# **Quantum Mechanical Treatment of Rotational Motion**

We have examined **translational** (the free particle) and **vibrational** (harmonic oscillator) motion. The latter serves as a useful model for the analysis of infrared spectra.

We will now examine the quantum mechanical treatment of **rotational motion**. Microwave spectroscopy can be used to measure the rotational states of molecules.
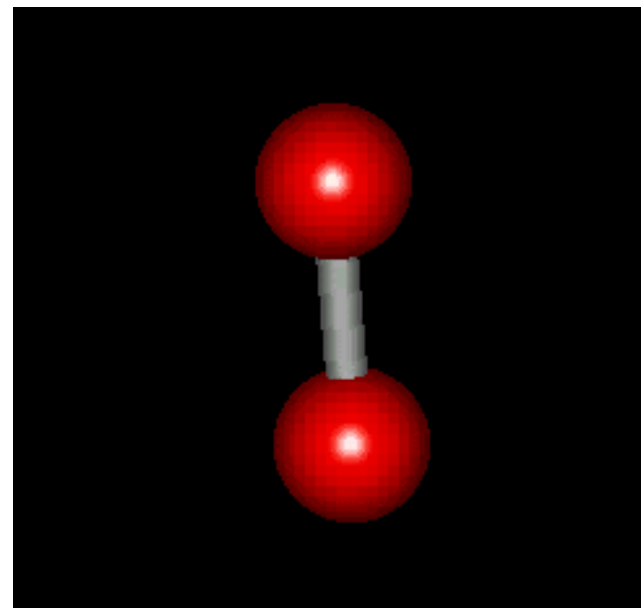
Rotational motion also provides a good introduction to chemical problems that have polar and spherical symmetry.

This will also lead to a discuss of **angular momentum**, an important topic in quantum chemistry.

The 2-D Rigid Rotor or Particle on a Ring

The 2-dimensional rigid rotor can be used to describe the rotational motion of a diatomic molecule constrained to rotate around one axis.

e.g. A rotating H$_2$ molecule adsorbed onto a surface.

The term *rigid* in this context means that the distance r (the bond length) is fixed. In other words, we are making the approximation that the molecule is not vibrating or stretching.
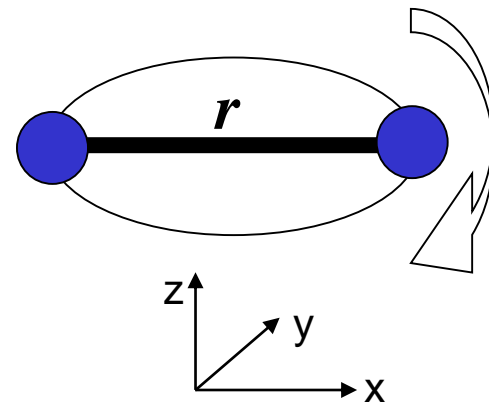
The rigid rotor model is a good approximation because, although molecules vibrate at room temperature, the vibrational amplitude is small compared to the bond lengths.

We can show that the 2-D rigid rotor is mathematically equivalent to a single particle constrained to move on a ring.
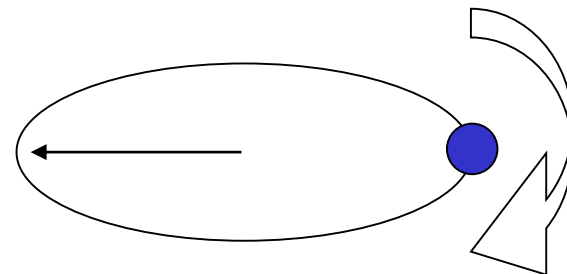
Reduction of the Dimensionality of the Problem

Recall with the Harmonic Oscillator, we reduced the two-body problem in 1-D into an effective one-body problem.

$$T = \frac{1}{2}\left(m_1 + m_2\right)\dot{X}_{CM}^2 \quad + \quad \frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}\dot{r}^2$$

We actually separated the problem into vibrational motion and the translational motion of the center of mass of the molecule.

Our current problem is similar, but now in 2-dimensions.

We can separate the problem into the center of mass motion and rotation about the center of mass.
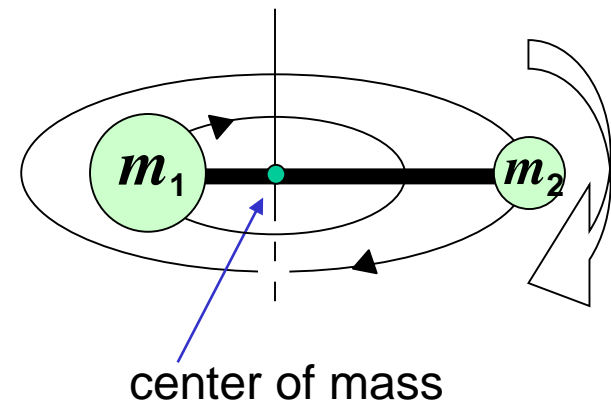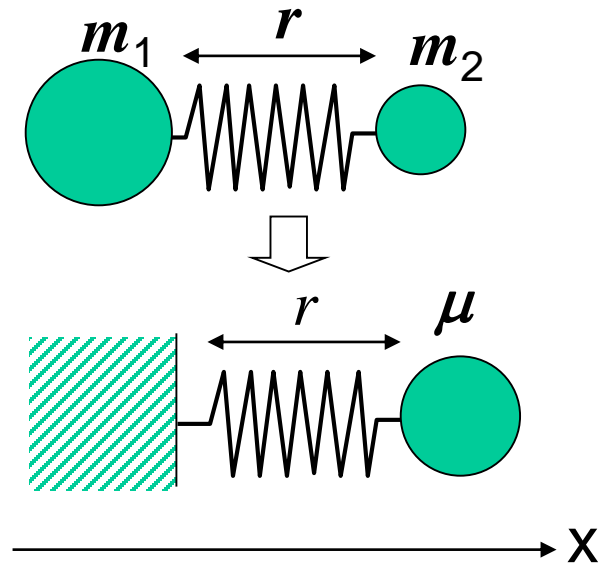
center of mass

Using the definition of the moment of inertia, it is straightforward to show that rotation of a rigid rotor of length r composed of two masses about the center of mass is equivalent to:
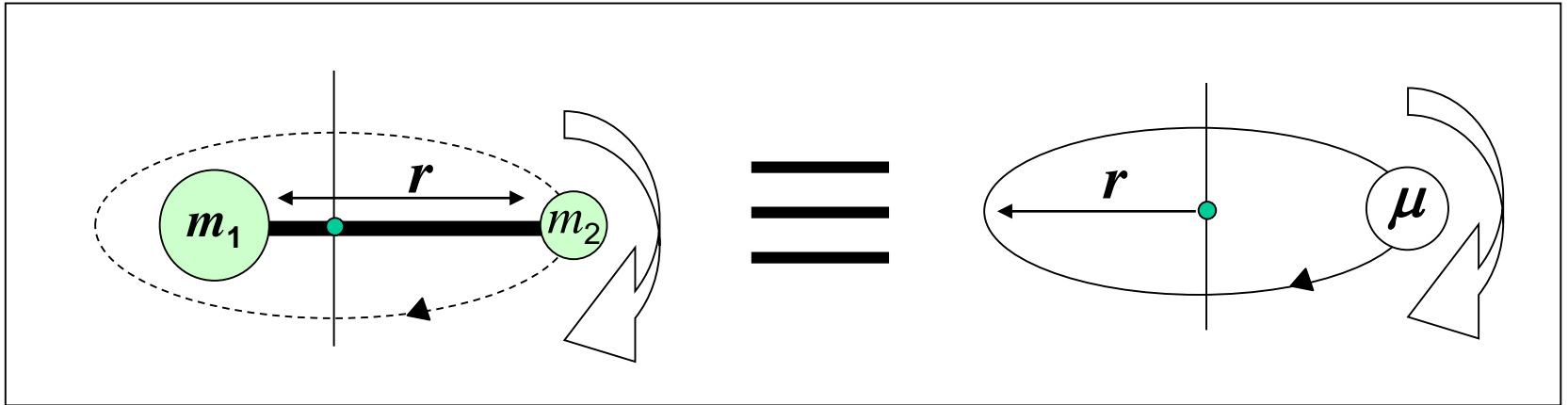
rotation of a single mass of μ, with a radius equal to r.

Where μ is the reduced mass we have encountered before: $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

We have again reduced our two-body problem into an **effective one-body problem**.

For our effective single-particle, what is the dimensionality of our problem?

What is the Hamiltonian of our problem?

## **Other Coordinate Systems can be More Convenient**

In this case, the Cartesian coordinate system may not be the best to use.

Instead, let's use a coordinate system that takes advantage of the natural symmetry of the problem, namely the **radial symmetry**.
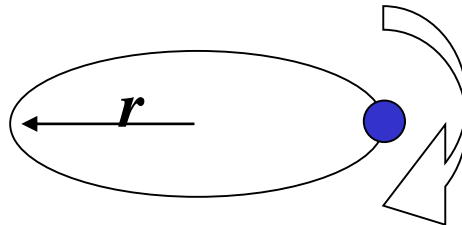
We'll see, if we use the polar coordinate system, our 2-dimensional problem will reduce into a 1-dimensional problem (a lot easier!).

The Polar Coordinate System

y

$(x, y) \equiv (r, \phi)$

r

ϕ

x

$0 \le r < \infty$

$0 \le \phi \le 2\pi$
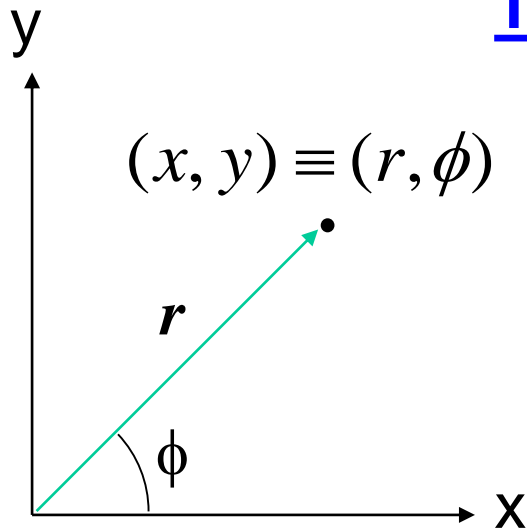
We can equivalently express any point in 2 dimensions with polar coordinates.

$$x = r\cos\phi \qquad\qquad r = \sqrt{x^2 + y^2}$$

$$\Longleftrightarrow$$

$$y = r\sin\phi \qquad\qquad \phi = \arctan(y/x)$$

It is easy enough to convert the coordinates x and y to r and ϕ using the expressions above.

Our wave function then becomes:

$$\psi(x, y) \implies \psi(r, \phi)$$

However, we must also convert our Hamiltonian into these coordinates.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \implies ? \text{ \textit{This is not trivial!}}$$

The Laplacian Can Be Expressed In A Variety Of Coordinate Systems

The difficulty with transforming our Hamiltonian into polar coordinates lies in the Laplacian operator.

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$$

We must convert these second derivatives in terms of r and ϕ.

Repeated application of the chain rule along with the equations that link (x,y) to (r,ϕ):

$$\frac{\partial}{\partial r} = \frac{\partial}{\partial x} \frac{\partial x}{\partial r} \qquad \begin{array}{l} x = r\cos\phi \\ y = r\sin\phi \end{array}$$

give the **Laplacian operator in polar coordinates**:

$$\nabla^2 = \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}$$

what does this mean?

Thus, our Hamiltonian in polar coordinates becomes:

$$\hat{H} = \hat{T} + V = -\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right)$$

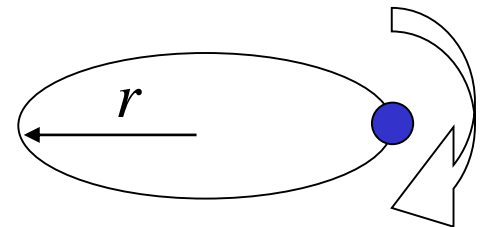We assume the particle is free to rotate so the potential is zero.

Our Schrödinger equation in polar coordinates is:

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right)\psi(r,\phi) = E\psi(r,\phi)$$

Our 2-D Rotor is Rigid (Fixed r)

Our wave function is a function of r, which is fixed, so it is not a variable. It is a constant in this problem.

$$\psi(r,\phi) \Rightarrow \psi(\phi)$$

Our Schrödinger equation for this problem is therefore:

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right)\psi(\phi)=E\psi(\phi)$$

Multiplying the wave function in on the left side gives:

$$-\frac{\hbar^2}{2\mu}\left(\underbrace{\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}\psi(\phi)}_{\text{zero}}+\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\psi(\phi)\right)=E\psi(\phi)$$

zero $\quad\dfrac{\partial}{\partial r}\psi(\phi)=0$ *(because ψ does not depend on r)*

So our two dimensional rotation reduces to a one-dimensional Schrödinger equation:

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial^2}{\partial\phi^2}\psi(\phi)=E\psi(\phi)\qquad 0\le\phi\le 2\pi$$

where *r* is a constant (the rotor is assumed to be rigid).

Rearranging to our standard DE form gives:

$$\frac{\partial^2}{\partial \phi^2}\psi(\phi) + \frac{2\mu r^2 E}{\hbar^2}\psi(\phi) = 0$$

Define the constant m as

$$m = \sqrt{\frac{2\mu r^2 E}{\hbar^2}}$$

The symbol 'm' is used here by convention, and does not represent the mass.

$$\frac{\partial^2}{\partial \phi^2}\psi(\phi) + m^2\psi(\phi) = 0$$

This DE is the same one that we get for the 1-D particle in a box or free particle!

