# Quantum Mechanics 2

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## Variational Principle

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# The Ritz Variational Principle

The prescription for the study of quantum mechanical system is straightforward. One simply has to solve an eigenvalue equation

$$Hu = Eu$$

where the Hamiltonian operator is defined as by

$$H = -\frac{\hbar^2}{2m}\nabla^2 - V(\vec{r})$$

There are however very few potentials for which an analytical solution of the eigenvalue equation described above could be found. More often than not, one has to resort to some approximation method.

One such method is the variational method. One start by guessing a trial solution $\tilde{\psi}$. Following the standard prescription of quantum mechanics, the energy of the system can be predicted to be

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

# The Ritz Variational Principle

Following the expansion postulate, any function can be expressed as a linear combination of a complete set of eigenkets

$$|\tilde{\psi}\rangle = \sum_n a_n |n\rangle$$

where

$$H|n\rangle = E_n|n\rangle$$

While $\tilde{\psi}$ is a guess, $|n\rangle$ are taken to be the true energy eigenkets, even if we do not know their true form. Then,

$$\frac{\langle\tilde{\psi}|H|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\sum_{n,m} a_n^\dagger a_m \langle n|H|m\rangle}{\sum_{n,m} a_n^\dagger a_m \langle n|m\rangle} = \frac{\sum_{n,m} a_n^\dagger a_m E_n \delta_{nm}}{\sum_{n,m} a_n^\dagger a_m \delta_{nm}} = \frac{\sum_n |a_n|^2 E_n}{\sum_n |a_n|^2}$$

The completeness of eigenkets guarantee that

$$\sum_{n,m} |a_n|^2 = 1$$

# The Ritz Variational Principle

On the other hand,

$$\sum_{n,m} |a_n|^2 E_n \geq E_0 \sum_{n,m} |a_n|^2 = E_0$$

since the ground state energy by definition is the lowest energy level. Thus,

$$\bar{H} = \frac{\langle\tilde{\psi}|H|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} \geq E_0$$

Which means that any construction $\bar{H}$ based even the wildest guess $\tilde{\psi}$ that satisfies the boundary conditions of the system will surely yield an expression that cannot be lower than the ground state energy.

The approximation can be enhanced by parametrizing $\tilde{\psi}$ by a variational parameter $\lambda$. The lowest value of $\bar{H}$ can be found by setting

$$\frac{\partial \bar{H}}{\partial \lambda} = 0$$

By virtue of the above construction, $\bar{H}$ calculated this way will be a best approximation for the ground state energy.