Quantum Mechanics and Atomic Physics

Lecture 15:
Quantization of Space
&
The Infinite and Finite Spherical Well

http://www.physics.rutgers.edu/ugrad/361

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Last time

- S.E. in 3D and in spherical coordinates
- For a mass $\mu$ moving in a central potential $V(r)$

$$\frac{-\hbar^2}{2\mu} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \psi(r, \theta, \phi)$$

$$+ V(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

- Solutions separated into angular and radial parts

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$$
Last time: Rewrite this in terms of angular momentum of the system

Recall:

\[
-\frac{\hbar^2}{2\mu} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \phi}{\partial r} \right) \right\} + \left[ V - \mathcal{E} \right] r^2
\]

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

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

\[
f(r) = g(\theta, \phi) = \text{const}
\]

\[
\Rightarrow -\frac{\hbar^2}{2\mu} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \phi}{\partial r} \right) \right\} + \left[ V - \mathcal{E} \right] r^2
\]

\[
= \text{const} = -\frac{1}{2\mu} \left[ L_{\phi}^2 \phi \right]
\]

\[
\text{const} = -\frac{\alpha \hbar^2}{2\mu}
\]
Last time

$$\Rightarrow -\frac{1}{2\mu} \left[ L_{\varphi}^2 Y \right] = -\frac{\alpha \hbar^2}{2\mu}$$

$$\Rightarrow L_{\varphi}^2 Y = \hbar^2 \alpha Y = \left[ \hbar^2 \left( \ell (\ell + 1) \right) \right] Y$$

$$\Rightarrow L = \sqrt{\ell (\ell + 1) \hbar} \quad \ell = 0, 1, 2, \ldots$$

So, \( \alpha = \ell (\ell + 1) \) and \( \ell = 0, 1, 2, \ldots \)

Total angular momentum is quantized!
What about $L_z$?

$$L_z = -i \hbar \frac{\partial}{\partial \varphi}$$

$$\Rightarrow L_z \Phi(\varphi) = -i \hbar \frac{\partial}{\partial \varphi} (A e^{i m \varphi})$$

$$= -i^2 \hbar m \hbar (A e^{i m \varphi})$$

$$= m \hbar \Phi$$

$$\Rightarrow L_z = m \hbar \text{ where } |m| \leq \ell$$

Since $L_z \leq |\hat{L}| \Rightarrow m \leq \sqrt{\ell (\ell + 1)}$

$$\Rightarrow |m| \leq \ell$$

- So, solutions exist only if $\ell$ is an integer and $\ell \geq m_\ell$
Summary: Angular Solutions

\[ \Phi(\varphi) = \sqrt{\frac{1}{\pi}} \, e^{im\varphi} \]

Magnetic quantum number \( m = 0, \pm 1, \pm 2, \ldots \)

\[ \Theta(\theta) = \text{Legendre polynomial} \]

Associated Legendre functions \( l = 0, 1, 2, 3, \ldots \)

\[ Y_l^m(\theta, \varphi) = \sqrt{\frac{2l+1}{4\pi}} \, \frac{d^m}{d\varphi^m}(\cos \theta) \]

Spherical harmonic functions \( l = 0, 1, 2, \ldots \)

\( |m| \leq l \)
Space Quantization

- The magnetic quantum number \( m_l \) expresses the quantization of direction of \( L \).

\[
L_z = m_l h \\
L_z = L \cos \theta
\]

\[
\Rightarrow \cos \theta = \frac{L_z}{L} = \frac{m_l h}{\sqrt{l(l+1)} h} = \frac{m_l}{\sqrt{l(l+1)}}
\]

- So \( L \) can assume only certain angles, given above, with respect to the \( z \)-axis.

- This is called space quantization.
Example

For a particle with $\ell=2$, what are the possible angles that $\mathbf{L}$ can make with the $z$-axis?

