

Solving the Schrodinger Equation using the Variational Method (and how to do it using MathCAD)

The Variational method is usually introduced as a way of getting the energy of the ground state solution to the Schrodinger Equation by optimizing coefficients of a trial wavefunction. The method is actually much more general: you can calculate the energy (and wavefunctions) for the ground and excited states of a system using the Variational method and some linear algebra. This method is very often used by chemists and physicists that solve the Schrodinger Equation as part of their research.

For a good, thorough introduction to the Variational method see Chapter 8 of the text by Levine (ref. [9]) or the MathCAD based introductions by Grubb (ref. [5]) and Dunn (ref. [6]).

Overview

The Schrodinger equation for a particle of mass μ in one dimensional potential $V(x)$ is

$$\frac{-\hbar^2}{2\cdot\mu} \cdot \frac{d^2}{dx^2} \Psi_n(x) + V(x) \cdot \Psi_n(x) = E_n \cdot \Psi_n(x) \quad (1)$$

The first term (with the derivatives) is the kinetic energy, the second term (with $V(x)$) is the potential energy.

Our goal is to calculate the wavefunctions $\Psi_n(x)$ and their energies E_n .

If we have another set of functions $\phi_j(x)$ (which we know) which can be integrated and which "span the space," then any well-behaved function can be written as a linear combination (a sum) of the ϕ_j . Thus, each wavefunction $\Psi_n(x)$ can be written in terms of the $\phi_j(x)$ (which are called the *basis functions*):

$$\Psi_n(x) = \sum_{j=1}^N C_{n,j} \cdot \phi_j(x) \quad (2)$$

In our case, we'll choose the basis functions $\phi_j(x)$ to be the solutions to the particle in a box Schrodinger Equation, for which $V(x) = 0$ if x is inside the box and $V(x)$ is infinite outside the box. Since we can solve the particle in a box Schrodinger equation, we know $\phi_j(x)$, so if we can calculate the coefficients $C_{n,j}$, then we'll have solved the Schrodinger equation for the potential $V(x)$.

Plugging equation (2) into the Schrodinger equation (1) gives

$$\sum_{j=1}^N C_{n,j} \cdot \left[\frac{-\hbar^2}{2\cdot\mu} \cdot \frac{d^2}{dx^2} \phi_j(x) + V(x) \cdot \phi_j(x) - E_n \cdot \phi_j(x) \right] = 0 \quad (3)$$

Multiplying on the left by $\phi_i(x)$ (note that this i, not j) gives

$$\sum_{j=1}^N C_{n,j} \left[\phi_i(x) \cdot \left[\frac{-\hbar^2}{2 \cdot \mu} \cdot \frac{d^2}{dx^2} \phi_j(x) \right] + \phi_i(x) \cdot V(x) \cdot \phi_j(x) - \phi_i(x) \cdot E_n \cdot \phi_j(x) \right] = 0 \quad (4)$$

Integrating over x gives

$$\sum_{j=1}^N C_{n,j} \left[\int \phi_i(x) \cdot \left[\frac{-\hbar^2}{2 \cdot \mu} \cdot \frac{d^2}{dx^2} \phi_j(x) \right] dx + \int \phi_i(x) \cdot V(x) \cdot \phi_j(x) dx - E_n \cdot \int \phi_i(x) \cdot \phi_j(x) dx \right] = 0 \quad (5)$$

This is a system of linear equations (there are N of them) that are called the Rayleigh-Ritz-Galerkin equation (this version of the Variational method is usually called the Rayleigh-Ritz Variational method) which is written as:

$$(T + U - E \cdot S) \cdot C = 0 \quad (6)$$

where T, U, E, S, and C are all NxN matrices

T is the kinetic energy matrix:

$$T_{i,j} = \int \phi_i(x) \cdot \left[\frac{-\hbar^2}{2 \cdot \mu} \cdot \frac{d^2}{dx^2} \phi_j(x) \right] dx \quad (7)$$

U is the potential energy matrix:

$$U_{i,j} = \int \phi_i(x) \cdot V(x) \cdot \phi_j(x) dx \quad (8)$$

The sum of the kinetic and potential energies is called the Hamiltonian, H:

$$H = T + U \quad (9)$$

S is the overlap matrix:

$$S_{i,j} = \int \phi_i(x) \cdot \phi_j(x) dx \quad (10)$$

E is a matrix that has the energies E_n on the diagonal (and is zero everywhere else)

C is the matrix of coefficients $C_{n,j}$ that give the wavefunctions (eq. 2)

Equation 6 is called a generalized eigenvalue equation - if you supply T, U and S, then the computer will solve for the energies E (also called the *eigenvalues*) and the coefficients C (also called the *eigenvectors*).

So far, this discussion has been pretty general. Because we're using a particle in a box basis set we can simplify these equations. From now on, $\phi_j(x)$ is the particle in a box wavefunction with quantum number j.

First, these wavefunctions are orthogonal and normalized, so $S_{i,j}=1$ if $i=j$ and is zero otherwise.

In the main program (Sch_Eq) we confirm this by calculating $S_{i,j}$.

So, S is the identity matrix and $E \cdot S$ is just E.

Equation 6 then simplifies to

$$(H - E) \cdot C = 0 \quad (11)$$

Second, the kinetic energy matrix T can be simplified. Recall that the potential for a particle in a box is zero inside the box and is infinite outside the box. So, the Schrodinger equation for a particle in a box contains only the kinetic energy term, and $T_{i,j}$ is the energy of the particle in a box wavefunction with quantum number j, if $i=j$, and is zero otherwise (this is because the wavefunctions are orthogonal and normalized). If the box extends from "start" to "end," and the length of the box is $A=end-start$, then

$$T_{i,j} = \frac{\pi^2 \cdot j^2}{2 \cdot \mu \cdot A^2} \quad \text{if } i=j \quad \text{and} \quad (12)$$

$$T_{i,j} = 0 \quad \text{otherwise.}$$

(This is how the kinetic energy T is defined in the main program).

- So, in order to solve the Schrodinger equation for a potential $V(x)$, the program
- defines the particle in a box basis functions $\phi_j(x)$.
 - calculates the kinetic energy T matrix using equation 12
 - calculates the potential energy U matrix using equation 8
 - sums them to get the Hamiltonian H matrix (equation 9)
 - uses the MathCAD function *eigenvals* to solve the eigenvalue equation 11 and find the eigenvalues (energies) E_j
 - uses the MathCAD function *eigenvecs* to find the eigenvector (the coefficients $C_{n,j}$) that correspond to a particular eigenvalue E_n
 - uses equation 2 to calculate the wavefunction $\Psi_n(x)$.