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**CHEMISTRY**
**PAPER:2, PHYSICAL CHEMISTRY-I**
**MODULE:13, APPROXIMATE METHOD – VARIATION  
METHOD**

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**CHEMISTRY**

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**MODULE:13, APPROXIMATE METHOD – VARIATION  
METHOD**

## 1. Learning Outcomes

After studying this module, you shall be able to

- Appreciate the application of variation method for studying complex chemical systems
- Identify the steps involved in studying a complex system quantum mechanically using variation method
- Identify suitable trial functions for application of variation method

## 2. Approximate Method – Variation method

Exact solution of the Schrödinger equation for any atom or molecule more complicated than the hydrogen atom or in other words for a multi-electron system is not possible.

Various approximate methods have been proposed to find eigenstates and eigenvalues of such complex systems. Two such approximate methods that have been most widely used are

- Perturbation theory
- Variation method

In this module, we shall develop the use of Variation method.

Variation method of approximating eigenfunctions and eigenvalues is of great importance in quantum chemistry and has been widely used for studying various complex chemical systems. Variation methods are more common and easier to apply than perturbation theory as variation method does not require a similar problem for which the exact solution is known previously. Valence band approach and molecular orbital approach come from variation method.

### 2.1 Variation theorem

Consider a quantum system for which the Schrödinger equation cannot be solved,

$$\hat{H} \psi_n = E_n \psi_n \dots(1)$$

Where  $\psi_n$  refers to the exact set of eigenfunctions for the system and  $E_n$  refers to the eigenvalues of the system.  $\Psi_0$  and  $E_0$  are ground state wave function and energy respectively but cannot be determined explicitly for the complex system. Variation principle provides a possible route to solve equation (1) which involves the following steps:

- Guess a ground state wave function for the system ( $\psi_a$ ). The guess for the wave function should be logical and based on various physical and chemical considerations.

$\psi_a \neq \psi_0$ , as  $\psi_a$  is an approximate wave function.

The approximate energy  $E_a$  is calculated using equation (2) and is always greater than the true energy  $E_0$

$$E_a = \frac{\int \psi_a^* \hat{H} \psi_a d\tau}{\int \psi_a^* \psi_a d\tau} \geq E_0 \dots(2)$$

Where  $d\tau$  represents the appropriate volume element. In equation (2),  $\hat{H}$  is exact but the wave function  $\psi_a$  is approximate. The approximate energy  $E_a$  is an estimate of the true energy and is called Rayleigh ratio.

- According to variation theorem,

$$E_a \geq E_0 \dots(3)$$

Variation theorem states that one can calculate an upper bound to the ground state energy  $E_0$  by using any appropriate guess/ trial function.

The closer  $\psi_a$  is to  $\psi_0$ , the closer  $E_a$  will be to  $E_0$ .

If  $\psi_a = \psi_0$ , then obviously  $E_a$  is equal to  $E_0$ . If two appropriate guess wave functions are used, then the wave function which gives  $E_a$  value closer to actual energy value  $E_0$  is better than the other one.

## 2.2 Linear Variation principle

Linear variation principle is widely used for studying complex systems. Linear variation principle employs a guess/trial function for solving the Schrödinger equation of complex system. The guess /trial function so considered is of the form

$$\psi_a = \sum a_n \Psi_n \dots\dots(4)$$

i.e., the guess/trial function is expressed as a linear combination of a complete set of normalized and orthogonal eigenfunctions  $\Psi_1, \Psi_2, \Psi_3, \dots\dots\dots$  of the same system. The coefficient  $a_n$  in equation (4) refers to some arbitrary parameters, called variational parameters / coefficients.

**Note:** Any guess function can be expanded as a linear combination of exact eigenfunctions  $\Psi_n$ . However, in practice, we don't need and don't happen to know  $\Psi_n$ 's, as we are applying variation method to a complex problem which we cannot solve analytically.

