10.3: The Variation Theorem in Dirac Notation

The recipe for calculating the expectation value for energy using a trial wave function is,

$$\langle E\rangle = \langle\psi|\hat{H}|\psi\rangle \tag{10.3.1}$$

Now suppose the eigenvalues of $\hat{H}$ are denoted by $|i\rangle$. Then,

$$\hat{H}|i\rangle = \varepsilon_i|i\rangle = |i\rangle\varepsilon_i \tag{10.3.2}$$

Next we write $|\psi\rangle$ as a superposition of the eigenfunctions $|i\rangle$,

$$|\psi\rangle = \sum_i |i\rangle\langle I|\psi\rangle$$

and substitute it into Equation 10.3.1.

$$\langle E\rangle = \sum_i \langle\psi|\hat{H}|i\rangle\langle i|\psi\rangle$$

Making use of Equation 10.3.2 yields,

$$\langle E\rangle = \sum_i \langle\psi|i\rangle\varepsilon_i\langle i|\psi\rangle$$

After rearrangement we have,

$$\langle E\rangle = \sum_i \varepsilon_i|\langle i|\psi\rangle|^2$$

However, $|\langle i|\psi\rangle|^2$ is the probability that ε_i will be observed, p_i.

$$\langle E\rangle = \sum_i \varepsilon_i p_i \geq \varepsilon_0$$

Thus, the expectation value obtained using the trial wave function is an upper bound to the true energy. In other words, in valid quantum mechanical calculations you can't get a lower energy than the true energy.