Recall:

$$\frac{\partial^2}{\partial x^2}\psi(x) + k^2\psi(x) = 0$$

Particle-in-a-box DE

We already know the general solutions of this problem, so what's different?
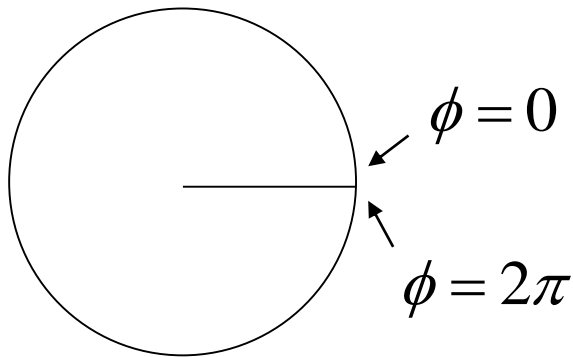
$$\frac{\partial^2}{\partial \phi^2} \psi(\phi) + m^2 \psi(\phi) = 0$$

The general solution to the above differential equation is:

$$\psi(\phi) = Ae^{im\phi} + Be^{-im\phi}$$

The difference between this problem, the 1-D particle in a box and the free particle are the boundary conditions.

$\phi = 0$

$\phi = 2\pi$

Our wave function has to match up at 0 and 2π, so our boundary condition is:

$$\psi(0) = \psi(2\pi)$$

The Angular Momentum is a Characteristic Property of the Rotor

Before we solve for the Schrödinger equation, let's use some principles that we learned earlier to simplify the problem.

Recall that the energy is always a property that characterizes the state of a conservative system.

In other words, the energy of a system is always definite.

We also said that other properties can characterize the state of a particular steady-state system.

Recall that if a physical property characterizes the system, the *wave function must be an eigenfunction of the operator corresponding to that property*.

The angular momentum of the rigid rotor is a characteristic property.

WHY?

Because the angular momentum is a characteristic property of the rigid rotor, the wave function must be an eigenfunction of the angular momentum operator, which is given by:

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

Use this to help us simplify our solution to the Schrödinger equation.

Recall that the general solution of the Schrödinger equation was:

$$\psi(\phi) = Ae^{im\phi} + Be^{-im\phi}$$

$$\hat{L}\psi(\phi) = -i\hbar im[A\exp(im\phi) - B\exp(-im\phi)]$$

Doesn't equal a constant times $\psi(\phi)$ unless A or B is zero!

Using the restriction that the wave function must be an eigenfunction of the linear momentum operator, we get the general form:

$$\psi(\phi) = A'e^{\pm im\phi} \qquad\qquad \psi(0) = \psi(2\pi)$$

It can be easily shown that, in order to satisfy the cyclic boundary conditions, m must be given by

$$m = 0, \pm 1, \pm 2, \pm 3...$$

with the wave function

$$\psi(\phi) = A'e^{im\phi}$$

notice the '±' is "gone"(it's now included in m).

If we can solve for the constant A', then we have our complete wave function.

How can we determine the constant A'?

Our complete wave function for our 2-D rigid rotor is given by:

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad m = 0, \pm 1, \pm 2, \pm 3 ...$$

What about the energy of these states?

The energy of the rotor is easily derived from the Schrodinger equation:

$$\frac{\partial^2}{\partial \phi^2} \psi(\phi) + \frac{2\mu r^2 E}{\hbar^2} \psi(\phi) = 0$$

we defined m as: $\qquad m = \sqrt{\dfrac{2\mu r^2 E}{\hbar^2}}$

Thus our energies are given by: $\quad E = \dfrac{m^2 \hbar^2}{2\mu r^2} \qquad m = 0, \pm 1, \pm 2, \pm 3 ...$
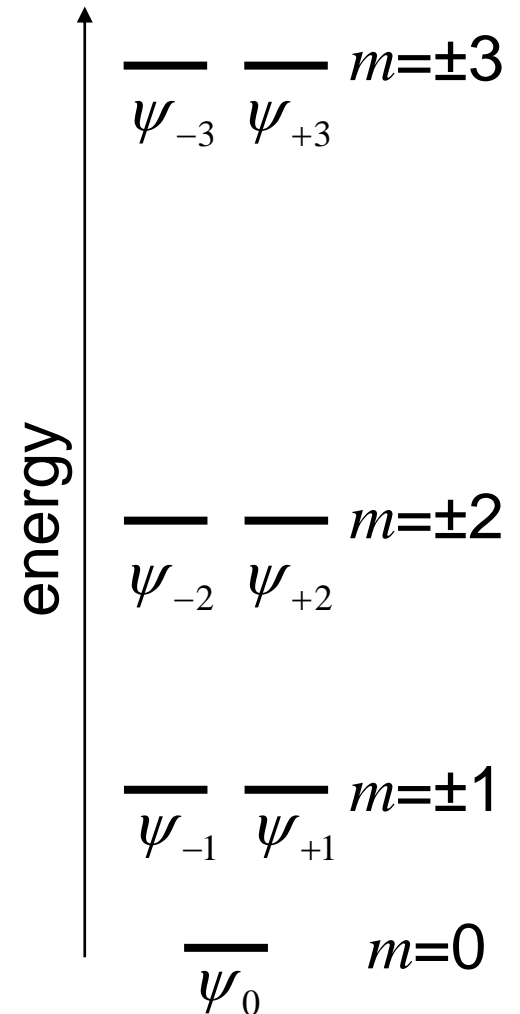
Labeling the wave functions and energies by their quantum number m gives:

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$E_m = \frac{m^2\hbar^2}{2\mu r^2} \qquad m = 0, \pm1, \pm2, \pm3 \dots$$
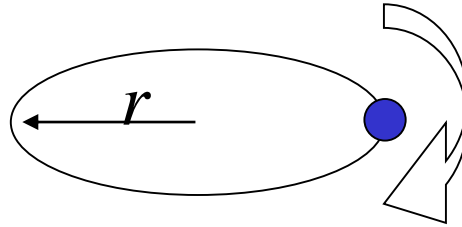
- The wave functions are all complex functions (except for $m = 0$)

- The energy levels are quantized.

- The energy levels are all doubly degenerate except for the ground state.

- The zero point energy for this system is zero.

$$E_0 = 0$$

energy

—— —— $m=\pm3$
ψ_{-3} ψ_{+3}

—— —— $m=\pm2$
ψ_{-2} ψ_{+2}

—— —— $m=\pm1$
ψ_{-1} ψ_{+1}

—— $m=0$
ψ_0

$$E_m = \frac{m^2 \hbar^2}{2\mu r^2} \qquad m = 0, \pm 1, \pm 2, \pm 3 \ldots$$

Because the potential energy is zero, $V(\phi) = 0$, all of the energy must be kinetic energy.

And the motion is all rotational, so all of the energy is rotational kinetic energy.

So **the rotational speed is also quantized.** In other words, the particle or rotor can only rotate at specific (discrete) speeds. This is again is in contrast to classical rotational motion (continuous speeds).

Can you explain why the energy levels are doubly degenerate?

The ground state with $m = 0$, corresponds to the rotor **not** rotating at all.
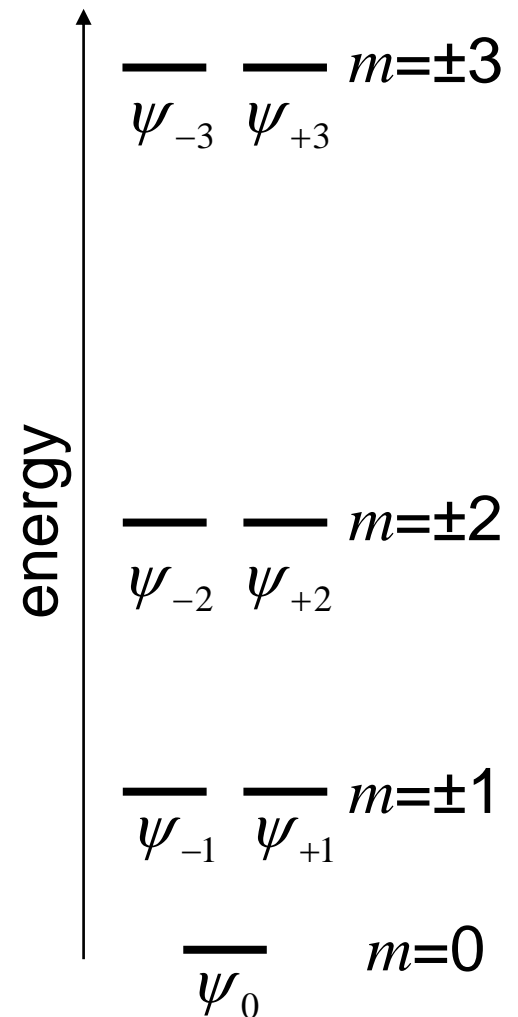
As m increases in magnitude, the system is rotating faster.

The sign of the quantum number m corresponds to the direction of rotation.

How can we verify the above statements?

What do the wave functions "look like"?

energy

$$\overline{} \quad \overline{} \quad m=\pm3$$
$$\psi_{-3} \quad \psi_{+3}$$

$$\overline{} \quad \overline{} \quad m=\pm2$$
$$\psi_{-2} \quad \psi_{+2}$$

$$\overline{} \quad \overline{} \quad m=\pm1$$
$$\psi_{-1} \quad \psi_{+1}$$

$$\overline{} \quad m=0$$
$$\psi_{0}$$

Recall what we learned earlier:

Consider a property, a, whose corresponding operator is given by $\underline{A}$. If $\underline{A}$ is happens to be an eigenfunction of the wave function of a state, then the variance in the measurement of that property is zero. In other words, the property 'a' of that state is definite.
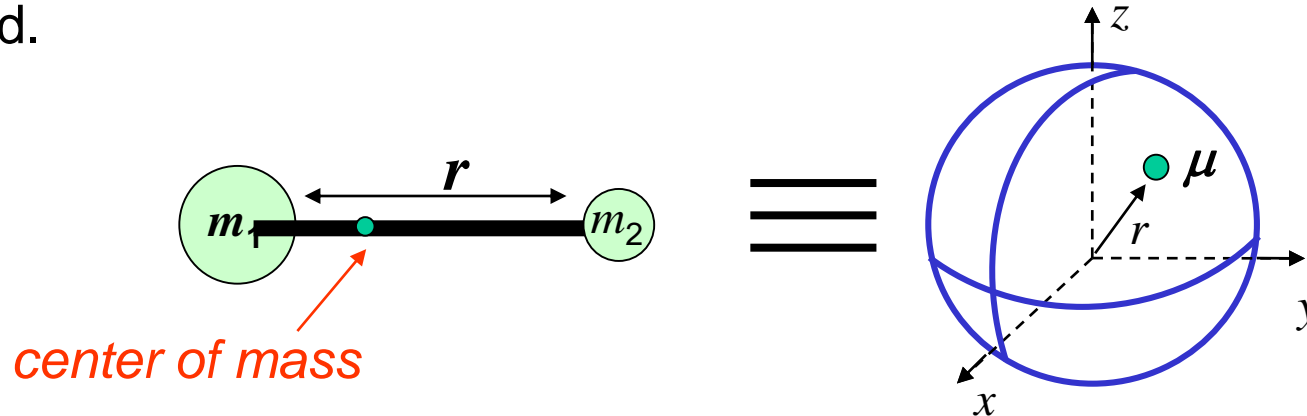
If $\quad \hat{A}\psi = a\psi \quad$ then $\quad \sigma_a^2 = \left\langle a^2 \right\rangle - \left\langle a \right\rangle^2 = 0$

Moreover, the value that will be measured is the eigenvalue 'a' such that:

$$\left\langle a \right\rangle = \int_{\text{all space}} \psi^* \hat{A}\psi \, d\tau = a$$

The 3-Dimensional Rigid Rotor

We now examine full 3-dimensional rotation. We will again consider the situation where our rotor is rigid. In other words, the bond distance is fixed.

center of mass

It can again be shown that full 3-D rotation of a two body system about the center of mass is equivalent to the rotation of a single effective body with mass μ.

Assuming the rotation is unhindered (free) so that the potential is zero, the Schrödinger equation is simply:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi = E\psi$$

Once again, Cartesian coordinates are not the most convenient representation. Here it is best to use **polar spherical coordinates**.

