Molecular Spectroscopy

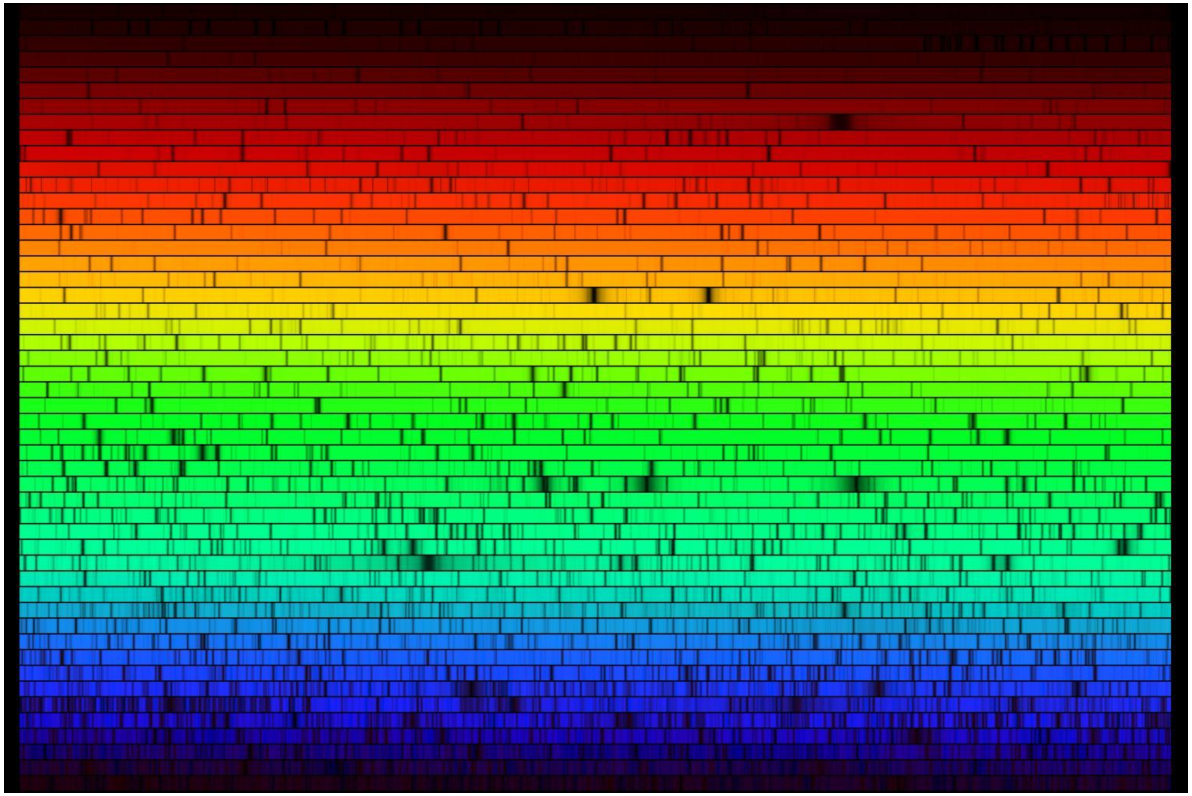
The hydrogen atom

NC State University

Experimental observation of hydrogen atom

- Hydrogen atom emission is “quantized”. It occurs at discrete wavelengths (and therefore at discrete energies).
- The Balmer series results from four visible lines at 410 nm, 434 nm, 496 nm and 656 nm.
- The relationship between these lines was shown to follow the Rydberg relation.

The Solar Spectrum



- There are gaps in the solar emission called Frauenhofer lines.
- The gaps arise from specific atoms in the sun that absorb radiation.

Atomic spectra

- Atomic spectra consist of series of narrow lines.
- Empirically it has been shown that the wavenumber of the spectral lines can be fit by

$$\Delta\tilde{\nu} = \tilde{R}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

where R is the Rydberg constant, and n_1 and n_2 are integers.

