7.2: Variational Method

The **variational method** is based on the Variational principle which says that a wavefunction that is not the true wavefunction will always yield a value for the energy that is greater than the true ground state energy of the system. This principle can be proven using the superposition theorem that was previously discussed.

Theorem 7.2.1: Variational Method

Assume a trial wavefunction $\psi(x)$ describing a particle in a box, that can be expressed as a linear combination of the normal particle in a box wavefunctions.

$$\psi(x) = \sum_n c_n \phi_n(x)$$

Assuming $\psi(x)$ is normalized, the expectation value of energy $\langle E \rangle$ is obtained from the expression

$$\langle E \rangle = \int \psi(x)\, \hat{H}\, \psi(x)\, d\tau$$

Substituting the expression for $\psi(x)$ from above

$$\langle E \rangle = \int \left(\sum_m c_m \phi_m \right) \hat{H} \left(\sum_n c_n \phi_n \right) d\tau$$

Noting that

$$\hat{H}\phi_n = E_n \phi_n$$

Substitution yields

$$\langle E \rangle = \int \left(\sum_m c_m \phi_m \right) \left(\sum_n c_n E_n \phi_n \right) d\tau$$

Gathering terms, one obtains

$$\begin{aligned} \langle E \rangle &= \int \left(\sum_m \sum_n c_m c_n E_n \phi_m \phi_n \right) d\tau \\ &= \sum_m \sum_n c_m c_n E_n \int (\phi_m \phi_n)\, d\tau \\ &= \sum_m \sum_n c_m c_n E_n \delta_{mn} \end{aligned}$$

The Kronecker delta will destroy one of the summations since it will pick out only one value to be non-zero.

$$\begin{aligned} \langle E \rangle &= \sum_m \sum_n c_m c_n E_n \delta_{mn} \\ &= \sum_n c_n^2 E_n \end{aligned}$$

Thus if any components of the linear combination have a non-zero contribution ($c_n \neq 0$ for $n > 1$) the expectation value has to be larger than E_1.

The Variational principle can be used to determine reasonable trial wavefunctions (Ψ) based on a set of approximate wavefunctions (ϕ_n). This is done by assuming the trial wavefunction can be expressed as a linear combination of the approximate wavefunctions

$$\Psi = \sum_n c_n \phi_n$$

and then determining the contribution to the trial function by minimizing the energy with respect to the coefficients (c_n) in the expansion.

$$\frac{\partial}{\partial c_n}\langle E\rangle = 0$$

This will produce n equations with n unknown values of c_n which can be simultaneously solved to yield the optimal values of c_n. This methodology is used to a great extent in computational chemistry methods.

Example 7.2.1

What is $\langle E\rangle$ for a system with the following wavefunction that approximates ψ_1 (x) for a particle in a box?

$$\psi(x) = \sqrt{\frac{30}{a^5}} \cdot x \cdot (a - x)$$

Solution

The wavefunction is a reasonable, but not perfect, approximation of the $n = 1$ level of a particle in a box.

$$\phi_1(x) = \sqrt{\frac{2}{a}} \cdot \sin\left(\frac{\pi \cdot x}{a}\right)$$

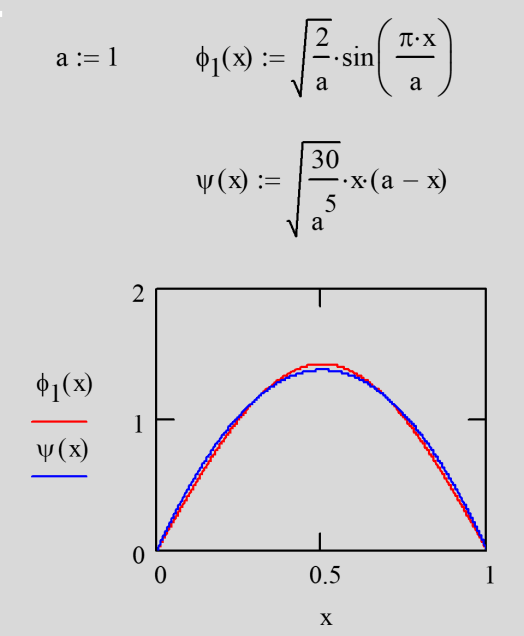

Figure 7.2.1

The expectation value of energy is found in the usual manner.

$$\begin{aligned}\langle E\rangle &= \int_0^a \psi \hat{H} \psi \, d\tau \\ &= -\frac{\hbar^2}{2m}\frac{30}{a^5}\int_0^a (ax - x^2)\frac{d^2}{dx^2}(ax - x^2)\,dx = -\frac{15\hbar^2}{ma^5}\int_0^a (ax - x^2)(-2)\,dx \\ &= \frac{30\hbar^2}{ma^5}\left[\frac{ax^2}{2} - \frac{x^3}{3}\right]_0^a = \frac{30\hbar^2}{ma^5}\left(\frac{a^3}{6}\right) \\ &= \frac{5\hbar^2}{ma^2}\end{aligned}$$

This result is slightly larger than $\frac{h^2}{8ma^2}$ since $\frac{5}{(2\pi)^2} = 0.127$ and $\frac{1}{8} = 0.125$.

> In the variational method, an approximate form of a wave function can be used

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