Last Time

1. Schrödinger Eq. in 2D

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

or

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

For 3D replace:

\[
\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \rightarrow \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}
\]

Now we looked for stationary states

\[
\Psi(x, y, t) = \Phi(x, y) e^{-iE \cdot t / \hbar}
\]

Then found the 2D time independent Schrödinger eq

\[
\left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + V(x, y) \right] \Phi(x, y) = E \Phi(x, y)
\]
Then example: Particle in 2D box

\[ \Psi = 0 \text{ outside box;} \]

\[ \Psi = 0 \text{ at edges of box.} \]

Then in side box: \( V = 0 \)

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

So try a solution:

\[ (\text{**}) \quad \Psi(x, y) = X(x) Y(y) \]

Boundary conditions: \( \Psi = 0 \) at edges:

\[ X \left|_{x = \pm a/2} \right. = 0 \quad Y \left|_{y = \pm a/2} \right. = 0 \]

Find plugging ** into *

\[ \frac{1}{X} \frac{\hbar^2}{2m} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\hbar^2}{2m} \frac{\partial^2 Y}{\partial y^2} = E \]

\[ E_n^x = \text{const} \quad E_m^y = \text{const} \]
Now have a particle in box in two direction (See handout)

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

\[ X_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos \left( \frac{n \pi x}{a} \right) & n = 1, 3, 5 \\ \cdots \sin \cdots & n = 2, 4, 6 \end{cases} \]

\[ Y_m(y) = \begin{cases} \sqrt{\frac{2}{a}} \cos \left( \frac{m \pi y}{a} \right) & m = 1, 3, 5 \\ \cdots \sin \cdots \end{cases} \]

The energies

\[ E_{nm} = E_n + E_m \]

\[ E = \frac{\hbar^2 \pi^2}{2ma^2} \left( n^2 + m^2 \right) \]

Then we have

\[ E_{11} = \frac{\hbar^2 \pi^2}{2ma^2} (1^2 + 1^2) \]

\[ E_{12} = E_{21} = \frac{\hbar^2 \pi^2}{2ma^2} (1^2 + 2^2) \leq \text{degeneracy} \]

\[ E_{22} = \frac{\hbar^2 \pi^2}{2ma^2} (2^2 + 2^2) \]
2D Particle in (Square) Box

1. For the particle in the two dimensional box the potential is

\[ V = \begin{cases} 
0 & \text{inside box } -L/2 < x, y < L/2 \\
\infty & \text{outside box}
\end{cases} \]  

(1)

We solved the Schrödinger equation

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

(2)

2. The wave functions are described by two quantum numbers \( n_x, n_y \) and are

\[ \Psi_{n_x, n_y}(x, y) = X_{n_x}(x)Y_{n_y}(y) \]  

(3)

with \( n_x = 1, 2, 3, \ldots \) and \( n_y = 1, 2, 3, \ldots \)  

(4)

Where

\[ X_{n_x}(x) = \begin{cases} 
\sqrt{\frac{2}{L}} \cos \left( \frac{n_x \pi x}{L} \right) & n_x = 1, 3, 5, \ldots \\
\sqrt{\frac{2}{L}} \sin \left( \frac{n_x \pi x}{L} \right) & n_x = 2, 4, 6, \ldots 
\end{cases} \]  

(5)

and similarly

\[ Y_{n_y}(y) = \begin{cases} 
\sqrt{\frac{2}{L}} \cos \left( \frac{n_y \pi y}{L} \right) & n_y = 1, 3, 5, \ldots \\
\sqrt{\frac{2}{L}} \sin \left( \frac{n_y \pi y}{L} \right) & n_y = 2, 4, 6, \ldots 
\end{cases} \]  

(6)

3. The Energies are a sum of the energies

\[ E_{n_x, n_y} = \epsilon_x + \epsilon_y \]  

(7)

\[ = \frac{\hbar^2 \pi^2}{2ML^2 n_x^2} + \frac{\hbar^2 \pi^2}{2ML^2 n_y^2} \]  

(8)
Comments and Vocabulary (see pictures)

\( n_x - 1 = \) \# of excitations in \( x\)-direction

\( n_y - 1 = \) \# of excitations in \( y\)-direction

\[ E_{21} = E_{21} = \text{same energy or degeneracy} \]

\[ E_{21} = \frac{\hbar^2}{2m} \left( \frac{1^2 + 2^2}{2m} \right) \]
Today Motion In 3D

\[ V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \]

\[ \vec{F}(r) = -\partial V \hat{r} = -\frac{e^2}{4\pi\varepsilon_0 r^2} \hat{r} \]

force

Want to solve for standing waves

\[(*) \quad \left[ -\hbar^2 \nabla^2 + V(r) \right] \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)\]

\[ \nabla^2 = \frac{1}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \]

\[ = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \]

