Lecture 8: Schrödinger Equation: Examples
Ref. Chapter 2.3
Recall, the analytical form of the Schrödinger Equation:

\[ i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = H \Psi(\vec{r}, t) \]

where

\[ H_{\alpha\beta} = -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \]

In numerical form:

\[ i\hbar \frac{\partial}{\partial t} \{\Psi\} = [H]\{\Psi\} \]

With the eigenvalue equation \([H]\{a\} = E_a \{a\}\)

And the corresponding eigenvectors and eigenvalues form a set by which wave functions may be represented as a linear combination of eigenvectors.

\[ \Psi = \sum_a C_a \{a\} e^{-iE_a \tau / \hbar} \]

Last time we looked at the Schrödinger Equation in one dimension. Along \(x\) a discrete set of lattice points were placed.

With the discrete set of lattice points shown on the right, the Schrödinger Equation was converted into a difference equation.
Computationally it is rather easy to find matrix eigenvectors and eigenvalues. For example in Matlab we simply call `[V,D]=eig(H)`.

Finally, it is important to emphasize that eigenvalues correspond to energies and eigenvectors to wavefunctions.

Matrix D provides the eigenvalues in a diagonal matrix and Matrix V provides the corresponding eigenvectors as columns of a square matrix.
The main advantage of the numerical method is that once it is solved for a particular dimensional structure, that same method may then be applied with little difficulty to other scenarios of the same nature.

Example: The slanted well has a complicated analytical solution (involving Airy Functions) but numerically the solution is the same as that implemented for the infinite square well.

So, how do we go beyond the one dimensional numerical solution seen thus far?

In two dimensions the Hamiltonian operator looks like:

\[ \hat{H}_{op} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + U(x, y) \]

The lattice for this operator is shown below.

It is straightforward to extend the finite difference method to two dimensions, the main problem is size. I.e.

100x100 pts = 10,000 pts
One solution is to separate the 2-D problem into two 1-D. However, this is only possible if the potential is separable:

\[ U(x, y) = U_x(x) + U_y(y) \]

Analytically this is done by separation of variables. Let,

\[ \Psi(x, y) = X(x) \times Y(y) \]

Thus,

\[ E_x X(x) = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U_x(x) \right] X(x) \]

\[ E_y Y(y) = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + U_y(y) \right] Y(y) \]

Where

\[ E = E_x + E_y \]

From,

\[ E \Psi(x, y) = \left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + U(x, y) \right] \Psi(x, y) \]

\[ \text{time independent form} \]

Numerically this translates into two 1-D lattices (one for the x-axis and one for the y-axis).

For example, take a two dimensional infinite square well:

2-D Infinite Square Well

\[ \text{Reducing the Lattice} \]
Numerically if we split the x and y lattices by 100 points. How many eigenvectors will result?

Ans: Total = 100 x 100 = 10000 eigenvectors.

We combine \( X(x) \) and \( Y(y) \) functions such that

\[ \psi_{nm}(x,y) = X_n(x) Y_m(y) \]

Notice that two eigenvectors with the same \( m+n \) value do not necessarily have the same energy:

Take eigenvectors \( \psi_{22} \) and \( \psi_{13} \), which has more energy?

Recall:

\[ E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \]

\[ \therefore (E_{13} + E_1 + E_3) > (E_{22} E_2 + E_2) \]

Now what about a 3-D infinite square well or a 3-D box? The same thing, separation of variables gives eigenfunctions of

\[ \psi_{111}, \psi_{112}, \ldots \text{etc.} \]
• Consider the Hydrogen Atom, can it be handled by separation of variables?

• The Hydrogen atom cannot be separated in Cartesian coordinates

\[ H_{\text{op}} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \]

\[ -\frac{q^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}} \]

But it can be separated in spherical coordinates such that \( U \) becomes

\[ -\frac{q^2}{4\pi\varepsilon_0 r} \]

• Note: A similar approach can be taken with all atoms but not with molecules because you don’t have this spherical symmetry.

• So separation of variables in spherical coordinates gives the radial Hamiltonian as:

\[ -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] + \frac{L(\theta, \phi)}{r^2} \]

\[ -\frac{q^2}{4\pi\varepsilon_0 r} \]

• In general \( \Psi \) becomes

\[ \Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \]
• Note: The radial equation

\[ ER(r) = \frac{-\hbar^2}{2m} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] R(r) \]

\[ + \left( \frac{-\hbar^2}{2m} \frac{l(l+1)}{r^2} - \frac{q^2}{4\pi\varepsilon r} \right) R(r) \]

can be simplified by letting \( R(r) = \frac{f(r)}{r} \)

Thus,

\[ \frac{dR(r)}{dr} = \frac{f'(r)}{r} - \frac{f(r)}{r^2} \]

\[ \frac{d^2R(r)}{dr^2} = \frac{f''(r)}{r} - \frac{f'(r)}{r^2} - \frac{f(r)}{r^3} + \frac{2f(r)}{r^4} \]

\[ \therefore \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) R(r) = \frac{f''(r)}{r} \]

• Hence, the entire radial equation simplifies to:

\[ E f(r) = \frac{-\hbar^2}{2m} \frac{d^2 f(r)}{dr^2} - \frac{q^2}{4\pi\varepsilon r} f(r) \]

\[ + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} f(r) \]

• Furthermore, the radial equation gives the s,p,d,... levels of the hydrogen atom for different values of "l":

s: l=0
p: l=1
D: l=2, etc
• How do we get a numerical solution to the hydrogen atom?
  • Ans: We set up a discrete axis along a radial axis and solve the appropriate radial Hamiltonian matrix for \( l = 0, 1, 2, \ldots \).

• Back to the hydrogen Hamiltonian, where does \( l(l+1) \) come from?
  • Ans: \( l(l+1) \) forms the eigenvalues of the spherical harmonics or angular part of the wave function.

\[
L(\theta, \phi) = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y_{lm}}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y_{lm}}{\partial \phi^2},
\]

and

\[
Y_{lm}'' = \Theta(\theta) \Phi_n(\phi)
\]

\[
L(\theta, \phi) Y_{lm}'' = -l(l+1) Y_{lm}''
\]

• Where, the angular term \( Y_{lm}'' \) is the same for all atoms which results in isotropic behavior. It is only the radial term that changes.
Closing Notes:

- For higher dimensions use separation of variables whenever possible.
- Separable solutions are of the form $\Psi(r, ?, f) = R(r)Y_m(?, f)$
- The angular term is the same for all separable spherical solutions.
- For hydrogen-like atoms the radial term can be treated as a 1-D numerical problem with coulomb potential $\frac{-Zq^2}{4\pi\epsilon r}$

and angular “potential” $\frac{h^2l(l+1)}{2mr^2}$.