

PH102: Interactive Lecture 3

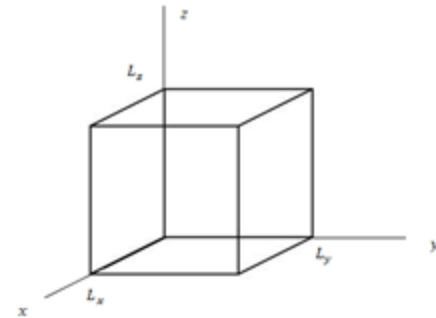
- Topics
 - Particle in a 3-D box
 - 3-D Schrodinger Equation for Hydrogen atom
 - $(x, y, z) \leftrightarrow (r, \theta, \phi)$
 - Separation of variables $R\Theta\Phi$
 - Three equations
 - Three quantum numbers (n, l, m_l)
 - Wave functions
 - Degeneracies

Particle in a 3-d infinite well

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E \psi(\vec{x})$$

In (x, y, z) coordinates, $\vec{x} = (x, y, z)$, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = -\frac{2m}{\hbar^2} (E - U(x, y, z)) \psi(x, y, z)$$



$$U(\vec{x}) = \begin{cases} 0 & 0 < x < L_x, 0 < y < L_y, 0 < z < L_z \\ \infty & \text{otherwise} \end{cases}$$

Wave functions exist only inside the 3-d infinite well.

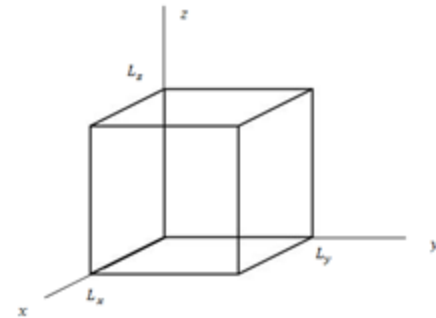
Separation of variables: $\psi(\vec{x}) = \psi(x, y, z) = F(x)G(y)H(z)$

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Wave functions exist only inside the 3-d infinite well.

Separation of variables: $\psi(\vec{x}) = \psi(x, y, z) = F(x)G(y)H(z)$

$$\frac{1}{F(x)} \frac{\partial^2 F(x)}{\partial x^2} + \frac{1}{G(y)} \frac{\partial^2 G(y)}{\partial y^2} + \frac{1}{H(z)} \frac{\partial^2 H(z)}{\partial z^2} = -\frac{2mE}{\hbar^2} \quad \text{=constant}$$

constant=Cx Constant=Cy Constant=Cz

$$Cx + Cy + Cz = -\frac{2mE}{\hbar^2}$$

Particle in a 3-d infinite well

1-D solutions:

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{2mE}{\hbar^2} \psi(x)$$

$$\text{Wave function: } \psi_{0 < x < L}(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$\text{Energy } E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

3-D solutions: wave functions

$$\begin{cases} \frac{d F(x)}{dx^2} = C_x F(x) \cdot \\ \frac{d G(y)}{dy^2} = C_y G(y) \cdot \\ \frac{d H(z)}{dz^2} = C_z H(z) \cdot \end{cases}$$

$$\rightarrow F(x) = A_x \sin \frac{n_x \pi x}{L_x}$$

$$\rightarrow G(y) = A_y \sin \frac{n_y \pi y}{L_y}$$

$$\rightarrow H(z) = A_z \sin \frac{n_z \pi z}{L_z}$$

Particle in a 3-d infinite well

1-D solutions:

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3-D solutions: wave functions

$$\begin{cases} \frac{dF(x)}{dx^2} = C_x F(x) & \rightarrow F(x) = A_x \sin \frac{n_x \pi x}{L_x} \\ \frac{dG(y)}{dy^2} = C_y G(y) & \rightarrow G(y) = A_y \sin \frac{n_y \pi y}{L_y} \\ \frac{dH(z)}{dz^2} = C_z H(z) & \rightarrow H(z) = A_z \sin \frac{n_z \pi z}{L_z} \end{cases}$$

$$C_x = -\frac{n_x^2 \pi^2}{L_x^2} \quad C_y = -\frac{n_y^2 \pi^2}{L_y^2} \quad C_z = -\frac{n_z^2 \pi^2}{L_z^2}$$

$$C_x + C_y + C_z = -\frac{2mE}{\hbar^2} = -\frac{n_x^2 \pi^2}{L_x^2} - \frac{n_y^2 \pi^2}{L_y^2} - \frac{n_z^2 \pi^2}{L_z^2}$$

Particle in a 3-D infinite well

$$E_{(n_x, n_y, n_z)} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

$$\psi(x, y, z) = F(x)G(y)H(z) = A \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}$$

$$\text{Lowest energy state} = E_{(1,1,1)} = \left(\frac{1^2}{L_x^2} + \frac{1^2}{L_y^2} + \frac{1^2}{L_z^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

$$\text{Wave function for the lowest energy state} = \psi_{(1,1,1)} = A \sin \frac{\pi x}{L_x} \sin \frac{\pi y}{L_y} \sin \frac{\pi z}{L_z}$$

$$E_{(n_x, n_y, n_z)} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

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An electron in a cubic 3d infinite well of 1 nm at the E(2,1,1) state

$$E_{(2,1,1)} = 6 \left(\frac{\pi^2 \hbar^2}{2mL^2} \right) = (2^2 + 1^2 + 1^2) \frac{\pi^2 (1.055 \times 10^{-34} \text{ J sec})^2}{2(9.11 \times 10^{-31} \text{ kg})(10^{-9} \text{ m})^2}$$

$$= 3.62 \times 10^{-19} \text{ J} = 2.26 \text{ eV (the same as } E_{(1,2,1)} = E_{(1,1,2)})$$

$$\text{Where } \begin{cases} \text{electron mass} = 9.11 \times 10^{-31} \text{ kg} \\ h = 1.055 \times 10^{-34} \text{ J sec} \\ L = 10^{-9} \text{ m} \end{cases} \quad \text{and } 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$E_{(n_x, n_y, n_z)} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

$$\psi(x, y, z) = F(x)G(y)H(z) = A \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}$$

Where is a particle with the value most likely to be found?

