9/11/2024

- Particle on a ring
  - Polar Coordinates
  - Laplacian and Hamiltonian operator
  - General solutions
  - Angular momentum
- Particle on a sphere
  - Spherical Coordinates
  - Laplacian and Hamiltonian operator
  - Spherical harmonics
  - Angular momentum

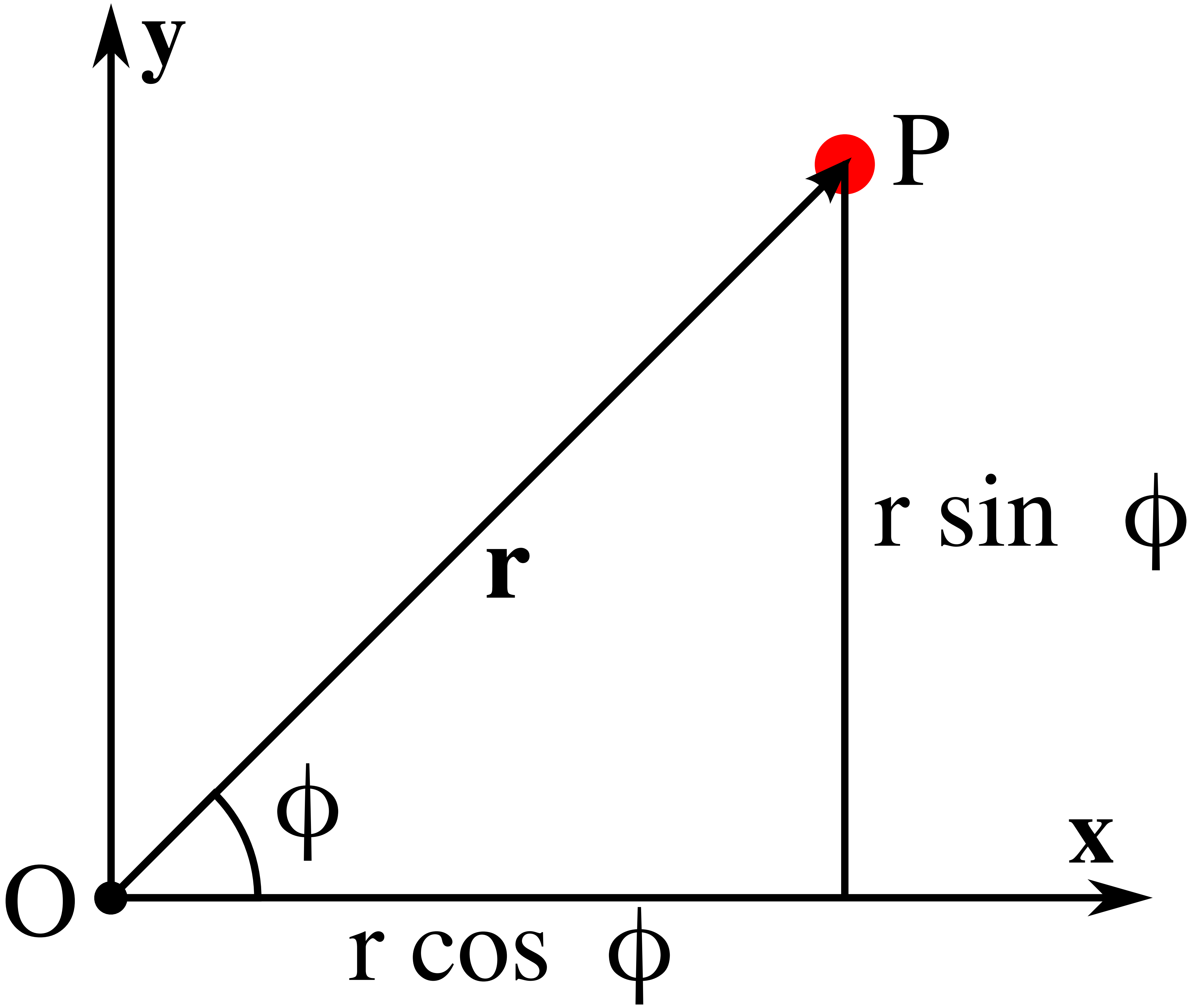
- This lecture is designed to help you achieve the following learning objectives
  - Obtain and interpret solutions of the Schrodinger equation for tractable systems including the particle in a box, harmonic oscillator, rigid rotor, and hydrogen atom
  - Describe how analytical models help interpret various experimental spectra