### 2.3 Proof of Variation theorem

In this section, we will prove that the variation theorem gives an approximate wave function which always gives higher energy than the ground state energy. The guess wave function  $\psi_a$  is so chosen that satisfies the same boundary conditions as the exact wave function and is generally taken as a linear combination of orthonormal set of independent functions.

$$\psi_a = \sum a_n \Psi_n$$

Using  $\psi_a$ , one can calculate  $E_a$  as,

$$E_a = \frac{\int \sum_n a_n \Psi_n^* \hat{H} \sum_n a_n \Psi_n d\tau}{\int \sum_n a_n \Psi_n^* \sum_n a_n \Psi_n d\tau} \quad \dots(5)$$

Considering the variational coefficients real,  $a_n^* = a_n$

Assuming  $\psi_a$  to be normalized, the denominator of equation (2) becomes,

$$\int \psi_a^* \psi_a d\tau = 1$$

Expressing the denominator of equation (2) in terms of linear variation function gives,

$$\int \sum_n a_n \Psi_n^* \sum_n a_n \Psi_n d\tau = \sum_n a_n^* a_n \int \Psi_n^* \Psi_n d\tau = \sum_n a_n^* a_n \int \Psi_n^* \Psi_n d\tau = 1$$

$$\sum_n a_n^* a_n = 1 \quad \dots(6)$$

Using equation (6) reduces equation (5),

$$E_a = \int \sum_n a_n \Psi_n^* \hat{H} \sum_n a_n \Psi_n d\tau \quad \dots(7)$$

Since,  $\hat{H} \Psi_n = E_n \Psi_n$

Equation (7) becomes,

$$E_a = \sum_n a_n^* a_n \int \Psi_n^* E_n \Psi_n d\tau = \sum_n a_n^* a_n E_n \quad \dots(8)$$

Subtracting  $E_o$  from both the sides of equation (8),

$$E_a - E_o = \sum_n a_n^* a_n (E_n - E_o), \quad \sum_n a_n^* a_n = 1 (\text{proved earlier})$$

$$E_n > E_o, \quad (E_n - E_o) > 0$$

$$\Rightarrow E_a > E_o$$

This proves that the variation method provides an upper bound to the ground state energy of the system.

## 2.4 Secular determinant

A trial function that depends linearly on the variational parameters leads to a secular determinant.

Considering the trial function as given in equation (4) with  $n = 2$  and  $a_1, a_2, \Psi_1$  and  $\Psi_2$  parameters real gives,

$$\psi_a = a_1\Psi_1 + a_2\Psi_2$$

Since  $a_1, a_2, \Psi_1$  and  $\Psi_2$  are all real,  $\psi_a^* = \psi_a$  .....(9)

The approximate energy  $E_a$  is calculated using equation (5)

$$E_a = \frac{\int \sum_n a_n \Psi_n^* \hat{H} \sum_n a_n \Psi_n d\tau}{\int \sum_n a_n \Psi_n^* \sum_n a_n \Psi_n d\tau}$$

where the numerator and denominator terms can be expressed individually in the form,

$$\begin{aligned} \int \psi_a^* \hat{H} \psi_a d\tau &= \int (a_1\Psi_1 + a_2\Psi_2) \hat{H} (a_1\Psi_1 + a_2\Psi_2) d\tau \\ &= a_1^2 \int \Psi_1 \hat{H} \Psi_1 d\tau + a_1 a_2 \int \Psi_1 \hat{H} \Psi_2 d\tau + a_1 a_2 \int \Psi_2 \hat{H} \Psi_1 d\tau + a_2^2 \int \Psi_2 \hat{H} \Psi_2 d\tau \quad \dots(10) \\ &= a_1^2 H_{11} + a_1 a_2 H_{12} + a_1 a_2 H_{21} + a_2^2 H_{22} \end{aligned}$$

$$\begin{aligned} \int \Psi_i \hat{H} \Psi_i &= H_{ii}, \int \Psi_j \hat{H} \Psi_j = H_{jj} \\ \int \Psi_i \hat{H} \Psi_j &= H_{ij} \\ \text{Since } \hat{H} \text{ is hermitian, } &H_{ij} = H_{ji} \end{aligned}$$

$$\int \psi_a^* \hat{H} \psi_a d\tau = a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22} \quad \dots(11)$$