Probability density

$$\circ \quad |\psi_{(2,1,1)}|^2 = A^2 \left(\sin \frac{2\pi x}{L} \right)^2 \left(\sin \frac{\pi y}{L} \right)^2 \left(\sin \frac{\pi z}{L} \right)^2$$

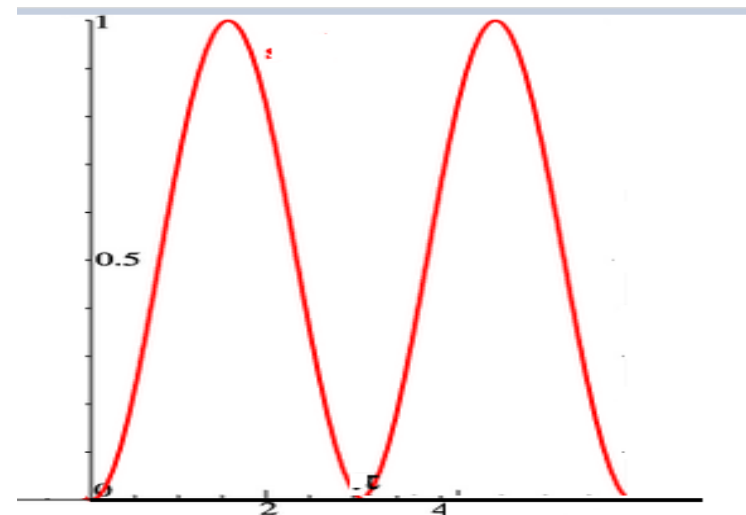
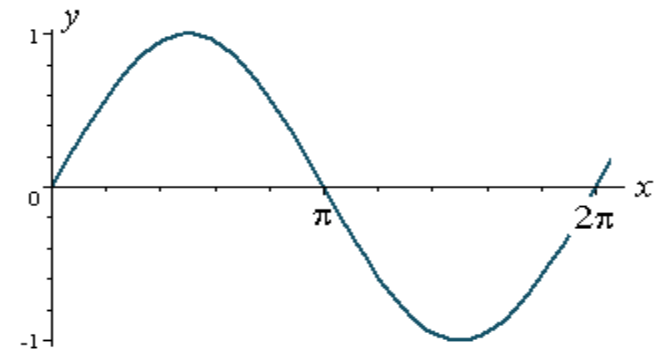
$$E_{(n_x, n_y, n_z)} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

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$$E_{(n_x, n_y, n_z)} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

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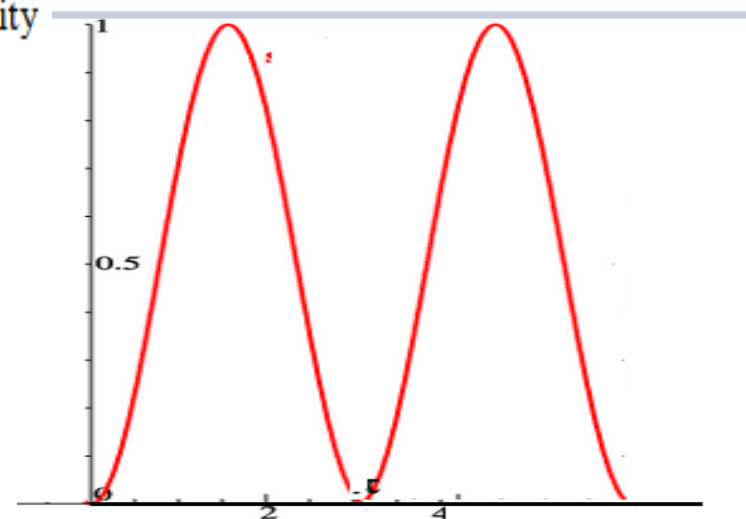
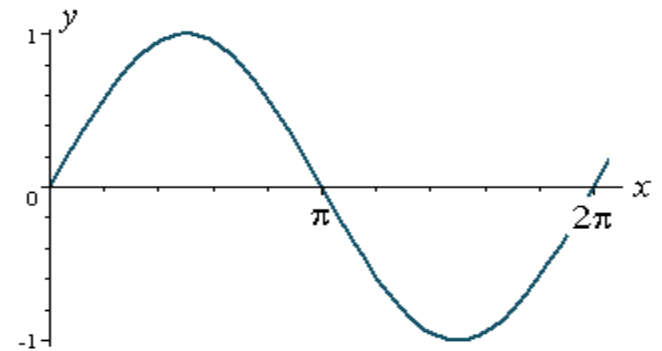
Where is a particle with the value most likely to be found?