Polar Spherical Coordinates

We can specify any point in 3-D space with the coordinates r, ϕ, θ as easily as we can with the Cartesian x, y, z coordinates.
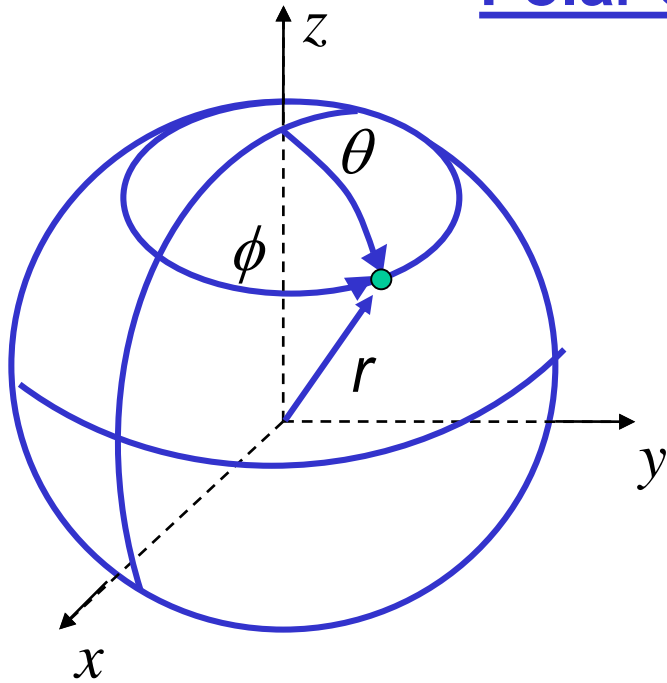
$$(x, y, z) \equiv (r, \theta, \phi)$$

r = distance from the origin
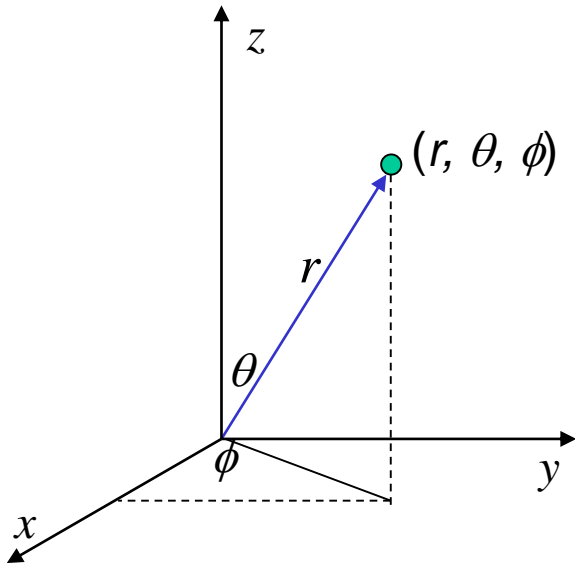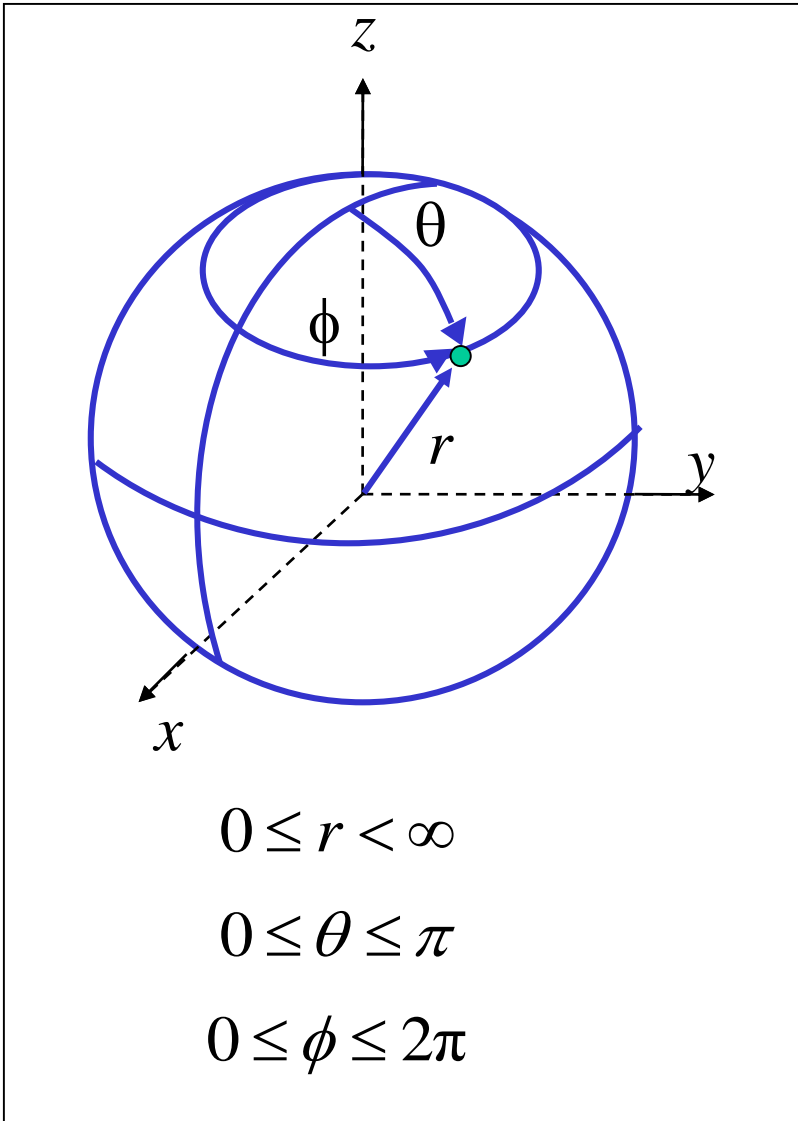$$0 \leq r < \infty$$

θ = angle line r makes with z-**axis**
$$0 \leq \theta \leq \pi$$

ϕ = angle about x-**axis**
$$0 \leq \phi \leq 2\pi$$

Polar Spherical Coordinates

$$0 \leq r < \infty$$
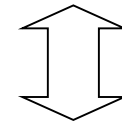
$$0 \leq \theta \leq \pi$$

$$0 \leq \phi \leq 2\pi$$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$\Updownarrow$$

$$r = (x^2 + y^2 + z^2)^{1/2}$$

$$\theta = \arccos \frac{z}{(x^2 + y^2 + z^2)^{1/2}}$$

$$\phi = \arctan \frac{y}{x}$$

Polar Spherical Coordinates

The **Laplacian operator** in polar spherical coordinates is not trivial to derive from

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

Again we have to repeatedly apply the chain rule to the second derivatives in terms of x, y, and z to convert the Laplacian to r, θ and ϕ.
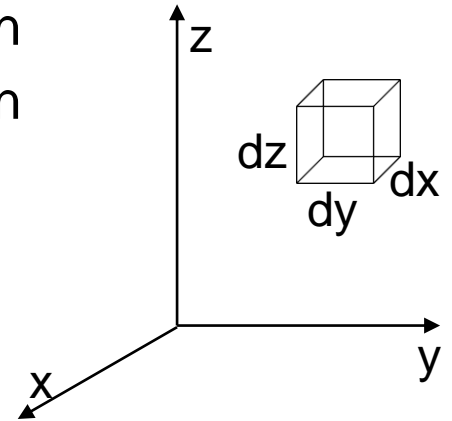
$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2}$$

(there is no need to memorize the above, but you should know how to work with it and what it means)

The Differential Volume Element or the Integration Element

In Cartesian coordinates, an infinitesimal change in dx, dy, dz maps out a cube whose volume is given by:
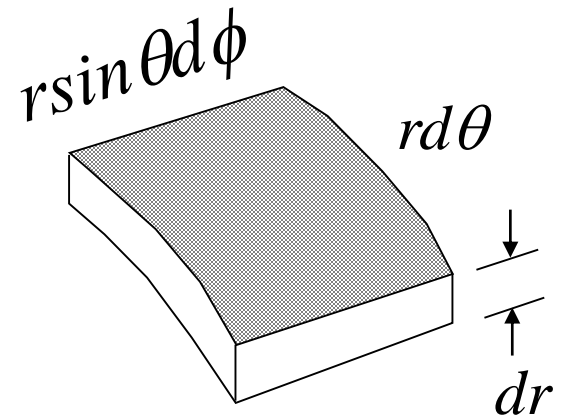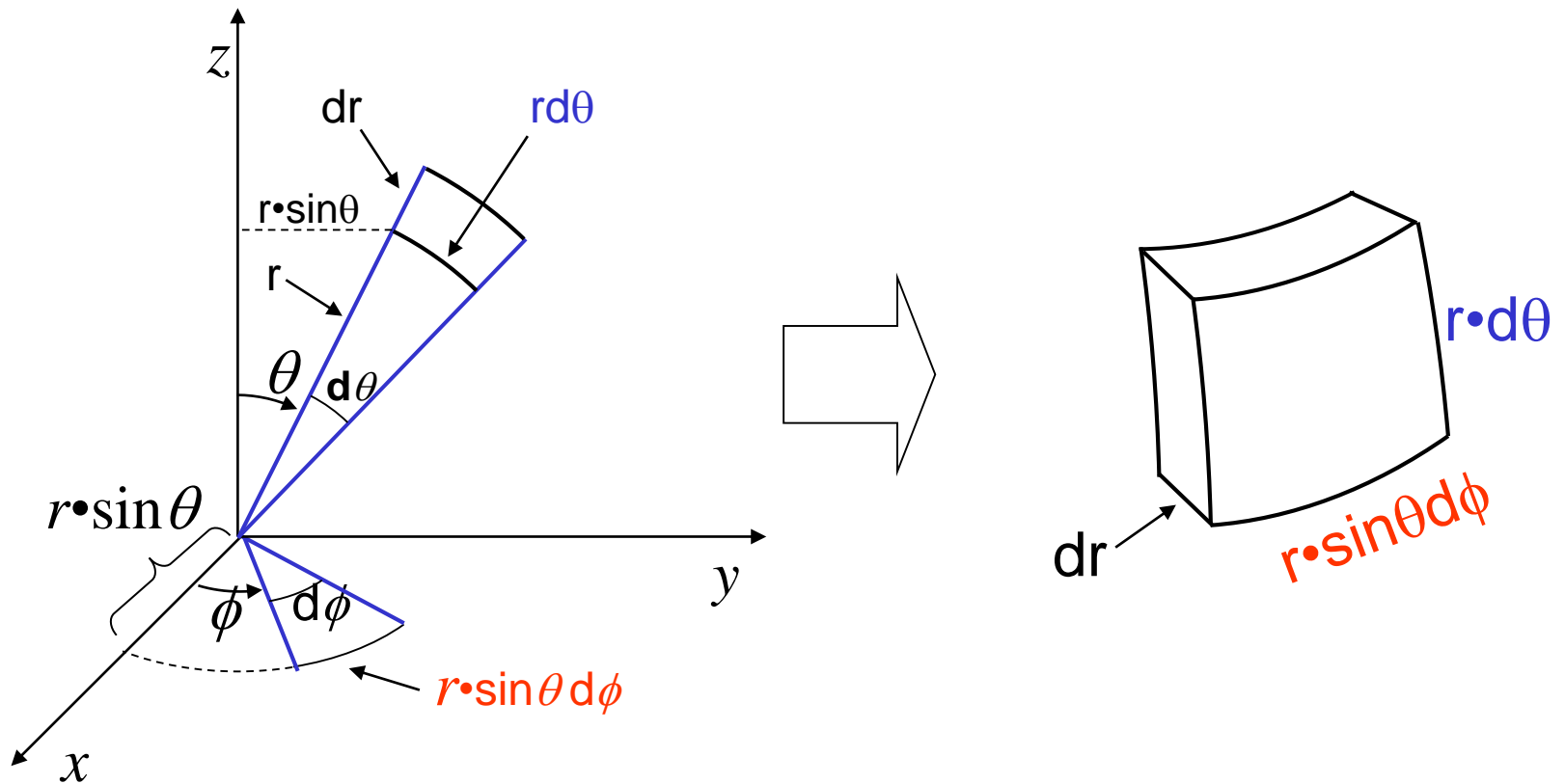
$$dV \equiv d\tau = dx\ dy\ dz$$

In polar spherical coordinates, when we change r, θ, and ϕ by an infinitesimal amount, it does not map out a perfect cube.

Indeed, the infinitesimal volume mapped out depends on r and θ.

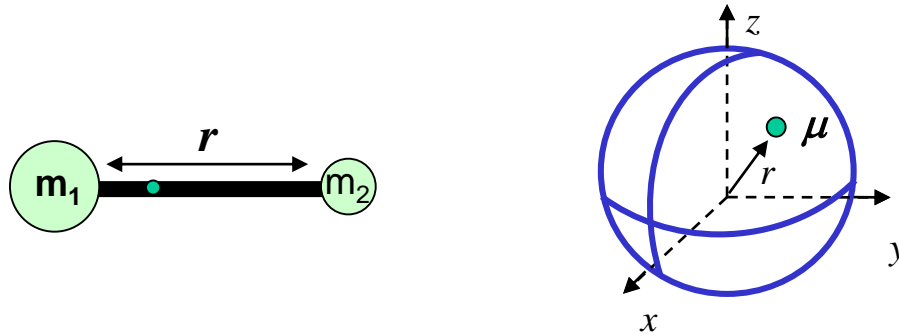The integration element in polar spherical coordinates is given by:

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

z

dr rdθ

r•sinθ

r

θ **d**θ

r•sinθ

ϕ dϕ

y

r•sinθ dϕ

x

r•dθ

dr

r•sinθdϕ

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

Back to our 3-Dimensional Rigid Rotor

Recall that r is fixed.

The Schrödinger equation for this problem is:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi = E\psi$$

$$-\frac{\hbar^2}{2\mu}\left(\underbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi = E\psi$$

This term is zero because our radius is fixed, and the wave function is a function of ϕ and θ, but not r.

$$\psi = \psi(\theta,\phi)$$

The Schrödinger equation for the 3-D rigid rotor problem becomes:

$$-\frac{\hbar^2}{2\mu r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}\psi(\theta,\phi)=E\psi(\theta,\phi)$$

Notice that the second term contains both θ and ϕ, so in this form, the problem is **not separable** and we cannot use that very nice theorem.

However, if we multiply both sides of the equation, by $\sin^2\theta$, the problem does become **pseudo-separable**.

$$-\sin^2\theta\frac{\hbar^2}{2\mu r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}\psi(\theta,\phi)=E\psi(\theta,\phi)\sin^2\theta$$

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

This suggests that there exists a solution of the form:

$$\psi(\theta,\phi) = \chi(\phi) \cdot \eta(\theta)$$

The above is a product of two independent functions, one dependent only on ϕ and the other only on θ.

