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CHEMICAL SCIENCES

CODE:01

2.2. Approximate Methods of Quantum Mechanics

At a Glance

Variation theorem and Secular Equation, Secular Equation, Application of Variation theorem, First order and Second order perturbation.



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Key Statements

Basic Key Statements: Variation theorem and Secular Equation (2.2.1),

Standard Key Statements: Secular Equation (2.2.2)

Advance Key Statements: First order and Second order perturbation (2.2.4/7)



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Key Facts**2.2.1. Variation theorem and Secular Equation:**

The calculation of multi-electronic system has two possible ways- (i) Perturbation theory (ii) Variation theory.

According to Variation principle it can be shown that, if ψ_0 is the correct wave function for a system, whose correct energy is E_0 than any other acceptable wave function ψ_1 will give energy greater E_0 .

2.2.2. Secular Equation:

Assuming $\psi = a_1\phi_1 + a_2\phi_2 + \dots \dots \dots a_i\phi_i$

$$\text{Now energy, } E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} = \frac{\int (a_1\phi_1 + a_2\phi_2)^* H (a_1\phi_1 + a_2\phi_2) d\tau}{\int (a_1\phi_1 + a_2\phi_2)^* (a_1\phi_1 + a_2\phi_2) d\tau}$$

Pursuing proper algebraic operation we have

$$a_1^2 H_{11} + a_2^2 H_{22} + a_1 a_2 H_{12} = E(a_1^2 S_{11} + a_2^2 S_{22} + a_1 a_2 S_{12})$$

Where, $\int \phi_i H \phi_j d\tau = H_{ij}$ and $\int \phi_i \phi_j d\tau = S_{ij}$

It is necessary to minimize E with respect to a_1 and a_2 .

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

$$\{(H_{21} - ES_{21})a_1 + (H_{22} - ES_{22})a_2 = 0$$

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \rightarrow \text{Secular determinant}$$

Differentiation:

$$E(a_1^2 S_{11} + a_2^2 S_{22} + a_1 a_2 S_{12}) = a_1^2 H_{11} + a_2^2 H_{22} + a_1 a_2 H_{12}$$

Diff. both side w.r.t. a_1 we have

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

$$E(2a_1 S_{11} + 0 + 2a_2 S_{12}) = [2a_1 H_{11} + 0 + 2a_2 H_{12}]$$

$$E a_1 S_{11} + E a_2 S_{12} = a_1 H_{11} + a_2 H_{12}$$

$$\text{Hence, } -a_2(H_{12} - ES_{12}) = a_1(H_{11} - ES_{11})$$

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

$$\text{So, } E(a_1^2 S_{11} + a_2^2 S_{22} + a_1 a_2 S_{12}) = (a_1^2 H_{11} + a_2^2 H_{22} + a_1 a_2 H_{12}) +$$

$$(a_1^2 S_{11} + a_2^2 S_{22} + a_1 a_2 S_{12}) \frac{\partial E}{\partial a_1}$$

Diff. both sides w.r.t. a_2 we have

$$E[0 + 2a_2S_{22} + 2a_1S_{12}] + (a_1^2S_{11} + a_2^2S_{22} + a_1a_2S_{12})\frac{\partial E}{\partial a_2} = (0 + 2a_2H_{22} + 2a_1H_{12})$$

$$\text{Hence, } -a_1(H_{12} - ES_{12}) + a_2(H_{22} - ES_{22}) = 0$$

2.2.3. Application:

- % error in energy by using variation principle and cross check of the function's validity.

$$\% \text{ error} = \frac{E_i - E_0}{E_0} \times 100\%$$

[NOTE]: If % error in negative, function is not acceptable.

2.2.4. First order Perturbation theorem:

Perturbation theory is as approximation method for finding out the method of way to the exact solution of any system with great accuracy.

Perturbation is of two types.

(1) Slow Perturbation

(2) Sudden

The energy correction is $\Delta E = \int \psi_0^* H^1 \psi_0 d\tau$, where H^1 is perturbed value.