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$$\circ |\psi_{(2,1,1)}|^2 = A^2 \left(\sin \frac{2\pi x}{L} \right)^2 \left(\sin \frac{\pi y}{L} \right)^2 \left(\sin \frac{\pi z}{L} \right)^2$$

Since the value of $(\sin\theta)^2$ is highest when $\theta = \frac{1}{2}\pi, \frac{3}{2}\pi, \text{etc.}$, the probability

$$\begin{cases} x = \frac{L}{4}, \frac{3L}{4} \\ y = \frac{L}{2} \\ z = \frac{L}{2} \end{cases}$$



Energy Split

Consider (that is, a slightly non-symmetric box along the z axis)

$$L_x = L_y = L_z = L \longrightarrow L_x = L_y = L, L_z = .9 L$$

$$E_{(1,1,1)} = (1^2 + 1^2 + 1^2) \left(\frac{\pi^2 \hbar^2}{2mL^2} \right) = 3 \left(\frac{\pi^2 \hbar^2}{2mL^2} \right)$$

$$E_{(2,1,1)} = E_{(1,2,1)} = E_{(1,1,2)} = (2^2 + 1^2 + 1^2) \left(\frac{\pi^2 \hbar^2}{2mL^2} \right) = 6 \left(\frac{\pi^2 \hbar^2}{2mL^2} \right)$$

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$$E_{(1,1,1)} = \left(\frac{1^2}{L^2} + \frac{1^2}{L^2} + \frac{1^2}{.9^2 L^2} \right) \left(\frac{\pi^2 \hbar^2}{2m} \right) = (1 + 1 + 1.23) \left(\frac{\pi^2 \hbar^2}{2mL^2} \right) = 3.23 \left(\frac{\pi^2 \hbar^2}{2mL^2} \right)$$

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Energy Split

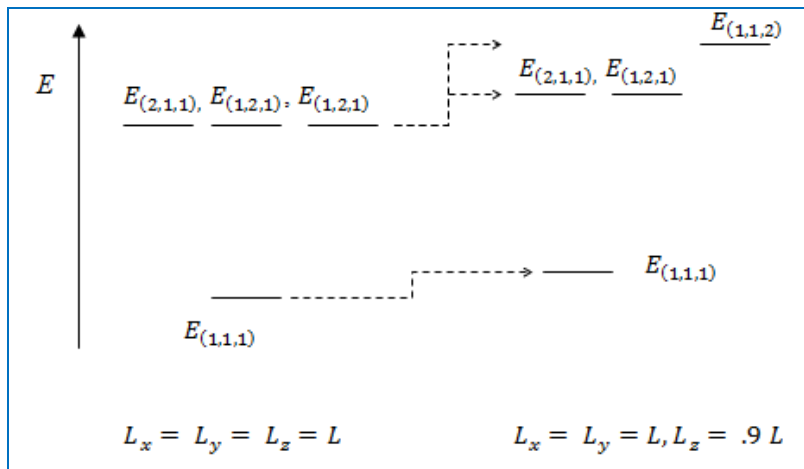
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$$E_{(1,1,1)} = \left(\frac{1^2}{L^2} + \frac{1^2}{L^2} + \frac{1^2}{.9^2 L^2} \right) \left(\frac{\pi^2 \hbar^2}{2m} \right) = (1 + 1 + 1.23) \left(\frac{\pi^2 \hbar^2}{2mL^2} \right) = 3.23 \left(\frac{\pi^2 \hbar^2}{2mL^2} \right)$$

$$E_{(2,1,1)} = E_{(1,2,1)} = E_{(1,1,2)} = (2^2 + 1^2 + 1^2) \left(\frac{\pi^2 \hbar^2}{2mL^2} \right) = 6 \left(\frac{\pi^2 \hbar^2}{2mL^2} \right)$$



$$E_{(1,1,2)} = \left(\frac{2^2}{L^2} + \frac{1^2}{L^2} + \frac{1^2}{.9^2 L^2} \right) \left(\frac{\pi^2 \hbar^2}{2m} \right) = (4 + 1 + 1.23) \left(\frac{\pi^2 \hbar^2}{2mL^2} \right) = 6.23 \left(\frac{\pi^2 \hbar^2}{2mL^2} \right)$$

$$E_{(1,1,2)} = \left(\frac{1^2}{L^2} + \frac{2^2}{.9^2 L^2} \right) \left(\frac{\pi^2 \hbar^2}{2m} \right) = (1 + 4.92) \left(\frac{\pi^2 \hbar^2}{2mL^2} \right) = 5.92 \left(\frac{\pi^2 \hbar^2}{2mL^2} \right)$$

Quantum Problem Solving Schema

- Think about **potential** energy and Hamiltonian
- **Divide** regions, if possible
- Choose appropriate **coordinates**
- Write **Schrodinger Equation** for each region
- **Separation of variables**, if possible
- Set “**constant**”s if applicable
- Solve for **wave function**
 - Boundary conditions
 - Normalization
- Solve for **energy**
- Build energy level diagrams and inspect for energy degeneracies

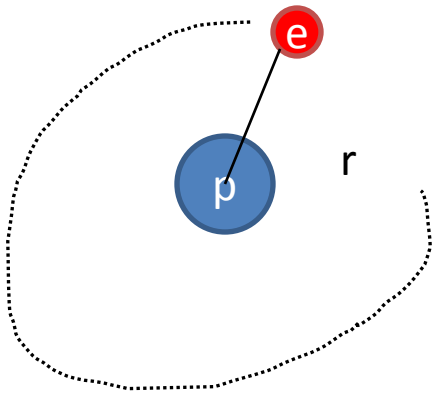
Hydrogen atom

- Potential created by Coulomb interactions between electron ($-e$) and proton ($+e$)