If we substitute this into our Schrödinger equation we have:

$$-\frac{\hbar^2}{2\mu r^2}\left\{\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right\}\chi(\phi)\cdot\eta(\theta) = E\sin^2\theta\cdot\chi(\phi)\cdot\eta(\theta)$$

We should be able to now collect all of the ϕ's on one side and all of the θs on the other side. If we can do this, then we can apply our standard **method of separation of variables**.

$$-\frac{\hbar^2}{2\mu r^2}\frac{1}{\chi(\phi)}\frac{\partial^2\chi(\phi)}{\partial\phi^2} = \lambda = \text{constant}$$

$$-\frac{\hbar^2}{2\mu r^2}\frac{1}{\eta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\eta(\theta) - E\sin^2\theta = \lambda = \text{same constant}$$

Let's solve for the ϕ term first. *It looks easier!*

$$-\frac{\hbar^2}{2\mu r^2}\frac{1}{\chi(\phi)}\frac{\partial^2\chi(\phi)}{\partial\phi^2} = \lambda$$

Moving the $1/\chi$ to the right side gives:

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial^2}{\partial\phi^2}\chi(\phi) = \lambda\chi(\phi)$$

Doesn't this look familiar?

Recall the Schrödinger equation from the 2-D rotor we just solved:

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial^2}{\partial \phi^2}\psi(\phi) = E\psi(\phi) \qquad 0 \le \phi \le 2\pi$$

It is identical except that we have a constant λ instead of the energy, E:

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial^2}{\partial \phi^2}\chi(\phi) = \lambda\chi(\phi) \qquad 0 \le \phi \le 2\pi$$

Our function $\chi(\phi)$ must satisfy the same boundary condition that

$$\chi(0) = \chi(2\pi)$$

So we know that our 2-D rigid rotor wave functions will satisfy this eigenvalue equation:

$$\chi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \qquad m = 0, \pm 1, \pm 2, \pm 3 \ldots$$

This is not the energy but $\longrightarrow$ $\lambda_m = \dfrac{m^2\hbar^2}{2\mu r^2}$
rather the constant λ.

Recall that we had

$$-\frac{\hbar^2}{2\mu r^2}\frac{1}{\chi(\phi)}\frac{\partial^2 \chi(\phi)}{\partial\phi^2} = \lambda = \text{ constant}$$

$$-\frac{\hbar^2}{2\mu r^2}\frac{1}{\eta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\eta(\theta) - E\sin^2\theta = \lambda = \text{ same constant}$$

Now that we have an expression for this constant λ, we have an equation for which we can solve for the function $\eta(\theta)$.

$$-\frac{\hbar^2}{2\mu r^2}\frac{1}{\eta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\eta(\theta) - E\sin^2\theta = \frac{m^2\hbar^2}{2\mu r^2}$$

Our total rigid rotor wave function will then be:

$$\psi(\theta,\phi) = \chi(\phi)\cdot\eta(\theta) = \frac{1}{\sqrt{2\pi}}e^{im\phi}\cdot\eta(\theta)$$

$$-\frac{\hbar^2}{2\mu r^2}\frac{1}{\eta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\eta(\theta)-E\sin^2\theta=\frac{m^2\hbar^2}{2\mu r^2}$$

We now have to solve the above differential equation for $\eta(\theta)$.

Rearranging gives:

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}-\frac{m^2}{\sin^2\theta}\right)\eta(\theta)=E\eta(\theta)$$

This differential equation is **not easy** to solve! Just like harmonic oscillator, it involves a power series solution.

Again, we will not solve this DE explicitly. Instead, the solutions will only be presented we will check their validity.

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}-\frac{m^2}{\sin^2\theta}\right)\eta(\theta)=E\eta(\theta)$$

The solution to the above differential equation that we derived is:

$$\eta(\theta)=(-1)^m\underbrace{\left[\frac{2\ell+1}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2}}P_\ell^{|m|}(\cos\theta)\qquad\begin{array}{l}\ell=0,1,2...\\[8pt]m=0,\pm1,\pm2,...\pm\ell\end{array}$$

ℓ and m are the quantum numbers. Notice that there are restrictions placed on m based on the value of ℓ . This actually results naturally from the solution of the differential equation.

These quantum numbers are not completely independent of one another because our problem was only pseudo-separable.

The first term is just a normalization constant.

$$\eta(\theta) = (-1)^m \left[\frac{2\ell+1}{2} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{1/2} P_\ell^{|m|}(\cos\theta)$$

$$\ell = 0, 1, 2...$$
$$m = 0, \pm 1, \pm 2, ... \pm \ell$$

The $P(\cos\theta)$'s are called the **associated Legendre Polynomials**. Notice $P(\cos\theta)$ is a function of the function $\cos\theta$. The first few of these polynomials are:

$$P_\ell^{|m|}(\cos\theta)$$

$P_0^0 = 1$	$P_1^0 = \cos\theta$	$P_2^0 = \frac{1}{2}\left(3\cos^2\theta - 1\right)$	$P_3^0 = \frac{1}{2}\left(5\cos^3\theta - 3\cos\theta\right)$
	$P_1^1 = \sin\theta$	$P_2^1 = \frac{1}{2}\sin\theta \cdot \cos\theta$	$P_3^1 = \frac{3}{2}\left(5\cos^2\theta - 1\right)\sin\theta$
		$P_2^2 = \sin^2\theta$	$P_3^2 = 15\cos\theta\sin^2\theta$
			$P_3^3 = 15\sin^3\theta$

Although P is a function of $\cos\theta$, some of the polynomials contain $\sin\theta$. The reason for this is that these particular polynomials involve the derivative of $\cos\theta$, which is $\sin\theta$.

The Wave Functions of the 3-D Rigid Rotor are Called Spherical Harmonics

Recall that the total wave function of our original Schrödinger equation was the product of $\chi(\phi)$ and $\eta(\theta)$.

$$Y_{\ell m}(\theta, \phi) = 0$$

For historical reasons, the wave functions are called **Spherical Harmonics** and are given the symbol Y. (They were used to describe the vibration of elastic spheres.)

$$\psi_{\ell m}(\theta, \phi) = Y_{\ell m}(\theta, \phi) = (-1)^m \left[\frac{2\ell+1}{2} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{1/2} P_\ell^{|m|}(\cos\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$\ell = 0, 1, 2...$$

$$m = 0, \pm 1, \pm 2, ... \pm \ell$$

Why <u>spherical harmonics</u>? What do they look like?

First, consider vibrations in **one dimension**.

Example   A <u>**vibrating string**</u> of length L is described
by functions such as

$$\sin(n_x \pi x/L)$$
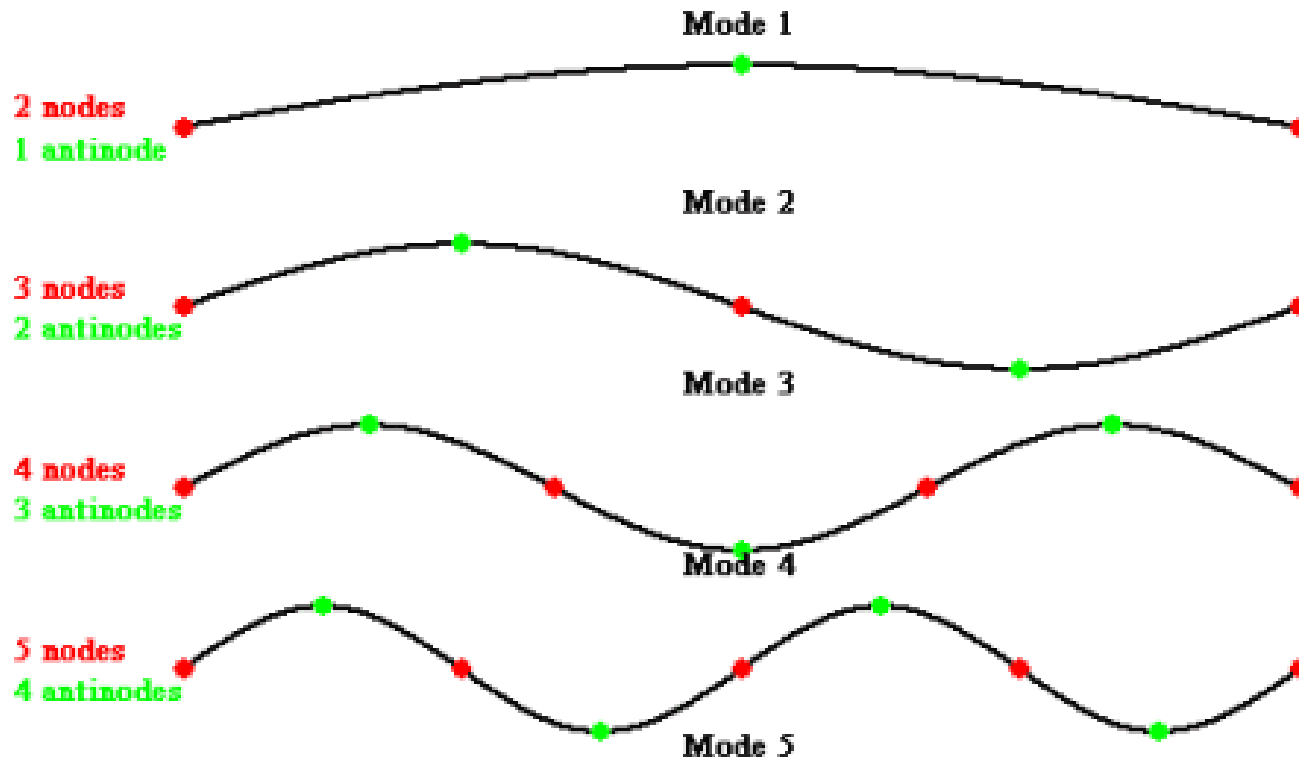
Next, consider vibrations in **two dimensions**.

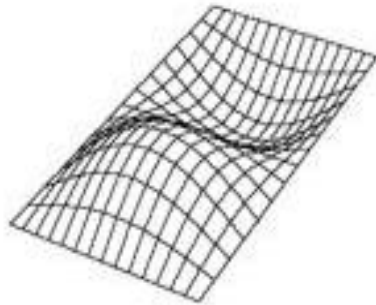**Example**   A **vibrating rectangular membrane** of length *L* and width *W*.

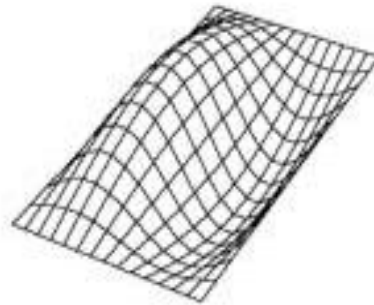Described by functions such as
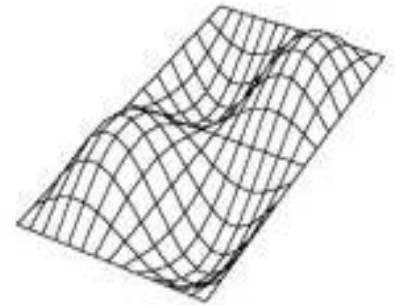
sin($n_x\pi$ x/L) sin(n_y π y/W)

(1,1) mode   (1,2) mode   (2,1) mode   (2,2) mode

Spherical Harmonics describe vibration in 3 dimensions

## Example   A vibrating spherical membrane

Many possibilities !

Zonal   Tesseral *   Sectoral

Types of Spherical Harmonics
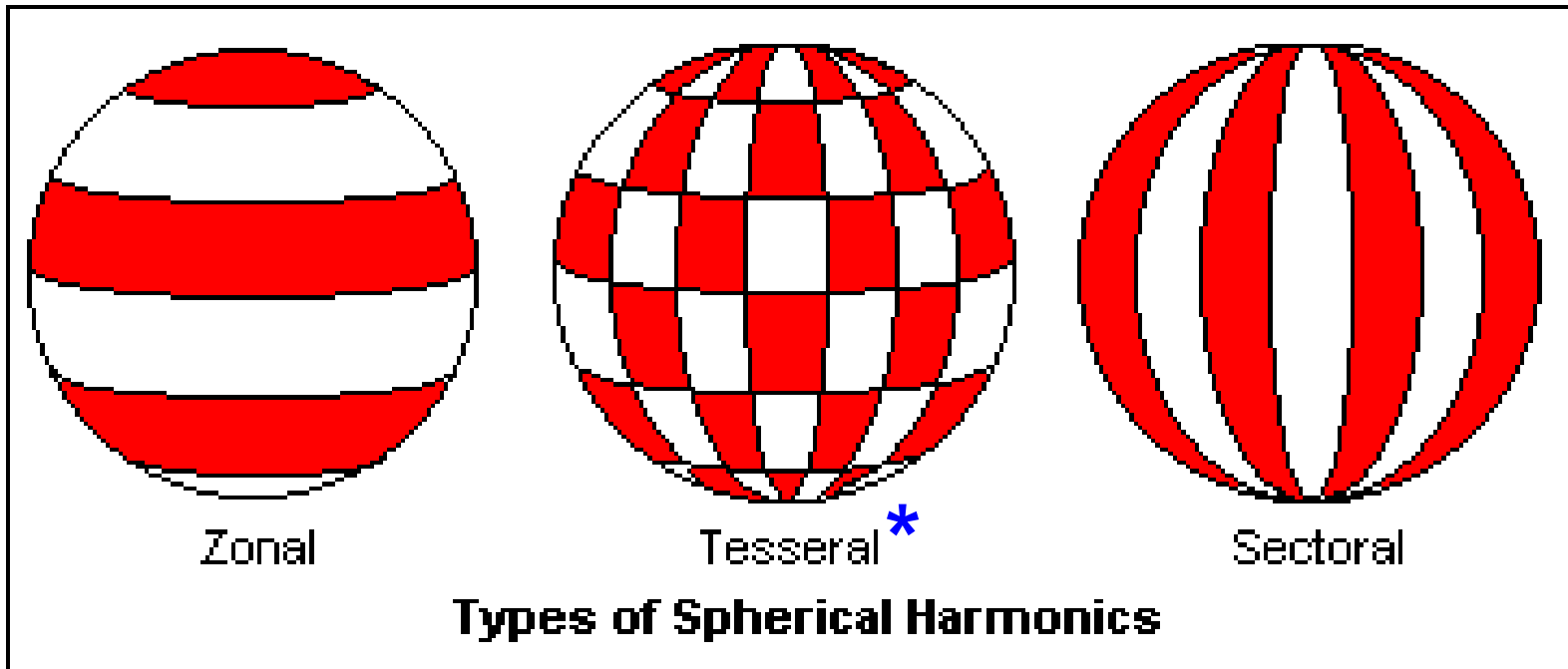
Red indicates **positive displacement**. **White** is negative displacement.