Particle on a Ring

- 1D Particle in a box, confined to a specific range of x.
  - Hamiltonian is $\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x}$.
- 2D Particle in a box, confined to a specific range of x and y.
  - Hamiltonian is $\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x} + \frac{\partial^2}{\partial y}\right)$
  - Alternatively, $\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\nabla^2$, where ∇^2 is the Laplacian operator.
- Particle on a ring, confined to a specific value of r. What is the kinetic energy?

Polar Coordinates

- $x = r\cos\phi$
- $y = r\sin\phi$
- $r = \sqrt{x^2 + y^2}$
- $\phi = \arctan\left(\dfrac{y}{x}\right)$



The Chain Rule

- $u(x, y)$ is a function that depends on x and y
- $\delta u(x, y) = \dfrac{\partial u}{\partial x}\delta x + \dfrac{\partial u}{\partial y}\delta y$ is differential for u
- Now let's say that $x = x(s, t)$ and $y = y(s, t)$. The chain rule says that, $\dfrac{\partial u}{\partial s} = \dfrac{\partial u}{\partial x}\dfrac{\partial x}{\partial s} + \dfrac{\partial u}{\partial y}\dfrac{\partial y}{\partial s}$.
- What about $\dfrac{\partial u}{\partial t}$?
  - $\dfrac{\partial u}{\partial t} = \dfrac{\partial u}{\partial x}\dfrac{\partial x}{\partial t} + \dfrac{\partial u}{\partial y}\dfrac{\partial y}{\partial t}$

Hamiltonian of POR

- Using the chain rule, one can obtain the Laplacian in polar coordinates as
$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$$
- $$\hat{\mathbf{H}} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)$$
- For a particle on a ring, r is constant, so $\hat{\mathbf{H}} = \dfrac{-\hbar^2}{2m}\left(\dfrac{1}{r^2}\dfrac{d^2}{d\phi^2}\right)$

Schrodinger Equation

- $\frac{-\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d^2}{d\phi^2}\right)\Psi = E\Psi$ is the Schrodinger equation for the system
- $\frac{d^2\Phi}{d\phi^2} = -\frac{2IE}{\hbar^2}\Phi$ (using $I = mr^2$ and swapping notation for the wavefunction)
- The general solution is $\Phi = Ae^{im_l\phi} + Be^{-im_l\phi}$, where $m_l = \sqrt{\frac{2IE}{\hbar^2}}$.

Schrodinger Equation Solutions

- $\Phi = Ae^{im_l\phi} + Be^{-im_l\phi}$, where $m_l = \sqrt{\dfrac{2IE}{\hbar^2}}$.
- The boundary conditions are $\Phi(\phi + 2\pi) = \Phi(\phi)$, or $Ae^{im_l\phi}e^{2\pi i m_l} + Be^{-im_l\phi}e^{2\pi i m_l} = Ae^{im_l\phi} + Be^{-im_l\phi}$
- Thus, $e^{2\pi i m_l} = \cos(2\pi m_l) + i\sin(2\pi m_l) = 1$ must be true.
- When is this true?
  - If m_l is an integer, $m_l = 0, \pm 1, \pm 2, \ldots$
- Given $m_l = \sqrt{\dfrac{2IE}{\hbar^2}}$, what are the energy levels of a particle on a ring?
  - $E_{m_l} = \dfrac{m_l^2\hbar^2}{2I}$
- Are there degenerate states (states with the same energy)?
  - Yes

