1. What is variation theorem ? Give a proof of the variation theorem. How is it used to find out the approximate solution for a multi-electron system ?

Ans. Variation theorem : The Schrodinger's equation can be solved exactly for hydrogen-like systems, i.e., single electron systems only. However, for systems having two or more electrons, the Schrodinger's equation can't be solved exactly because the presence of more than one electron introduces the electron repulsion terms, i.e., $\frac{e^2}{r_{ij}}$ where r_{ij} is the distance between i^{th} and j^{th} electrons, in the Hamiltonian. The separation of variables can't be possible now owing to the dependence of r_{ij} on θ and ϕ coordinates. Therefore, for systems having more than one electrons, the Schrodinger's equation has to be solved approximately. The variation method is one of the methods for finding out the approximate solution of Schrodinger's equation for a multi-electron system.

According to the variation theorem, also called variation method, if we can make a guess of an approximate wave function of a system based on the physical and chemical considerations, then the energy of the system is approximately given by

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi \psi^* \, d\tau} = \frac{< \psi^* \mid \hat{H} \mid \psi >}{< \psi^* \mid \psi >}.$$

Here ψ^* is the complex conjugate of ψ, the guessed wavefunction for the system. If the wavefunction is real, $\psi^* = \psi$, and we can write.

$$E = \frac{\langle \psi \mid \hat{H} \mid \psi \rangle}{\langle \psi \mid \psi \rangle} \qquad \ldots (1)$$

If the chosen function ψ is normalised, then E can be given as

$$E = \langle \psi \mid \hat{H} \mid \Psi \rangle \qquad \ldots (2)$$

Where $\hat{H}$ is the complete Hamiltonian of the system. According to the variation theorem, the energy E is always greater than the true energy E_0, the lowest eigen value of $\hat{H}$, of the system in its ground state. In other words, if we make several guesses of wavefucntions, ψ_1 and ψ_2 which lead to E_1 and E_2 respectively as eigenvalues according to equation (1) or (2) then, in accordance with variation principle, if $E_1 < E_2$, E_1 is the better approximation to the true energy E_0 than E_2. Thus, the corresponding wavefunction ψ_1 is a better wavefunction of the system than ψ_2.

The variation theorem may thus be stated as follows :

"If ψ be the trial wavefunction of a system whose Hamiltonian $\hat{H}$ has a discrete eigen spectrum, then

$$\langle \psi \mid \hat{H} \mid \psi \rangle \geq E_0 \qquad \ldots (3)$$

Where E_0 is the lowest exact eigen value of $\hat{H}$ assuming that the trial wave function ψ is normalised."

Proof of variation theorem : Let $\phi_0, \phi_1, \phi_2, \phi_3....$ be the set of normalised and mutually orthogonal eigen functions of $\hat{H}$ with discrete eigen values such as E_0, E_1, E_2, E_3 ... etc., respectively. Thus,

$$\hat{H}\,\phi_i = E\phi_i,\ i = 0, 1, 2, 3, \qquad ...(4)$$

Now, ψ is expanded in terms of the set of eigen functions ϕ_i as

$$\psi = \sum_i C_i\phi_i \qquad ...(5)$$

Since $\langle \psi \,|\, \psi \rangle = 1$, we have

$$\Sigma\, C_i^2 = 1 \qquad ... (6)$$

Moreover,

$$\langle \phi_i \,|\, \hat{H} \,|\, \phi_i \rangle = E_i \qquad ...(7)$$

and $\langle \phi_i \,|\, \hat{H} \,|\, \phi_j \rangle = E_j \langle \phi_i / \phi_j \rangle = 0 \qquad ... (8)$

Let us consider the integral

$$E = \langle \psi \,|\, \hat{H} \,|\, \psi \rangle = \langle \sum_i C_i\phi_i \,|\, \hat{H} \,|\sum_i C_i\,\phi_i \rangle$$

$$= \sum_i C_i^2 \langle \phi_i \,|\, \hat{H} \,|\, \phi_i \rangle$$

$$= \sum_i C_i^2\, E_i \qquad ...(9)$$

If E_0 be the lowest eigen value of $\hat{H}$, we can write

$$E - E_0 = \sum_i C_i^2 E_i - E_0$$

$$= \sum_i C_i^2 E_i - \sum_i C_i^2 E_0 \ (\because \sum_i C_i^2 = 1)$$

$$= \sum_i C_i^2\,(E_i - E_0) \qquad ...(10)$$

The quantity $(E_i - E_0)$ must be positive or zero for all values of i and since C_i^2 is always positive, it is seen that the right hand side of equation (10) must always be positive or zero. It, therefore, follows that

$$E - E_0 \geq 0$$

or,

$$E \geq E_0$$

or,

$$\langle \psi | \hat{H} | \psi \rangle \geq E_0$$

In other words, if the trial wave function ψ happens to be the true wave function of the system in its lowest energy state, we get true energy E_0. Otherwise the variation method always gives an upper bound to the true energy without giving any information regarding how far the true energy is different from the calculated value.

Determination of approximate solution using variation method :

Following steps are applied for finding out approximate solution using variation method—

(i) A trial function (ψ) is selected with some variable parameters.

(ii) The integral, $\langle \psi | \hat{H} | \psi \rangle = E$, is evaluated.

(iii) Since this integral always gives an upper bound to the true energy unless the chosen function ψ happens to be the exact solution, the integral is minimised with respect to the variable parameters.

(iv) The function ψ with the optimum value of the parameters is the best approximation to the true wave function.

(v) The lowest value of $\langle \psi | \hat{H} | \psi \rangle$ is the nearest approximation to the true energy, for all trial functions belonging to the same class.