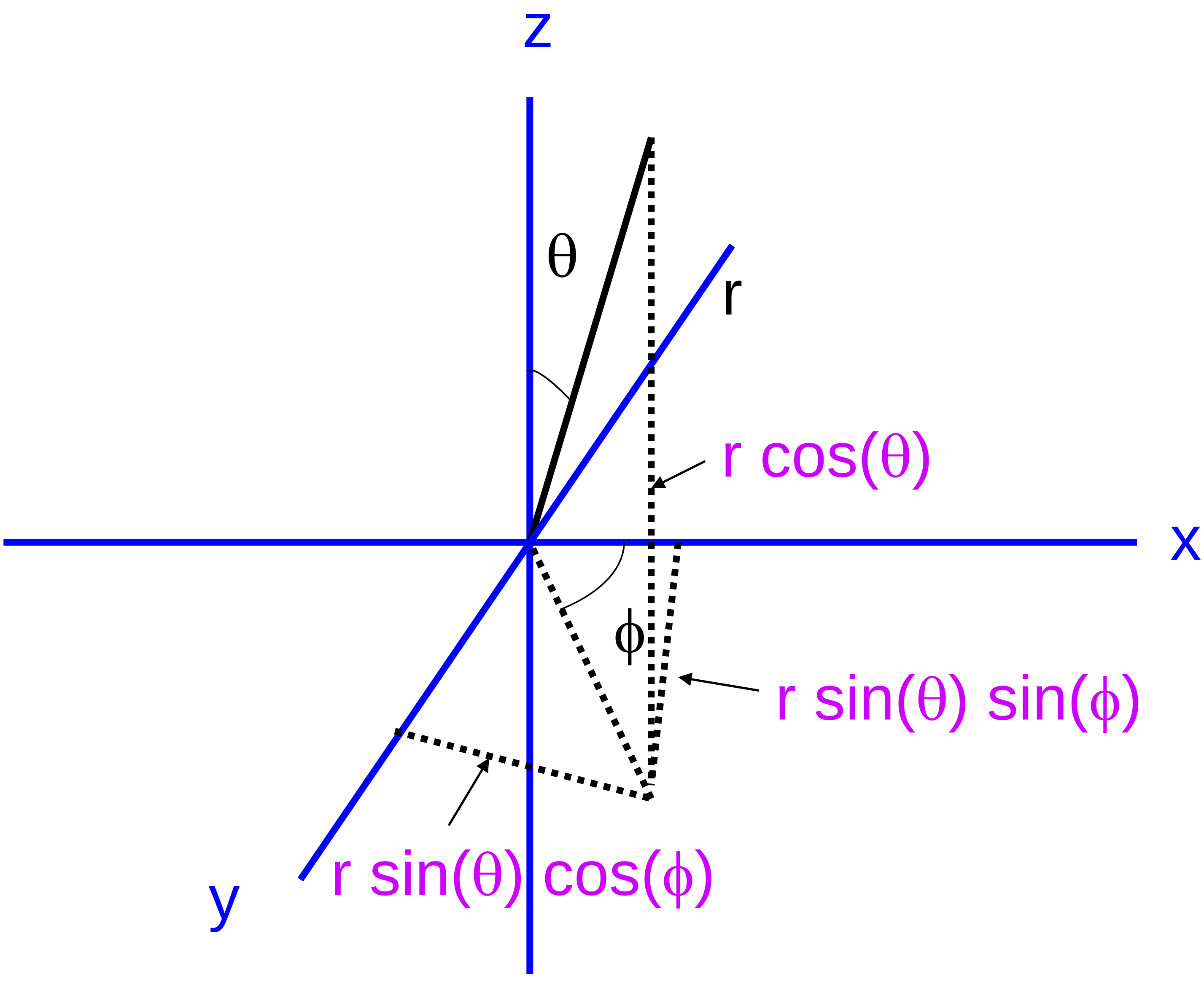
Spherical Polar Coordinates



The volume element in spherical polar coordinates

To solve the Schrodinger equation we need to integrate of all space.   This is the same thing as performing a volume integral. The volume element is:

$$dV = r^2 dr\ sin\theta d\theta\ d\phi$$

This integrates to 4π, which is the normalization constant. 4π stearadians also gives the solid angle of a sphere.

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.

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

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

Separation of variables

The spherical harmonics arise from the product of $\Theta\Phi$ after substituting $Y = \Theta\Phi$

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

Multiply through by $\sin^2\theta/\hbar^2$.

$$\frac{\partial^2}{\partial\phi^2}\Phi\Theta+sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\Phi\Theta\right)=-sin^2\theta\frac{\beta}{\hbar^2}\Phi\Theta$$

Separation of variables

The operators in variables θ and ϕ operate on function Θ and Φ , respectively, so we can write

$$\Theta \frac{\partial^2}{\partial \phi^2}\Phi + \Phi sin\theta \frac{\partial}{\partial \theta}\left(sin\theta \frac{\partial}{\partial \theta}\Theta\right) = -sin^2\theta \frac{\beta}{\hbar^2}\Phi\Theta$$