Normalization

- If B = 0, then $\Phi = Ae^{im_l\phi}$
- What is A?
  - $\int_0^{2\pi} \Phi^*\Phi d\phi = |A|^2 \int_0^{2\pi} e^{-im_l\phi} e^{im_l\phi} d\phi = |A|^2 \int_0^{2\pi} d\phi = |A|^2 2\pi$
  - $|A| = \sqrt{\dfrac{1}{2\pi}}$

Angular Momentum

- In classical mechanics, angular momentum is the cross product of the position $\mathbf{r}$ and momentum vectors $\mathbf{p}$, $l = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_z & p_y & p_z \end{vmatrix}$
- The z component is $l_z = xp_y - yp_x$
- Using the momentum operator in the position representation,
$$\hat{\mathbf{l}}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} + y\frac{\partial}{\partial x}\right) = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$
- If $\Phi = Ae^{im_l\phi}$, what is the angular momentum?
    - Applying the operator to the wavefunction gives $\hat{\mathbf{l}}_z\Phi = \frac{\hbar}{i}im_l\Phi = m_l\hbar\Phi$
    - Thus the momentum is $m_l\hbar$

Postulate 3 Self-Test

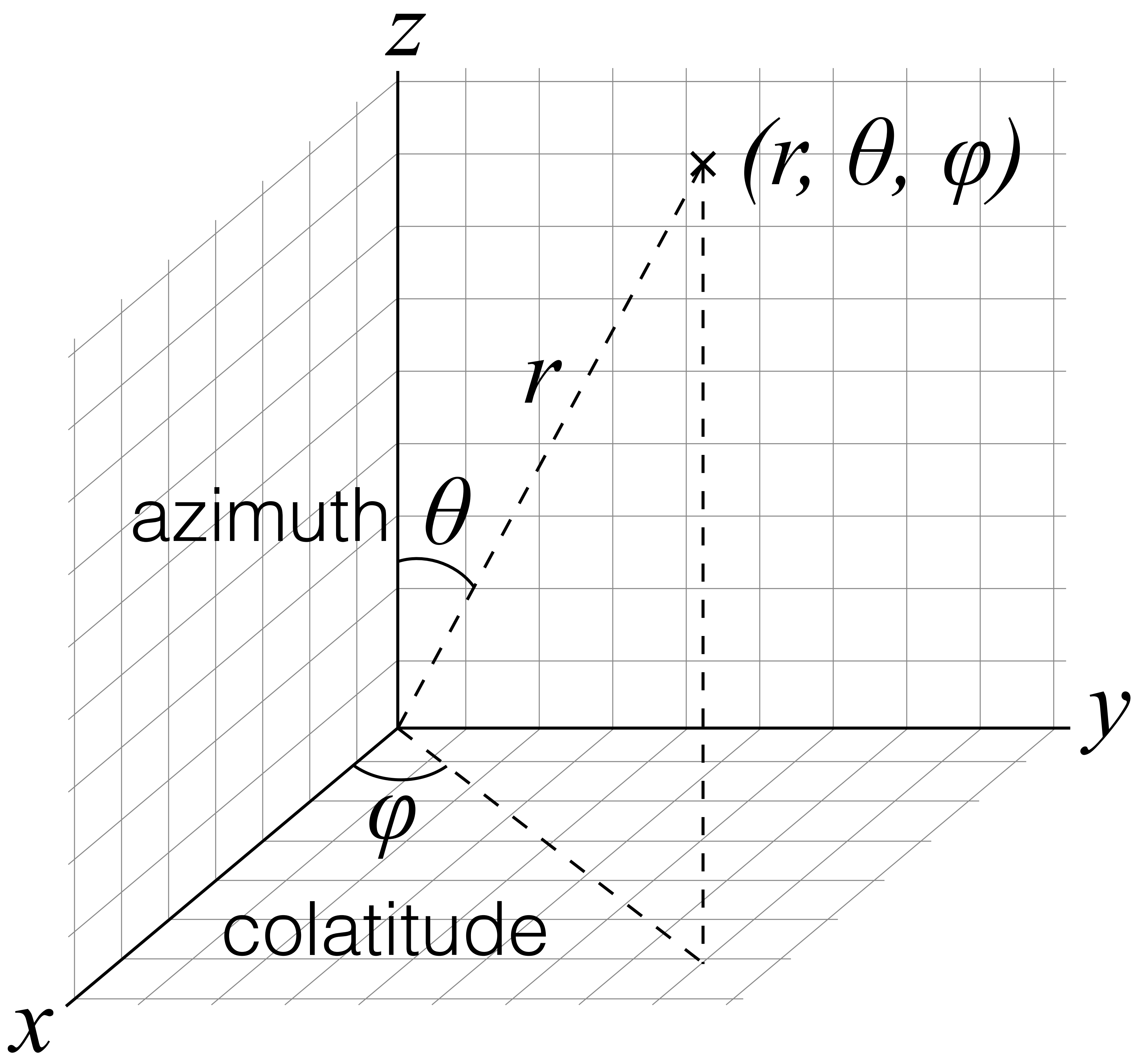
- $$\Phi = \sqrt{\frac{1}{3}}\sqrt{\frac{1}{2\pi}} - \sqrt{\frac{2}{3}}\sqrt{\frac{1}{2\pi}}e^{-2i\phi}$$
- What are the angular momentum quantum numbers?
- What are the normalized wavefunctions ϕ_n?
- What the the coefficients c_n?

