Applications of Calculus II

Applications of Polar Coordinates in Chemistry

Dr. Christian Clausen III
Department of Chemistry

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Calculus – Topic

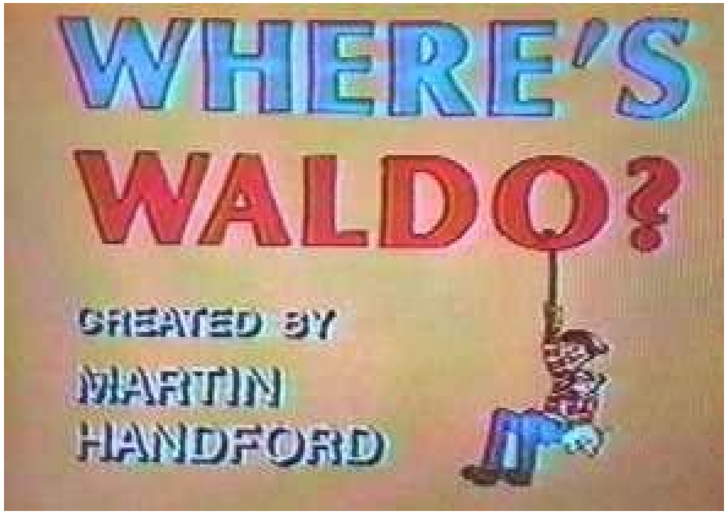
- Polar Coordinates
  - Covered in Section 11.3, page 705 of your textbook

Polar Coordinates

- We will use Polar Coordinates to help us define the electronic structure of an ATOM

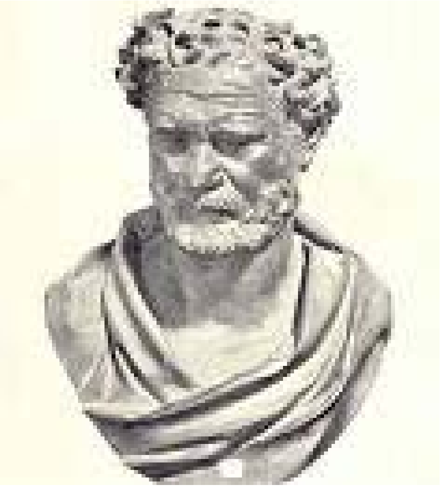
A Little Background Info

- As a child growing up you probably read one popular books dealing with “Where’s Waldo”
- Now the question is where are the electrons in an ATOM



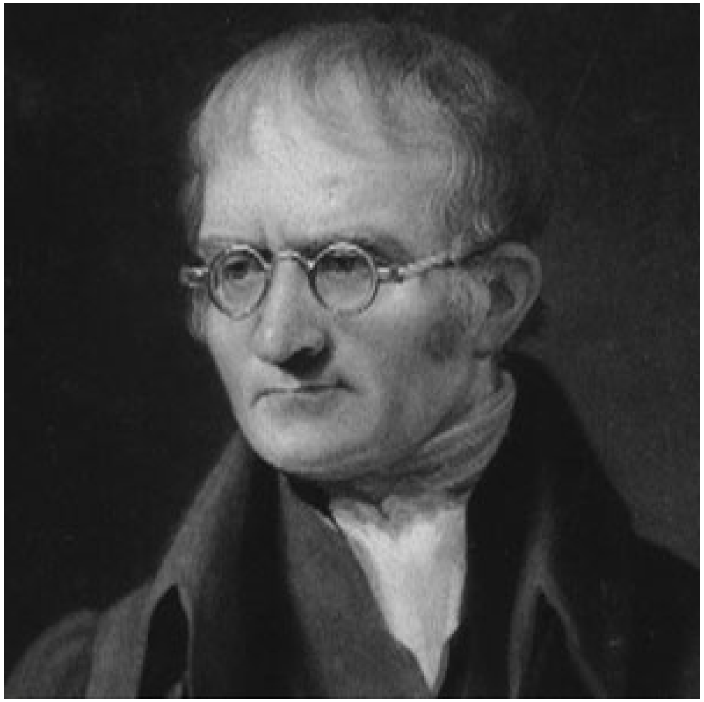
First, What is an ATOM?

- 1st Century AD Greek Philosopher said that if you take a piece of Gold and divided it into smaller and smaller pieces you would ultimately end up with the smallest particle that is still Gold and they called this an ATOM



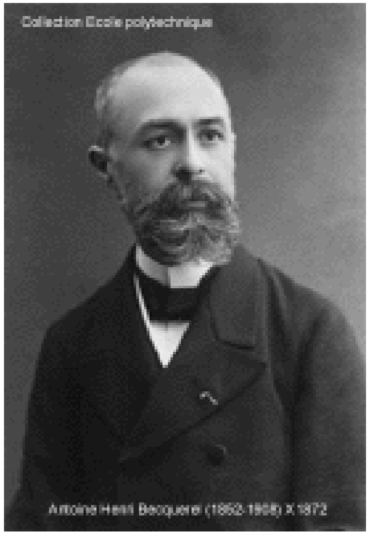
Dalton's Theory of Matter

- Nothing much happened for 1800 years (Alchemy period) to tell us much of anything about the ATOM, until 1808 when John Dalton proposed his theory on the structure of matter
  - One postulate was that all matter consists of ATOMs, tiny indivisible particles of an element that cannot be created or destroyed



Radioactivity

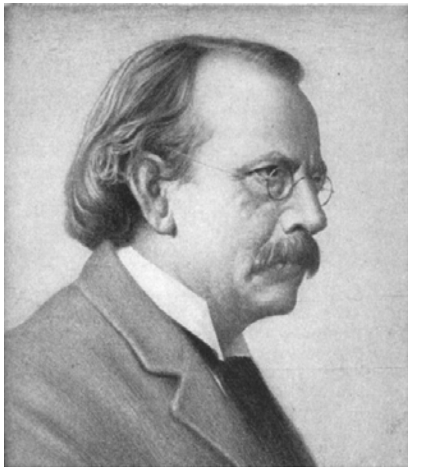
- The discovery of Radioactivity (the spontaneous emission of subatomic particles) in 1896 by Henri Becquerel proved that ATOMS could be broken down into smaller particles

