Rayleigh Ritz Variation Method

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1 A Theorem

Let $E_0, E_1, E_2, \cdots$ be the exact energy eigenvalues of Hamiltonian of a system corresponding to the ground state, the first excited state, the second excited state etc., respectively,

$$Hu_\alpha = E_\alpha u_\alpha \tag{1}$$

where u_α are eigenfunctions corresponding to eigenvalue E_α. Let ψ be any square integrable function then we have the following results.

$$E_\alpha \leq \frac{\int \psi^* H \psi d^2x}{\int \psi^* \psi d^3x} \tag{2}$$

2 Proof of the Theorem

Let ψ be expanded as

$$\psi = \sum C_n u_n \tag{3}$$

Then

$$(\psi, \psi) = \int \psi^* \psi d^3x = \sum_n |C_n|^2 \tag{4}$$

and

$$\begin{aligned}
\int \psi^* H \psi d^3x &= \left(\sum_n C_n u_n, H \sum C_n u_m \right) \\
&= \sum_n \sum_m C_n^* C_m (u_n, H u_m) \\
&= \sum_n \sum_m C_n^* C_m E_m (u_n, H u_m) \\
&= \sum_n \sum_m C_n^* C_m \delta_{mn} E_m \\
&= \sum_{n=o} E_n |C_n|^2
\end{aligned} \tag{5}$$

Consider

$$\int \psi^* H\psi d^3x - E_0 \int d^3x \psi^* \psi = \sum_{n=o}^{\infty} E_n |C_n|^2 - E_0 \sum_{n=0}^{\infty} |C_n|^2 \quad (6)$$

$$= \sum_{n=1}^{\infty} (E_n - E_0)|C_n|^2 \quad (7)$$

The right hand side is positive because $E_n - E_0 > 0$, for all $n \neq 0$. Hence

$$\therefore \int \psi^* H\psi d^3x - E_0 \int \psi^* \psi d^3x \geq 0 \ . \quad (8)$$

or

$$\int \psi^* H\psi d^3x \geq E_0 \int \psi^* \psi d^3x \ . \quad (9)$$

or

$$\frac{\int \psi^* H\psi d^3x}{\int \psi^* \psi d^3x} \geq E_0 \ . \quad (10)$$

Thus we have

$$E_0 \leq \frac{\int \psi^* H\psi d^3x}{\int \psi^* \psi d^3x} \quad (11)$$

for all square integrable ψ.

3 Ritz Variation method

The above result can be used to estimate the ground state energy as follows

1. Choose a trial wave function ψ which is square integrable.

2. Normalize it to unity $\int \psi^* \psi d^3x = 1$.

3. Compute

$$E_\psi \equiv \int \psi^* H\psi d^3x \quad (12)$$

4. The trial wave function will contain some unknown parameter(s). Let the unknown parameter be called α. Fix α such that E_ψ is minimum by demanding

$$\frac{\partial E_\psi}{\partial \alpha} = 0 \quad (13)$$

The value α_0, for which E_ψ is minimum, can now be used for calculating E_ψ which gives an estimate for the ground state energy. A good choice of trial wave function can lead to very good estimate for the ground state energy. The variation method has been successfully applied to the energy for ground state of He atom. The variation method is most useful for the ground state energy although it can be modified to estimate energies of excited states also.