Electronic Structure of Hydrogen

The Schrödinger equation for hydrogen

Separation of variables: Radial and angular parts

Hydrogen atom wavefunctions Expectation values

Spectroscopy of atomic hydrogen

Schrödinger equation for hydrogen: The form of the potential

- The Coulomb potential between the electron and the proton is

$$V = -Ze^2/4\pi\varepsilon_0 r$$

- The hamiltonian for both the proton and electron is:

$$-\frac{\hbar^2}{2m_e}\nabla^2{}_{\mathrm{elec}}\Psi - \frac{\hbar^2}{2m_N}\nabla^2{}_{\mathrm{nuc}}\Psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = \mathbf{E}\Psi$$

- Separation of nuclear and electronic variables results in an electronic equation in the center-of-mass coordinates:

$$-\frac{\hbar^2}{2\mu}\nabla^2{}_{\mathrm{elec}}\psi_{\mathrm{elec}} - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi_{\mathrm{elec}} = \mathbf{E}_{\mathbf{elec}}\psi_{\mathrm{elec}}$$

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

Schrödinger equation for hydrogen: The kinetic energy operator

The Schrödinger equation in three dimensions is:

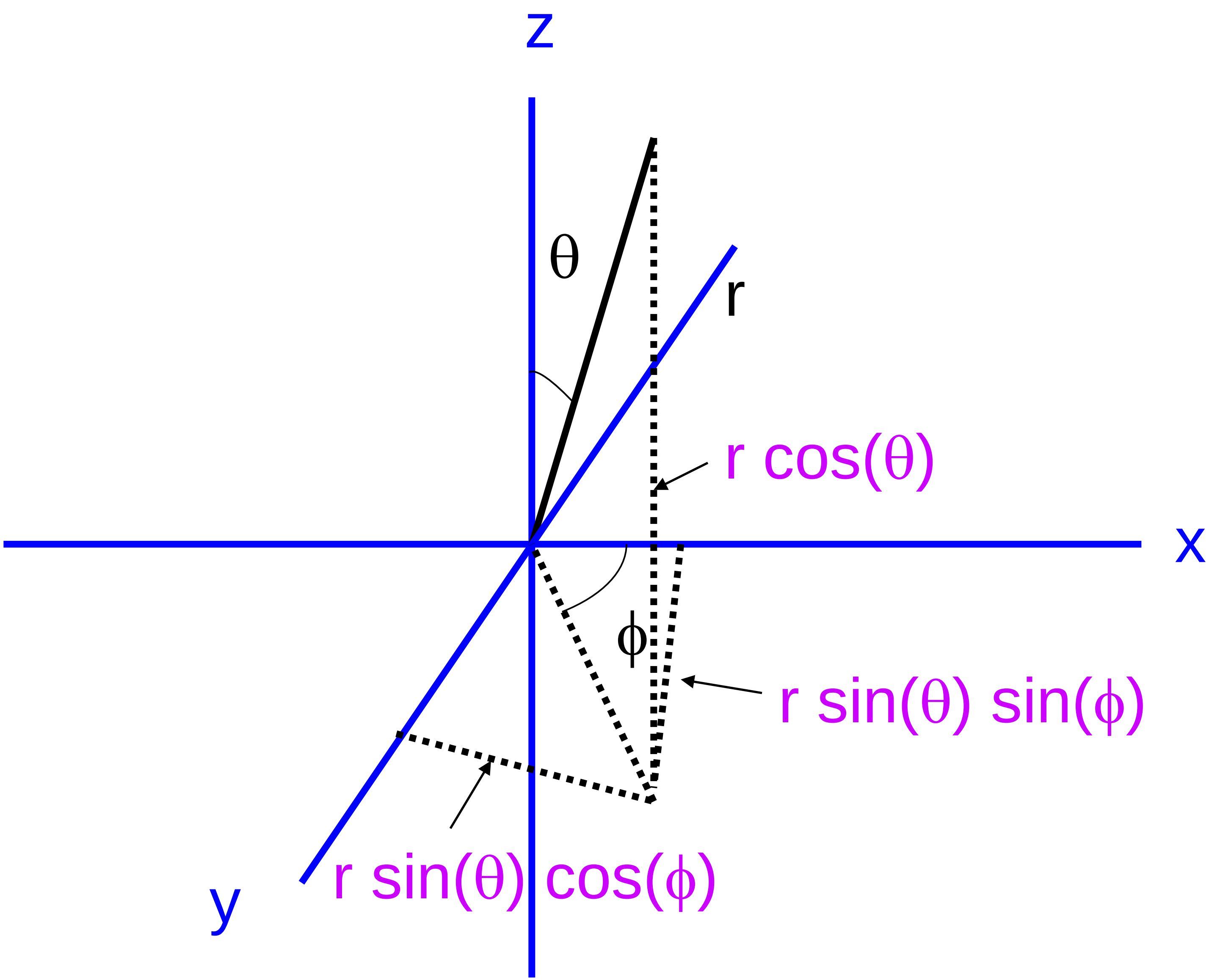
$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi + V\Psi = E\Psi$$