Hydrogen atom

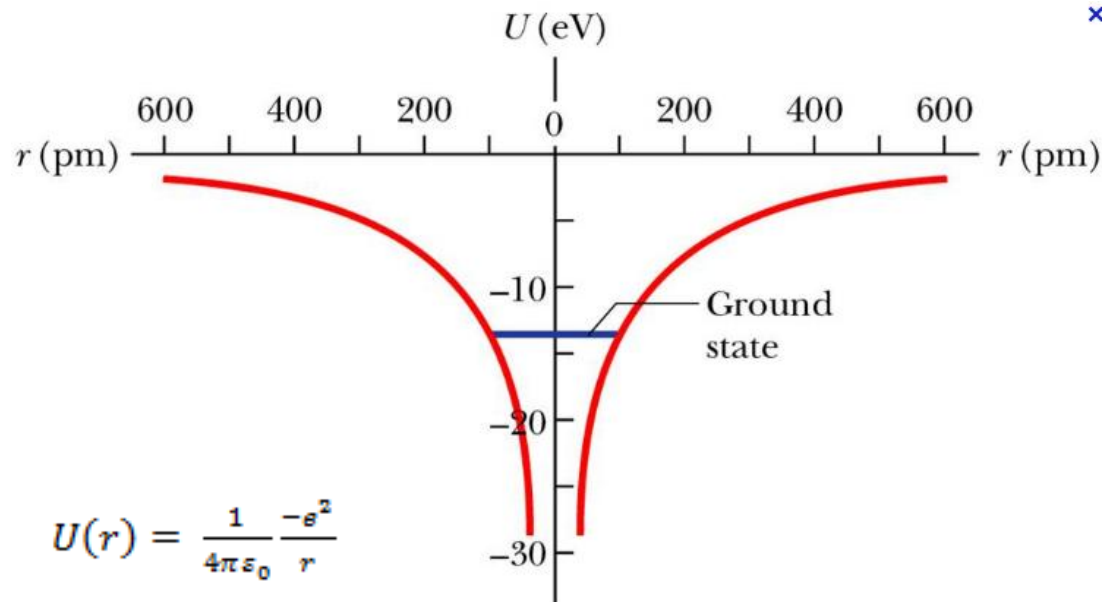
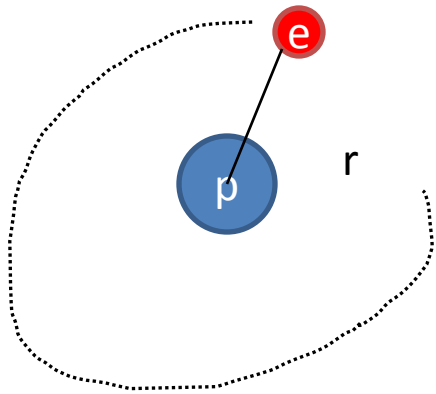
- Potential created by Coulomb interactions between electron ($-e$) and proton ($+e$)

$$U(r) = \frac{1}{4\pi\epsilon_0} \frac{-e^2}{r}$$



Hydrogen atom

- Potential created by Coulomb interactions between electron ($-e$) and proton ($+e$)



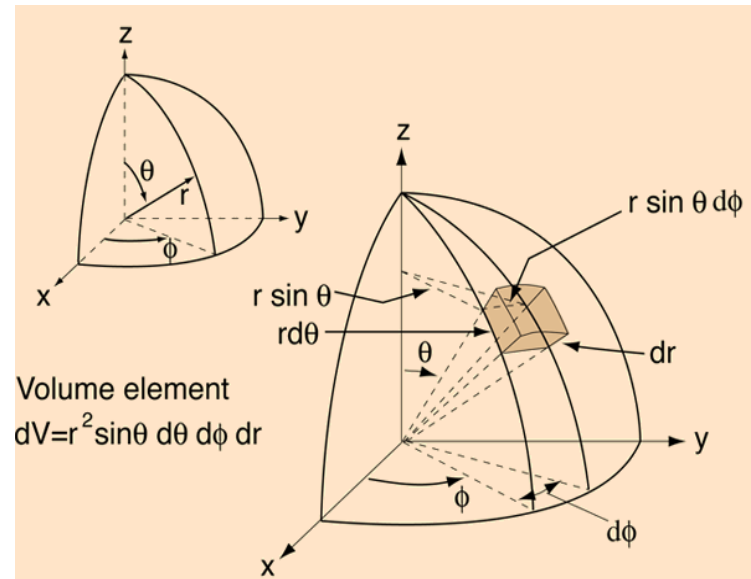
$$(x, y, z) \leftrightarrow (r, \theta, \phi)$$

$$\begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \phi = \tan^{-1} \frac{y}{x} \\ \theta = \cos^{-1} \frac{z}{r} \end{cases}$$

$$\begin{cases} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{cases}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \csc \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \csc^2 \theta \frac{\partial}{\partial \phi^2} \right] \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2} \end{aligned}$$



Schrodinger Equation

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E \psi(\vec{x})$$

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

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$$\frac{-\hbar^2}{2m} \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) + U(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

Schrodinger Equation

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E \psi(\vec{x})$$

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

$$\frac{-\hbar^2}{2m} \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) + U(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

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

Schrodinger Equation

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E \psi(\vec{x})$$

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

$$\frac{-\hbar^2}{2m} \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) + U(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

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

$$\left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = - \frac{2mr^2}{\hbar^2} (E - U) \psi$$

Schrodinger Equation

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E \psi(\vec{x})$$

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

$$\frac{-\hbar^2}{2m} \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) + U(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

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

$$\left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = - \frac{2mr^2}{\hbar^2} (E - U) \psi$$

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \psi + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) \psi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \psi = - \frac{2mr^2}{\hbar^2} (E - U) \psi$$

Schrodinger Equation

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E \psi(\vec{x})$$

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

$$\frac{-\hbar^2}{2m} \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) + U(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

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

$$\left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = - \frac{2mr^2}{\hbar^2} (E - U) \psi$$

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \psi + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) \psi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \psi = - \frac{2mr^2}{\hbar^2} (E - U) \psi$$

$$\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) \psi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \psi = \left[- \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) \right] \psi$$

Schrodinger Equation

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) \psi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \psi = \left[-\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) \right] \psi$$

Separation of variables

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Schrodinger Equation

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) \psi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \psi = \left[-\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) \right] \psi$$

