Approximate Methods - I

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APPROXIMATE METHODS

An exact solution of schrodinger wave equation for H atom is possible only when the system contains a single electron. If the system contains several electrons, the solution of the schrodinger wave equation for a polyelectron system is very difficult. In such a case, we use some approximate methods viz. variation theory and perturbation theory.

Perturbation theory

The perturbation theory is another way for approximate solution of the problem. The method is based on the fact that the actual problem can be treated as a slight modification or perturbation of another problem capable of exact solution. If $\hat{H}\psi = E\psi$ represents the actual schrodinger's wave equation to be solved then it is assumed that an exact solution is available for $\hat{H}_0\psi_0 = E_0\psi_0$ where $\hat{H}_0$ differ slightly from Hamiltonian for the actual problem.

This method may be illustrated by taking the state of any system (say that of H-atom) characterised

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by the wave the wave fuction ψ. when acted on by external electrical field, it's electronic state will be changed. Let the wave function of the perturbed state is $(\psi + \phi)$.

The Hamiltonian will also change due to the change in potential energy. Let $\hat{H}$ be the Hamiltonian in the unperturbed state and $(\hat{H} + \hat{H}_1)$ that of the perturbed state and $(\hat{H} + \hat{H}_1)$ that of the perturbed state. $\hat{H}_1$ is called the amount of perturbation. Suppose ψ_0, ψ_1 .... are the solutions of eto the equation is unperturbed state. Since these are solutions of the schrodinger's wave equation, they must from an orthogonal set. Thus, ϕ must be represented as

$$\phi = c_1\psi_1 + c_2\psi_2 \quad - (1)$$

where c_1, c_2 and ψ_1, ψ_2 are very small quanties.

Let a perturbed state of the system is ψ. The wave funtion in the perturbed state is given by $(\psi_2 + \phi)$ ie

$$\psi = \psi_2 + c_1\psi_1 + c_3\psi_3 \quad -(2)$$

Since $c_2\psi_2$ makes no contribution hence

it does not appear in the Perturbed state of B.
from Schrodinger's wave equation, $\hat{H}\psi = E\psi$.
In the present case $(\hat{H}+\hat{H}_1)\psi = E\psi$ where
E is energy in the perturbed state.

$$(\hat{H}+\hat{H}_1)(\psi_2 + c_1\psi_1 + c_3\psi_3) = E(\psi_2 + c_1\psi_1 + c_3\psi_3)$$

$$\hat{H}\psi_2 + c\hat{H}\psi_1 + c_3\hat{H}\psi_3 + \hat{H}_1\psi_2 + c_1\hat{H}_1\psi_1 + c_3\hat{H}_1\psi_3 = E\psi_2 + Ec_1\psi_1 + Ec_3\psi_3 \quad (3)$$

Since c_1, c_3 and $\hat{H}_1$ are small quantities, the term $c_1\hat{H}_1\psi_1$ and $\hat{H}_1 c_3\psi_3$ can be neglected from equation (3). Thus, we get-

$$E\psi_2 - \hat{H}\psi_2 + Ec_1\psi_1 - c_2\hat{H}_1\psi_1 + Ec_3\psi_3 - c_3\hat{H}\psi_3 = \hat{H}_1\psi_2 \quad (4)$$

Multiplying equation (4) by ψ_2 and then integrating over the entire configuration space, we get

$$\int \psi_2 (E-H)\psi_2\, d\tau + c_1\int \psi_2(E-H)\psi_2\, d\tau + c_3\int \psi_2(E-H)\psi_3\, d\tau = \int \psi_2 \hat{H}_1 \psi_2\, d\tau \quad (5)$$

or $\int \psi_2 E\psi_2\, d\tau - \int \psi_2 \hat{H}\psi_2\, d\tau = \psi_2 H_1 \psi_2\, d\tau$

or $\int \psi_2 E\psi_2\, d\tau = \int \psi_2 \hat{H}\psi_2\, d\tau + \psi_2 \hat{H}_1\psi_2\, d\tau$

$$E = E_0 + \int \psi_2 \hat{H}_1 \psi_2\, d\tau$$

$$E = E_0 + \int \psi_2 \hat{H}_1 \psi_2\, d\tau \quad (7)$$

where E_0 = Energy of unperturbed state.

The value of $\hat{H}_1$ is given by $\hat{H}_1 = eEX$ where e is the electric charge. E is the strength of electrical field and X is the coordinate of the system in the direction of field. Thus,

$$E = E_0 + Ee\int \psi_2 X\, d\tau$$

Since all the terms of the right-hand side of the above equation can be known and hence E can be found out. The wave function of the perturbed state is given by

$$(E-\hat{H})\psi_2 + c_2(E-\hat{H})\psi_1 + c_3(E-H)\psi_3 = \hat{H}_1\psi_2$$

or $\int \psi_1 (E-\hat{H})\psi_2 d\tau + c_1 \int \phi_1 [E-\hat{H}]\psi_1 d\tau + c_3 \int \psi_1 [E-\hat{H}]\psi_3 d\tau = \int \psi_1 \hat{H}_1 \psi_2 d\tau$

or $c_1 \int \psi_1 E \psi_1 d\tau + c_1 \int \psi_1 \hat{H} \psi_1 d\tau = \int \psi_1 \hat{H}_1 \psi_2 d\tau$

or $c_1 E + c_1 \int \psi_1 \hat{H} \psi_1 d\tau = \psi_1 \hat{H}_1 \psi_2 d\tau$

Since all the terms are known, we can calculate c_1.

Similarly, multiplying equation $\hat{H}\psi = E\psi$ by ψ_3, we can calculate c_3. Thus, $\psi = \psi_2 + c_2\psi_1 + c_3\psi_3$ can be known since ψ_1, ψ_2 and ψ_3 can be easily known.

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