Probability	Energy	Angular Momentum
Expectation		

Particle on a Sphere

Spherical Polar Coordinates

- The mapping from spherical polar to Cartesian coordinates is,
  - $x = r\sin\theta\cos\phi$
  - $y = r\sin\theta\sin\phi$
  - $z = r\cos\theta$
- The Laplacian is,
  - $\hat{\nabla}^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\hat{\mathbf{\Lambda}}^2$
  - $\hat{\mathbf{\Lambda}}^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$ is called the Legendrian



Schrodinger Equation

- $\hat{\mathbf{H}} = \frac{-\hbar^2}{2m}\hat{\nabla}^2 = \frac{-\hbar^2}{2mr^2}\hat{\mathbf{\Lambda}}^2$ is the Hamiltonian if r is constant
- $\hat{\mathbf{\Lambda}}^2\Psi = -\frac{2IE}{\hbar^2}\Psi$ is the Schrodinger equation
- $\hat{\mathbf{\Lambda}}^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$

Separation of Variables

- Applying the Legendrian to $\Psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ gives
- $\hat{\boldsymbol{\Lambda}}^2\Theta\Phi = \Theta\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Phi + \Phi\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta = -\frac{2IE}{\hbar^2}\Theta\Phi$
- $\frac{1}{\Phi}\frac{\partial^2}{\partial\phi^2}\Phi + \frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta = -\frac{2IE}{\hbar^2}\sin^2\theta$ by rearrangement
- For Φ, this has the form $\frac{d^2}{d\phi^2}\Phi = k\Phi$, the same as the particle on the ring
- For Θ, the solutions are known as *Spherical Harmonics*

Spherical Harmonics

- The spherical harmonics, $Y_{lm_l}(\theta, \phi) = \Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$, are separable solutions to the Schrodinger equation

- For these equations, applying the Legendrian operator yields
  - $\hat{\mathbf{\Lambda}}^2 Y_{lm_l} = -l(l+1)Y_{lm_l}$, where Y_{lm_l} are spherical harmonics
  - $l = 0,1,2,...$
  - $m_l = l, l-1, l-2, ..., -l$

- Be rearranging $\dfrac{2IE_{lm_l}}{\hbar^2} = -l(l+1)$, we see that the allowed energy levels are, $E_{lm_l} = \dfrac{\hbar^2 l(l+1)}{2I}$. Notably, this does not depend on m_l.