The operator del-squared is:

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

The procedure uses a spherical polar coordinate system.
Instead of x, y and z the coordiantes are θ, ϕ and r.

Spherical Polar Coordinates



Separation of variables

The del-squared operator in spherical polar coordinates is:

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

It is not possible to solve the equation with all three variables simultaneously. Instead a procedure known as separation of variables is used.

The steps are:

1. Multiply both sides by $2\mu r^2$
2. Substitute in $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$
3. Divide both sides by $R(r)Y(\theta,\phi)$

Using a separation constant called β we can write the Schrodinger equation as two separate equations.

$$-\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi - \mathbf{E}\psi = -\beta\psi$$

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

We write the total wave function as a product of two wave functions. $\psi(r,\theta,\phi) = R(r)Y_m^\ell(\theta,\phi)$

Then we divide the radial equation by Y_m^l and the angular equation by R to get two separate equations.

$$-\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)\mathrm{R} - \frac{Ze^2}{4\pi\varepsilon_0 r}\mathrm{R} - \mathbf{E}\mathrm{R} = -\beta\mathrm{R}$$

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

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.

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.

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

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \qquad Y_2^0 = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_2^{\pm 1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_1^{\pm 1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi} \qquad Y_2^2 = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi}$$

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

Euler relation

Linear combinations are formed using the Euler relation

$e^{+i\phi} = \cos\phi + i \sin\phi$, $e^{-i\phi} = \cos\phi - i \sin\phi$

$\cos\phi = \dfrac{e^{+i\phi} + e^{-i\phi}}{\mathbf{2}}$, $\sin\phi = \dfrac{e^{+i\phi} - e^{-i\phi}}{\mathbf{2i}}$

Projection along the z-axis is usually taken using $z = r\cos\theta$. Projection in the x,y plane is taken using $x = r\sin\theta\cos\phi$ and $y = r\sin\theta\sin\phi$

Solutions to the 3-D rotational hamiltonian

- There are two quantum numbers

  ℓ is the total angular momentum quantum number

  m is the z-component of the angular momentum
- The spherical harmonics called $Y_{\ell m}$ are functions whose probability $|Y_{\ell m}|^2$ has the well known shape of the s, p and d orbitals etc.

