

Approximate Methods - III

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APPROXIMATE METHOD

VARIATION METHOD

The variation theorem is very in the treatment of chemical bond. In this method a trial function is reasonably guessed and is used to calculate the energy expectation value.

The Schrodinger's wave equation is

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \text{--- (1)}$$

$$\text{or } \left(-\frac{h^2 \nabla^2}{8\pi^2 m} + V \right) \psi = E \psi \quad \text{--- (2)}$$

The term on the left hand side of equation (2) can be considered to be an operator acting on ψ . Thus, equation (2) may be written as

$$\hat{H}\psi = E\psi \quad \text{--- (3)}$$

where \hat{H} is known as Hamiltonian operator. Multiplying both sides of equation (3) by ψ^* and then integrating over the configuration space, we have

$$\int \psi^* \hat{H}\psi d\tau = E \int \psi \psi^* d\tau$$

$$E = \frac{\int \psi^* \hat{H}\psi d\tau}{\int \psi \psi^* d\tau} \quad \text{--- (4)}$$

Variation theory presumes that the calculate value

$$E \geq E^0$$

where E^0 is the true energy, and the equality

(2)

holds when $\psi = \psi_0$
 If the trial function is ~~chosen~~ contains some variable parameters (α, β, \dots) then the best function is obtained by minimizing the energy with respect to α, β, \dots i.e. by setting

$$\frac{\delta E}{\delta \alpha} = \frac{\delta E}{\delta \beta} = \dots = 0$$

if the trial function is a linear combination of some basis functions $\phi_1, \phi_2, \dots, \phi_n$ i.e.
 $\psi = a_1 \phi_1 + a_2 \phi_2 + \dots + a_n \phi_n$ then the energy minimisation leads to linear secular equation of the type

$$a_1(H_{11} - ES_{11}) + a_2(H_{12} - ES_{12}) + \dots + a_n(H_{1n} - ES_{1n}) = 0$$

$$a_1(H_{n1} - ES_{n1}) + a_2(H_{n2} - ES_{n2}) + \dots + a_n(H_{nn} - ES_{nn}) = 0$$

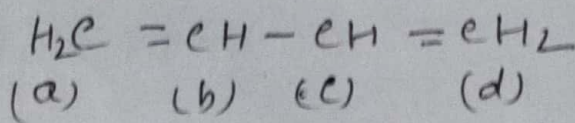
and the corresponding secular determinant or secular equation.

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

where $H_{ij} = \int \phi_i \hat{H} \phi_j$ are called the matrix elements of \hat{H} .

Slater functions :-

For a system of n electrons that are involved in bonding in a polyatomic molecule e.g.



Slater functions have the form

(3)

$$\phi = N \begin{vmatrix} a_1 & b_1 & c_1 & d_1 \\ a_2 & b_2 & c_2 & d_2 \\ a_3 & b_3 & c_3 & d_3 \\ a_4 & b_4 & c_4 & d_4 \end{vmatrix}$$

where $a(i), b(i) \dots$ may be $a(i)\alpha(i)$ or $a(i)\beta(i)$ and so on.

N is the normalization factor. There will be

$2^4 = 16$ such determinants as each column may have either α or β spin. Each determinant is a eigenfunction of S_z as each term on its expansion is an eigenfunction with the same eigen value. If the number of columns with spin α and n_α and the number with spin β is n_β , the eigen value is

$$\frac{1}{2} (n_\alpha - n_\beta) \frac{h}{2\pi}$$

if we denote the Slater determinants through their diagonal elements only, then, for example,

$$\hat{S}_z | a(1) b(2) c(3) d(4) | = \frac{1}{2} (3-1) \cdot \frac{h}{2\pi} | a(1) b(2) c(3) d(4) |$$

The 16 Slater functions may thus be classified according to their eigen values. Normalizing a Slater function means developing the determinant into a polynomial, iterating its square and equating the result to unity. Each term of the polynomial results from one of the $4!$ possible permutations of the electrons in the 4 spin orbitals.