13.1: Variational Principle

Suppose that we wish to solve the time-independent Schrödinger equation

$$H\,\psi = E\,\psi, \tag{13.1.1}$$

where H is a known (presumably complicated) time-independent Hamiltonian. Let ψ be a properly normalized trial solution to the previous equation. The variational principle states, quite simply, that the ground-state energy, E_0, is always less than or equal to the expectation value of H calculated with the trial wavefunction: that is,

$$E_0 \leq \langle \psi | H | \psi \rangle. \tag{13.1.2}$$

Thus, by varying ψ until the expectation value of H is minimized, we can obtain approximations to the wavefunction and the energy of the ground-state.

Let us prove the variational principle. Suppose that the ψ_n and the E_n are the true eigenstates and eigenvalues of H: that is,

$$H\,\psi_n = E_n\,\psi_n. \tag{13.1.3}$$

Furthermore, let

$$E_0 < E_1 < E_2 < \cdots, \tag{13.1.4}$$

so that ψ_0 is the ground-state, ψ_1 the first excited state, et cetera. The ψ_n are assumed to be orthonormal: that is,

$$\langle \psi_n | \psi_m \rangle = \delta_{nm}. \tag{13.1.5}$$

If our trial wavefunction ψ is properly normalized then we can write

$$\psi = \sum_n c_n\,\psi_n, \tag{13.1.6}$$

where

$$\sum_n |c_n|^2 = 1. \tag{13.1.7}$$

Now, the expectation value of H, calculated with ψ, takes the form

$$\begin{aligned}\langle \psi | H | \psi \rangle &= \left\langle \sum_n c_n\,\psi_n \middle| H \middle| \sum_m c_m\,\psi_m \right\rangle = \sum_{n,m} c_n^*\,c_m\,\langle \psi_n | H | \psi_m \rangle \\ &= \sum_n c_n^*\,c_m\,E_m\,\langle \psi_n | \psi_m \rangle = \sum_n E_n\,|c_n|^2,\end{aligned}$$

where use has been made of Equations 13.1.3 and 13.1.5. So, we can write

$$\langle \psi | H | \psi \rangle = |c_0|^2\,E_0 + \sum_{n>0} |c_n|^2\,E_n. \tag{13.1.8}$$

However, Equation 13.1.7 can be rearranged to give

$$|c_0|^2 = 1 - \sum_{n>0} |c_n|^2. \tag{13.1.9}$$

Combining the previous two equations, we obtain

$$\langle \psi | H | \psi \rangle = E_0 + \sum_{n>0} |c_n|^2\,(E_n - E_0). \tag{13.1.10}$$

The second term on the right-hand side of the previous expression is positive definite, because $E_n - E_0 > 0$ for all $n > 0$ (Equation 13.1.4). Hence, we obtain the desired result

$$\langle \psi | H | \psi \rangle \geq E_0. \tag{13.1.11}$$

Excited States

Suppose that we have found a good approximation, $\tilde{\psi}_0$, to the ground-state wavefunction. If ψ is a normalized trial wavefunction that is orthogonal to $\tilde{\psi}_0$ (i.e., $\langle\psi|\tilde{\psi}_0\rangle = 0$) then, by repeating the previous analysis, we can easily demonstrate that

$$\langle\psi|H|\psi\rangle \geq E_1. \tag{13.1.12}$$

Thus, by varying ψ until the expectation value of H is minimized, we can obtain approximations to the wavefunction and the energy of the first excited state. Obviously, we can continue this process until we have approximations to all of the stationary eigenstates. Note, however, that the errors are clearly cumulative in this method, so that any approximations to highly excited states are unlikely to be very accurate. For this reason, the variational method is generally only used to calculate the ground-state and first few excited states of complicated quantum systems.

Contributors and Attributions

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