3-D Infinite Potential Well

Use conservation of energy

\[ E = KE + V = \frac{p^2}{2m} + V \]

+ expand \( p^2 \) given operator definition \( \hat{p}_i = -i\hbar \frac{\partial}{\partial x_i} \), we get

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

- or -

\[ \frac{-\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi \]

Interpretation of \( \psi \):

\[ \psi^* \psi = \text{Probability density} \]

\[ \text{Volume} \]

Normalization in 3-D:

\[ \int \psi^* \psi \, dV = 1 \]
To arrive at a solution, take the approach of separation of variables, i.e.

$$\psi(x, y, z) = F(x)G(y)H(z)$$

We will use this technique a bit later for the hydrogen atom potential. For 3-D infinite potential well, Cartesian coordinates are sensible.

$$\psi(\mathbf{r}) = A_x \sin(k_x x) A_y \sin(k_y y) A_z \sin(k_z z)$$

General notation:

$$A \sin(k_x x) A \sin(k_y y) A \sin(k_z z)$$

for 3-D vector.

As in 1-D case, $$\psi = 0$$ at:

- $$x = 0$$ and $$x = L$$;

$$k_i L = n_i \pi$$

for $$i = 1, 2, 3 \ldots$$

and independently:

3-D means 3 quantum numbers.
3.8 Infinite Potential Well:

\[ V = \begin{cases} 0 & 0 < x < L_x, \ 0 < y < L_y, \ 0 < z < L_z \\ \infty & \text{everywhere else} \end{cases} \]
Energy levels turn out to be

\[ E = \frac{n_1^2 \hbar^2}{2mL^2} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right) \]

would define quantum state by \( n_i \):

<table>
<thead>
<tr>
<th>( n_1 )</th>
<th>( n_2 )</th>
<th>( n_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

If \( L_1 = L_2 = L_3 \), then

\[ E_n = \frac{n_1^2 \hbar^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2) \]

cases B, C & D above termed 'degenerate' different quantum states give same energy
Hydrogen Atom

In 3-D, the Coulomb Potential is

\[ V(r) = \frac{-e^2}{4\pi\epsilon_0 r} \]

Spherically symmetric potential

Will be very painful to solve Schröd. e.g. in Cartesian coordinates

\[ \Rightarrow \text{convert to spherical coordinates} \]
Spherical Coordinates 101

We talk about 'polar' (θ) and 'azimuthal' (φ) angles around the axis.

Some useful conversions:

\[ r = \sqrt{x^2 + y^2 + z^2} \]
\[ \theta = \cos^{-1} \frac{2}{r} = \cos^{-1} \left( \frac{2}{\sqrt{x^2 + y^2 + z^2}} \right) \]
\[ \phi = \tan^{-1} \frac{y}{x} \]
Schrödinger Eq. in polar coordinates:

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} - \frac{2m}{\hbar^2} (\varepsilon - V(r)) \psi = 0
\]

Multiplying both sides by \( r^2 \) and substituting \( \psi(r) = R(r) \Theta(\theta) \Phi(\phi) \) to perform separation of variables,

\[
\Theta \Phi \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Theta}{\partial r} \right) + R \Phi \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Phi}{\partial \theta} \right) + \frac{R \Theta}{\sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} = -\frac{2m r^2}{\hbar^2} (\varepsilon - V(r)) R \Phi \Theta
\]

Divide by \( \Theta \Phi R \) and rearrange:

\[
\frac{1}{\Omega} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Omega}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Omega}{\partial \phi^2} = -\frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Omega}{\partial r} \right) - \frac{2m r^2}{\hbar^2} (\varepsilon - V(r))
\]

Since both sides depend on different variables, they must each equal a constant:

\[
-\frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Omega}{\partial r} \right) - \frac{2m r^2}{\hbar^2} (\varepsilon - V(r)) = C
\]

Radial Equation
Separating Angular Variables

We know
\[ \frac{1}{\Theta \sin \Theta} \frac{\partial}{\partial \Theta} \left( \frac{2}{\sin \Theta} \frac{\partial \Theta}{\partial \Theta} \right) + \frac{1}{\sin^2 \Theta} \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \Phi^2} = C \]

Multiply both sides by \( \sin^2 \Theta \) and rearrange:
\[ \sin \Theta \frac{\partial}{\partial \Theta} \left( \frac{2}{\sin \Theta} \frac{\partial \Theta}{\partial \Theta} \right) - C \sin^2 \Theta = - \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \Phi^2} \]

Again, both sides must equal a constant

\[ \sin \Theta \frac{\partial}{\partial \Theta} \left( \frac{2}{\sin \Theta} \frac{\partial \Theta}{\partial \Theta} \right) - C \sin^2 \Theta = \lambda \]

Polar Equation

\[ - \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \Phi^2} = \lambda \]

Azimuthal Equation
Azimuthal Equation

\[ \frac{d^2 \Phi}{d\phi^2} = -D \Phi(\phi) \]

If \( D < 0 \): exponential solution
- not physical since \( \phi \) is an angular variable & \( \Phi \) must come back to itself

If \( D > 0 \): sinusoidal solution
- has proper behavior for \( \Phi \) to repeat every \( 2\pi \)
  
  when
  \[ JD = m = 0, \pm 1, \pm 2, \pm 3, \ldots \]

  - and -
  \[ \Phi(\phi) = e^{im\phi} \]

\( m \) is a quantum \# associated with azimuthal degree of freedom

\[ \frac{d^2 \Phi(\phi)}{d\phi^2} = -m^2 \Phi(\phi) \]
What is physical property quantized?