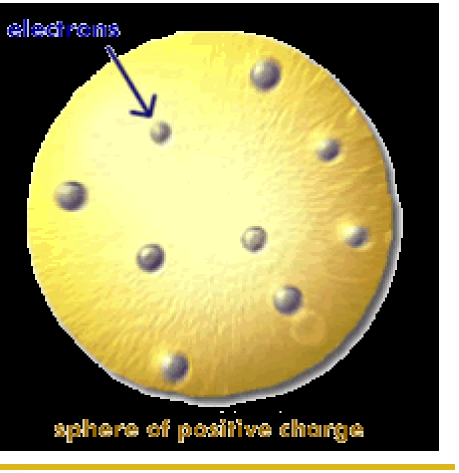


- So what discovery came next…

The Discovery of the Electron

- By J. J. Thomson
- Cathode ray tube experiments documented that all atoms contained small negatively charged particles of very little mass that were called "Electrons"
  - Thomson's Plum Pudding Model of the ATOM





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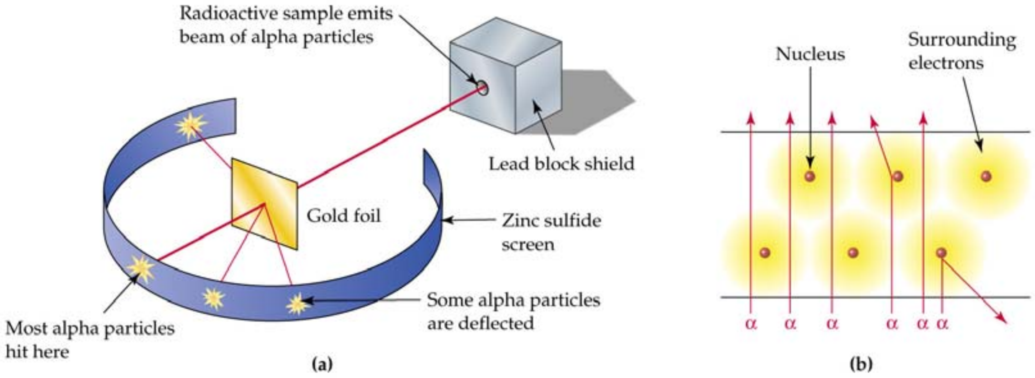
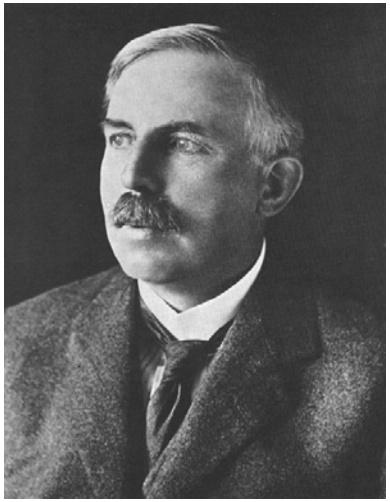
A Great Experiment

- Rutherford's Gold Foil α particle scattering experiment (1910)

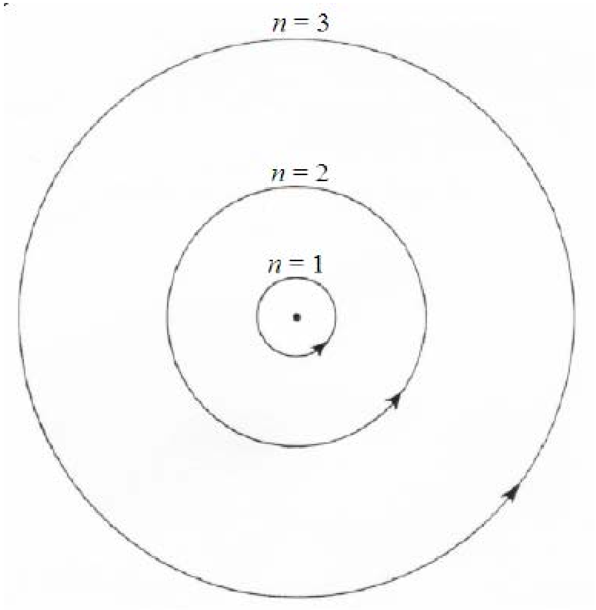




- The nuclear model of the atom, with a positive massive nucleus, electrons outside the nucleus

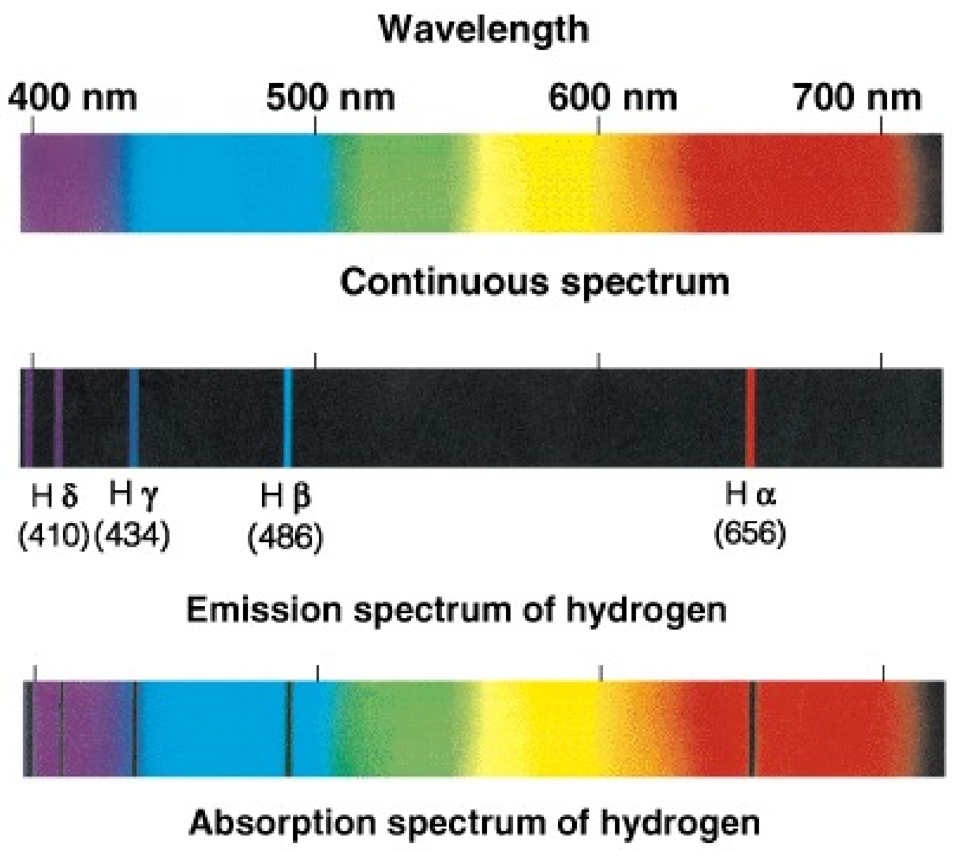
Bohr Model

- Why don't the electron's spiral into the positive nucleus?
- Why and how do atoms (when heated) emit electromagnetic radiation of certain wavelengths?