*from tessera, a square piece of mosaic tile

Spherical Harmonics can be visualized by considering **nodal lines** where $Y_{\ell m}(\theta, \phi) = 0$

$\ell - |m|$ latitudinal nodes

$2|m|$ longitudinal nodes

Zonal   Tesseral   Sectoral

Types of Spherical Harmonics
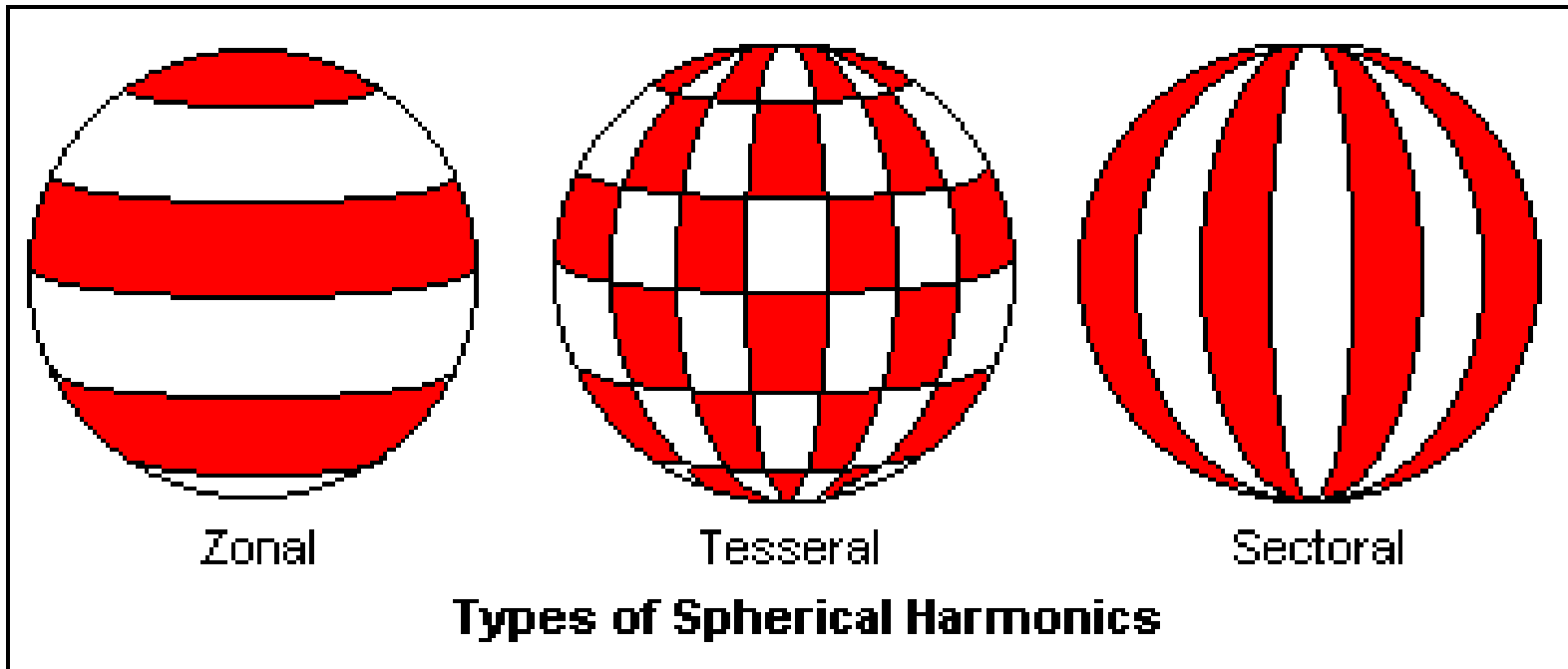
Much wider significance of spherical harmonics:

Just as sine and cosine functions provide an **orthogonal basis set of functions** for **one-dimensional** systems

$$f(x) \ = \ \sum_i [A_i \cos(a_i x) \ + \ B_i \sin(b_i x)]$$

spherical harmonics provide an **orthogonal basis set of functions** for **spherical** systems

$$f(\theta, \phi) \ = \ \sum_\ell \sum_m A_{\ell m} Y_{\ell m}(\theta, \phi)$$

in convenient angular coordinates.

Can you suggest why spherical harmonics are very widely used in geology, astronomy, acoustics, quantum chemistry, …

The first few wave functions of the 3-D rigid rotor are:

$$Y_{\ell m}(\theta, \phi) \qquad \ell = 0, 1, 2...$$

$$m = 0, \pm 1, \pm 2,... \pm \ell$$

$\ell = 0$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$\ell = 2$

$$Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2} \left(3\cos^2 \theta - 1\right)$$

$\ell = 1$

$$Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

$$Y_{2\pm 1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cdot \cos \theta \cdot e^{\pm i\phi}$$

$$Y_{1\pm 1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta \cdot e^{\pm i\phi}$$

$$Y_{2\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta \cdot e^{\pm 2i\phi}$$

There is no need to memorize these functions, but you should be know how to work with them and be familiar with their interpretation.

The 3-D Rigid Rotor Wave Functions are Orthonormal

Because the spherical harmonics are also the wave functions of the 3-D rigid rotor, and satisfy the corresponding Schrödinger equation, we would expect the spherical harmonics to be orthonormal.

Recall that the orthonormalization condition is given generically as:

[$\delta_{ii} = 1$, δ_{ik} if $i \neq k$ (Kronecker's delta)]

$$\int f_i^* f_j \mathrm{d}\tau = \delta_{ij}$$

Explicitly, show that the Y_{00} spherical harmonic is normalized and orthogonal to Y_{11}.

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \qquad Y_{1\pm1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \cdot e^{\pm i\phi}$$

The 3-D Rigid Rotor Energy Levels

As with the wave functions, we simply present the energies obtained from solving the rigid-rotor Schrödinger equation:

$$E_{\ell m} = \ell(\ell+1)\frac{\hbar^2}{2\mu r^2} \qquad \begin{array}{l} \ell = 0,\ 1,\ 2... \\[1ex] m = 0,\ \pm1,\ \pm2,...\ \pm\ell \end{array}$$

Notice that the total energy <u>does not depend</u> on the quantum number m
We will discuss the physical interpretation of this shortly.

• Zero-point energy is zero, just like the 2-D rotor. $\qquad E_{00} = 0$

• Energy levels increase with ℓ $\qquad\qquad E_{\ell m} = \left(\ell^2 + \ell\right)\frac{\hbar^2}{2\mu r^2}$

• Degeneracies. $g_\ell = 2\ell + 1$
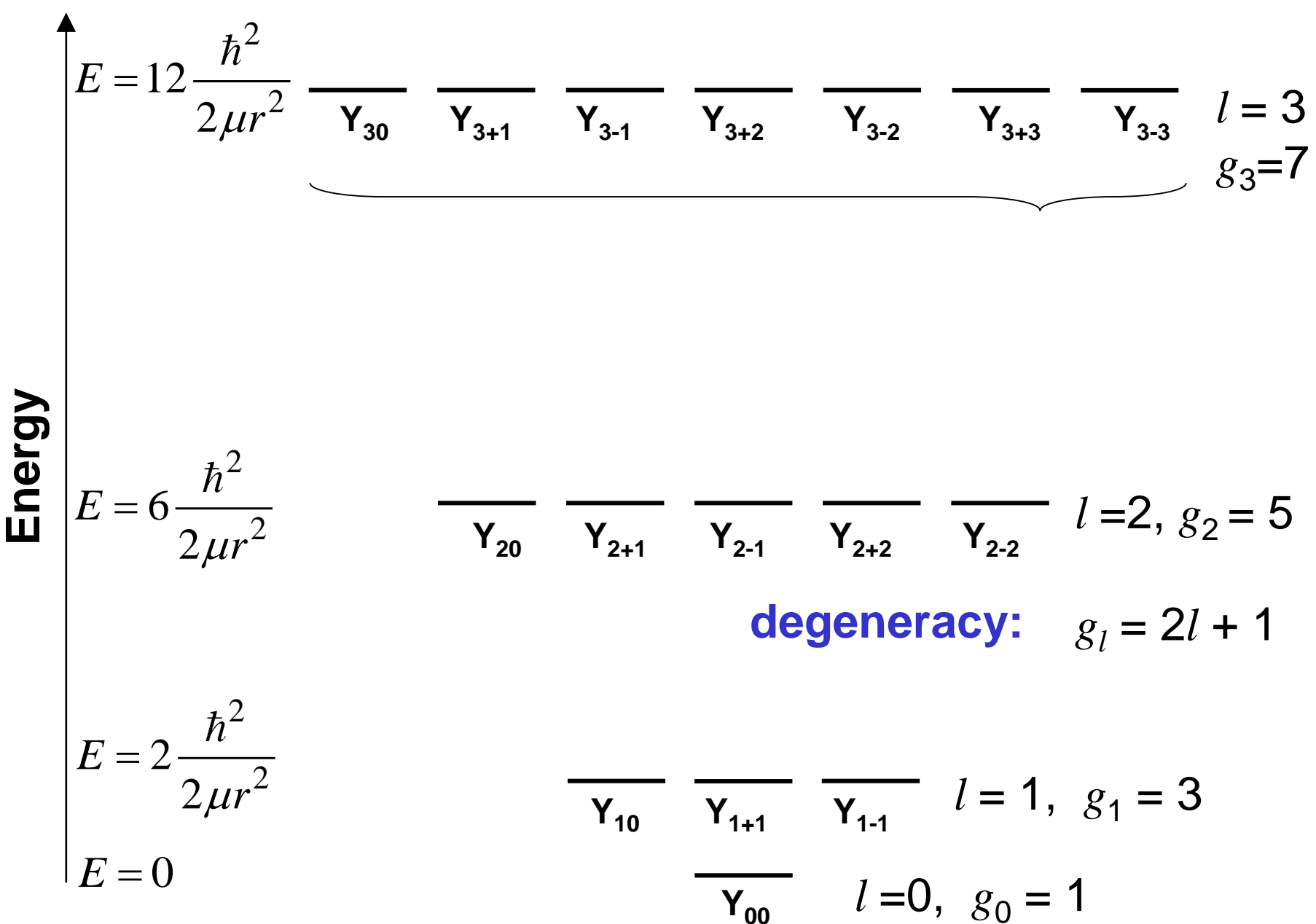
What do the Wave Functions Look Like?

The visualization of the spherical harmonics is complicated by the fact that the functions have imaginary components and because of the 3-dimensionality of the problem.
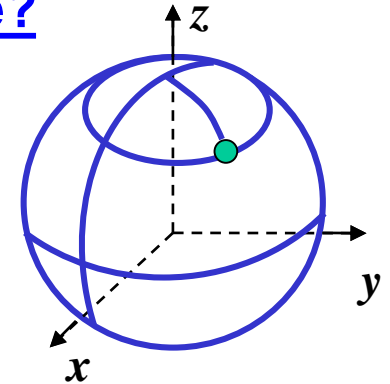
The complex nature of the wave functions means that we must plot the real or imaginary parts of the wave function separately, or plot the square of the wave function.

$$\text{Re}\left(Y_{\ell m}(\theta,\phi)\right) \qquad \text{Im}\left(Y_{\ell m}(\theta,\phi)\right) \qquad \left|Y_{\ell m}(\theta,\phi)\right|^2$$

One obvious way to visual the spherical harmonics is to plot the function on the surface of the sphere.

Recall we have an effective one-particle on the sphere and the square of the wave function will give the probability of finding the particle at that point on the sphere.

What do the **probability distribution functions** of the following spherical harmonics look like?