Separation of variables

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) R\Theta\Phi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} R\Theta\Phi = \left[-\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) \right] R\Theta\Phi$$

$$\begin{aligned} \frac{\partial\psi}{\partial r} &= \Theta\Phi \frac{\partial R}{\partial r} \\ \frac{\partial\psi}{\partial\theta} &= R\Phi \frac{\partial\Theta}{\partial\theta} \\ \frac{\partial^2\psi}{\partial\phi^2} &= R\Theta \frac{\partial^2\Phi}{\partial\phi^2} \end{aligned}$$

Schrodinger Equation

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) \psi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \psi = \left[-\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) \right] \psi$$

Separation of variables

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) R\Theta\Phi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} R\Theta\Phi = \left[-\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) \right] R\Theta\Phi$$

$$\begin{aligned} \frac{\partial\psi}{\partial r} &= \Theta\Phi \frac{\partial R}{\partial r} \\ \frac{\partial\psi}{\partial\theta} &= R\Phi \frac{\partial\Theta}{\partial\theta} \\ \frac{\partial^2\psi}{\partial\phi^2} &= R\Theta \frac{\partial^2\Phi}{\partial\phi^2} \end{aligned}$$

$$R\Phi \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + R\Theta \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = -\Theta\Phi \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) R\Theta\Phi$$

Schrodinger Equation

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) \psi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \psi = \left[-\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) \right] \psi$$

Separation of variables

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) R\Theta\Phi + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} R\Theta\Phi = \left[-\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) \right] R\Theta\Phi$$

$$\begin{aligned} \frac{\partial\psi}{\partial r} &= \Theta\Phi \frac{\partial R}{\partial r} \\ \frac{\partial\psi}{\partial\theta} &= R\Phi \frac{\partial\Theta}{\partial\theta} \\ \frac{\partial^2\psi}{\partial\phi^2} &= R\Theta \frac{\partial^2\Phi}{\partial\phi^2} \end{aligned}$$

$$R\Phi \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + R\Theta \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = -\Theta\Phi \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) R\Theta\Phi$$

$$\frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U)$$

Schrodinger Equation

$$\frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) = C \text{ (Constant)}$$

Angular part

Radial part

$-l(l+1)$

Schrodinger Equation

$$\frac{1}{\theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Phi}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) = C \text{ (Constant)}$$

$-l(l+1)$

Angular part

$-l(l+1)$

Radial part

$-l(l+1)$

Schrodinger Equation

$$\frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) = C \text{ (Constant)}$$

Angular part

$$-l(l+1)$$

Radial part

$$-l(l+1)$$

$$-l(l+1)$$

$$\begin{cases} -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C = -l(l+1) \\ \frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = C = -l(l+1) \end{cases}$$

Schrodinger Equation

$$\frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) = C \text{ (Constant)}$$

Angular part

$$-l(l+1)$$

Radial part

$$-l(l+1)$$

$$-l(l+1)$$

$$\begin{cases} -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C = -l(l+1) \\ \frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = C = -l(l+1) \end{cases}$$

multiply $\sin^2\theta$.

Schrodinger Equation

$$\frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) = C \text{ (Constant)}$$

Angular part

$$-l(l+1)$$

Radial part

$$-l(l+1)$$

$$\begin{cases} -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C = -l(l+1) \\ \frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = C = -l(l+1) \end{cases}$$

multiply $\sin^2\theta$. $\frac{1}{\Theta} \sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} = -l(l+1) \sin^2\theta$

Schrodinger Equation

$$\frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U) = C \text{ (Constant)}$$

Angular part

$$-l(l+1)$$

Radial part

$$-l(l+1)$$

$$-l(l+1)$$

$$\begin{cases} -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C = -l(l+1) \\ \frac{1}{\Theta} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} = C = -l(l+1) \end{cases}$$

multiply $\sin^2\theta$. $\frac{1}{\Theta} \sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + \frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} = -l(l+1) \sin^2\theta$

$$\begin{aligned} \frac{1}{\Theta} \sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + l(l+1) \sin^2\theta &= -\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} \\ &= m_l^2 \text{ (another constant)} \end{aligned}$$

Schrodinger Equation

$$\left\{ \begin{array}{ll} \frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi & \text{Azimuthal Equation} \\ \sin\theta \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \Theta}{\partial \theta} \right) + [l(l+1)\sin^2\theta - m_l^2]\Theta = 0 & \text{Polar Equation} \\ \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} (E - U(r))R - l(l+1)R = 0 & \text{Radial Equation} \end{array} \right.$$

Azimuthal Equation

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

Wave function

Boundary condition

Quantization

Azimuthal Equation

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

Wave function $\Phi(\phi) = A e^{im_l \phi}$

Boundary condition

Quantization

Azimuthal Equation

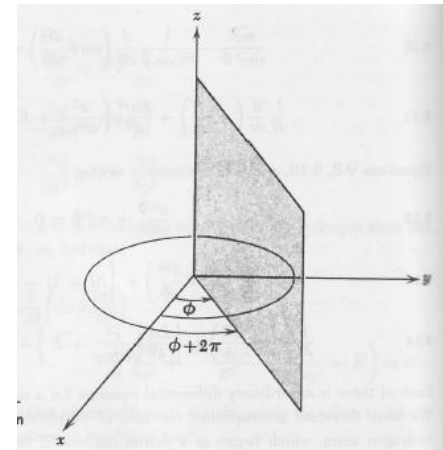
$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

Wave function

$$\Phi(\phi) = A e^{im_l \phi}$$

Boundary condition

Quantization



Azimuthal Equation

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

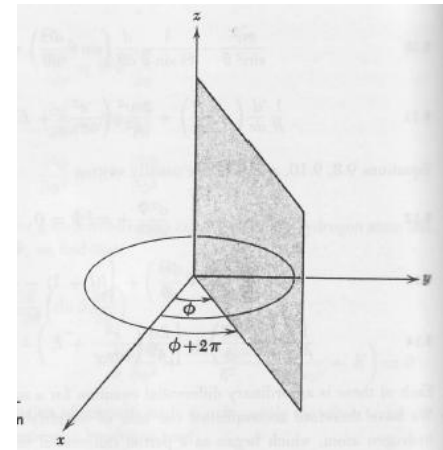
Wave function $\Phi(\phi) = A e^{im_l \phi}$