The Bohr Model of the ATOM (1914)

H Atom Emission Spectra



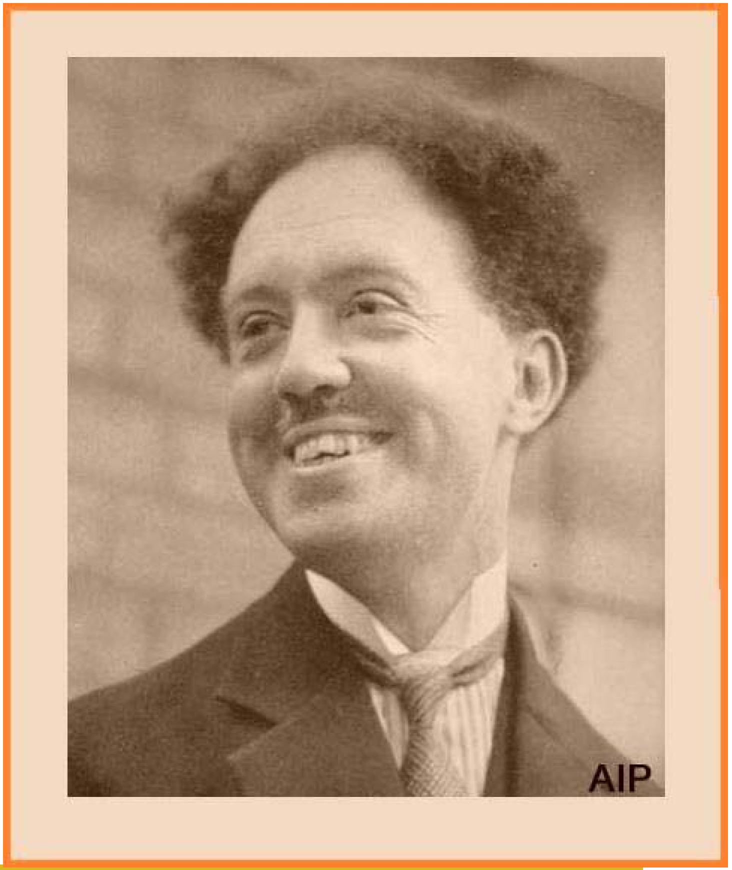
Unfortunately…

- The Bohr model failed to predict the line spectra of any model other than the H atom therefore the model cannot be correct.
- What Next?

- Particles having wavelike properties and Quantum Mechanics

What is Wrong with the Bohr Model?

- The e^- was treated like a particle but Louis deBroglie said it should be treated like it had wave-like motion (1922)
  - This was later proven to be true by experiment



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Uncertainty Principle

- If the e^- is in an orbit then we know where it is but in 1925 Werner Heisenberg postulated the uncertainty principle which states, "It is impossible to know the exact position and momentum of the e^- simultaneously"

Quantum Mechanics

- How do we deal with these issues?
  - Quantum Mechanics which examines the wave nature of objects on the atomic scale
- In 1926, Erwin Schrödinger derived an equation that is the basis for the quantum-mechanical model of the hydrogen atom.

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The Schrödinger Wave Equation

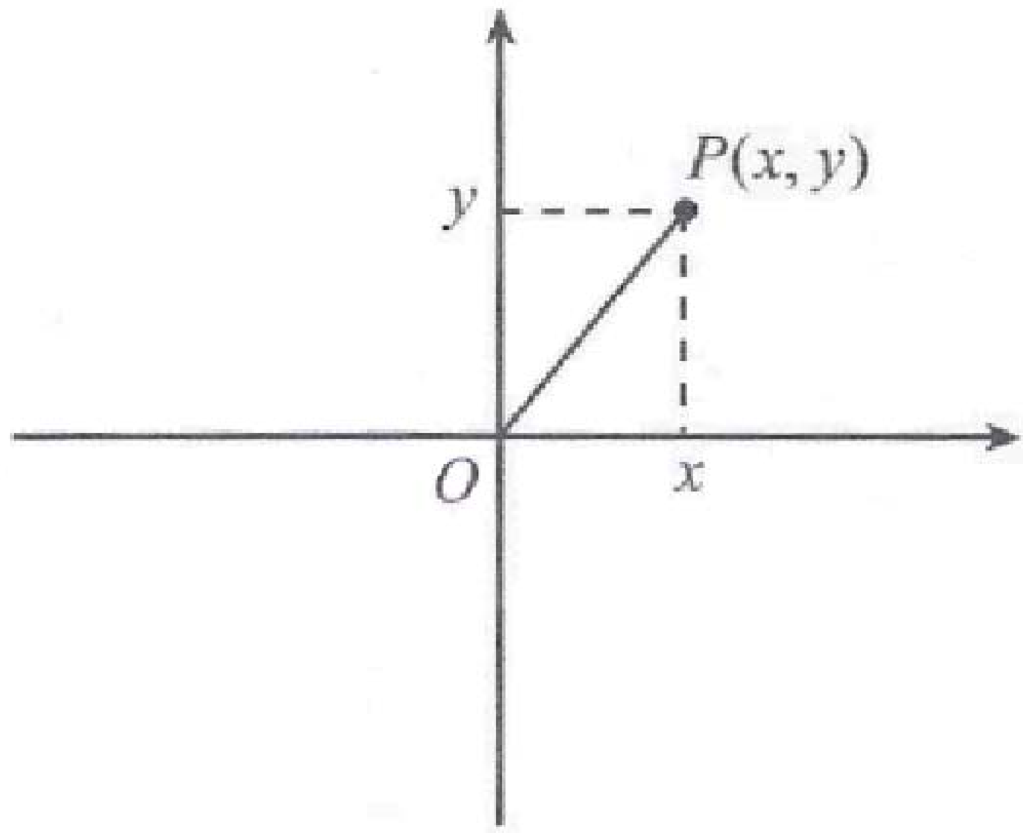
$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + (8\pi^2 m/h^2)(E - V)\Psi = 0$$

