Variation Principle

To approximate

$$\hat{H}\psi = E\psi$$

Take any function $\tilde{\psi}$ that satisfies the same boundary conditions as ψ and calculate

$$\tilde{E} = \frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle}$$

where $\hat{H}$ is the correct Born-Oppenheimer (Electronic) Hamiltonian, then

$$\hat{E} \geq E$$

and $\tilde{E} = E$, when

$$\tilde{\psi} = \psi$$