Variational Theorem (Proof)

Theorem: In a system where $\hat{H}$ is a time-independent Hamiltonian and $|\Phi\rangle$ is a well-behaved 'trial' wave function that satisfies the boundary conditions of the system, the Rayleigh quotient (ρ)

$$\rho = \frac{\langle\Phi|\,\hat{H}\,|\Phi\rangle}{\langle\Phi|\Phi\rangle} \geq E_0 \;\; \text{(the system's ground-state energy).} \tag{1}$$

Proof: Assuming, WLOG, that $|\Phi\rangle$ is normalized, we want to show: $\rho = \langle\Phi|\,\hat{H}\,|\Phi\rangle \geq E_0$.

Furthermore, by normalization of $|\Phi\rangle$,

$$\sum_{k=0}^{\infty} |a_k|^2 = 1. \tag{2}$$

The key concept is to expand the trial function $|\Phi\rangle$ in the complete basis of eigenfunctions of $\hat{H}$, $\{\psi_k\}$.

$$|\Phi\rangle = \sum_{k=0}^{\infty} a_k\,|\psi_k\rangle \tag{3}$$

Where we construct the basis to be orthonormal ($\langle\psi_j|\psi_k\rangle$).
Now we are in a position to evaluate the energy expectation value

$$\begin{aligned}\langle\Phi|\,\hat{H}\,|\Phi\rangle &= \left(\sum_{j=0}^{\infty} a_j^*\,\langle\psi_j|\right)\left(\sum_{k=0}^{\infty} \hat{H} a_k\,|\psi_k\rangle\right) = \sum_{j=0}^{\infty}\sum_{k=0}^{\infty} a_j^* a_k\,\langle\psi_j|\,\hat{H}\,|\psi_k\rangle \\ &= \sum_{j=0}^{\infty}\sum_{k=0}^{\infty} a_j^* a_k E_k\,\langle\psi_j|\psi_k\rangle = \sum_{j=0}^{\infty}\sum_{k=0}^{\infty} a_j^* a_k E_k \delta_{jk}\end{aligned}$$

Which yields the final result

$$\langle\Phi|\,\hat{H}\,|\Phi\rangle = \sum_{k=0}^{\infty} |a_k|^2 E_k \tag{4}$$

With some foresight, rewrite this equation as

$$\langle\Phi|\,\hat{H}\,|\Phi\rangle = E_0|a_0|^2 + \sum_{k=1}^{\infty} |a_k|^2 E_k \tag{5}$$

Applying the normalization of the trial function,

$$\begin{aligned}\langle\Phi|\,\hat{H}\,|\Phi\rangle &= E_0\left(1 - \sum_{k=1}^{\infty}|a_k|^2\right) + \sum_{k=1}^{\infty}|a_k|^2 E_k \\ &= E_0 + \sum_{k=1}^{\infty}|a_k|^2(E_k - E_0)\end{aligned}$$

The last assumption we'll make (WLOG) will be that the the eigenvalues are ordered, $E_0 \leq E_1 \leq ... \leq E_n$, so

$$\sum_{k=1}^{\infty}|a_k|^2(E_k - E_0) \geq 0. \tag{6}$$

Thus,

$$\langle\Phi|\,\hat{H}\,|\Phi\rangle \geq E_0 + 0 \;\; \blacksquare. \tag{7}$$

Clearly equality holds when $|\Phi\rangle = |\Psi\rangle$, the exact ground-state wavefunction in the specified basis representation. In practice, this means that minimizing the energy expectation value yields the ground state energy of the system.

What is the variational method // how do we use it?

We can restate the variational principle in matrix form:

$$\frac{\mathbf{c}^{\dagger}\mathbf{H}\,\mathbf{c}}{\mathbf{c}^{\dagger}\mathbf{c}} \geq E_0, \tag{8}$$

where, in a given basis set, $\mathbf{H}$ is the matrix representation of the Hamiltonian $\hat{H}$, and $\mathbf{c}$ is the coefficient vector of the basis functions of the system's ground-state wave function $|\Psi\rangle$.

Claim: A vector $\mathbf{c}$ that minimizes $\mathbf{c}^{\dagger}\mathbf{H}\,\mathbf{c}$ is the ground-state eigenvector of $\mathbf{H}$.

Proof:

We'll show that minimizing the expectation value $\mathbf{c}^{\dagger}\mathbf{H}\,\mathbf{c}$ (with $\mathbf{c}^{\dagger}\mathbf{c} = 1$) is equivalent to solving a matrix eigenvalue problem.

A good way to minimize $\mathbf{c}^{\dagger}\mathbf{H}\,\mathbf{c}$ with respect to the constraint $\mathbf{c}^{\dagger}\mathbf{c} = 1$ is by using a Lagrangian optimization:

$$\mathcal{L}\{\mathbf{c}, \lambda\} = \mathbf{c}^{\dagger}\mathbf{H}\,\mathbf{c} - \lambda(\mathbf{c}^{\dagger}\mathbf{c} - \mathbf{1}) \tag{9}$$

$$= \sum_{ij} c_i^* H_{ij} c_j - \lambda \left(\sum_i c_i^* c_i - 1 \right) \tag{10}$$

The Lagrange optimization procedure requires $\frac{\partial \mathcal{L}}{\partial \lambda} = \frac{\partial \mathcal{L}}{\partial \mathbf{c}} = 0$. Consider the derivative with respect to $\mathbf{c}$:

$$0 = \frac{\partial \mathcal{L}}{\partial c_k} = \sum_{ij} \left[\frac{\partial c_i}{\partial c_k} H_{ij} c_j + c_i H_{ij} \frac{\partial c_j}{\partial c_k} \right] - \lambda \sum_i \frac{\partial}{\partial c_k} c_i^2 \tag{11}$$

$$= \sum_{ij} \delta_{ik} H_{ij} c_j + \sum_{ij} c_i H_{ij} \delta_{jk} - \lambda \sum_i 2c_i^2 \delta_{ik} \tag{12}$$

$$= \sum_j H_{kj} c_j + \sum_i c_i H_{ik} - \lambda 2c_k^2 \tag{13}$$

Since summed-over indices are just dummy variables (interchangeable),

$$= \sum_i H_{ki} c_i + \sum_i c_i H_{ik} - \lambda 2c_k^2 \tag{14}$$

Since $\mathbf{H}$ is symmetric,

$$= \sum_i H_{ki} c_i + \sum_i -\lambda 2c_k^2 \tag{15}$$

So we have arrived at

$$0 = 2 \left(\sum_i H_{ik} c_i - \lambda c_k \right) \tag{16}$$

Which we rearrange to identify as an eigenvalue problem:

$$\sum_i H_{ki} c_i = \lambda c_k, \tag{17}$$

In matrix form this equation is $\mathbf{H}\mathbf{c_k} = \lambda_k \mathbf{c_k}$.

Conclude: This is very significant, because it means that solving for lowest eigenvalue and its associated eigenvector of $\mathbf{H}$ corresponds physically to finding the ground state energy of the system.