- Before we can solve this equation we need to convert it into Polar Coordinates, thus this will be the Chemistry Application

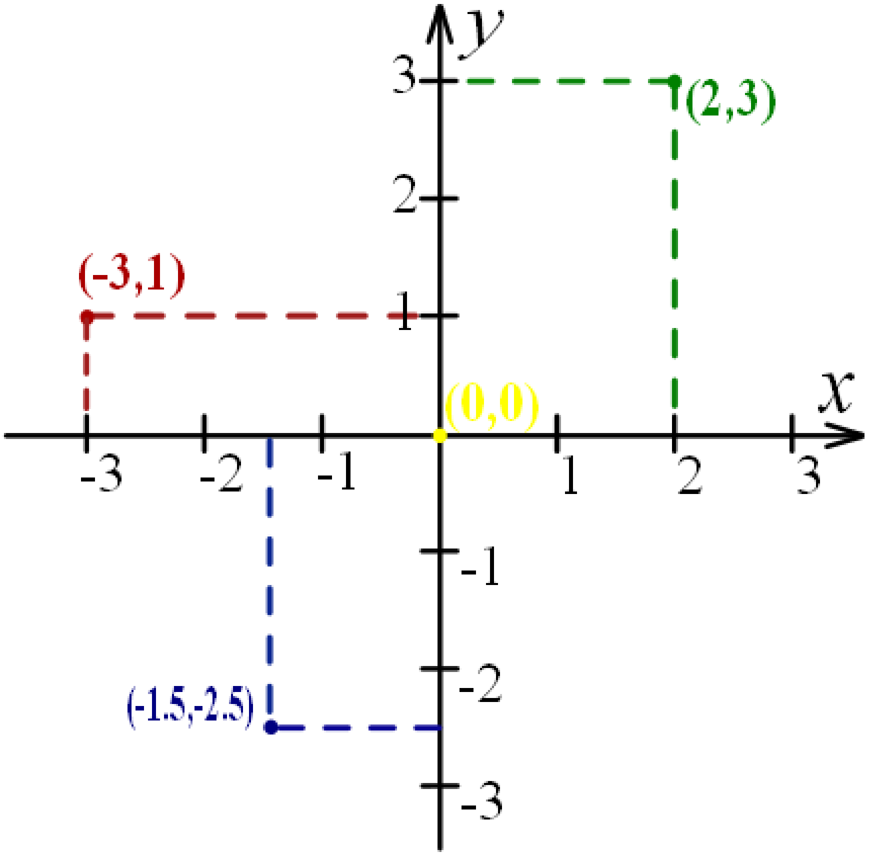
Polar Coordinates

- A review of Polar Coordinates before moving on to the CHEMISTRY APPLICATIONS
  - The Cartesian Coordinate System