Boundary condition

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$
$$A e^{im_l \phi} = A e^{im_l(\phi + 2\pi)} = A e^{im_l \phi} e^{i2\pi m_l}$$



Quantization



Azimuthal Equation

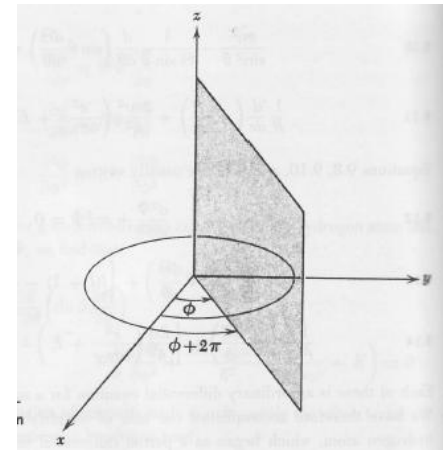
$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

Wave function $\Phi(\phi) = A e^{im_l \phi}$

Boundary condition

$$\begin{aligned}\Phi(\phi) &= \Phi(\phi + 2\pi) \\ A e^{im_l \phi} &= A e^{im_l(\phi + 2\pi)} = A e^{im_l \phi} e^{i2\pi m_l} \\ e^{i2\pi m_l} &= 1 = \cos 2\pi m_l + i \sin 2\pi m_l\end{aligned}$$

Quantization



Azimuthal Equation

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

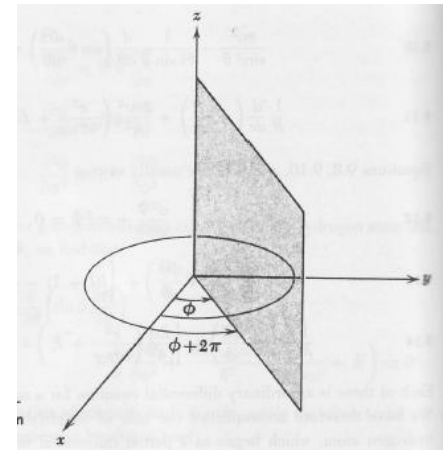
Wave function $\Phi(\phi) = A e^{im_l \phi}$

Boundary condition

$$\begin{aligned}\Phi(\phi) &= \Phi(\phi + 2\pi) \\ A e^{im_l \phi} &= A e^{im_l(\phi + 2\pi)} = A e^{im_l \phi} e^{i2\pi m_l} \\ e^{i2\pi m_l} &= 1 = \cos 2\pi m_l + i \sin 2\pi m_l\end{aligned}$$

Quantization

$$m_l = 0, \pm 1, \pm 2, \pm 3, \text{ etc.}$$



Azimuthal Equation

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

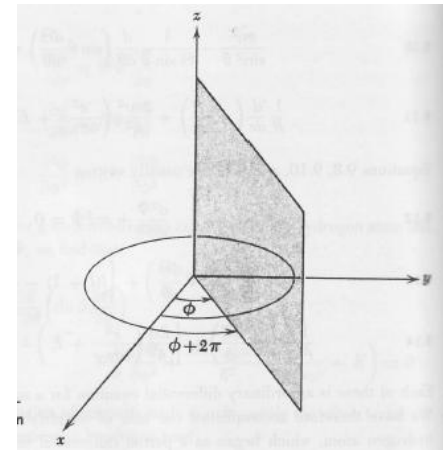
Wave function $\Phi(\phi) = A e^{im_l \phi}$

Boundary condition

$$\begin{aligned}\Phi(\phi) &= \Phi(\phi + 2\pi) \\ A e^{im_l \phi} &= A e^{im_l(\phi + 2\pi)} = A e^{im_l \phi} e^{i2\pi m_l} \\ e^{i2\pi m_l} &= 1 = \cos 2\pi m_l + i \sin 2\pi m_l\end{aligned}$$

Quantization

$$m_l = 0, \pm 1, \pm 2, \pm 3, \text{ etc.}$$



Magnetic quantum number

Polar Equation

$$\sin\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Theta}{\partial\theta} \right) + [l(l+1)\sin^2\theta - m_l^2]\Theta = 0$$

Solutions: Associated Legendre Functions

Quantization

any given l , m_l values can be $0, \pm 1, \pm 2, \dots, \pm l$

→ **Orbital quantum number**

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{+i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{+i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{+i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{+2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{+2i\phi}$

Radial Equation

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} (E - U(r))R - l(l+1)R = 0$$

Solutions: associated Laguerre functions

Quantization:

$$E_n = - \frac{m e^4}{32 \pi \epsilon_0^2 \hbar^2} \left(\frac{1}{n^2} \right) \text{ where } n \text{ is an integer}$$

$n \rightarrow$ **Principal quantum number**

$$l = 0, 1, 2, \dots, (n-1)$$

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{+i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{+i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{+i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{+2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{+2i\phi}$

Hydrogen atom Solutions

- Principal quantum number, $n = 1, 2, 3, \dots$
- Orbital quantum number, $l = 0, 1, 2, \dots (n - 1)$ where $l = 1(s), = 2(p), = 3(d), = 4(f), \text{ etc.}$
- Magnetic quantum number, $m_l = 0, \pm 1, \pm 2, \dots \pm l$

Wave function = $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l}$
where $\Theta_{l,m_l}\Phi_{m_l} = Y_l^{m_l}$ (Spherical harmonics)