Visualizing Spherical Harmonics

http://demonstrations.wolfram.com/SphericalHarmonics/

What is the relationship between l, m_l, and the number of angular nodes?

Angular Momentum: Components

- Recall that the z component of angular momentum is
$$\hat{\mathbf{l}}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} + y\frac{\partial}{\partial x}\right) = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$

- $\hat{\mathbf{l}}_z Y_{lm_l} = m_l \hbar Y_{lm_l}$, the same as a particle on a ring

- Due to the uncertainty principle, x and y components cannot be simultaneously determined

Angular Momentum: Magnitude

- Classical energy
  - Linear momentum: $E = \frac{1}{2}mv^2$. $p = mv$. $E = \frac{p^2}{2m}$.
  - Angular momentum: $E = \frac{1}{2}I\omega^2$. $L = I\omega$. $E = \frac{L^2}{2I}$.
- $\hat{\mathbf{L}}^2 = 2I\hat{\mathbf{H}} = 2I\frac{-\hbar^2}{2I}\hat{\mathbf{\Lambda}}^2 = -\hbar^2\hat{\mathbf{\Lambda}}^2$ is the square magnitude of the linear momentum
- Since $\hat{\mathbf{L}}^2 Y_{lm_l} = l(l+1)\hbar^2$, the angular momentum is quantized as $\sqrt{l(l+1)}\hbar$, where $l = 0,1,2,...$ is the angular momentum quantum number

Diatomic Rigid Rotor

- The mathematics of this model, two particles a specific distance apart, can be posed the same way as a Particle on a Sphere
- For two free particles, the Hamiltonian is $\hat{\mathbf{H}} = -\frac{\hbar^2}{2m_1}\hat{\nabla}_{\mathbf{1}}{}^2 - -\frac{\hbar^2}{2m_1}\hat{\nabla}_{\mathbf{1}}{}^2$.
- To consider a rigid rotor, we will simply the expression using, $\frac{1}{m_1}\nabla_1^2 + \frac{1}{m_2}\nabla_2^2 = \frac{1}{m}\nabla_{cm}^2 + \frac{1}{\mu}\nabla^2$, where
  - $m = m_1 + m_2$ is the total mass of the system
  - $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ is the reduced mass (also seen for harmonic oscillator)
  - ∇^2 pertains to relative coordinates of the two atoms.

Solutions to the RR

- $-\frac{\hbar^2}{2m}\hat{\nabla}^2_{cm}\Psi - \frac{\hbar^2}{2\mu}\hat{\nabla}^2\Psi = E_{total}\Psi$ is the Schrodinger equation
- Separation of variables $\Psi = \Psi_{cm}\Psi$ leads to
  - $-\frac{\hbar^2}{2m}\nabla^2_{cm}\Psi_{cm} = E_{cm}\Psi_{cm}$, which is a free particle
  - $-\frac{\hbar^2}{2\mu}\nabla^2\Psi = E\Psi$
  - $E_{total} = E + E_{cm}$
- Since the separation between particles, a, is constant, $-\frac{\hbar^2}{2\mu a^2}\Lambda^2\Psi = E\Psi$. With $I = \mu a^2$, this is a particle on the sphere!
  - Solutions are spherical harmonics
  - Energy levels $E_{JM_J} = J(J+1)\frac{\hbar^2}{2I}$
  - Model for microwave spectroscopy

Review

- Compare the allowed quantum numbers, energy levels, and energy gaps for a particle in a box, harmonic oscillator, particle on a ring, and particle on a sphere
- What are spherical harmonics?
- What is the relationship between l, m_l, and the number of angular nodes?
- Which analytical systems are models for infrared and microwave spectroscopy?