Cartesian Coordinate System



Cartesian Coordinate System



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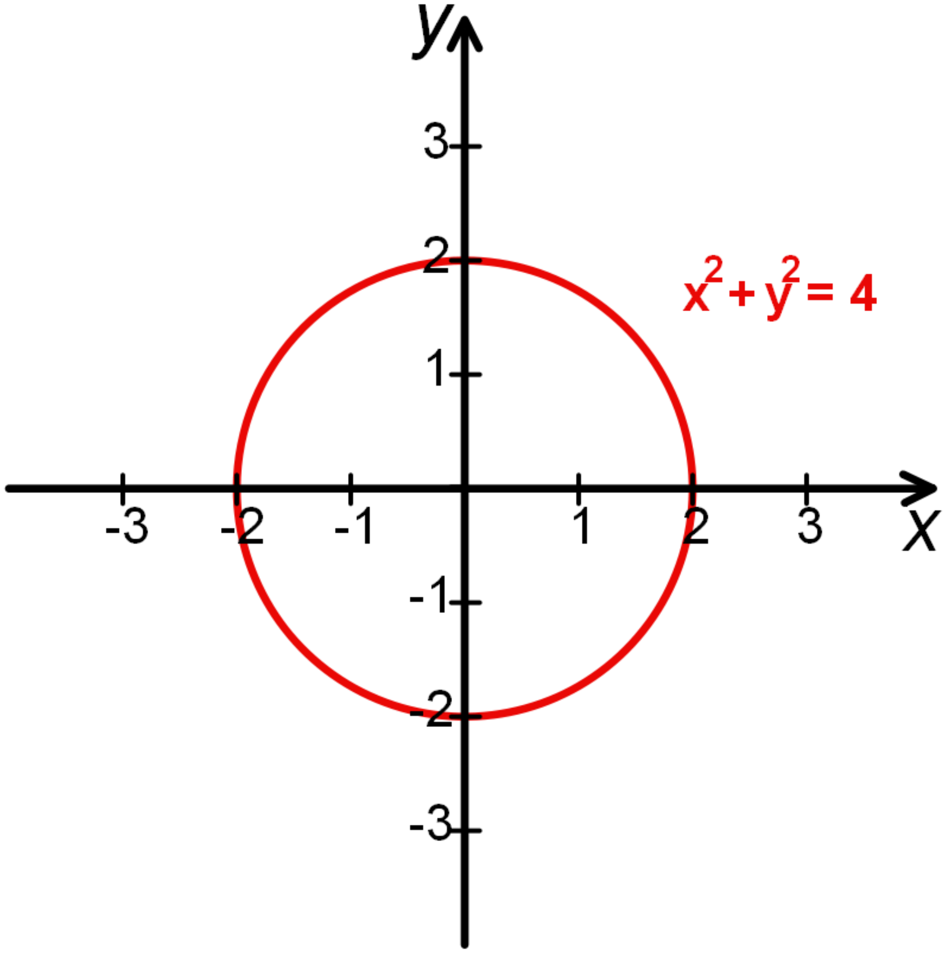
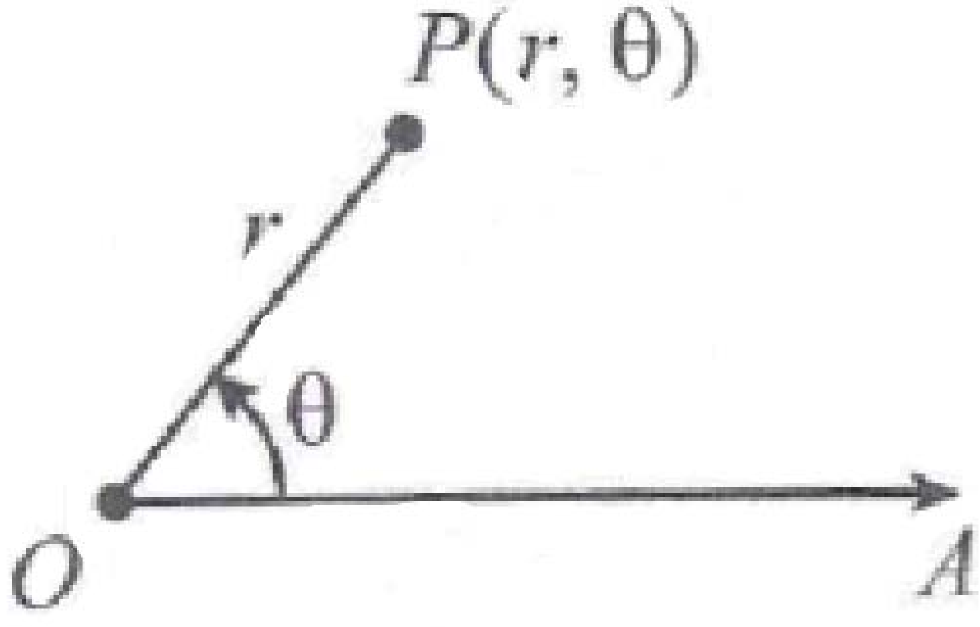
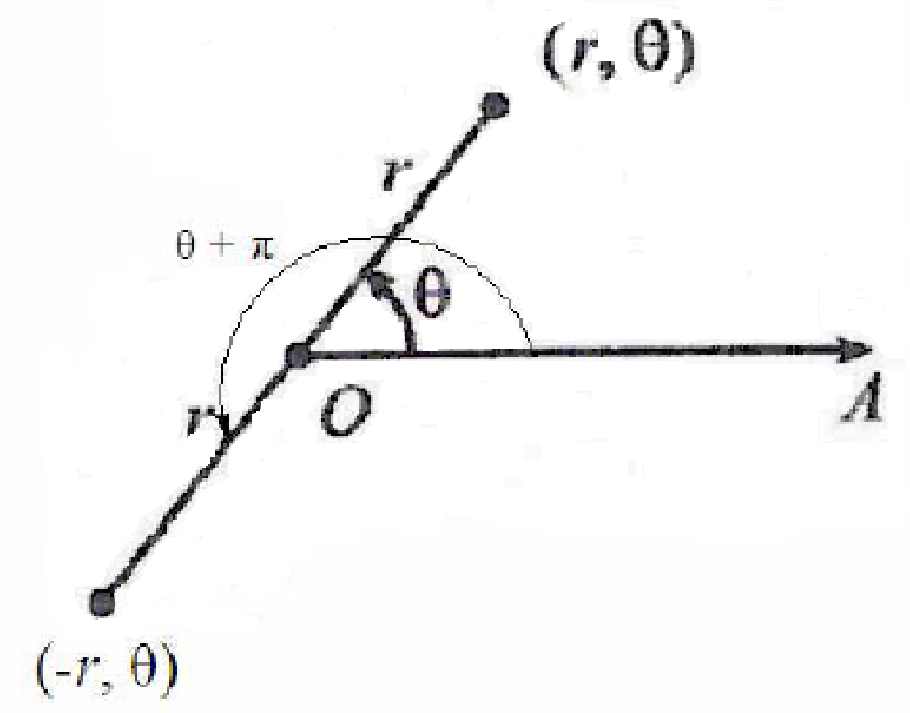
Cartesian Coordinate System



Polar Coordinate System

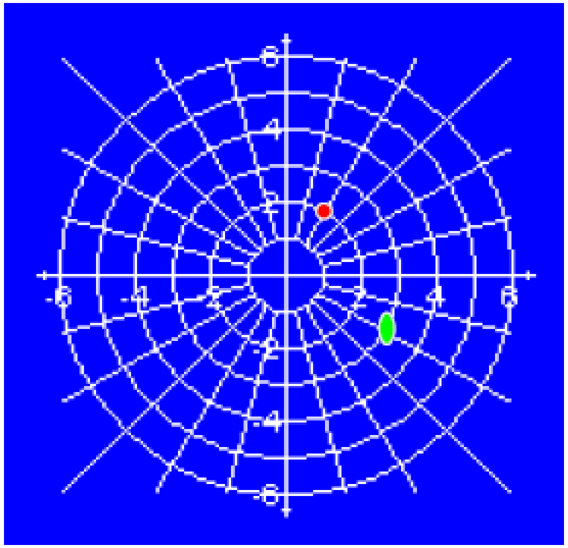


Relationship of (r,θ) to $(-r,\theta)$



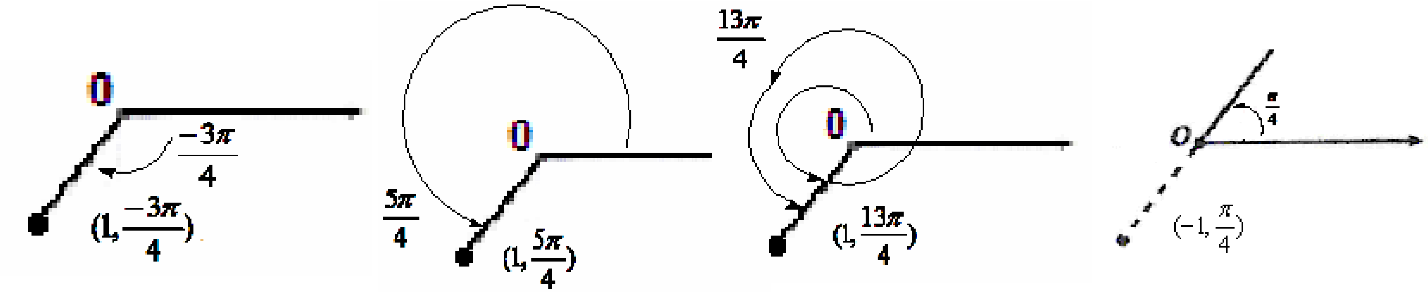
Plotting Points in the Polar Coordinate System

