

Energy Expectation Values and the Origin of the Variation Principle

A system is in the state $|\Psi\rangle$, which is not an eigenfunction of the energy operator, \hat{H} . A statistically meaningful number of such states are available for the purpose of measuring the energy. Quantum mechanical principles state that an energy measurement must yield one of the energy eigenvalues, ϵ_i , of the energy operator. Therefore, the average value of the energy measurements is calculated as,

$$\langle E \rangle = \frac{\sum_i n_i \epsilon_i}{N} \quad (1)$$

where n_i is the number of times ϵ_i is measured, and N is the total number of measurements. Therefore, $p_i = n_i/N$, is the probability that ϵ_i will be observed. Equation (1) becomes

$$\langle E \rangle = \sum_i p_i \epsilon_i \geq \epsilon_1 = \epsilon_{gs} \quad (2)$$

where gs stands for ground state. As shown above, it is clear that the average energy has to be greater than ($p_1 < 1$) or equal to ($p_1 = 1$) the lowest energy. This is the origin of the quantum mechanical variational theorem.

According to quantum mechanics, for a system in the state $|\Psi\rangle$, $p_i = \langle \Psi | i \rangle \langle i | \Psi \rangle$, where the $|i\rangle$ are the eigenfunctions of the energy operator. Equation (2) can now be re-written as,

$$\langle E \rangle = \sum_i \langle \Psi | i \rangle \langle i | \Psi \rangle \epsilon_i = \sum_i \langle \Psi | i \rangle \epsilon_i \langle i | \Psi \rangle \quad (3)$$

However, it is also true that

$$\hat{H} |i\rangle = \epsilon_i |i\rangle = |i\rangle \epsilon_i \quad (4)$$

Substitution of equation (4) into (3) yields

$$\langle E \rangle = \sum_i \langle \Psi | \hat{H} |i\rangle \langle i | \Psi \rangle \quad (5)$$

As eigenfunctions of the energy operator, the $|i\rangle$ form a complete basis set, making available the discrete completeness relation, $\sum_i |i\rangle \langle i| = \mathbf{1}$, the use of which in equation (5) yields

$$\langle E \rangle = \langle \Psi | \hat{H} | \Psi \rangle \geq \epsilon_{gs} \quad (6)$$

Chemists generally evaluate expectation values in coordinate space, so we now insert the continuous completeness relationship of coordinate space, $\int |x\rangle\langle x| dx = \mathbf{1}$, in equation (6) which gives us,

$$\langle E \rangle = \int \langle \Psi | x \rangle \langle x | \hat{H} | \Psi \rangle dx = \int \langle \Psi | x \rangle \hat{H}(x) \langle x | \Psi \rangle dx \quad (7)$$

where

$$\hat{H}(x) = -\frac{\hbar^2}{2m} \frac{d}{dx^2} + V(x) \quad (8)$$