

Chapter 7: Approximate Methods

The previous chapters all dealt with problems that can be solved analytically. However, there are many problems that are of chemical interest that cannot be solved exactly. For these problems, we must employ some methods that will approximate a correct and complete solution. Two such methods will be discussed in this chapter.

Perturbation Theory

Oftentimes, a system represents only a small difference from an exactly solvable system. In these instances, **perturbation theory** can be used to describe the system. To use perturbation theory, one must separate the Hamiltonian into two parts: one for which the solution is known ($\hat{H}^{(0)}$) and the other part which will represent the perturbation to the system ($\hat{H}^{(1)}$).

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

The solution for the unperturbed system is known.

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

The energy levels and wavefunctions for the perturbed system are determined by applying a series of corrections (referred to as first order, second order, etc.)

$$\begin{aligned} E_n &= E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots \\ \psi_n &= \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} + \dots \end{aligned}$$

Oftentimes only the first and second order corrections are needed to give a reasonable description of the system. The first order correction to the energy is given by

$$E_n^{(1)} = \int \psi_n^{(0)} \hat{H}^{(1)} \psi_n^{(0)} d\tau$$

The second order correction to the energy depends on the first order correction to the wavefunctions.

$$E_n^{(2)} = \int \psi_n^{(0)} \hat{H}^{(1)} \psi_n^{(1)} d\tau$$

The formula for generating the first order corrections to the wavefunctions is given by

$$\psi_n^{(1)} \sum_{i \neq n} \psi_i^{(0)} \frac{\int \psi_i^{(0)} \hat{H}^{(0)} \psi_n^{(0)} d\tau}{E_n^{(0)} - E_i^{(0)}}$$

Substitution into the expression for $E_n^{(2)}$ yields

$$E_n^{(2)} = \sum_{i \neq n} \frac{\left| \int \psi_n^{(0)} H^{(1)} \psi_n^{(0)} d\tau \right|^2}{E_n^{(0)} - E_i^{(0)}}$$

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.

Proof:

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: What is $\langle E \rangle$ for a system with the following wavefunction that approximates $\psi_1(x)$ for a particle in a box?

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

Solution:

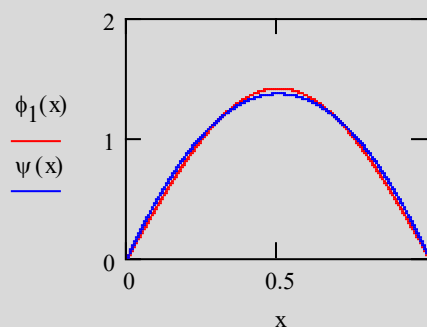
The wavefunction is a reasonable, but not perfect, approximation of the $n=1$ level of a particle in a box.

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

$$a := 1 \quad \phi_1(x) := \sqrt{\frac{2}{a}} \cdot \sin\left(\frac{\pi \cdot x}{a}\right)$$

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

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



This result is slightly larger than $\hbar^2/8ma^2$ since $5/(2\pi)^2 = 0.127$ and $1/8 = 0.125$.

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

Vocabulary and Concepts

perturbation theory 169

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Problems

1. Consider a particle of mass m in a box defined between $x = 0$ and $x = a$, that is prepared in the $n = 1$ state. If the wavefunction is approximated by

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

- a. Show that the expectation value of $\langle E \rangle$ exceeds E_1 for a particle in a box.
- b. By what percentage does the approximate energy exceed that of the $n = 1$ energy?