- The point $(r,\theta) = (2, \pi/3)$ lies two units from the pole on the terminal side angle $\theta = \pi/3$
- The point $(r,\theta) = (3, -\pi/6)$ lies three units from the pole on the terminal side of the angle $\theta = -\pi/6$
- The point $(r,\theta) = (3, 11\pi/6)$ coincides with the point $(r,\theta) = (3, -\pi/6)$



Multiple Representation for Polar Coordinates

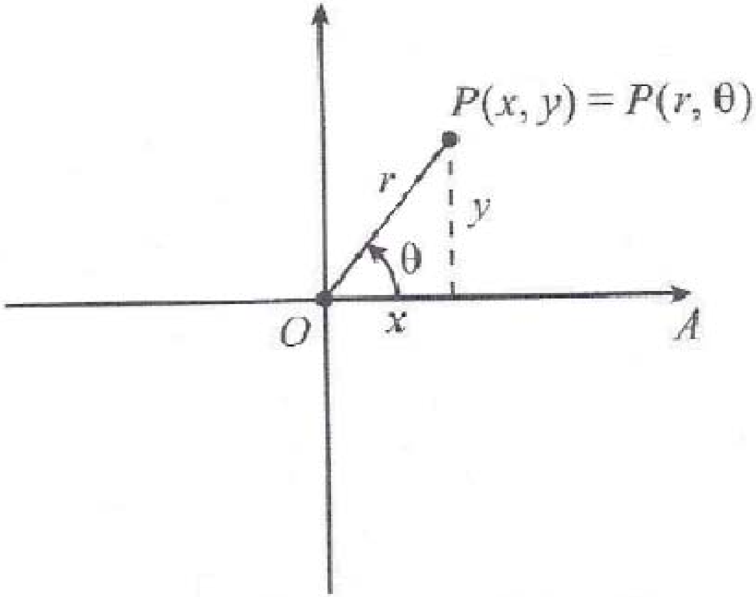
- In the Cartesian Coordinate system every point has only one representation but in the polar coordinate system each point has many representations
- For Example
  - What are other ways to express the polar coordinates (1, -3π/4)?



Converting between the two systems

- Cartesian (x,y) to Polar (r,θ)

  $r^2 = x^2 + y^2$, $\tan(\theta) = y/x$



Example

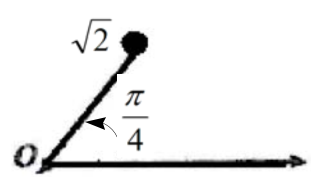
- Convert the point (1,1) to polar coordinates

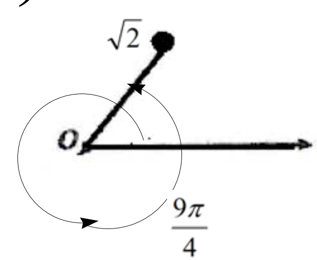
  $r^2 = x^2 + y^2 = 1 + 1$, $r = \sqrt{2}$

  $\tan(\theta) = x/y = 1$

  $\theta = \text{atan}(1) = 45°$ or $\pi/4$

  One answer is ($\sqrt{2}$, $\pi/4$) while another is ($\sqrt{2}$, $9\pi/4$)





Converting between the two systems

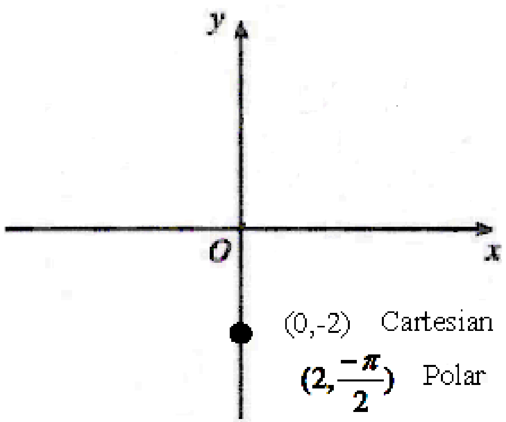
- To convert from Polar Coordinates to Cartesian Coordinates we use

  $x = r\cos(\theta)$, $y = r\sin(\theta)$

- Example: convert $(2, -\pi/2)$

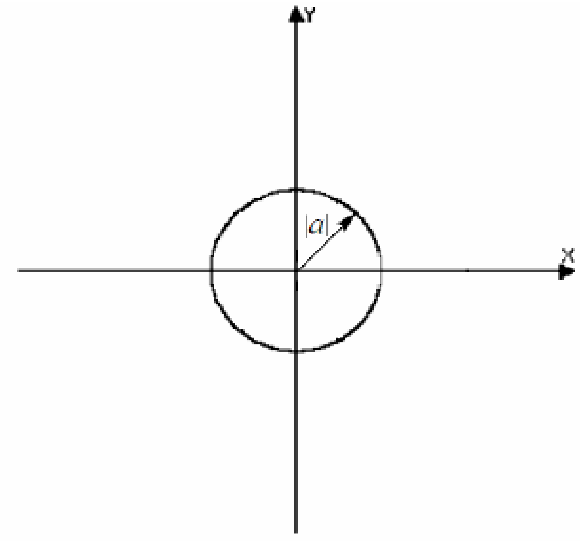
  $x = 2\cos(-\pi/2) = 0$

  $y = 2\sin(-\pi/2) = -2$



Plotting Curves in Polar Coordinates

- Example: Graph r = f(θ) when r = 4
  - The curve consists of all points (r, θ), with r = 4