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{+i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{+i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{+i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{+i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{+2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{+2i\phi}$

Schrodinger Equation: Hydrogen Atom

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E \psi(\vec{x}) \quad U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

$$\underline{\left[\frac{-\hbar^2}{2m} \nabla^2 + U(\vec{x}) \right] \psi(\vec{x}) = E \psi(\vec{x})}$$

Hamiltonian (H) = T (kinetic) + U (Potential)

Kinetic energy w.r.t. r + Kinetic energy w.r.t. rotation

$$\left\{ \begin{array}{l} -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C = -l(l+1) \\ \frac{1}{\Theta} \csc\theta \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{\Phi} \csc^2\theta \frac{\partial^2 \Phi}{\partial \phi^2} = C = -l(l+1) \end{array} \right.$$

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

Schrodinger Equation: Hydrogen Atom

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E \psi(\vec{x})$$

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

$$\underline{\left[\frac{-\hbar^2}{2m} \nabla^2 + U(\vec{x}) \right] \psi(\vec{x}) = E \psi(\vec{x})}$$

$$\mathbf{H}\psi_{n,l,m_l} = E_n \psi_{n,l,m_l}$$

Hamiltonian (H) = T (kinetic) + U (Potential)

Kinetic energy w.r.t. r + Kinetic energy w.r.t. rotation

$$\left\{ \begin{array}{l} -\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C = -l(l+1) - \\ \frac{1}{\Theta} \csc\theta \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{\Phi} \csc^2\theta \frac{\partial^2 \Phi}{\partial \phi^2} = C = -l(l+1) \end{array} \right.$$

$$\mathbf{L}^2 \psi_{n,l,m_l} = l(l+1) \hbar^2 \psi_{n,l,m_l}$$

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m_l^2 \Phi$$

$$\mathbf{L}_z \psi_{n,l,m_l} = m_l \hbar \psi_{n,l,m_l}$$

The angular momentum \mathbf{L} of a particle at the position \mathbf{r} whose linear momentum is \mathbf{p} is defined by the vector formula

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

- (a) From the above expression, explain how three Cartesian components of \mathbf{L} can be written as:

$$\begin{cases} L_x = yp_z - zp_y \\ L_y = zp_x - xp_z \\ L_z = xp_y - yp_x \end{cases}$$

- (b) Using the momentum operators such as $p_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$, etc. express three Cartesian angular momentum operators L_x, L_y, L_z
- (c) Prove that the three Cartesian angular momentum operators in spherical polar coordinates can be written as:

$$\begin{aligned} L_x &= \frac{\hbar}{i} \left(-\sin\phi \frac{\partial}{\partial \theta} - \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right) \\ L_y &= \frac{\hbar}{i} \left(\cos\phi \frac{\partial}{\partial \theta} - \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right) \\ L_z &= \frac{\hbar}{i} \frac{\partial}{\partial \phi} \end{aligned}$$

- (d) L^2 operator is defined by:

$$\mathbf{L}^2 = L_x L_x + L_y L_y + L_z L_z$$

Prove that

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

- (e) Using $L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$ and $\Phi(\phi) = A e^{im_l \phi}$ prove that

$$L_z \psi = m_l \hbar \psi$$

- (f) Using $\mathbf{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right]$

$$\Phi(\phi) = A e^{im_l \phi}$$

$$\sin\theta \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \Theta}{\partial \theta} \right) + [l(l+1)\sin^2\theta - m_l^2] \Theta = 0$$

Prove that

$$\mathbf{L}^2 \psi = l(l+1)\hbar^2 \psi$$

Three quantum numbers

- Principal quantum number: n

$$E_n = -\frac{m e^4}{32 \pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8 \pi \epsilon_0}\right) \left(\frac{m e^2}{4 \pi \epsilon_0 \hbar^2}\right) \left(\frac{1}{n^2}\right) =$$
$$-\left(\frac{e^2}{8 \pi \epsilon_0 a_0}\right) \left(\frac{1}{n^2}\right) = -13.6 \text{ eV} \left(\frac{1}{n^2}\right)$$

$$L^2 = l(l+1)\hbar^2$$

$$L_z = m_l \hbar$$

- Orbital quantum number: $l = 0, 1, 2, \dots, (n-1)$
- Magnetic quantum number: $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

Degeneracies

$$\psi(r, \theta, \phi) = \psi_{n,l,m_l} = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l} = R_{n,l}Y_l^{m_l}$$

where $\Theta_{l,m_l}\Phi_{m_l} = Y_l^{m_l}$ (Spherical harmonics)

$$\mathbf{L}^2\psi_{n,l,m_l} = l(l+1)\hbar^2\psi_{n,l,m_l}$$

$$\mathbf{L}_z\psi_{n,l,m_l} = m_l\hbar\psi_{n,l,m_l}$$

n	l	m_l	E_n (eV)	$ L $	L_z	$\psi_{n,l,m_l} =$	$R_{n,l}Y_l^{m_l}$	<u>degeneracies</u>	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}Y_0^0$	Non-degenerate	1s

Degeneracies

$$\psi(r, \theta, \phi) = \psi_{n,l,m_l} = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l} = R_{n,l}Y_l^{m_l}$$

where $\Theta_{l,m_l}\Phi_{m_l} = Y_l^{m_l}$ (Spherical harmonics)

$$\mathbf{L}^2\psi_{n,l,m_l} = l(l+1)\hbar^2\psi_{n,l,m_l}$$

$$L_z\psi_{n,l,m_l} = m_l\hbar\psi_{n,l,m_l}$$

n	l	m_l	E_n (eV)	$ L $	L_z	$\psi_{n,l,m_l} =$	$R_{n,l}Y_l^{m_l}$	<u>degeneracies</u>	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}Y_0^0$	Non-degenerate	1s
2	0	0							
	1	-1							
		0							
		1							