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

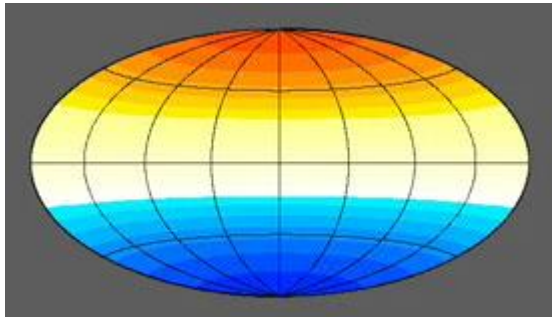$$Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$
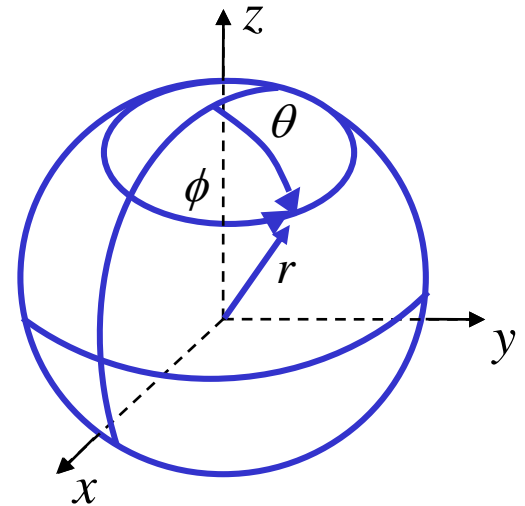
$$0 \leq \theta \leq \pi$$

$$0 \leq \phi \leq 2\pi$$

One way to interpret the spherical harmonics are as **standing waves on the surface of a sphere**.

It turns out that the above is not a common visualization of the spherical harmonics because one has to use a different intensity of shading to represent different probabilities.

$\ell = 1 \ m=0$

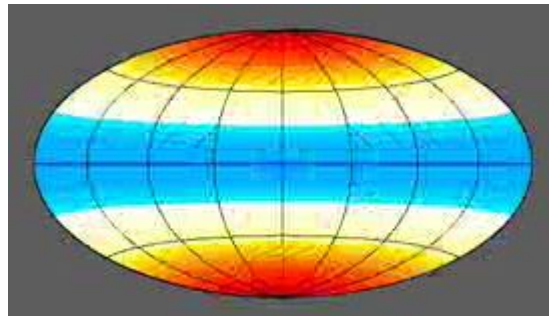Plots of the real component of the spherical harmonics on the 'flattened' spheres:

$$\mathrm{Re}\big(Y_{\ell m}(\theta,\phi)\big)$$
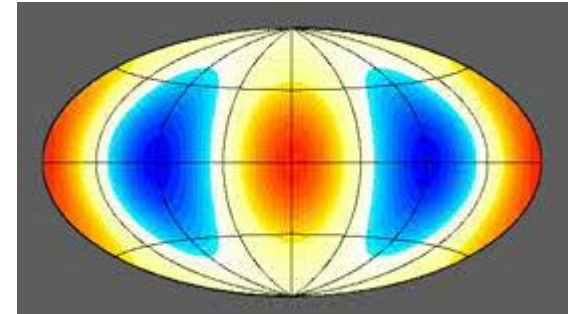
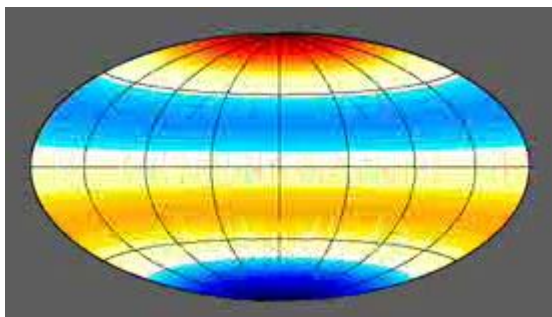**What do the different colors represent?**
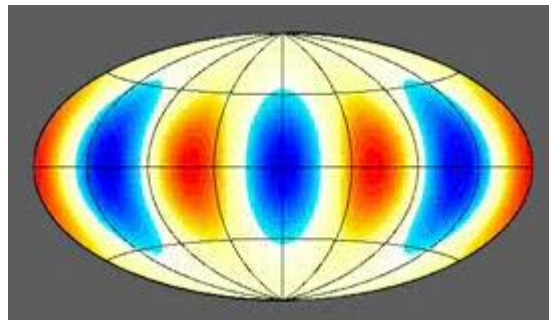
$\ell = 1 \quad m=1$
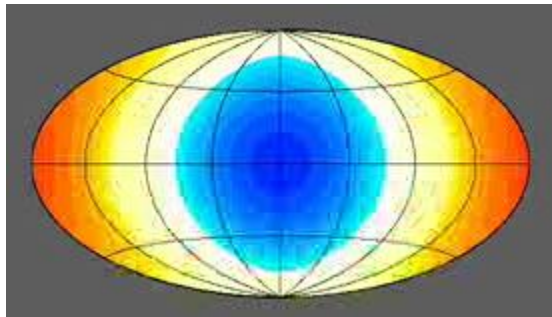
$\ell = 2 \quad m=0$

$\ell = 2 \quad m=2$
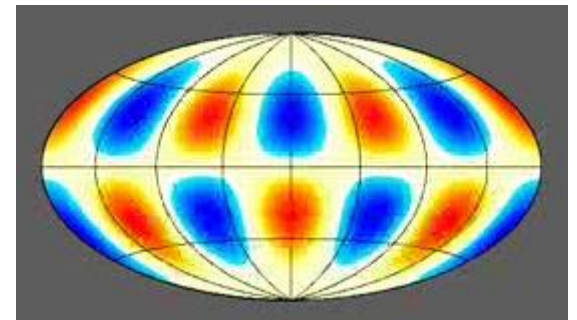

$\ell = 3 \quad m=0$

$\ell = 3 \quad m=3$

$\ell = 4 \quad m=3$

Another way to represent the spherical harmonic functions is to **plot the magnitude of the probability density as a *distance from the origin*.**

The greater the probability density for any θ and ϕ, the longer the distance from the origin.

Let's do this for the θ dependence of the following spherical harmonics.

$$|Y_{00}|^2 = \left|\frac{1}{\sqrt{4\pi}}\right|^2 \qquad\qquad |Y_{10}|^2 = \left|\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta\right|^2$$
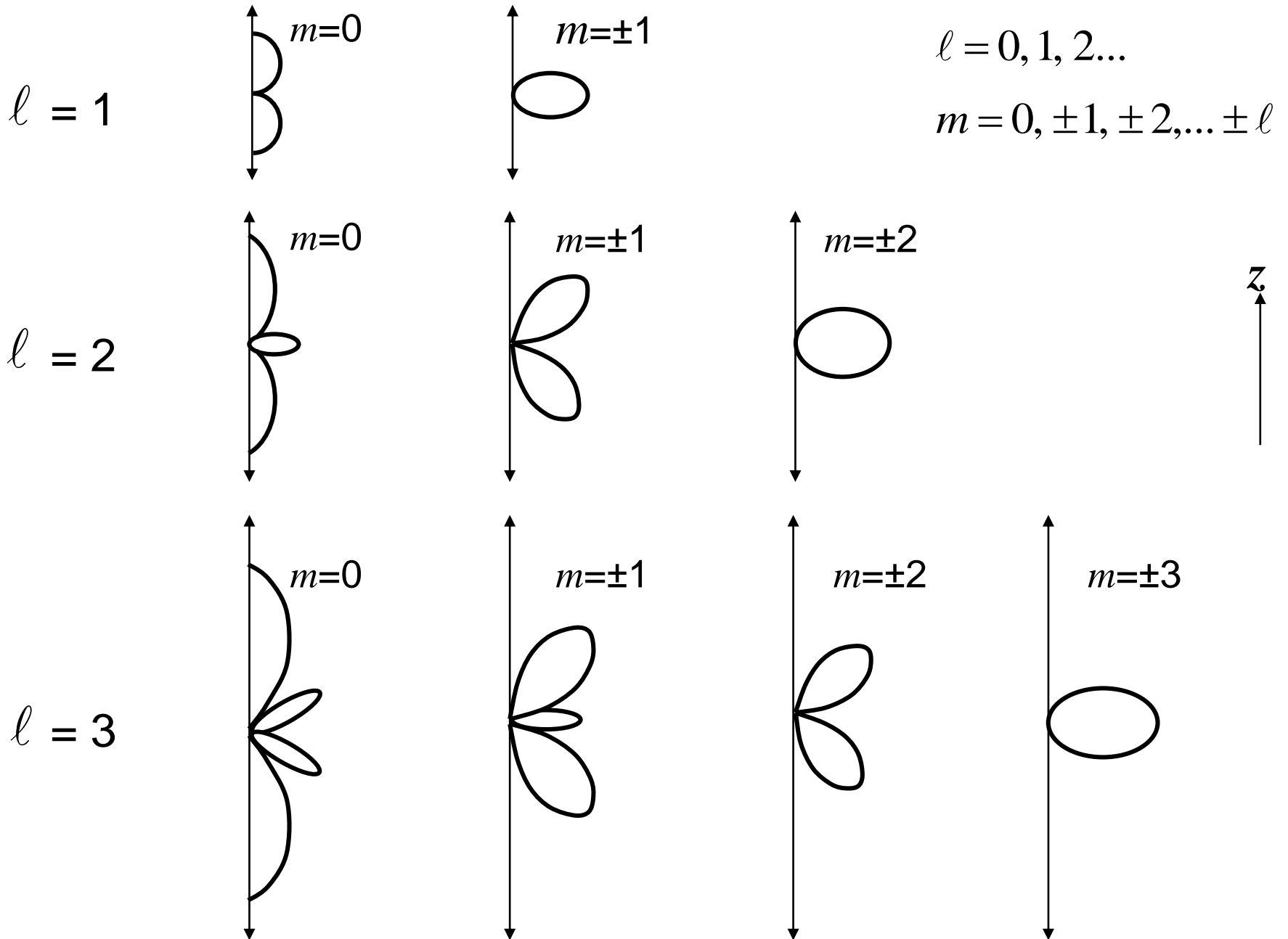
$$|Y_{11}|^2 = \left|\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta \cdot e^{+i\phi}\right|^2$$

Consider the θ dependence of:

$$Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$
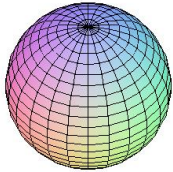
θ dependence of the $|Y_{lm}|^2$

$\ell = 0, 1, 2...$

$m = 0, \pm 1, \pm 2,... \pm \ell$

$\ell = 1$

$m{=}0$ $m{=}\pm 1$

$\ell = 2$

$m{=}0$ $m{=}\pm 1$ $m{=}\pm 2$

z

$\ell = 3$

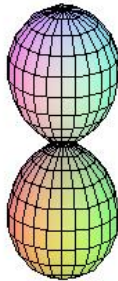$m{=}0$ $m{=}\pm 1$ $m{=}\pm 2$ $m{=}\pm 3$
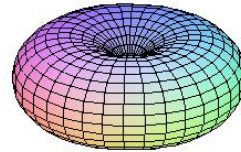
θ and ϕ dependence of the $|Y_{lm}|^2$
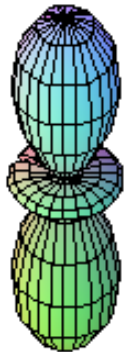

$\ell = 0$

$|Y_{00}|^2$

$\ell = 1$

$|Y_{10}|^2$ $|Y_{1\pm1}|^2$

$\ell = 2$

$|Y_{20}|^2$ $|Y_{2\pm1}|^2$ $|Y_{2\pm2}|^2$
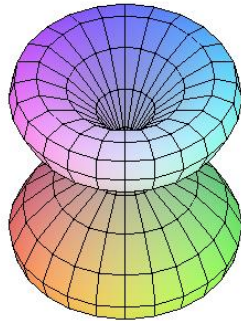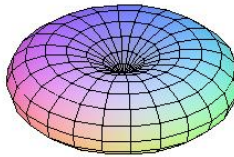
$\ell = 3$
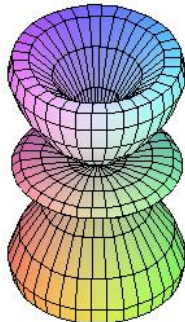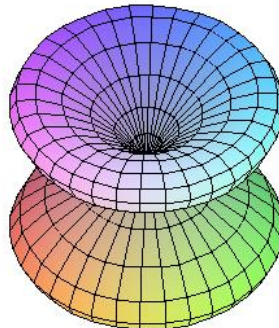
$|Y_{30}|^2$ $|Y_{3\pm1}|^2$ $|Y_{3\pm2}|^2$ $|Y_{3\pm3}|^2$

Real and Imaginary Components

$\left|\text{Re}\left(Y_{1+1}\right)\right|$ $\left|\text{Im}\left(Y_{1+1}\right)\right|$

$\left|\text{Re}\left(Y_{2+1}\right)\right|$ $\left|\text{Im}\left(Y_{2+1}\right)\right|$