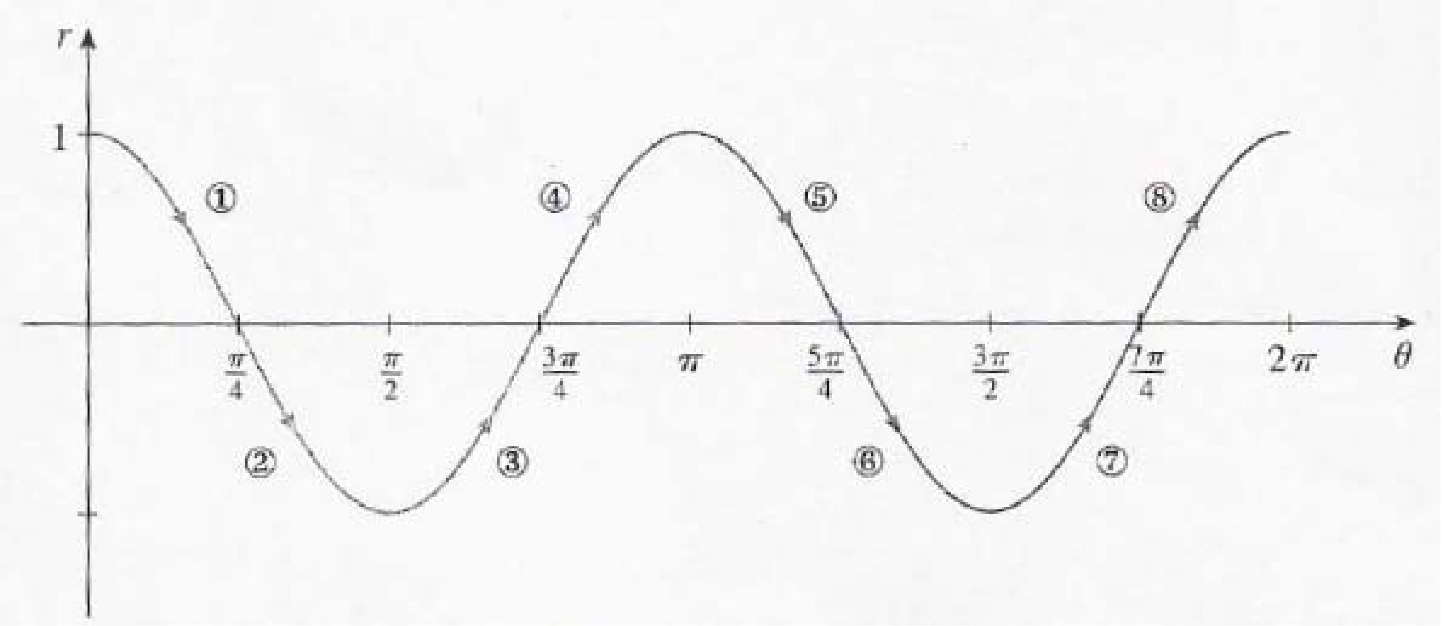


Sketching Coordinates

- When the polar equations become more complicated than the example we just did then it helps to sketch out the equation in Cartesian Coordinates
- For example: sketch the curve $r = \cos(2\theta)$ first in Cartesian Coordinates and then in Polar Coordinates

Cartesian Coordinate Solution

- $r = \cos(2\theta)$



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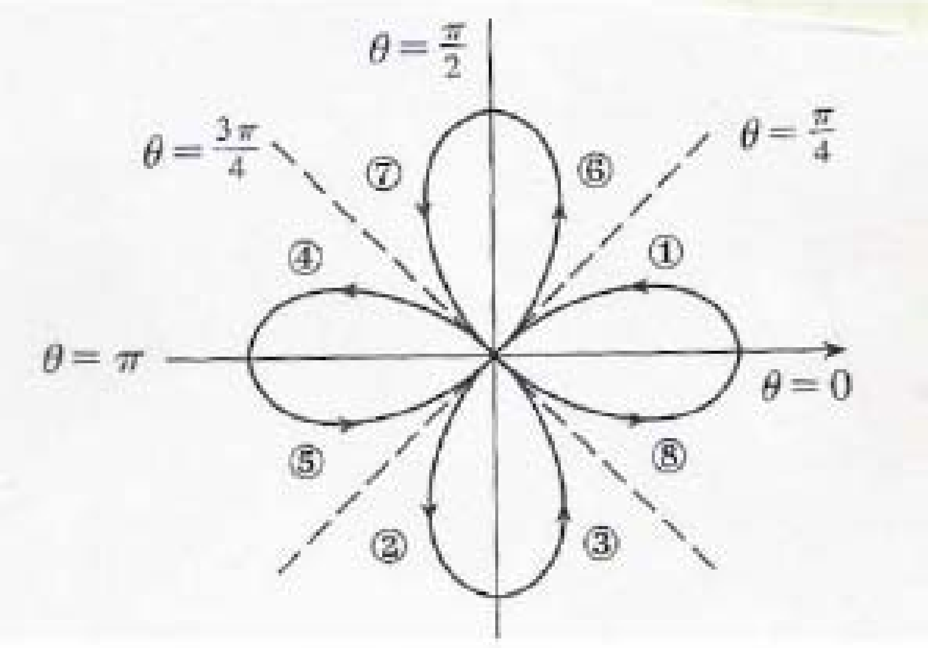
Polar Coordinate Solution

- $r = \cos(2\theta)$



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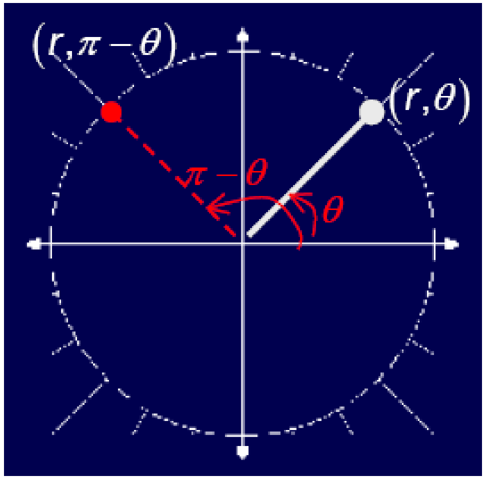
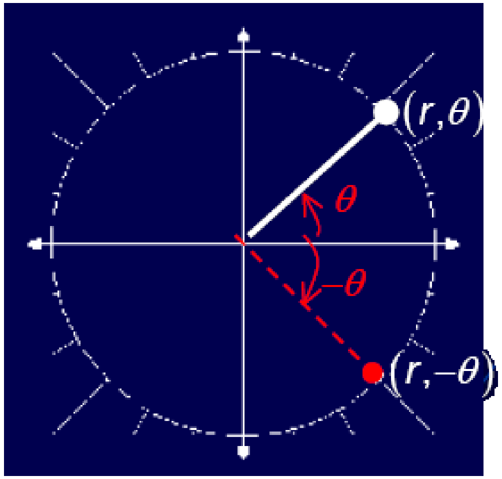
Using Symmetry to Sketch a Polar Graph

