The Variational Methods

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INTRODUCTION

This presentation shows a technique of how to solve for the approximate ground state energy using Schrodinger Equation in which the solution for wave function is not on hand.

The intended reader of this presentation were physics students. The author already assumed that the reader knows Dirac Braket notation.

This presentation was made to facilitate learning in quantum mechanics.

Consider a quantum system described by a Hamiltonian with a series of eigenstates with corresponding energy eigenvalues

The Time-Independent Schrödinger Equation:

$$H\psi_i = E_i\psi_i$$

TASK:

Suppose you want to calculate the ground-state energy for a system described by the Hamiltonian, but you are unable to solve the Time-Independent Schrödinger Equation.

THEOREM:

$$E_g \le \langle \psi | H | \psi \rangle \equiv \langle H \rangle$$

That is , the expectation value of H in the state ψ is certain to overestimate the ground-state energy. Of course if ψ just happens to be one of the excited states, then obviously $\langle H \rangle$ exceeds E_g ; but the theorem says that the same holds for any psi whatsoever

PROOF:

Since the (unknown) eigenfunctions of H form a complete set, we can express ψ as linear combination of them:

$$\psi_{trial} = \sum_n c_n \psi_n \qquad \text{with} \qquad H\psi_n = E_n \psi_n$$

Since ψ is normalized,

$$\langle \psi | \psi \rangle = \left\langle \sum_m c_m \psi_m \middle| \sum_n c_n \psi_n \right\rangle$$

$$= \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle$$

$$1 = \sum_m \sum_n c_m^* c_n \delta_{mn} = \sum_n |c_n|^2$$

Assuming the eigenfunctions have been orthonormalized

The expectation value for the Hamiltonian choosing the trial function will be

$$\langle H \rangle = \left\langle \sum_m c_m \psi_m \middle| H \sum_n c_n \psi_n \right\rangle$$

$$= \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle$$

$$= \sum_n E_n |c_n|^2$$

But the ground-state energy is, by definition, the smallest eigenvalue, so $E_g \leq E_n$, and hence

$$\langle H \rangle \geq E_g \sum_n |c_n|^2 = E_g$$