$\Psi$ is a standing wave

$m_\ell$ indicates

$\ell$ fits in circumference when consider real part of wave function (i.e. $2\pi r = m_\ell\ell$)

$\ell$ can be related to angular momentum

$$L_\ell = mL = \frac{m_\ell h}{2\pi r} r = m_\ell \frac{h}{2\pi}$$

So $m_\ell$ is associated with the angular momentum in $z$-direction.

$m_\ell$ termed "magnetic quantum number."
Polar Equation

\[
\frac{\sin \theta}{\theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\theta}{d\theta} \right) - c \sin^2 \theta = 0
\]

\[
\lambda \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\theta}{d\theta} \right) - c \sin^2 \theta = \lambda \theta^2
\]

Solution is complicated but again considering boundary conditions

\[ c = \text{negative integer} = 0, -2, -6, -12, \ldots \]

Express this as

\[ c = -\lambda (l+1) \] where \( l = 0, 1, 2, \ldots \)

Quantum number \( l \) associated with polar angle \( \theta \) dimension. It's quantization corresponds to standing wave conditions in \( \theta \).

It turns out \( m \) and \( l \) are connected

\[ m = 0, \pm 1, \pm 2, \ldots \pm l \]
What does it quantize?

Go back to the Angular Eq.

\[ \frac{1}{\Theta \sin \Theta} \frac{d}{d\Theta} \left( \Theta \sin \Theta \frac{d \Phi}{d\Theta} \right) + \frac{1}{\sin^2 \Theta} \frac{d^2 \Phi}{d\theta^2} = \xi \]

Substituting for \( \xi \) and multiplying by \( \Theta \Phi \),

\[ \frac{1}{\sin \Theta} \frac{d}{d\Theta} \left( \sin \Theta \frac{d \Phi}{d\Theta} \right) \Theta \Phi + \frac{1}{\sin^2 \Theta} \frac{d^2 \Phi}{d\theta^2} = -\xi (l+1) \]

we can think of an angular momentum operator \( \hat{L} \) such that

\[ \hat{L}^2 = -\frac{\hbar^2}{\sin \Theta} \frac{d}{d\Theta} \left( \sin \Theta \frac{d}{d\Theta} \right) - \frac{\hbar^2}{\sin^2 \Theta} \frac{d^2}{d\theta^2} \]

The angular differential Eq. would then be

\[ \hat{L}^2 \ Y_{l,m}(\theta, \phi) = \xi (l+1) \hbar^2 \ Y_{l,m}(\theta, \phi) \]

where \( Y_{l,m}(\theta, \phi) = \Theta \Phi \) and are called "spherical harmonics". We get

\[ |\xi| = \sqrt{l(l+1) \hbar^2} \]

\( l = 0, 1, 2, \ldots \)

So \( l \) quantizes the total angular momentum, \( \hat{L} \).
Space Quantization

Since \( |m_\ell| = \ell \) and

\[
L_2 = m_\ell \hbar \quad \text{and} \quad |L| = \ell (\ell + 1) \hbar
\]

\( L_2 \) is always less than \( |L| \).

Also, \( L_2 / |L| \) takes on discrete ratios for a given \( \ell \).

**Example**

If \( \ell = 3 \), what is the smallest polar angle?

\( \theta \) minimized by maximizing \( L_2 \).

\[
\therefore m_\ell = +3
\]

\[
\cos \theta = \frac{L_2}{|L|} = \frac{3\hbar}{\sqrt{3(3+1) \hbar}} = \frac{3}{\sqrt{12}}
\]

\[
\theta = \cos^{-1}\left(\frac{\sqrt{3}}{2}\right) = 30^\circ
\]
The Radial Equation

Substituting for $L$ and rearranging,

$$-\frac{\hbar^2}{2m} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) + \frac{\hbar^2}{2m r^2} (\ell+1) \psi - \frac{\hbar^2}{2mr^2} + U(r) \psi = \epsilon \psi$$

**KE**

**rad**

**KE**

By supposition, considering other terms:

- KE corresponding to motion toward or away from nucleus.

If use Coulomb potential:

$$U(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

only see physical results when

$$\epsilon = \frac{-m \epsilon_0^4}{2(4\pi\epsilon_0 \hbar^2)} \frac{1}{n^2}$$

$n = 1, 2, 3, \ldots$

and $l$ is constrained as

$l = 0, 1, 2, \ldots, n-1$
Solutions to Radial Eq.

When \( l = 0 \), no angular momentum
- 2nd term \( (K\Sigma_{l=0}) \rightarrow 0 \)

Wave function

Spherically symmetric wave function

\[ R(r) = A e^{-r/a_0} \rightarrow a_0 = \frac{\sqrt{\hbar^2}}{m e^2} \]

Bohr radius!

Ground state energy

\[ E = -\frac{\hbar^2}{2m a_0^2} = -E_0 = -13.6 \, eV \]

Ground state energy of Bohr atom!

Fact that \( n \) comes from radial Eq. indicating some relation between "size of shell" \( e^- \) harbors +\( \Sigma n \)
- lower \( n \), smaller orbits, more tightly bound \( e^- \)
Quantum #5

\[ n > 0 \quad \rightarrow \quad E_n \]
\[ l < n \quad \rightarrow \quad l \pm 1 \]
\[ |m| \leq l \quad \rightarrow \quad l_s \]

Example: what are quantum #s for \( n = 4 \) state?

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l )</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1</td>
<td>-1, 0, +1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>-2, -1, 0, +1, +2</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>-3, -2, -1, 0, +1, +2, +3</td>
</tr>
</tbody>
</table>

Terminology

\( l = 0, 1, 2, 3, 4, 5 \)

Spectroscopic notation:

- \( n = 2, l = 1 \): "2p state"
- \( n = 4, l = 2 \): "4d state"