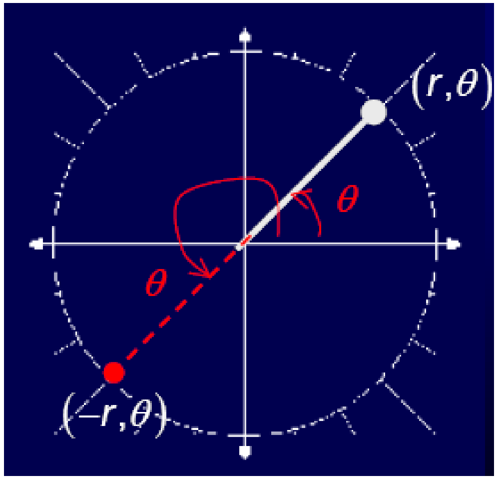
Symmetry with respect to
The line $\theta = \frac{\pi}{2}$



Symmetry with respect
To the Polar Axis



Symmetry with respect
to the pole



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Tests for Symmetry

- The graph of a polar equation is symmetric with respect to the following if the given substitution yields an equivalent equation

1. The line $\theta = \frac{\pi}{2}$: Replace (r,θ) with (r, π – θ)
2. The Polar Axis: Replace (r,θ) with (r,-θ)
3. The pole: Replace (r,θ) with (-r,θ)

Using Symmetry to Sketch

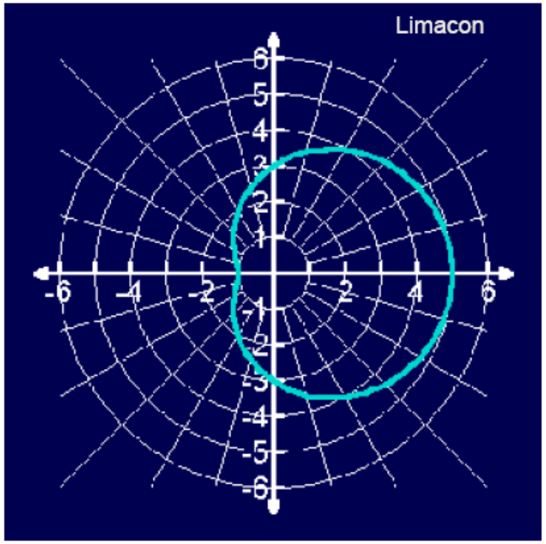
- Graph: $r = 3 + 2\cos(\theta)$ Replacing (r,θ) by $(r,-\theta)$ produces

$$r = 3 + 2\cos(-\theta)$$

$$r = 3 + 2\cos$$

Thus, the graph is symmetric with respect to the polar axis, and you need only plot points from 0 to π

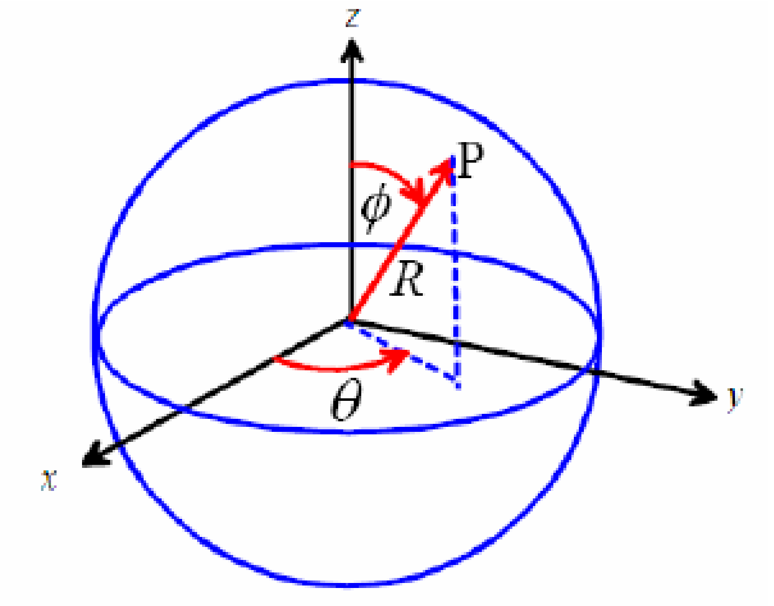
θ	r
0	5
$\frac{\pi}{6}$	$3+\sqrt{3}$
$\frac{\pi}{3}$	4
$\frac{\pi}{2}$	3
$\frac{2\pi}{3}$	2
$\frac{5\pi}{6}$	$3-\sqrt{3}$
π	1



Spherical Polar Coordinates

- We are almost ready to attack the Schrödinger equation but first we need to add a 3rd dimension to our polar coordinate system
  - It is then called Spherical Polar Coordinates

Spherical Polar Coordinates



$x = r\cos\theta$; $y = r\sin\theta$; $z = r\cos\varphi$

The Schrödinger Equation in Spherical Polar Coordinates

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial\psi}{\partial\varphi}\right)+\frac{1}{r^2\sin^2\varphi}\frac{\partial^2\psi}{\partial\theta^2}+\frac{8\pi^2 m}{h^2}(E+V)\psi=0$$

Solving the Schrödinger Equation

- To solve the equation we write the wave function ψ, which is a function of r, θ and φ as the product of three functions R(r), $\Theta(\theta)$ and $\Phi(\varphi)$

Manipulation of the Schrödinger Equation

- Substitution into the Schrödinger Equation and division by RΘΦ gives:

$$\frac{1}{r^2 R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{r^2\sin\varphi\Phi}\frac{d}{d\varphi}\left(\sin\theta\frac{d\Phi}{d\varphi}\right)+\frac{1}{r^2\sin^2\varphi}\left(\frac{1}{\Theta}\frac{d^2\theta}{d\theta^2}\right)+\frac{8\pi^2 m}{h^2}(E+V)\psi=0$$