  $\ell = 0$ is s , $m = 0$

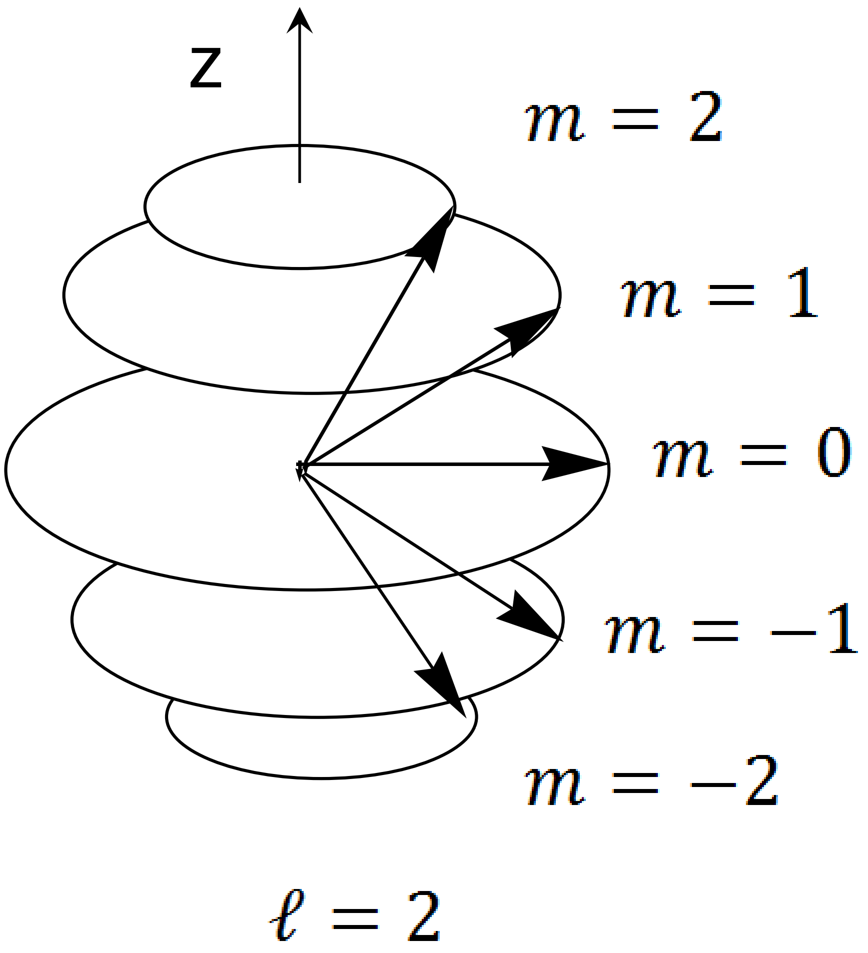
  $\ell = 1$ is p , $m = -1, 0, 1$

  $\ell = 2$ is d , $m = -2, -1, 0, 1, 2$

  $\ell = 3$ is f , $m = -3, -2, -1, 0, 1, 2, 3$

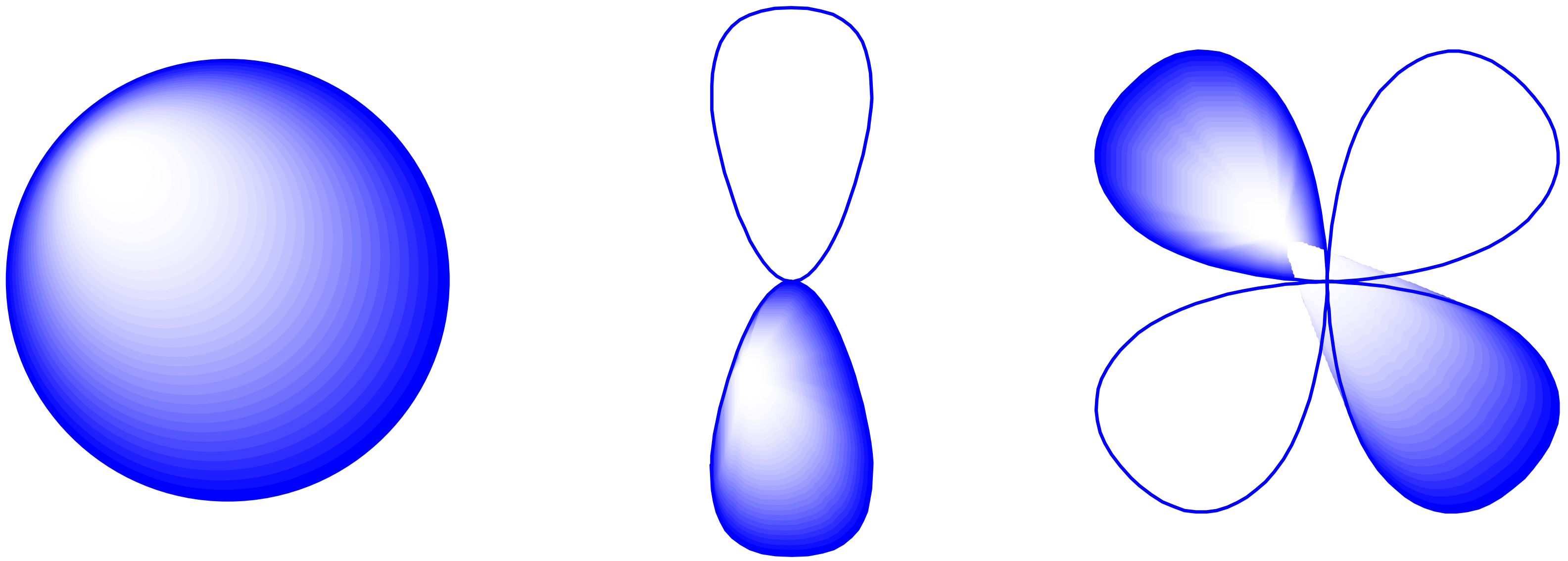
  etc.

Space quantization in 3D



- Specification of the azimuthal quantum number m_z implies that the angular momentum about the z-axis is $J_z = \hbar m$.
- This implies a fixed orientation between the total angular momentum and the z component.
- The x and y components cannot be known due to the Uncertainty principle.

Standing waves on a sphere



$\ell = 0$ $\quad$ $\ell = 1$ $\quad$ $\ell = 2$

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

Orthogonality of wavefunctions

- 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 $\sin\theta d\theta d\phi/4\pi$
- The limits $\theta = 0$ to π and $\phi = 0$ to 2π.
- The angular wavefunctions are orthogonal.