Degeneracies

$$\psi(r, \theta, \phi) = \psi_{n,l,m_l} = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l} = R_{n,l}Y_l^{m_l}$$

where $\Theta_{l,m_l}\Phi_{m_l} = Y_l^{m_l}$ (Spherical harmonics)

$$\mathbf{L}^2\psi_{n,l,m_l} = l(l+1)\hbar^2\psi_{n,l,m_l}$$

$$\mathbf{L}_z\psi_{n,l,m_l} = m_l\hbar\psi_{n,l,m_l}$$

n	l	m_l	E_n (eV)	$ L $	L_z	$\psi_{n,l,m_l} =$	$R_{n,l}Y_l^{m_l}$	degeneracies	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}Y_0^0$	Non-degenerate	1s
2	0	0	-3.40	0	0				
	1	-1		$\sqrt{2}\hbar$	$-\hbar$				
		0			0				
		1			$+\hbar$				

Degeneracies

$$\psi(r, \theta, \phi) = \psi_{n,l,m_l} = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l} = R_{n,l}Y_l^{m_l}$$

where $\Theta_{l,m_l}\Phi_{m_l} = Y_l^{m_l}$ (Spherical harmonics)

$$\mathbf{L}^2\psi_{n,l,m_l} = l(l+1)\hbar^2\psi_{n,l,m_l}$$

$$\mathbf{L}_z\psi_{n,l,m_l} = m_l\hbar\psi_{n,l,m_l}$$

n	l	m_l	E_n (eV)	$ L $	L_z	$\psi_{n,l,m_l} =$	$R_{n,l}Y_l^{m_l}$	<u>degeneracies</u>	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}Y_0^0$	Non-degenerate	1s
2	1	0	-3.40	$\sqrt{2}\hbar$	0	ψ_{200}	$R_{20}Y_0^0$		
		-1			$-\hbar$	ψ_{21-1}	$R_{21}Y_1^{-1}$		
		0			0	ψ_{210}	$R_{21}Y_1^0$		
		1			$+\hbar$	ψ_{211}	$R_{21}Y_1^{+1}$		

Degeneracies

$$\psi(r, \theta, \phi) = \psi_{n,l,m_l} = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l} = R_{n,l}Y_l^{m_l}$$

where $\Theta_{l,m_l}\Phi_{m_l} = Y_l^{m_l}$ (Spherical harmonics)

$$\mathbf{L}^2\psi_{n,l,m_l} = l(l+1)\hbar^2\psi_{n,l,m_l}$$

$$\mathbf{L}_z\psi_{n,l,m_l} = m_l\hbar\psi_{n,l,m_l}$$

n	l	m_l	E_n (eV)	$ L $	L_z	$\psi_{n,l,m_l} =$	$R_{n,l}Y_l^{m_l}$	degeneracies	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}Y_0^0$	Non-degenerate	1s
2	1	0	-3.40	0	0	ψ_{200}	$R_{20}Y_0^0$	4 (=2 ²)	2p
		-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{21-1}	$R_{21}Y_1^{-1}$		
		0			0	ψ_{210}	$R_{21}Y_1^0$		
		1			$+\hbar$	ψ_{211}	$R_{21}Y_1^{+1}$		

n	l	m_l	$E_n(\text{eV})$	$ L $	L_z	$\psi_{n,l,m_l} =$	$R_{n,l} Y_l^{m_l}$	<u>degeneracies</u>	Orbital name	
1	0	0	-13.6	0	0	ψ_{100}	$R_{10} Y_0^0$	Non-degenerate	1s	
2	0	0	-3.40	0	0	ψ_{200}	$R_{20} Y_0^0$	4 ($=2^2$)	2s	
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{21-1}	$R_{21} Y_1^{-1}$		2p	
		0			0	ψ_{210}	$R_{21} Y_1^0$			
		1			$+\hbar$	ψ_{211}	$R_{21} Y_1^{+1}$			
3	0	0	-1.51							
	1	-1								
		0								
		1								
	2	-2								
		-1								
		0								
		1								
	2									

n	l	m_l	$E_n(\text{eV})$	$ L $	L_z	$\psi_{n,l,m_l} =$	$R_{n,l} Y_l^{m_l}$	<u>degeneracies</u>	Orbital name	
1	0	0	-13.6	0	0	ψ_{100}	$R_{10} Y_0^0$	Non-degenerate	1s	
2	0	0	-3.40	$\sqrt{2}\hbar$	0	ψ_{200}	$R_{20} Y_0^0$	4 (=2 ²)	2s	
	1	-1			$-\hbar$	ψ_{21-1}	$R_{21} Y_1^{-1}$		2p	
		0			0	ψ_{210}	$R_{21} Y_1^0$			
	1	1	$+\hbar$	ψ_{211}	$R_{21} Y_1^{+1}$					
3	0	0	-1.51	$\sqrt{2}\hbar$	0	ψ_{300}	$R_{30} Y_0^0$	9 (=3 ²)	3s	
	1	-1			$-\hbar$	ψ_{31-1}	$R_{31} Y_1^{-1}$		3p	
		0			0	ψ_{310}	$R_{31} Y_1^0$			
		1			$+\hbar$	ψ_{311}	$R_{31} Y_1^1$			
	2	-2			$\sqrt{6}\hbar$	$-2\hbar$	ψ_{32-2}		$R_{32} Y_2^{-2}$	3d
		-1			$-\hbar$	ψ_{32-1}	$R_{32} Y_2^{-1}$			
		0			0	ψ_{320}	$R_{32} Y_2^0$			
		1			$+\hbar$	ψ_{321}	$R_{32} Y_2^1$			
		2			$+2\hbar$	ψ_{322}	$R_{32} Y_2^2$			