Try separation of variables

\[(***) \quad \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)\]

Substitute (***) into (*) and find an equation for \( R \Theta \Phi \) separately. But it's a little complicated because of the spherical geometry.
Wave functions are characterized by three quantum numbers

\[ \psi_{n\ell m} = R_{n\ell}(r) \Theta_{\ell m}(\theta) \Phi_m(\varphi) \]

Wave functions have radial and angular excitations in \( \Theta \) and \( \Phi \)

1. \( n = \) principle quantum number

   \( n-1 = \) "total number of excitations" angular or radial

   \[ E_{nn} = 1, 2, 3, 4, 5, \ldots \]

   \[ E_{nt} = -13.6 \text{ eV} \]

   This is specific to \( V \) potential in general, \( E \) depends on \( l \)

2. \( \ell = \) angular quantum number

   \( \ell = 0, 1, 2, 3, \ldots n-1 \)

   \( \ell = 0, 1, 2 \) are also known as \( s, p, d \)

   "sharp, principle, diffuse"
a) Number of radial excitations = \( n - 1 - \ell \)

b) \[
L^2 = \text{average angular momentum squared} = L_x^2 + L_y^2 + L_z^2
\]

\[
L^2 = \ell(\ell+1)\frac{\hbar^2}{2m}
\]
we will show later

m = magnetic quantum \#

\[
|m| = \pm \ell \text{ # of excitations around z-axis }\]

= 0, \pm 1, \pm 2, \ldots, \pm \ell

Sign indicates whether angular excitation is spinning clockwise or counter clockwise

9) \[
L_z = m \hbar
\]
we will show later
Wave functions Hydrogen

- We will solve the Shrödinger equation for the Coulomb potential

\[
V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \quad r = \sqrt{x^2 + y^2 + z^2}
\]

(9)

- The wave functions are

\[
\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\varphi)
\]

(10)

Here the labels \(n, l\) and \(m\) are the quantum numbers. One for each dimension \(r, \theta, \varphi\).

- In general the wave functions are characterized by the three quantum numbers

1. The **principle** quantum number

\[
n = 1, 2, 3, 4 \ldots
\]

(11)

\(n - 1\) is the “total number of excitations in either the radial or angular directions”.

\[
E_n = -\frac{\hbar^2}{2ma_0^2} \frac{1}{n^2} = \frac{13.6 \text{ eV}}{n^3}
\]

(12)

2. The **angular** quantum number is the total number of angular excitations which should be less than or equal to the total number of excitations, \((n - 1)\):

\[
l = 0, 1, \ldots n - 1
\]

(13)

\((n-1)-\ell\) is the number of radial excitations. \(\ell\) labels the total angular momentum of this wave functions:

\[
\vec{L}^2 = \ell(\ell + 1)\hbar^2.
\]

(14)

For \(\ell = 0, 1, 2, 3, 4 \ldots\) these wave-fcn's also called by the names

\[
\ell = s, p, d, f, g
\]

(15)

i.e. an “s-wave” is another name for the \(\ell = 0\) wave function.

3. And a “magnetic” quantum number which labels the \(z\) component of the angular momentum

\[
\vec{L}_z = mh
\]

with

\[
m = -\ell, -\ell + 1, \ldots, \ell - 1, \ell
\]

(16)

<table>
<thead>
<tr>
<th>(n )</th>
<th>(\ell )</th>
<th>(m )</th>
<th>(\Phi_m(\varphi))</th>
<th>(\Theta_{lm}(\theta))</th>
<th>(R_{nl}(r))</th>
<th>(\psi_{nlm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1s</td>
<td>1</td>
<td>(\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0})</td>
<td>(\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0})</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2s</td>
<td>1</td>
<td>(\sqrt{2} \cos(\theta))</td>
<td>(\frac{1}{\sqrt{32\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0})</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>2p</td>
<td>(\sqrt{3} \cos(\theta))</td>
<td>(\frac{1}{\sqrt{96\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0})</td>
<td>(\frac{1}{\sqrt{32\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \cos(\theta))</td>
</tr>
<tr>
<td>2</td>
<td>\pm 1</td>
<td>2p</td>
<td>(e^{\pm i\varphi})</td>
<td>(\sqrt{3} \sin(\theta))</td>
<td>(\frac{1}{\sqrt{96\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0})</td>
<td>(\frac{1}{\sqrt{64\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin(\theta) e^{\pm i\varphi})</td>
</tr>
</tbody>
</table>
Then we usually draw the energy level diagram.

\[ E_n \text{, this state has } n=0 \text{ } l=3 \]
\[ -\frac{13.6}{n^2} \]
\[ -\frac{13.6}{l^2} \]

\[ n=0 \quad l=0 \]
\[ n=1 \quad l=1 \]
\[ n=2 \quad l=2 \]
\[ n=3 \quad l=3 \]
\[ n=2 \quad l=0 \quad n=2 \quad l=1 \]