Orthogonality of wavefunctions

- For the theta integrals we can use the substitution
- $x = \cos\theta$ and $dx = \sin\theta d\theta$
- For example, for s and p-type rotational wave functions we have

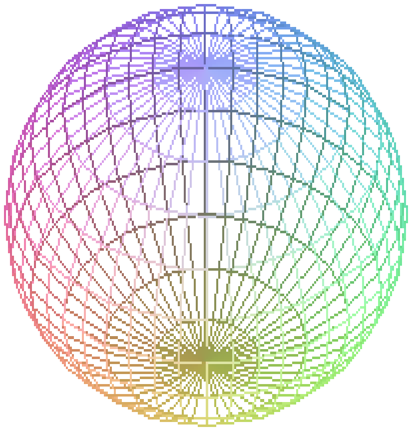
$$< s \,|\, p > \propto \int_0^{\pi} \cos\theta \,\sin\theta \; d\theta = \int_1^{-1} x \, dx = \left.\frac{x^2}{2}\right|_{-1}^{-1} = \frac{1}{2} - \frac{1}{2} = 0$$

MAPLE worksheet on spherical harmonics

- The form of the spherical harmonics $Y_{lm}(\theta,\phi)$ is quite familiar. The shape of the s-orbital resembles the first spherical harmonic Y_{00}.
- Attached to this lecture are three MAPLE worksheets that illustrate the s, p and d orbitals respectively. The idea is to obtain an interactive picture of the mathematical form and the plots of the functions.
- Disclaimer: The spherical harmonics have been simplified by formation of linear combinations to remove any complex numbers.

