Lecture 7: Schrödinger Equation: Method of Finite Differences

Ref. Chapter 2.2
• Last time, we discussed the Schrödinger Equation:

\[ i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U(r)\Psi \]

• We began with the simplest case, the Hydrogen atom. It is the simplest because there are no electron-electron interactions.

• Experimentally discrete energy levels are observed.

Discrete Energy Levels

\[ E_n = -\frac{\hbar^2}{2m} \frac{1}{n^2} \]

- \( n = 1 \)
- \( n = 2 \)
- \( n = 3 \)
- \( n = 4 \)
Today: How to solve the Schrödinger Equation numerically using the method of finite differences.

Start with the 1-Dimensional Schrödinger equation:

\[ i \hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U(x) \psi \]

In essence we want to convert the Schrödinger Equation into a matrix equation.

First create a lattice for the 1-D problem.

\[ \psi_n = \begin{pmatrix} \psi(x_1) \\ \psi(x_2) \\ \vdots \\ \psi(x_n) \end{pmatrix} \]

\( (x,t) \) therefore becomes a column vector telling the value of \( \psi \) at different points at any given instant of time:
Similarly, the entire 1-D Schrödinger Equation becomes:

\[ i \hbar \frac{d}{dt} \begin{bmatrix} \Psi_1 \\ \vdots \\ \Psi_n \end{bmatrix} = \begin{bmatrix} H \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \vdots \\ \Psi_n \end{bmatrix} \]

How do we convert the Hamiltonian operator into a matrix?

First try writing the matrix for \( U(x) \) and then the matrix for \( \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \).

The total Hamiltonian should be a sum of these two.

Formulating Schrödinger’s Equation in the following form:

\[ \begin{bmatrix} i \hbar \frac{d}{dt} \end{bmatrix} _{x=x_n} = \begin{bmatrix} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \end{bmatrix} _{x=x_n} + \begin{bmatrix} U(x) \end{bmatrix} _{x=x_n} \]

The second term on the right side equation can be written down easily and it is \( U(x) \times \Psi \) for any given point ‘n’ of the lattice. Note that \( \Psi \) only depends on \( \Psi_n \) and this indicates that potential term \( U(x) \) appears on the diagonal of Hamiltonian only.
• First try to write \[ \frac{d^2}{dx^2} \].

\[
\begin{bmatrix}
\frac{d}{dx}
\end{bmatrix}_{n}\begin{bmatrix}
\frac{d}{dx}
\end{bmatrix}_{n+1} = \frac{n+1 - n}{a}
\]

\[
\begin{bmatrix}
\frac{d}{dx}
\end{bmatrix}_{n}\begin{bmatrix}
\frac{d}{dx}
\end{bmatrix}_{n-1} = \frac{n - n-1}{a}
\]

• Then,

\[
\begin{bmatrix}
\frac{d^2}{dx^2}
\end{bmatrix}_{n} = \begin{bmatrix}
\frac{d}{dx}
\end{bmatrix}_{n+1}\begin{bmatrix}
\frac{d}{dx}
\end{bmatrix}_{n-1} - \begin{bmatrix}
\frac{d}{dx}
\end{bmatrix}_{n}\begin{bmatrix}
\frac{d}{dx}
\end{bmatrix}_{n-1}
\]

\[
= \frac{n+1 - 2 \cdot n + n-1}{a^2}
\]

Which is the representation of a second derivative in the finite differences method.
Generalizing the numerical expression for the second derivative we get:

\[
i\hbar \frac{d^2}{dt^2} \approx \frac{-\hbar^2}{2ma^2} \left[ 2 \cdot \sum_{i=0}^{n-1} - \cdot \sum_{i=0}^{n+1} \right] + U(x_n) \cdot \sum_{i=0}^{n} \frac{\partial^2}{\partial t^2}
\]

Let \( t_0 = \frac{\hbar^2}{2ma} \) so the Hamiltonian matrix \( i\hbar \frac{\partial}{\partial t} \{ \{ H \} \} \) now looks like…

\[
\begin{bmatrix}
\cdot & -t_0 & 0 & 0 & 0 & 0 \\
-t_0 & \cdot & -t_0 & 0 & 0 & 0 \\
0 & -t_0 & \cdot & \cdot & \cdot & \cdot \\
0 & 0 & \cdot & \cdot & \cdot & \cdot \\
0 & 0 & 0 & \cdot & \cdot & \cdot \\
0 & 0 & 0 & 0 & -t_0 & 2t_0 + U(x_N)
\end{bmatrix}
\]
• What about the time derivative
  \[ i\hbar \frac{d \psi}{dt} \]
  i.e. How do we calculate \( \{ \psi(t) \} \) given some initial state \( \{ \psi(0) \} \)?