$l=2$, $L = \sqrt{6}\hbar$  
$L_z = m\hbar$

$m_{\ell} = -2, -1, 0, 1, 2$

$$\cos \theta = \frac{m_{\ell}}{\sqrt{\ell(\ell+1)}} = \frac{m_{\ell}}{\sqrt{6}}$$

- $m_{\ell} = 2 \Rightarrow \cos \theta = \frac{2}{\sqrt{6}} \Rightarrow \theta = 35.3^\circ$
- $m_{\ell} = 1 \Rightarrow \cos \theta = \frac{1}{\sqrt{6}} \Rightarrow \theta = 65.9^\circ$
- $m_{\ell} = 0 \Rightarrow \cos \theta = 0 \Rightarrow \theta = 90^\circ$
- $m_{\ell} = -1 \Rightarrow \cos \theta = -\frac{1}{\sqrt{6}} \Rightarrow \theta = 114^\circ$ or $-66^\circ$
- $m_{\ell} = -2 \Rightarrow \cos \theta = \frac{2}{\sqrt{6}} \Rightarrow \theta = 145^\circ$  
  or $-35^\circ$

Figure 6.5 Possible orientations of $\mathbf{L}$ for $\ell = 2$, $|\mathbf{L}| = \sqrt{6}\hbar$. 
Plot of Spherical harmonics

- “3D” plots of:
  \[ y_{\ell m}(\theta, \phi) \]

- \( \theta \) is vertically up
- Independent of \( \phi \)
  - So rotationally symmetric around z-axis

- We will see later these will manifest themselves as the probability distributions
Summary: Quantization of $L$, $L_z$ and space

$$L_c^2 Y^\prime_{\ell, m}\left(0, \varphi\right) = \left[\hbar^2 \ell (\ell + 1)\right] Y_{\ell, m\ell}\left(0, \varphi\right)$$

$$\Rightarrow L = \sqrt{\ell (\ell + 1)} \hbar$$

$$(L_3)_{op} \Phi(\varphi) = m_e \hbar \Phi(\varphi)$$

$$\Rightarrow L_3 = m_e \hbar$$

$$\cos \theta = \frac{L_3}{L} = \frac{m_e}{\sqrt{\ell (\ell + 1)}}$$

Reed: Chapter 6
Radial Solutions

To find radial solutions:

\[-\frac{\hbar^2}{2\mu} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right\} \right\} + (V(r) - E) r^2 = -\frac{\hbar^2}{2\mu} \left[ k^2_{\text{op}} + l(l+1) \right] \gamma\]

\[\Rightarrow -\frac{\hbar^2}{2\mu} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - l(l+1) \right\} + V(r) r^2 = E r^2\]

This is called the radial equation
Solving the radial equation

Note:

\[
\frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) = \frac{r}{R} \frac{\partial^2 \psi}{\partial r^2} (r R)
\]

\[
\Rightarrow \quad -\frac{\hbar^2}{2\mu} \left\{ \frac{r}{R} \frac{\partial^2 \psi}{\partial r^2} (r R) - \ell (\ell+1) \right\} + V(r) r^2 = E r^2
\]

Let’s introduce the auxiliary function:

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

And plug it in above
\[ -\frac{\hbar^2}{2\mu} \left( \frac{2}{r^2} (U) - l(l+1) \right) + V(r) \frac{U}{R^2} - E \frac{U^2}{R^2} = 0 \]

Multiply by \( \frac{R^2}{U} \)

\[ -\frac{\hbar^2}{2\mu} \left( \frac{2}{r^2} U - l(l+1) \frac{R^2}{U} \right) + U(V-E) = 0 \]

Multiply by \( -\frac{2\mu}{\hbar^2} \) and \( \frac{2}{r^2} \Rightarrow \frac{d^2}{dr^2} \)

\[ \Rightarrow \frac{d^2}{dr^2} U + \frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{l(l+1)}{r^2} \cdot \frac{\hbar^2}{2\mu} \right] U = 0 \]
The Total Wavefunction

- The total wavefunction

\[ \psi_{n \ell m, \theta} (r, \theta, \phi) = R_n (r) Y_{\ell m} (\theta, \phi) = \frac{U_n (r)}{r} Y_{\ell, m} (\theta, \phi) \]