MAPLE
worksheet on spherical harmonics

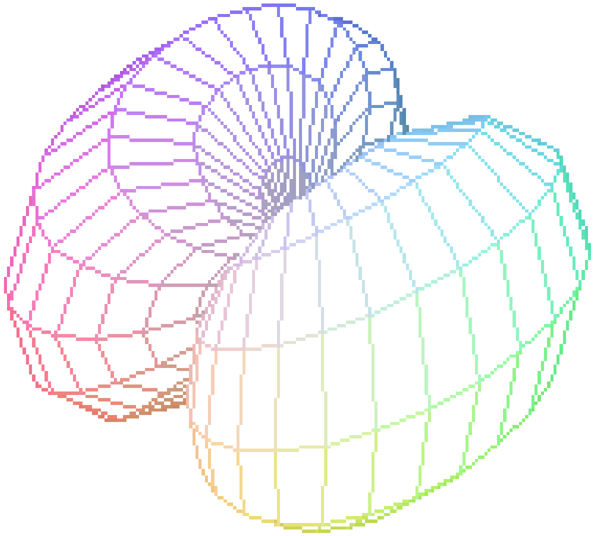
- The Y_{00} spherical harmonic has the form of an s-orbital.



- There is only one angular function for $\ell = 0$

MAPLE worksheet on spherical harmonics

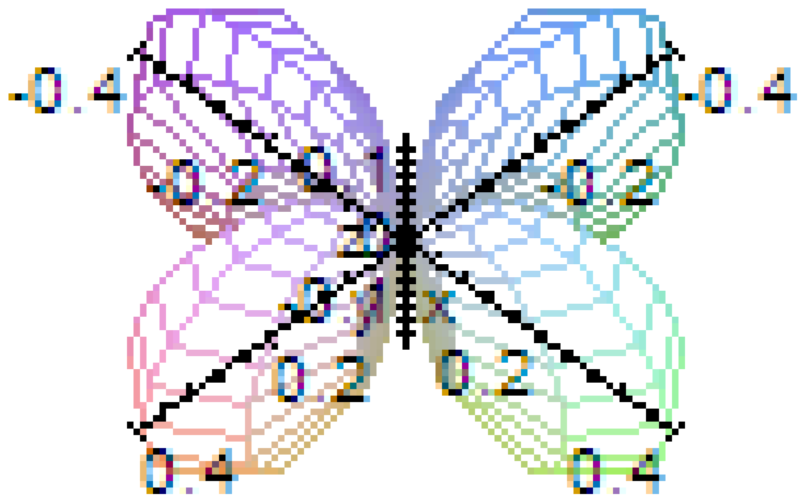
- The Y_{10} Y_{11} , and $Y_{1,-1}$ spherical harmonics have the form of p-orbitals.



- There are three angular functions for $\ell = 1$

MAPLE
worksheet on spherical harmonics

- The Y_{20} , Y_{21} , $Y_{2,-1}$, $Y_{2,2}$ and $Y_{2,-2}$ spherical harmonics have the form of d-orbitals.



- There are five angular functions for. $\ell = 2$

Angular momentum operators

The definition of the angular momentum operators in spherical polar coordinates are:

$$\hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

The total angular momentum is:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

which can be expressed in terms of the angular derivatives,

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

Raising and lowering operators

We can define a raising and lowering operator for angular momentum using the definition:

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y$$

This is also known as the ladder operator, and it has the form,

$$\hat{L}_{\pm} = -i\hbar e^{\pm i\phi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right)$$

We can prove the valuation of the angular momentum commutators

$$\left[\hat{L}_z, \hat{L}_{\pm}\right] = \pm\hbar\hat{L}_{\pm} \qquad \left[\hat{L}_+, \hat{L}_-\right] = 2\hbar\hat{L}_z$$