• Answer: Find the eigenvalues \( E_\alpha \) and eigenvectors \( \{ \alpha \} \) of the matrix \([H]\). Such that,
  \[ [H]\{ \alpha \} = E_\alpha \{ \alpha \} \]

• Using the eigenvectors as a basis set, by substitution it can be shown that
  \[ \{ \psi(t) \} = \{ \alpha \} e^{-iE_\alpha t/\hbar} \] satisfies the matrix form of the Schrödinger Equation

• And similarly, so does any linear combination of basis functions
  \[ \{ \Psi(t) \} = \sum_\alpha C_\alpha e^{-iE_\alpha t/\hbar} \{ \alpha \} \]

• What is not clear, is what the coefficients \( C_\alpha \) are. This depends on the problem

But first step is to find the eigen value \( E_\alpha \)
And the eigen vector \( \{ \alpha \} \)
• What do we do when we get near a boundary?

• In the case of infinite-wall boundary conditions, such as the infinite square well, 
  \(-t_0 ?_0 \pm (2t_0 + U_1) ?_1 - t_0 ?_2\)
  is replaced by 
  \(2t_0 + U_1) ?_1 - 2 ?_2\)

and

\(-t_0 ?_{N+1} \pm (2t_0 + U_N) ?_{N+1} - t_0 ?_{N+1}\)

by

\(-t_0 ?_{N+1} \pm (2t_0 + U_N) ?_{N+1}\)

Meaning, \(?_0\) and \(?_{N+1}\) are considered equal to zero

• For periodic boundary conditions, such as a particle on a ring, we let
  \(?_0 = ?_N\) and \(?_{N+1} = ?_1\)

• Unlike the infinite-wall scenario, periodic boundary conditions have a slightly different Hamiltonian matrix:

\[
[H] = \begin{pmatrix}
2t_0 + U(x_1) & -t_0 & \cdots & \cdots & -t_0 \\
-t_0 & 2t_0 + U(x_2) & \cdots & \cdots & \cdots \\
\vdots & \vdots & \ddots & \ddots & \vdots \\
\vdots & \vdots & \ddots & \ddots & \ddots \\
-t_0 & \cdots & \cdots & -t_0 & 2t_0 + U(x_N)
\end{pmatrix}
\]

• Sub-note: Most Hamiltonians are normally Hermitian:

\[H = (H^*)^T = H\]
• For periodic boundary conditions eigenvalues come in degenerate pairs

• Whereas for BOX boundary conditions the eigenvalues are non degenerate

**Degenerate Eigenvalues**

![Graph showing degenerate eigenvalues](image1)

• This is because the eigenfunctions for the periodic case are:
  \[ \sin \left( \frac{ka}{L} \right) \text{ and } \cos \left( \frac{ka}{L} \right) \]
  with \( k_{a} = \frac{a2\pi}{L}, a = 1,2,\ldots \)

**Non-Degenerate Eigenvalues**

![Graph showing non-degenerate eigenvalues](image2)

• This is because the eigenfunctions for the this case are:
  \[ \sin \left( \frac{ka}{L} \right) \text{ with } k_{a} = \frac{a\pi}{L}, a = 1,2,\ldots \]
Finally note that numerical analysis yields eigenvalues close to analytical result only for low energies.

For example a 100 point lattice in the infinite square well yields the following…

Where the analytical result is given by $E_a = \frac{(\hbar^2 a^2 p^2)}{2mL^2}$

This occurs because at very high energies the wave function oscillates very fast and the wide lattice spacing does not capture the whole story.