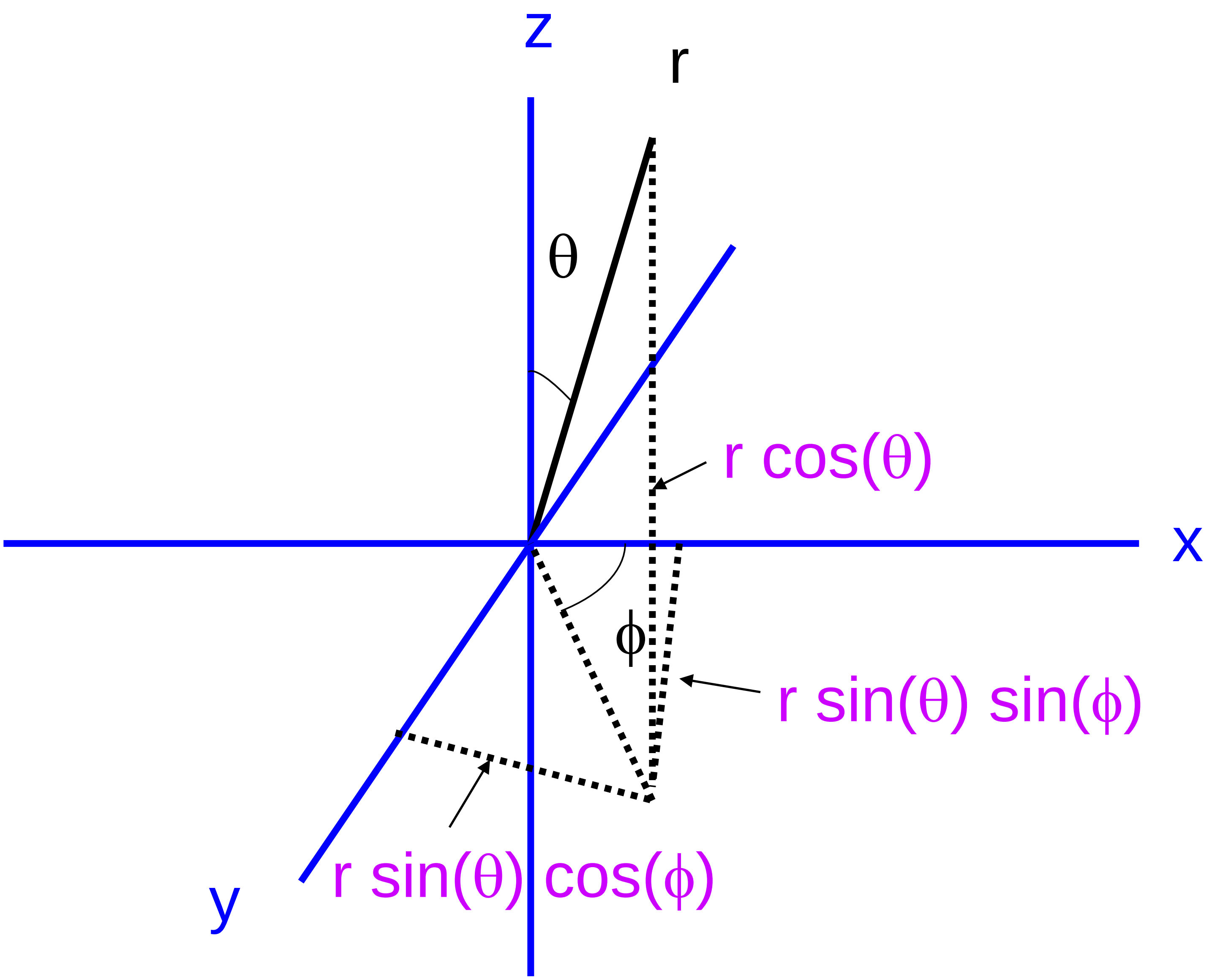
Spherical Polar Coordinates



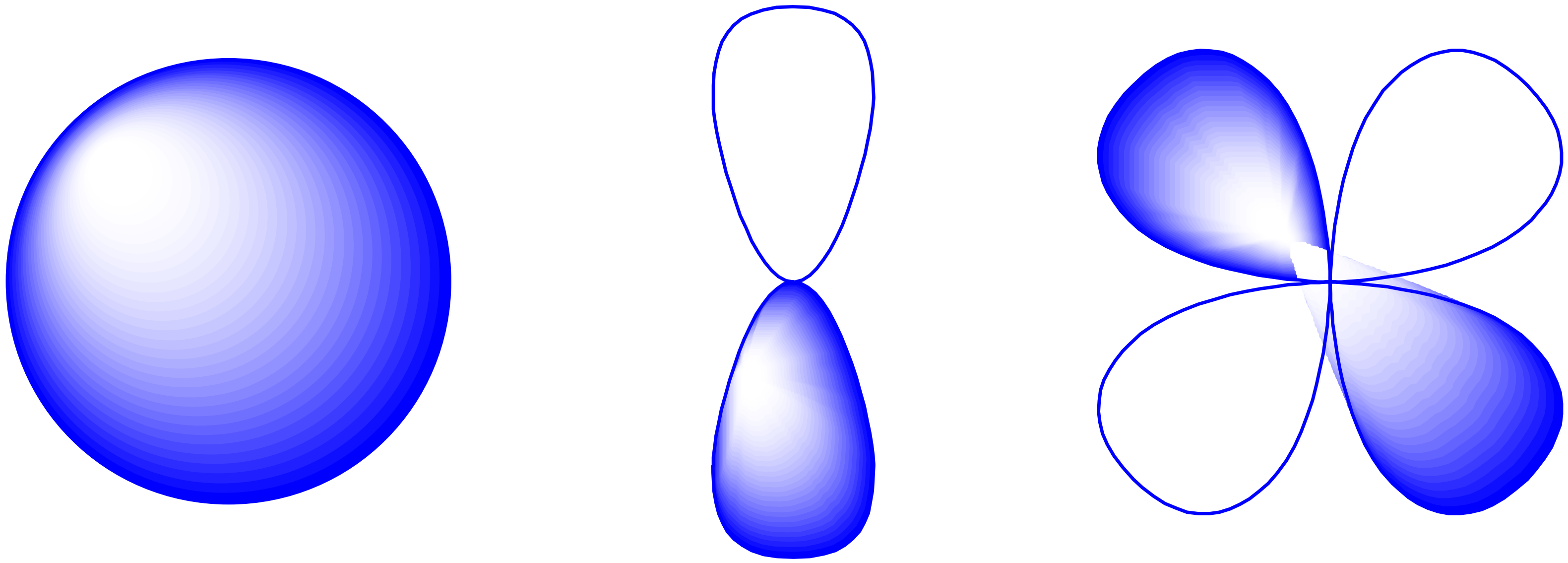
The wavefunctions of a rigid rotor are called spherical harmonics

The solutions to the θ and ϕ equation (angular part) are the spherical harmonics $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$
Separation of variables using the functions $\Theta(\theta)$ and $\Phi(\phi)$ allows solution of the rotational wave equation.

$$-\frac{\hbar^2}{2I}\left(\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)\right)=EY$$

We can obtain a θ and ϕ equation from the above equation.

Rotational Wavefunctions



J = 0 J = 1 J = 2

These are the spherical harmonics Y_{JM}, which are solutions of the angular Schrodinger equation.

The form of the spherical harmonics

Including normalization the spherical harmonics are

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_1^{\pm 1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$$

$$Y_2^{\pm 1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_2^2 = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi}$$

The form commonly used to represent p and d orbitals are linear combinations of these functions

Solutions to the 3-D rotational hamiltonian

- There are two quantum numbers

  J is the total angular momentum quantum number

  M is the z-component of the angular momentum

- The spherical harmonics called Y_{JM} are functions whose probability $|Y_{JM}|^2$ has the well known shape of the s, p and d orbitals etc.