And 
$$\int \psi_a^* \psi_a d\tau = \int (a_1\Psi_1 + a_2\Psi_2)^2 d\tau$$

$$\begin{aligned} \int \Psi_i \Psi_i &= S_{ii}, \int \Psi_j \Psi_j = S_{jj} \\ \int \Psi_i \Psi_j &= S_{ij} \end{aligned}$$



$$\begin{aligned}
 &= a_1^2 \int \Psi_1 \Psi_1 d\tau + a_1 a_2 \int \Psi_1 \Psi_2 d\tau + a_1 a_2 \int \Psi_2 \Psi_1 d\tau + a_2^2 \int \Psi_2 \Psi_2 d\tau \\
 &= a_1^2 S_{11} + a_1 a_2 S_{12} + a_1 a_2 S_{21} + a_2^2 S_{22}
 \end{aligned}$$

$$\int \psi_a^* \psi_a d\tau = a_1^2 S_{11} + 2a_1 a_2 S_{12} + a_2^2 S_{22} \dots$$

The integral quantities  $H_{ij}$  and  $S_{ij}$  are called matrix elements and modify equation (5) to

$$E_a = \frac{a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22}}{a_1^2 S_{11} + 2a_1 a_2 S_{12} + a_2^2 S_{22}} \dots (12)$$

Rearranging equation (12) gives

$$E_a (a_1^2 S_{11} + 2a_1 a_2 S_{12} + a_2^2 S_{22}) = a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22} \dots (13)$$

Differentiating equation (13) with respect to  $a_1$  and equating the differential to zero as we are minimizing energy gives,

$$a_1 (H_{11} - ES_{11}) + a_2 (H_{12} - ES_{12}) = 0 \dots (14)$$

Differentiating equation (13) with respect to  $a_2$  and equating the differential to zero as we are minimizing energy gives,

$$a_1 (H_{12} - ES_{12}) + a_2 (H_{22} - ES_{22}) = 0 \dots (15)$$

Equations (14) and (15) constitute a pair of linear algebraic equations for  $a_1$  and  $a_2$ .

Differentiation of energy with respect to the variational parameters yields a non-trivial solution only if the determinant of coefficients equals to zero.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \dots (16)$$

The determinant in equation (16) is called the secular determinant. The solution of this determinant gives a 2<sup>nd</sup> order secular equation as an approximation to ground state energy.

For  $n$  functions,  $n \times n$  secular determinant is obtained which gives  $n^{\text{th}}$  order secular equation as an approximation to the energy.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots\dots\dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots\dots\dots & \dots\dots\dots \\ \dots\dots\dots & \dots\dots\dots & \dots\dots\dots & \dots\dots\dots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots\dots\dots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

### 3. Summary

1. Variation method is an approximate approach used in quantum mechanics.
2. The basic principle of variation method is to guess a trial wave function for the problem, which consists of some adjustable parameters called variational parameters. These variational parameters are fixed to minimize the energy of trial wave function. The resulting trial wave function and corresponding energy are variation method approximations to exact wave function and energy.
3. Variation method calculates an upper bound ( $E_a$ ) to the ground state energy  $E_o$  by using any appropriate guess/ trial function ( $\psi_a$ ).

$$E_a = \frac{\int \psi_a^* \hat{H} \psi_a d\tau}{\int \psi_a^* \psi_a d\tau} \geq E_o$$

4. The trial/guess function so chosen should satisfy same boundary conditions as the exact wavefunction and should be normalized.

5. The most important step for solving eigenvalues of complex systems using variation method is choosing or guessing the right guess/trial function  $\psi_a$  which determines the success of the variation method.
6. A trial function can be taken as a linear combination of  $n$  linearly independent functions.

$$\psi_a = \sum a_n \Psi_n, \text{ where } a_n \text{ refers to the variational parameters.}$$

7. A trial function that depends linearly on the variational parameters leads to a secular determinant which gives secular equation as an approximation to the energy.

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