The variation Method

The variational method is based on the following variational theorem:

Variation Theorem

The essential idea of the method is to evaluate the expectation value $\langle H \rangle$ of the Hamiltonian operator H of the system with respect to a trial wavefunction Ø. The variation theorem states that the ground state energy.

$$E_1 \leq \langle H \rangle = \langle \emptyset | H | \emptyset \rangle \quad \rightarrow (1)$$

The equality holds if the trial wavefunction is the same as the ground state wavefunction of the system and the value $\langle H \rangle$ is an upper limit to the ground state energy. If the trial wavefunction is not normalized.

$$\langle H \rangle = \frac{\langle \emptyset | H | \emptyset \rangle}{\langle \emptyset | \emptyset \rangle} \quad \longrightarrow (2)$$

The ratio is often referred as *Rayleigh ratio.*

Proof

For the proof of the theorem, express the trial wavefunction $\emptyset$ as a linear combination of the true wavefunction Ψ_1, Ψ_2, Ψ_3 , ...of the Hamiltonian of the system corresponding to Eigenvalues $E_1, E_2, E_3, \ldots\ldots$

$$\emptyset = \sum_i a_i \, |\Psi_i\rangle \quad \rightarrow (3)$$

And $$\langle H \rangle = \sum_i \sum_j a_i^* \, a_j \, \langle \Psi_i | H | \Psi_j \rangle$$

$$= \sum_i \sum_j a_i^* \, a_j \, E_j \, \langle \Psi_i | \Psi_j \rangle$$

$$= \sum_i |a_i|^2 \, E_i$$

Writing $E_i = E_1 + \Delta E_i$, where E_1 is the ground state energy, we get

$$\langle H \rangle = E_1 \sum_i |a_i|^2 + \sum_i |a_i|^2 \Delta E_i$$

Since $\sum_i |a_i|^2 = 1$ and ΔE_i is positive,

$$\langle H \rangle \geq E_1$$

The variational procedure described above is due to Lord Rayleigh. In practice, the trial wavefunction Ø is selected in terms of one or more variable parameters and the value $\langle H \rangle$ evaluated. The value of $\langle H \rangle$ when minimized with respect to each other of the parameter, one gets the closest estimate possible with the selected trial function. A good trial function is a slight modification of a known wavefunction.