  J = 0 is s , M = 0

  J = 1 is p , M = -1, 0 , 1

  J = 2 is d , M = -2 , -1, 0 , 1, 2

  J = 3 is f , M = -3 , -2 , -1, 0 , 1, 2, 3

  etc.

The degeneracy of the solutions

- The solutions form a set of 2J + 1 functions at each energy (the energies are

$$E = \frac{\hbar^2}{2I} J(J+1)$$

- A set of levels that are equal in energy is called a degenerate set.

Orthogonality of wavefunctions

- The rotational wavefunctions can be represented as the product of sines and cosines.
- Ignoring normalization we have:
- s 1
- p $\cos\theta$, $\sin\theta\cos\phi$, $\sin\theta\sin\phi$
- d $1/2(3\cos^2\theta - 1)$, $\cos^2\theta\cos 2\phi$, $\cos^2\theta\sin 2\phi$,
  $\cos\theta\sin\theta\cos\phi$, $\cos\theta\sin\theta\sin\phi$
- The differential angular element is $\sin\theta d\theta d\phi/4\pi$ over
- the limits $\theta = 0$ to π and $\phi = 0$ to 2π.
- The angular wavefunctions are orthogonal.

The moment of inertia

The kinetic energy of a rotating body is $1/2I\omega^2$.
The moment of inertia is given by:

$$I = \sum_{i=1}^{\infty} m_i r_i^2$$

The rigid rotor approximation assumes that molecules do not distort under rotation. The types or rotor are (with moments I_a , I_b , I_c)

- Spherical: Three equal moments (CH_4, SF_6)
  (Note: No dipole moment)
- Symmetric: Two equal moments (NH_3, CH_3CN)
- Linear: One moment (CO_2, HCl, HCN)
  (Note: Dipole moment depends on asymmetry)
- Asymmetric: Three unequal moments (H_2O)