When we divide by Y = $\Theta\Phi$, we obtain

$$\frac{1}{\Phi}\frac{\partial^2}{\partial \phi^2}\Phi + \frac{1}{\Theta} sin\theta \frac{\partial}{\partial \theta}\left(sin\theta \frac{\partial}{\partial \theta}\Theta\right) + sin^2\theta \frac{\beta}{\hbar^2} = 0$$

Now, these equations can be separated using separation constant m^2.

$$\frac{1}{\Phi}\frac{\partial^2}{\partial \phi^2}\Phi = -\mathrm{m}^2 \qquad \frac{1}{\Theta} sin\theta \frac{\partial}{\partial \theta}\left(sin\theta \frac{\partial}{\partial \theta}\Theta\right) + sin^2\theta \frac{\beta}{\hbar^2} = \mathrm{m}^2$$

The Φ equation

We have already seen the solution to the ϕ equation from the example of rotation in two dimensions.

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

which has solutions

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im\phi}, m = \pm 1, \pm 2, \pm 3, \ldots$$

Now that we have defined the values of m as positive and negative integers, the θ equation is also defined.

Convert the θ-equation into the LeGendre polynomial generating equation

$$\frac{1}{\Theta} sin\theta \frac{\partial}{\partial\theta}\left(sin\theta \frac{\partial}{\partial\theta}\Theta\right) + \frac{1}{\Theta} sin^2\theta \frac{\beta}{\hbar^2}\Theta = \mathrm{m}^2$$

Can be written as

$$sin\theta \frac{\partial}{\partial\theta}\left(sin\theta \frac{\partial}{\partial\theta}\Theta\right) + sin^2\theta \frac{\beta}{\hbar^2}\Theta - \mathrm{m}^2\Theta = 0$$

Let x = cosθ.

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial\, cos\theta} = \frac{\partial\theta}{\partial\, cos\theta}\ \frac{\partial}{\partial\theta}$$

$$\frac{\partial\theta}{\partial\, cos\theta} = \frac{-1}{sin\theta}$$

Therefore

$$\frac{\partial}{\partial\theta} = -\sqrt{(1 - x^2)}\frac{\partial}{\partial x}$$

$$\sqrt{(1-x^2)}\left(-\sqrt{(1-x^2)}\frac{\partial}{\partial x}\right)\left(\sqrt{(1-x^2)}\left(-\sqrt{(1-x^2)}\right)\frac{\partial}{\partial x}\mathrm{P(x)}\right)$$

$$+\left((1-x^2)\frac{\beta}{\hbar^2}-\mathrm{m}^2\right)\mathrm{P(x)}=0$$

$$(1-x^2)\frac{\partial}{\partial x}\left((1-x^2)\frac{\partial}{\partial x}\mathrm{P(x)}\right)+\left((1-x^2)\frac{\beta}{\hbar^2}-\mathrm{m}^2\right)\mathrm{P(x)}=0$$

$$\frac{\partial}{\partial x}\left((1-x^2)\frac{\partial}{\partial x}\mathrm{P(x)}\right)+\left(\frac{\beta}{\hbar^2}-\frac{\mathrm{m}^2}{(1-x^2)}\right)\mathrm{P(x)}=0$$

we find,

$$\beta=\hbar^2\ell(\ell+1)$$

Using the product rule to take the derivative with respect to x, and making the substitution

$$(1-x^2)\frac{\partial^2 P}{\partial x^2}-2x\frac{\partial P}{\partial x}+\left(\ell(\ell+1)-\frac{m^2}{1-x^2}\right)P=0$$

The solution of θ equation gives Legendre polynomials

Substitute x = cosθ and the equation becomes:

$$(1-x^2)\frac{\partial^2 P}{\partial x^2} - 2x\frac{\partial P}{\partial x} + \left(\beta - \frac{m^2}{1-x^2}\right)P = 0$$

The solution requires that β = $\ell(\ell+1)$ with ℓ = 0,1,2..
Where ℓ is the rotational quantum number.
The azimuthal quantum number is m.
The magnitude of $|m| \leq \ell$. The solutions are Legendre polynomials

$P_0(x)=1$

$P_1(x)=x$

$P_2(x)=1/2\ (3x^2 - 1)$

$P_3(x)=1/2\ (5x^3 - 3x)$

The spherical harmonics as solutions to the rotational hamiltonian

The spherical harmonics are the product of the solutions to the θ and ϕ equations. With norm-
-alization these solutions are

$$Y(\theta,\phi) = N_{\ell,m} P_{\ell}{}^{m}(cos\,\theta) e^{im\phi}$$

The m quantum number corresponds the z component of angular momentum.
The normalization constant is

$$N_{\ell,m} = \sqrt{\frac{(2\ell+1)(\ell-|m|)}{4\pi(\ell+|m|)}}$$

The form of the spherical harmonics

Including normalization the spherical harmonics are

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

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

$$Y_1^{\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$$

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

$$Y_2^{\pm1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}$$

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

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