$\left|\text{Re}\left(Y_{2+2}\right)\right|$ $\left|\text{Im}\left(Y_{2+2}\right)\right|$
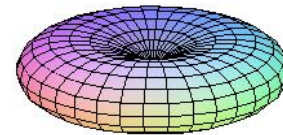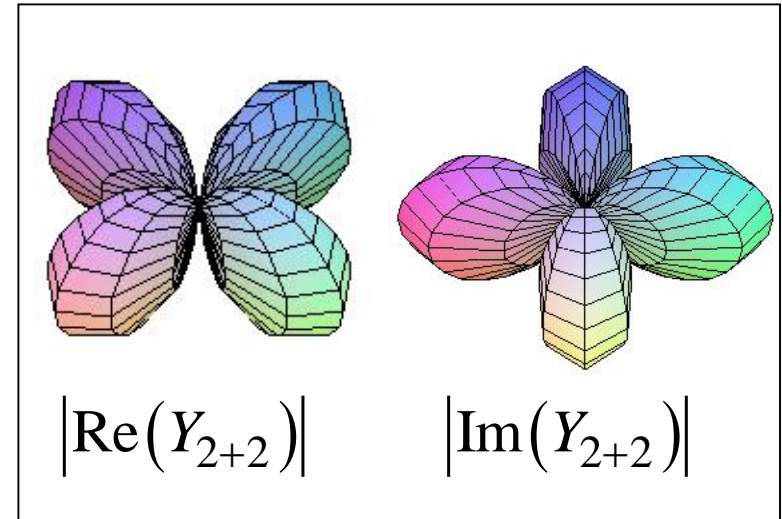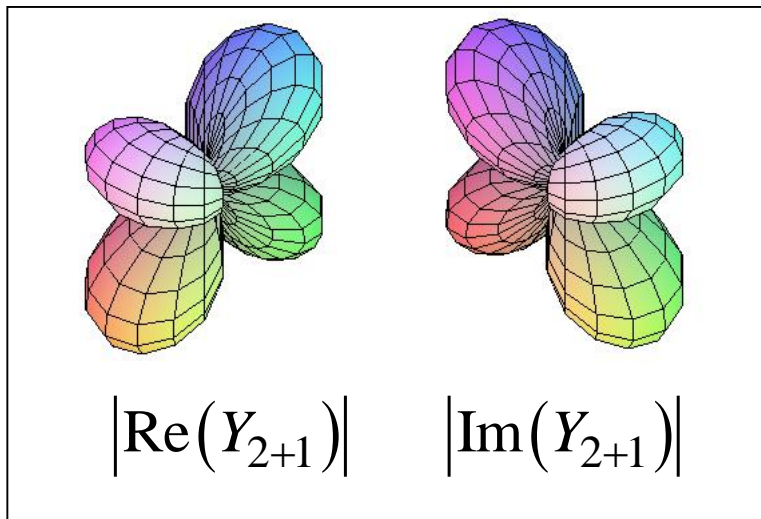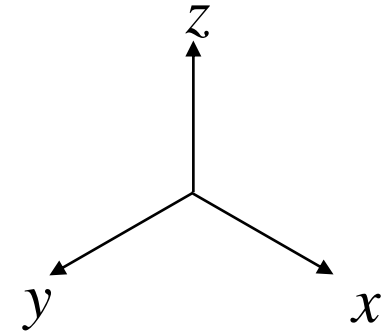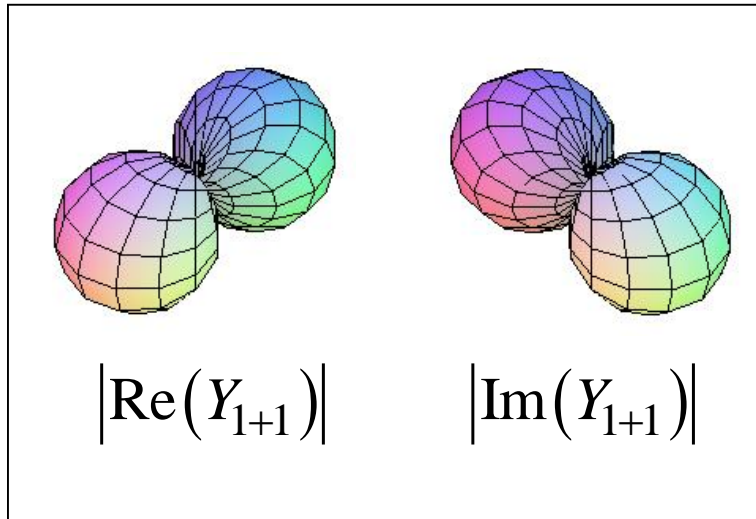
Notice that the real and imaginary components of each function are orthogonal to one another.

Angular Momentum Characterizes the Rigid Rotor States

For the 2-D rigid rotor, the angular momentum defined the state. In other words, each 2-D rotor state had a definite angular momentum.

One would expect this to be the same for the 3-D rigid rotor. This is indeed the case and we will see that the spherical harmonics are eigenfunctions of the angular momentum operators.

It turns out that the spherical harmonics are closely connected to our quantum mechanical interpretation of angular momentum.

Angular momentum is very important when discussing molecules because much of the motion of electrons in molecules is angular in nature.

We will now examine this relationship, to help us interpret the rigid rotor wave functions.

Linear Motion and Angular Motion
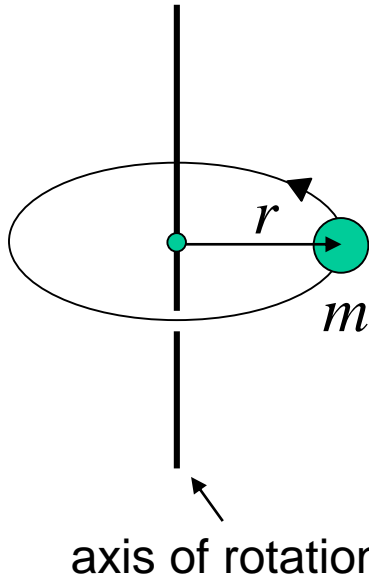
Recall the analogy between classical linear motion and classical angular motion:

axis of rotation
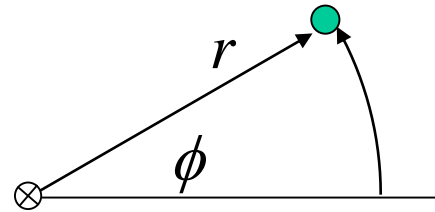
	linear	angular	
position	x	ϕ	angular position
mass	m	$I = mr^2$	moment of inertia
velocity	$\dot{x} = v$	$\dot{\phi} = \omega$	angular velocity
momentum	$p = mv$	$L = I\omega$	angular momentum
kinetic energy	$\dfrac{p^2}{2m}$	$\dfrac{L^2}{2I}$	angular kinetic energy

Classical Angular Momentum

The classical definition of angular momentum in Cartesian coordinates is

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (yp_z - zp_y)\hat{\mathbf{i}} - (xp_z - zp_x)\hat{\mathbf{j}} + (xp_y - yp_x)\hat{\mathbf{k}}$$

Angular momentum is a 3-D vector quantity.
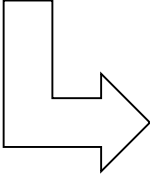
Using the right-hand-rule:

The faster the system is spinning, the greater the magnitude of the angular momentum.
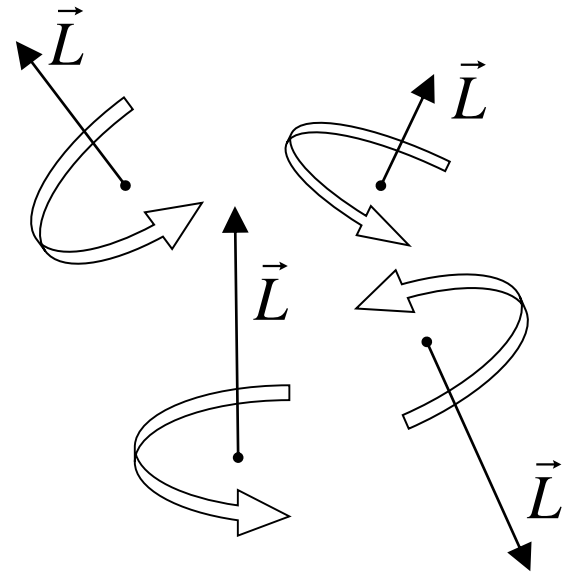
Angular momentum can be expressed in terms of its components

$$\vec{L} = \vec{r} \times \vec{p}$$

$$= (yp_z - zp_y)\hat{\mathbf{i}} - (xp_z - zp_x)\hat{\mathbf{j}} + (xp_y - yp_x)\hat{\mathbf{k}}$$

$$= L_x\hat{\mathbf{i}} + L_y\hat{\mathbf{j}} + L_z\hat{\mathbf{k}}$$

$$L_x = (yp_z - zp_y)$$
$$L_y = (zp_x - xp_z)$$
$$L_z = (xp_y - yp_x)$$
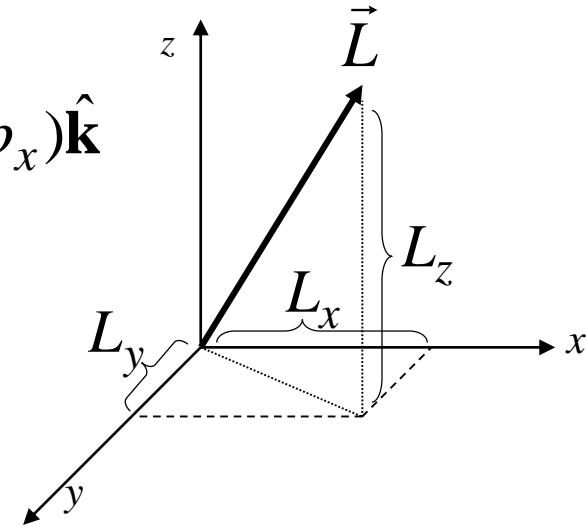
The components, L_x, L_y, and L_z are scalar quantities.

The Magnitude of the Angular Momentum

$$L^2 = \vec{L} \bullet \vec{L} = L_x^2 + L_y^2 + L_z^2$$

$$\left|\vec{L}\right| = \sqrt{L_x^2 + L_y^2 + L_z^2}$$
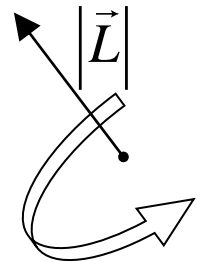
$|L|$ is the length of the angular momentum vector.

Quantum Mechanical Angular Momentum

Because angular momentum is a physical observable, it will be represented by a quantum mechanical linear Hermitian operator.

To obtain the quantum mechanical operator for angular momentum, we use the postulate telling us to express classical expressions in Cartesian coordinates and then make the following substitutions.

$$p_x \Rightarrow \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \qquad p_z \Rightarrow \hat{p}_z = -i\hbar \frac{\partial}{\partial z} \qquad p_z \Rightarrow \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

$$x \Rightarrow \hat{x} = x \qquad y \Rightarrow \hat{y} = y \qquad z \Rightarrow \hat{z} = z$$

The angular momentum operators in Cartesian coordinates are:

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \qquad \hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \qquad \hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

In polar spherical coordinates, the angular momentum operators (after lengthy derivations!) are:

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

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

And the L^2 operator is:

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

Angular Momentum Observables In Quantum Mechanics

Recall postulate 3.

For any measurement of the observable associated with the operator $\underline{A}$, the only values that will ever be observed are the eigenvalues a_n, which satisfy:

$$\hat{A}\phi_n = a_n\phi_n$$

Consider the square of the angular momentum. What are the eigenfunctions of the L^2 operator?

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

Let's find the eigenfunctions of the square of the angular momentum operator,

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

The L^2 operator is almost identical to the Hamiltonian operator for the 3-D rigid rotor given by:

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

They differ only by a constant, and therefore for the 3-D rigid rotor:

$$\hat{H} = \frac{\hat{L}^2}{2\mu r^2}$$

From the above, what do you think are eigenfunctions of the L^2 operator? What are the eigenvalues?

The following expression will be useful: $E_{\ell m} = \ell(\ell+1)\dfrac{\hbar^2}{2\mu r^2}$

Spherical Harmonics are Eigenfunctions of the L^2 operator

$$\hat{L}^2 Y_{\ell m}(\theta, \phi) = \hbar^2 \ell(\ell+1) \cdot Y_{\ell m}(\theta, \phi)$$

From the 3rd postulate, we find that the allowed values of the magnitude of the angular momentum are:

$$L^2 = \ell(\ell+1)\hbar^2 \qquad \ell = 0, 1, 2, 3 \ldots.$$

$$|L| = \sqrt{\ell(\ell+1)}\hbar$$

So, angular momentum is quantized.

Classically, angular momentum can take any value. But in reality, it is a quantized property.

If we could make very precise measurements, we would find we could only accelerate the rotation of a ball in steps, not smoothly and continuously!

$\sqrt{12}\hbar$

$\sqrt{6}\hbar$

$\sqrt{2}\hbar$

0
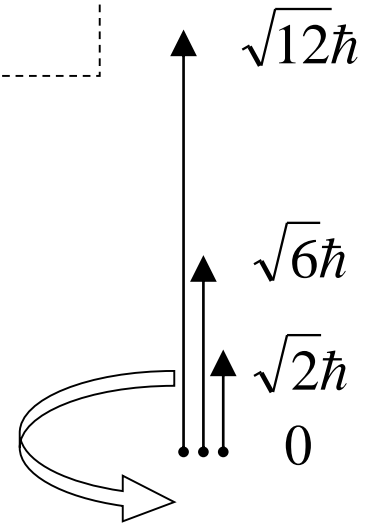
Precise Values of the Three Components of Angular Momentum Cannot Be Measured Simultaneously

Surprisingly, the angular momentum vector cannot be specified precisely. The reason for this is that the operators L_x, L_y and L_z do not commute.