Examples:

1. Thus for \( n=2 \) states we are referring to:
   \[ n=2 \quad l=0 \quad m=0 \]
   \[ n=2 \quad l=1 \quad m=0, \pm 1 \]

2. When we refer to a 3d state we mean:
   \[ n=3 \quad l=2 \quad m=0, \pm 1, \pm 2 \]

\[ L^2 = 2(2l+1) \frac{n^2}{\hbar^2} \]
\[ L_z = 0, \pm \hbar, \pm 2\hbar \]

3. What is the degeneracy of the no3 level?
Solution:

\[
\begin{align*}
&n=3 \quad l=0 \quad \leftarrow \quad 1 \text{ state } = (2l+1) \\
&n=3 \quad l=1 \quad m=0, \pm 1 \quad \leftarrow \quad 3 \text{ states } = (2l+1) \\
&n=3 \quad l=2 \quad m=0, \pm 1, \pm 2 \quad \leftarrow \quad 5 \text{ states } = (2l+1)
\end{align*}
\]

So the total degeneracy is

\[
1 + 3 + 5 = 9 \quad \Rightarrow \quad \text{generally } \sum_{l=0}^{n-1} (2l+1) = n^2
\]

\[
= 3^2
\]
Radial Probability density:

\[ dP = 12r^2 \, dV \]

\( \uparrow \) probability per volume

Take \( l=0 \), \( m=0 \) waves (no angular dependence or excitations)

\( \Theta = 1 \) and \( \Phi = 1 \)

Then:

\[ 2\psi = R(r) \]

\[ dP = 12\psi^2 \, dV = R^2(r) 4\pi r^2 \, dr = \text{probability} \]

= probability to find electron between \( r+dr \) at any angle
Actually this works for $l + m = 0$

\[ dp = 12^l \, dV \]

\[ dp = \int_{\text{sphere}} r^2 \, dr \, d\Omega \]

\[ = 1R^2 \, \pi^2 \, dr \int d\Omega \, l \theta^2 l \phi^2 \]

constant:

\[ \text{can choose to be } 4\pi \]

\[ dp = \frac{1R^2}{n^2} \, 4\pi \, r^2 \, dr \, d\Omega = \rho(r) \, dr \]

\[ \rho(r) = \frac{1R^2}{n^2} \, 4\pi \, r^2 \]

\[ \text{probability per unit } r \]
Example: The ground state wave function of hydrogen is (see table)

\[ \psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \]

1. Graph the probability density \( P(r) \).

Solution: \( R_{ne} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \) \( \Phi = \Theta = 1 \)

\[ P(r) = R^2 4\pi r^2 \, dr = \frac{4\pi}{\pi a_0^3} r^2 e^{-2r/a_0} \]

\[ \int P(r) \, dr \text{ integral under this curve is one} \]

Kinds of problems one can now pose

1. \( 1 = \int_0^\infty P(r) \, dr \) \( \Phi \) \( \text{normalize the wave function, electron must be somewhere} \)
See example 7.3 of book
2. \[ P_{ab} = \# \text{prob between } a \text{ and } b \]
\[ = \int_a^b \rho(r) \, dr \]

3. \[ \bar{r} = \int_0^\infty \, \rho(r) \, r \, dr \]
\[ \bar{r}^2 = \int_0^\infty \, \rho(r) \, r^2 \, dr \]
\[ \Delta r^2 = \bar{r}^2 - \bar{r}^2 \]

4. most probable \[ \frac{\partial \rho}{\partial r} \bigg|_{r_{mp}} = 0 \]

* Bohr model often gives the right order of magnitude for these averages
  * Sometimes it's exactly right
\[ r = \int_0^\infty dr \, P(r) \, r \]

\[ r = a \int_0^\infty dr \, \frac{4\pi r^2}{\pi a_0^3} \, e^{-2r/a_0} \, r \]

\[ = 4a_0 \int_0^\infty dr \, \left( \frac{r}{a_0} \right)^2 \, e^{-2r/a_0} \, r \]

Divide by \( a_0 \) and bring on \( a_0 \)

\[ u = \frac{r}{a_0} \]

\[ r = 4a_0 \int_0^u du \, u^3 \, e^{-2u} \]

Note:
\[ \int_0^\infty dx \, x^n \, e^{-x} = n! \]

So let \( x = 2u \)

\[ F = \frac{4a_0}{16} \int_0^\infty dx \, x^3 \, e^{-x} = \frac{4 \cdot 3 \cdot 2 \cdot a_0}{16} = \frac{3 a_0}{2} \]

\[ r = \frac{3 a_0}{2} \]