + C^*_3 C_3 \alpha_3 + C^*_4 C_4 \alpha_4 + \dots + C^*_n C_n \alpha_n \text{-- (9)}$$

According to five postulates of quantum mechanics, the right side of equation -9 represents **the average value of an unobservable quantity that's suitable to the mathematical operator** when the system in the state of Ψ , by using the average value (\bar{a})...Can be written eq-9 as:

$$\bar{a} = \int \Psi^* \hat{A} \Psi d\tau \text{----- (10)}$$

By this equation can find a lot of measuring for $\alpha_1, \alpha_2 \dots$ etc. for any physical measuring quantity. The average value is equal to the summation of measuring divided by the number of measuring. this equation is transferred from the pure mathematical quantum mechanics theory into a real physical system.

7-Application:

Example// 1

Prove that $C_1^* C_1 + C_2^* C_2 = 1$, According to $\Psi = C_1 \Psi_1 + C_2 \Psi_2$ where C_1 , and C_2 are constants of system case and the probability of a_1 value equal to $C_1^* C_1$ and a_2 equal to $C_2^* C_2$, since a_1 and a_2 are Eigenvalues for functions Ψ_1, Ψ_2 respectively.

Answer: -

Normalization condition is $\int \Psi^* \Psi d\tau = 1$; so that

$$\int \Psi^* \Psi d\tau = 1 = \int (C_1 \Psi_1 + C_2 \Psi_2)^* (C_1 \Psi_1 + C_2 \Psi_2) d\tau \text{ therefore}$$

$$C_1^* C_1 \int \Psi_1^* \Psi_1 d\tau + C_1^* C_2 \int \Psi_1^* \Psi_2 d\tau + C_2^* C_1 \int \Psi_2^* \Psi_1 d\tau + C_2^* C_2 \int \Psi_2^* \Psi_2 d\tau = 1$$

$$\int \Psi_1^* \Psi_2 d\tau = 0, \int \Psi_2^* \Psi_1 d\tau = 0 \text{ (orthogonal conditions) and } \int \Psi_1^* \Psi_1 d\tau = 1, \\ \int \Psi_2^* \Psi_2 d\tau = 1 \text{ (normalization condition) ; so that } C_1^* C_1 + C_2^* C_2 = 1$$

Example// 2

If that a_i and a_j are Eigenvalues for functions Ψ_i, Ψ_j for mathematical operator \hat{O} respectively. Prove that integral of $\int \Psi_i^* \hat{O} \Psi_j d\tau = 0$, taking in your mind the functions are orthogonal.

Answer:-

By using the fourth postulate of quantum mechanics

$$\hat{O} \Psi_j = a_j \Psi_j \text{-----1}$$

Multiple eq.1 with conjugated complex of Ψ_i and integrated respect to element of volume

$$\Psi_i^* \hat{O} \Psi_j = \Psi_i^* a_j \Psi_j \text{-----2}$$

$$\int \Psi_i^* \hat{O} \Psi_j d\tau = a_j \int \Psi_i^* \Psi_j d\tau \text{-----3}$$

Due to that condition of question, functions are orthogonal functions.

$$\text{Then } \int \Psi_i^* \Psi_j d\tau = 0$$

$$\text{So that } \int \Psi_i^* \hat{O} \Psi_j d\tau = 0$$