To prove that these are the commutators we need to evaluate the eigenvalues. We can use the nomenclature

$$Y_m^{\ell}(\theta, \phi) = |\ell, m>$$

From the known properties of the angular momentum operator in obtained in the solution of the angular equation we have:

$$\hat{L}_z|\ell, m> = \hbar m|\ell, m>$$

$$\hat{L}^2|\ell, m> = \hbar^2 \ell(\ell + 1)|\ell, m>$$

We want to evaluate the ladder operator using $\hat{L}_{\pm}|\ell, m>$

We can use the commutator to evaluate the ladder operator,

$$\hat{L}_z\left(\hat{L}_{\pm}|\ell, m>\right)$$

Using the definition of the commutator we have

$$\hat{L}_z\hat{L}_{\pm} - \hat{L}_{\pm}\hat{L}_z = \pm\hbar\hat{L}_{\pm}$$

Eigenvalues for the raising and lowering operators

$$\hat{L}_z \hat{L}_\pm |\ell, m> = \hat{L}_\pm \hat{L}_z |\ell, m> \pm \hbar \hat{L}_\pm |\ell, m>$$

$$\hat{L}_z \hat{L}_\pm |\ell, m> = \hat{L}_\pm \hbar m |\ell, m> \pm \hbar \hat{L}_\pm |\ell, m>$$

.

$$\hat{L}_z \hat{L}_\pm |\ell, m> = \hbar (m \pm 1) \hat{L}_\pm |\ell, m>$$

Thus, we see that $\hat{L}_\pm |\ell, m>$ is an eigenstate of $\hat{L}_z$ with eigenvalue $\hbar (m \pm 1)$

This above result leads to an operator equation for the Raising and lowering operators. Now we must calculate the Eigenvalue:

$$\hat{L}_\pm |\ell, m> = c^\pm |\ell, m \pm 1>$$

Properties of raising and lowering operators

From the definition of the total angular moment, we can replace the x and y terms using the definition of the ladder operator,

$$\hat{L}_x^2 + \hat{L}_y^2 = \left(\hat{L}_x + i\hat{L}_y\right)\left(\hat{L}_x - \ i\hat{L}_y\right) = \frac{1}{2}\hat{L}_+\hat{L}_-$$

From the commutator

$$\hat{L}_+\hat{L}_- = \hat{L}_-\hat{L}_+ + 2\hbar\hat{L}_z$$

Therefore,

$$\hat{L}^2 = \frac{1}{2}\hat{L}_-\hat{L}_+ + \hbar\hat{L}_z + \hat{L}_z^2$$

There are $2\ell + 1$ values of m, which range from -ℓ to ℓ.

If we operate with the $\hat{L}_+$ ladder operator on the highest eigenvalue, ℓ we obtain

$$\hat{L}_+|\ell, \ell > = 0$$

Likewise, we obtain 0 when using the lowering operator on the lowest state

.

$$\hat{\mathrm{L}}_-|\ell,-\ell> = 0$$

Thus, if we choose $|\ell,\ell>$ as our test function we have,

$$\hat{\mathrm{L}}^2|\ell,\ell> = 0 + \ \hbar(\hbar\ell)|\ell,\ell> + (\hbar\ell)^2|\ell,\ell>$$

This gives,

$$\hat{\mathrm{L}}^2\Bigg|\ell,\ell> = \frac{1}{2}\hat{\mathrm{L}}_-\hat{\mathrm{L}}_+\Bigg|\ell,\ell> + \hbar\hat{\mathrm{L}}_{\mathrm{z}}\,|\ell,\ell> + \hat{\mathrm{L}}_{\mathrm{z}}^2\,|\ell,\ell>$$

Thus,

$$\hat{\mathrm{L}}^2|\ell,\ell> = \ \hbar^2\ell(\ell+1)|\ell,\ell>$$

We can show that the eigenvalue for the ladder operators is,

$$\mathrm{c}^{\pm} = \hbar\sqrt{\ell(\ell+1) - \mathrm{m}(\mathrm{m}\pm 1)}$$