Assuming an eigen system $H_0\psi_0 = E_0\psi_0$

Where, ψ_0 and E_0 are clearly known and effect of H^1 is not more because it is a first order effect. Now we perturbed the Hamiltonian as follows

$$H = H_0 + H^1 \dots\dots\dots(i)$$

$$E = E_0 + \Delta E \dots\dots\dots(ii)$$

$$\psi = \psi_0 + \Delta\psi \dots\dots\dots(ii)$$

Since from (i), $H\psi^1 = E\psi^1$

$$(H_0 + H^1)(\psi_0 + \Delta\psi) = (E_0 + \Delta E)(\psi_0 + \Delta\psi)$$

$$\Rightarrow H^1\psi_0 + H_0\Delta\psi + H^1\Delta\psi = \Delta E\psi_0 + E_0\Delta\psi + \Delta E\psi_0$$

In addition to it we shall neglect the last term of each side may be neglected because multiplication of these two small term is further small.

$$H^1\psi_0 + H_0\Delta\psi = \Delta E\psi_0 + E_0\Delta\psi$$

This equation in which unperturbed and another small quantity is present be called as **First order perturbation**.

2.2.5. The two term we neglected are 2nd order term,

$$H^1\psi_0 + (H_0 - E_0)\Delta\psi = \Delta E\psi_0 \dots\dots(iv)$$

Multiplying both sides by ψ_0^* from left and integrating both sides with respect to τ we get

$$\int \psi_0^* H^1 \psi_0 d\tau + \int \psi_0^* (H_0 - E_0) \Delta\psi d\tau = \int \psi_0^* \Delta E \psi_0 d\tau$$

$$\Delta E = \int \psi_0^* (H_0 - E_0) \Delta\psi d\tau + \int \psi_0^* H^1 \psi_0 d\tau \dots\dots(v)$$

$$\text{Now, } \int \psi_0^* (H_0 - E_0) \Delta\psi d\tau = \int \Delta\psi (H_0 - E_0)^* \psi_0^* d\tau = \int \Delta\psi (H_0 \psi_0 - E_0 \psi_0)^* d\tau = \int \Delta\psi \times 0 \times d\tau = 0$$

$$\text{Thus from (v) we have } \Delta E = \int \psi_0^* H^1 \psi_0 d\tau$$

This method is very suitable and nearest to Hamiltonian, H which has been perturbed.

$$\text{So, } H_{\text{original}} + H_{\text{perturbed}} = H$$

Again, we know that $H_p \ll H_0$

$$H_p = \lambda W \quad \lambda \ll 1$$

So, the eigen value problem becomes dependent upon $H_0 + d\lambda$.

2.2.6. In perturbation theory generally two cases generates:

- (i) Non-degenerate perturbation theory & (ii) Degenerate perturbation theory.

In case of H_0 has non-degenerate eigen values,

$$H_0 |\phi_n\rangle = \varepsilon_n^{(0)} |\phi_n\rangle$$

$$\text{Where, } \varepsilon_n = \varepsilon_n^{(0)} + \varepsilon_n^{(1)} + \varepsilon_n^{(2)} + \dots$$

$$|\psi_n\rangle = |\phi_n^{(0)}\rangle + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots$$

$$\text{Now, } H_0 |\phi_n^{(0)}\rangle + H_0 \lambda |\psi_n^{(1)}\rangle + H_0 \lambda^2 |\psi_n^{(2)}\rangle + \lambda \omega |\phi_n^{(0)}\rangle + \lambda^2 \omega |\psi_n^{(1)}\rangle + \lambda^3 \omega |\psi_n^{(2)}\rangle \dots$$

$$\varepsilon_n^{(0)} |\phi_n^{(0)}\rangle + \lambda \varepsilon_n^{(0)} |\psi_n^{(1)}\rangle + \lambda^2 \varepsilon_n^{(0)} |\psi_n^{(2)}\rangle + \lambda \varepsilon_n^{(1)} |\phi_n^{(0)}\rangle + \lambda^2 \varepsilon_n^{(1)} |\psi_n^{(1)}\rangle + \lambda^2 \varepsilon_n^{(2)} |\psi_n^{(2)}\rangle \dots$$

$$\text{Now, } \langle \phi_m^{(0)} | \psi_n^{(0)} \rangle = \frac{\langle \phi_m^{(0)} | \omega | \phi_n^{(0)} \rangle}{\varepsilon_n^{(0)} - \varepsilon_m^{(0)}}$$

But,

$$\varepsilon_n^2 = \sum \langle \phi_n^{(0)} | \omega | \phi_m^{(0)} \rangle \left| \frac{\langle \phi_m^{(0)} | \omega | \phi_n^{(0)} \rangle}{\varepsilon_n^{(0)} - \varepsilon_m^{(0)}} \right|$$

2.2.7. Second order perturbation:

The corrected form of energy, $E_n^2 = \sum_{m \neq n} \frac{\langle \phi_m | W | \phi_n \rangle^2}{E_n^{(0)} - E_m^{(0)}}$.