- We will soon define \( n \) to be the quantum number that dictates the quantization of energy

- First let’s solve this for two simple cases
  - Infinite and finite spherical wells
  - Spherical analogs of particle in a box
  - Interest in nuclear physics: nuclei modeled as spherical potential wells 10’s of MeV deep and 10\(^{-14}\) m in radius

- Then we will obtain a detailed solution to the Coulomb potential for hydrogen (next time)
The Infinite Spherical Well

- A particle of mass $\mu$ is trapped in a spherical region of space with radius $a$ and an impenetrable barrier

$$V(r) = \begin{cases} \infty & r > a \\ 0 & r < a \end{cases}$$

- We will only deal with the simplest case is for zero angular momentum

$$l = 0$$

- (Otherwise: $l \neq 0 \Rightarrow$ Bessel & Neumann Functions.)
Looks just like for 1D infinite potential well!

So solutions are:

\[ U_0(r) = A \sin(kr) + B \cos(kr) \]
Boundary Conditions

- Recall: \( R = \frac{\mathcal{U}}{r} \)

- **Boundary conditions should prevent divergence as** \( r \to 0 \)
  \[
  \Rightarrow \quad U(r = 0) = 0 \quad \Rightarrow \quad B = 0
  \]

- **Boundary conditions also require that the barrier is impenetrable:**
  \[
  \Rightarrow \quad U|_{r=a} = 0 \quad \Rightarrow \quad 0 = A \sin \kappa a \quad \Rightarrow \quad \kappa a = n\pi
  \]

- **This gives us quantization of energy:**
  \[
  \Rightarrow \quad \varepsilon_n(l=0) = \frac{n^2 \pi^2 \hbar^2}{2\mu a^2}
  \]
Total Wavefunction

\[ \Psi_{n\ell m}(r, \theta, \varphi) = R_n(r) Y_{\ell m}^m(\theta, \varphi) \]

\[ = \frac{A}{\sqrt{4\pi r}} \sin \left( \frac{n\pi r}{a} \right) \]

Since: \( Y_{0,0} = \frac{1}{\sqrt{4\pi}} \) and

\[ R_n(r) = \frac{U_n(r)}{r} = \frac{A}{r} \sin \left( \frac{n\pi r}{a} \right) \]

- To obtain A, we apply normalization …
Normalization

\[ \int_0^a \int_0^{2\pi} \int_0^{2\pi} r^2 \sin \theta \psi^* \psi \, r^2 \sin \theta \, d\phi \, d\theta \, dr = 1 \]

\[ \int_0^a \int_0^{2\pi} \int_0^{2\pi} \frac{A^2}{4\pi r^2} \sin^2 \left( \frac{n\pi r}{a} \right) \cdot r^2 \sin \theta \psi^* \psi \, d\phi \, d\theta \, dr = 1 \]

\[ \int_0^{2\pi} d\phi = 2\pi, \quad \int_0^{\pi} \sin \theta d\theta = 2, \quad \int_0^a \sin^2 \left( \frac{n\pi r}{a} \right) \, dr = \frac{a}{2} \]

\[ \Rightarrow \quad \frac{A^2}{4\pi} \cdot 2\pi \cdot 2 \cdot \frac{a}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{a}} \]

\[ S_{01} \]

\[ \psi_{n, 0, 0} = \frac{1}{\sqrt{2\pi a r}} \sin \left( \frac{n\pi r}{a} \right) \]
Example: what is $\langle r \rangle$ for a particle in an infinite spherical well?

$$\langle r \rangle = \int_0^a \int_0^{2\pi} \int_0^\pi \left[ \frac{\Psi^*_{n\ell m} \cdot r \cdot \Psi_{n\ell m}}{r} \right] r^2 \sin \theta \, d\theta \, d\phi \, dr$$

$$= \frac{1}{2\pi a} \left[ \int_0^a \left( r \sin^2 \left( \frac{n\pi r}{a} \right) \right) \, dr \right] \frac{\pi}{\sin \theta} \, d\theta \, d\phi$$

$$= \frac{2}{a} \int_0^a r \sin^2 \left( \frac{n\pi r}{a} \right) \, dr$$

$$= \frac{2}{a} \left[ \frac{r^2}{4} - \frac{r \sin \left( \frac{n\pi r}{a} \right)}{\frac{n\pi r}{a}} - \frac{\cos \left( \frac{n\pi r}{a} \right)}{8 \left( \frac{n\pi r}{a} \right)^2} \right]_0^a$$

$$= \frac{2}{a} \cdot \frac{a^2}{4} = \frac{a}{2}$$

$\langle r \rangle$ is independent of $n$!

Increasing the energy of the particle changes the probability distribution but not it’s average position.

This is not the case for non-zero angular momentum!
The Finite Spherical Well

- Analog of 1-D finite potential well.
- Could describe a particle trapped inside a nucleus

\[
V(r) = \begin{cases} 
  V_0 & r \geq a \\
  0 & r < a
\end{cases}
\]

Let’s find the bound state solutions, \( E < V_0 \)
Inside and outside the well

- **Inside the well**
  
  \[ \frac{d^2 U_0^{\text{in}}}{dr^2} + \kappa_1^2 U_0^{\text{in}} = 0 \]
  
  \[ \kappa_1^2 = \frac{2\mu E}{\hbar^2} \]
  
  Just like infinite spherical well
  
  \[ R_0^{\text{inside}}(r) = \frac{A \sin \kappa_1 r}{r} \quad \text{for} \quad r < a \]

- **Outside the well**
  
  \[ \frac{d^2 U_0^{\text{out}}}{dr^2} = \kappa_2^2 U_0^{\text{out}} \]
  
  \[ \kappa_2^2 = \frac{2\mu}{\hbar^2} (V_0 - E) \]

  \[ U_0^{\text{out}}(r) = Ce^{k_2r} + De^{-k_2r} \]

  \[ \Rightarrow R_0^{\text{out}}(r) = \frac{Ce^{k_1r}}{r} + \frac{De^{-k_1r}}{r} \]
Boundary conditions outside the well

- Boundary condition at \( r \to \infty \), \( U(1r) \to 0 \)
  
  \[ \Rightarrow C = 0 \]

\[ R_{\text{out}}(r) = \frac{D e^{-kr}}{r} \]

- Continuity at \( r = a \) of \( R \) and \( \frac{dR}{dr} \)

\[ A \sin \kappa a = D e^{-k_2 a} \]

\[-\frac{A \sin \kappa a}{a^2} + \frac{A \kappa \cos \kappa a}{a} = -\frac{D k_2 e^{-k_2 a}}{a} - \frac{D e^{-k_2 a}}{a^2} \]

\[ \Rightarrow A \left[ k_2 \cos \kappa a - \sin \kappa a \right] = -D e^{-k_2 a} (a \kappa^2 + 1) \]
Divide the two equations:

\[ n_{1a} \cot n_{1a} - 1 = -\left( a \frac{\pi}{2} + 1 \right) \]
\[ n_{2a} \cot n_{2a} = -a \frac{\pi}{2} \]

Define:

\[ \zeta = n_{1a}, \quad \eta = n_{2a} \]
\[ \zeta \cot \zeta = -\eta \]

This is a transcendental equation!

\[ \zeta^2 + \eta^2 = a^2 \left( k_1^2 + k_2^2 \right) = a^2 \left[ \frac{2mE}{h^2} + \frac{2m}{h^2} (V_0 - E) \right] \]
\[ = a^2 \cdot \frac{2mV_0}{h^2} = \text{const} \cdot \rho^2 \]

\( \rho^2 \) is the strength parameter

To be continued next time…
Summary/Announcements

- **Next time:**
  - Finish Finite Spherical Well
  - The Coulomb Potential of the Hydrogen atom

- No homework today.

- **Next homework due on Monday Nov 6.**

- You will have a QUIZ next Wednesday Nov 8 on Chapter 6

- Stay tuned for midterm exam grades this week …