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \qquad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

Each of the x, y and z components of the angular momentum, do however, commute with the square of the angular momentum operator:

$$[\hat{L}^2, \hat{L}_x] = 0 \qquad [\hat{L}^2, \hat{L}_z] = 0 \qquad [\hat{L}^2, \hat{L}_y] = 0$$

So, **we can precisely determine the <u>magnitude</u> of the angular momentum and only <u>one of its components</u> simultaneously.**

Commuting Operators and the Uncertainty Principle

$$[\hat{F}, \hat{G}] \; = \; \hat{F}\hat{G} \; - \; \hat{G}\hat{F}$$

Commuting Operators

$$[\hat{F}, \hat{G}] \; = \; 0 \qquad\qquad \hat{F}\hat{G} \; = \; \hat{G}\hat{F}$$

$$\sigma_F{}^2 \sigma_G{}^2 \; = \; 0$$

Non-Commuting Operators

$$[\hat{F}, \hat{G}] \; \neq \; 0 \qquad\qquad \sigma_F{}^2 \sigma_G{}^2 \; \geq \; -\frac{1}{4}\left(\int \psi * [\hat{F}, \hat{G}] \psi \, \mathrm{d}\tau\right)^2$$

Suppose we choose to determine L^2 and the z component of the angular momentum vector:

If we specify the z-component of the angular momentum, then the x and y components will be uncertain.

This uncertainty is represented in this picture as a

"cone of uncertainty"

z-axis

L_z

$\vec{L}$

z

x

$\hat{y}$
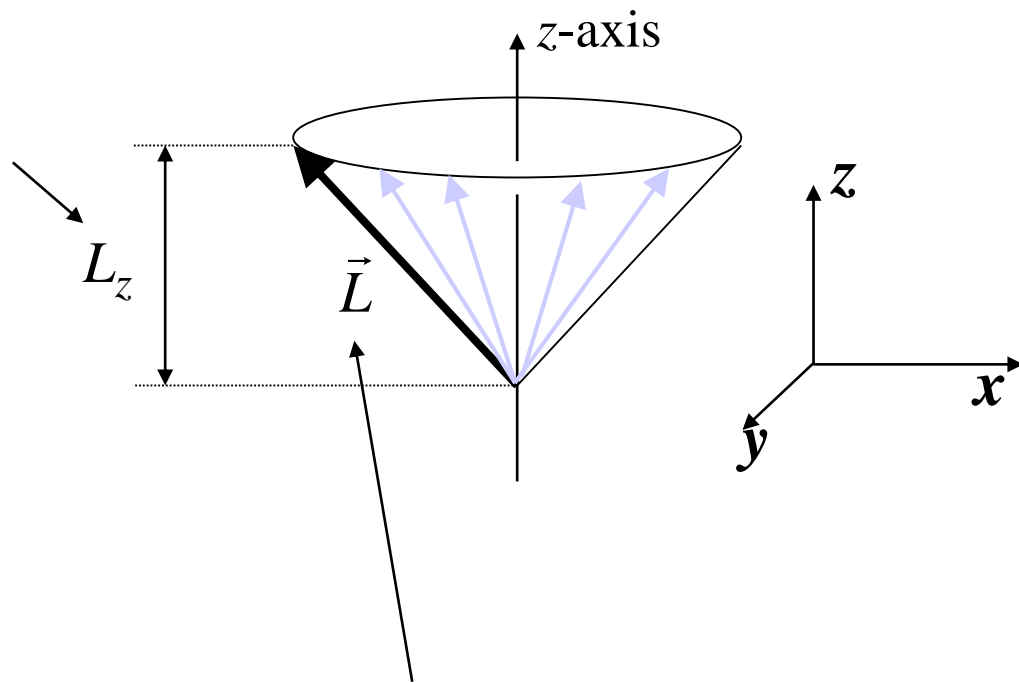
The magnitude of the angular momentum vector is given by:

$$\left|\vec{L}\right| = \sqrt{\ell(\ell+1)}\,\hbar$$

Spherical Harmonics are Also Eigenfunctions of the L_z Operator

We can simultaneously specify only one of the components of the angular momentum vector, and so it is by convention we specify the z-component of the angular momentum. *(NOTE: there is nothing special about the z-component of the angular momentum vector. It is traditional to use it.)*

The L_z operator is given by: $\quad \hat{L}_z = -i\hbar \dfrac{\partial}{\partial \phi}$

The spherical Harmonics are also eigenfunctions of the L_z operator.

$$Y_{\ell m}(\theta, \phi) \qquad \begin{array}{l} \ell = 0, 1, 2... \\ m = 0, \pm 1, \pm 2, ... \pm \ell \end{array}$$

What are the eigenvalues of the spherical harmonics with the L_z operator?

$$\hat{L}_z Y_{\ell m} = ?$$

Consequently, the only values of the z-component of the angular momentum that will be observed are:

$$L_z = m\hbar \qquad m = 0, \pm 1, \pm 2, \ldots$$

NOTE: Only integer values of $\hbar$-bar for the measurement of the angular momentum are allowed.

This is true for the measurement of the angular momentum for *any* system, not just for observations of the rigid rotor.

Expectation Values and Variances

If we want to measure a property of a given state, the expectation value gives the average that we will measure:

$$\langle a \rangle = \int\limits_{\text{all space}} \psi^* \hat{A} \psi \, d\tau$$

In the above, $\underline{A}$ is the operator corresponding to the property of interest, Ψ is the wave function of the given system we are interested in measuring.

In general there will be a spread in our measurements, and the above only gives the average.

The spread in the measurement can be quantified by the variance:

$$\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2$$

$$= \int \psi^* \hat{A}^2 \psi \, d\tau - \left(\int \psi^* \hat{A} \psi \, d\tau \right)^2$$

When Ψ is an Eigenfunction of A, the Variance is Zero

If the wave function of the state of interest, Ψ, happens to be an eigenfunction of the operator A, then there is no spread in the measurement of that property.

$$\text{If} \quad \hat{A}\psi = a\psi \quad \text{then} \quad \sigma_a^2 = \left\langle a^2 \right\rangle - \left\langle a \right\rangle^2 = 0$$

Moreover, the value that will be measured is the eigenvalue 'a' such that:

$$\left\langle a \right\rangle = \int_{\text{all space}} \psi^* \hat{A}\psi \, d\tau = \int_{\text{all space}} \psi^* a\psi \, d\tau = a \int_{\text{all space}} \psi^* \psi \, d\tau = a$$

normalized

For that system, the property, 'a', has a definite value that can be used to characterize the system.

Back to the 3-D Rigid Rotor

Because the 3D rigid rotor wave functions are eigenfunctions of the L^2 and L_z operators, we know that L^2 and L_z characterize the states of the rigid rotor.

In other words, each 3D rigid rotor state will have a unique combination of L^2 and L_z that defines the state.

$\overline{}$ $\overline{}$ $\overline{}$ $\overline{}$ $\overline{}$ $\ell = 2$

Y_{20} Y_{2+1} Y_{2-1} Y_{2+2} Y_{2-2}

$$E_{\ell m} = \ell(\ell+1)\frac{\hbar^2}{2\mu r^2}$$

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

$\overline{}$ $\overline{}$ $\overline{}$ $\ell = 1$

Y_{10} Y_{1+1} Y_{1-1}

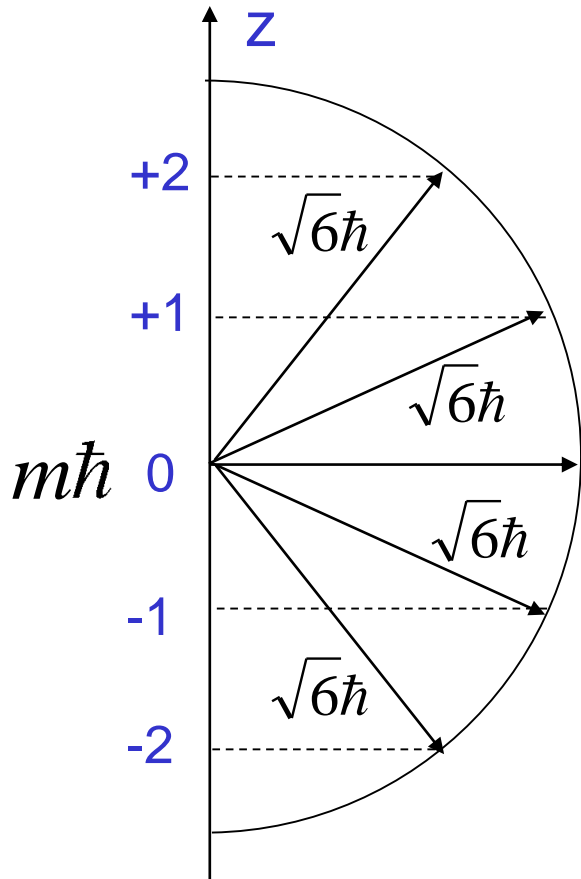$\overline{}$ $\ell = 0$

Y_{00}

$$L_z = m\hbar$$

For a rigid rotor, sketch the possible angular momentum vectors that are consistent with an ℓ = 0, 1 and 2 states.

Consider an $\ell = 2$ state. $|L| = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$

There are 5 allowed states with $m = -2, -1, 0, +1, +2$

$m\hbar$

z

+2 $\sqrt{6}\hbar$

+1 $\sqrt{6}\hbar$

0

$\sqrt{6}\hbar$

-1

$\sqrt{6}\hbar$

-2

From this depiction of the quantized angular momentum, we see the m quantum number defines the orientation of the angular momentum vector. This is sometimes referred to as *space quantization*.

It is important to realize that a state can only have one value of ℓ and m at one time.

Rotational Excited States of a Diatomic Molecule are Significantly Populated at Room Temperature

We can estimate the relative population of the rotational energy states by using the Boltzmann distribution law:

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{-\Delta E / kT} \qquad \Delta E = E_i - E_j$$

$$\overline{\text{Y}_{10}} \quad \overline{\text{Y}_{1+1}} \quad \overline{\text{Y}_{1-1}}$$

$$\overline{\text{Y}_{00}}$$

N_i/N_j is the ratio of the molecules in the ith and j^{th} rotational states. The g_i's are the degeneracies of these states. k is Boltzmann's constant and T is the temperature.

The ratio of the number of molecules in the ℓth rotational state and the ground rotational state is therefore (remember the degeneracy of the rotational states):

$$\frac{N_\ell}{N_0} = (2\ell + 1)e^{-\frac{\hbar^2}{2\mu r^2 kT}\ell(\ell+1)}$$

Rotational Spectra

The energy levels of the 3-D rigid rotor are given by:

$$E_{\ell m} = \ell(\ell+1)\frac{\hbar^2}{2\mu r^2} \qquad \begin{array}{l} \ell = 0,\ 1,\ 2... \\ m = 0,\ \pm 1,\ \pm 2,...\ \pm\ell \end{array}$$

Rotational Spectra Selection Rules

Not all transitions are allowed. Using the results of time-dependent perturbation theory, it can be shown that transitions are allowed only if the following integral is non-zero:

for a $\ell m \rightarrow \ell' m'$ transition

$$\int Y_{\ell m}^{*}\,\hat{\mu}\,Y_{\ell' m'}d\tau = \int_{0}^{2\pi}\int_{0}^{\pi} Y_{\ell m}^{*}\,\hat{\mu}\,Y_{\ell' m'}\sin\theta d\theta\,d\phi$$

where μ is the dipole moment operator (not the effective mass). $\hat{\mu} = e\vec{r}$

Using the 3-D rigid rotor wave functions, these integrals are only non-zero when:

$$\Delta \ell = \pm 1 \qquad \Delta m = \pm 1$$

and, **for diatomics, there must be a permanent dipole moment**.

These are the selection rules for rotational transitions.

Because the energy depends only on the quantum number ℓ we have for the **absorption transition** (molecular energy increasing):

$$E_\ell \rightarrow E_{\ell+1}$$

$$\Delta E_\ell = (\ell+1)(\ell+2)\frac{\hbar^2}{2\mu r^2} - \ell(\ell+1)\frac{\hbar^2}{2\mu r^2}$$

$$\Delta E_\ell = \frac{\hbar^2}{\mu r^2}(\ell+1)$$

← *notice the transition energy depends on the quantum number of the initial state*

$$\Delta E_\ell = \frac{\hbar^2}{\mu r^2}(\ell+1) = h\nu$$

For a typical diatomic molecule:

$$m = 10^{-25} \text{ to } 10^{-26} \text{ kg} \qquad r = 10^{-10} \text{ m}$$

If we use these values in the above equation for the transition energy, starting from $\ell = 0$, we find that the absorption frequencies of pure rotational spectra are 2 x 10^{10} to 10^{11} Hz

This is in the microwave region of the EM spectrum and the study of rotational transitions in molecules is called **microwave spectroscopy.**

Practical application:

Microwave ovens actually excite the rotational states of water molecules.

Microwave Spectroscopy has its Own Naming Conventions

In the field of microwave spectroscopy, it is conventional to use the symbols J and M for the quantum numbers ℓ and m, respectively:

$$\ell \to J \qquad m \to M$$

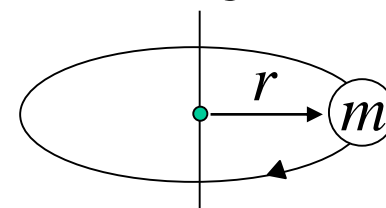*(We won't use this notation, but be aware of it.)*

Recall the definition of the **moment of inertia**:

$$I = \sum_i m_i r_i^2$$

← *distance of the ith particle from the origin.*

For a diatomic molecule, the moment of inertia is:

$$I = \mu r^2$$

So the transition energy is usually written as:

$$\Delta E_\ell = \frac{\hbar^2}{\mu r^2}(\ell + 1) \implies \Delta E = \frac{\hbar^2}{I}(\ell + 1)$$

It is also common practice to write the transition energy in terms of wave numbers (cm⁻¹) and a rotational constant of the molecule, B.

$$\Delta \tilde{E}_\ell = \tilde{\nu} = 2\tilde{B}(\ell+1) \qquad \tilde{B} = \frac{h}{8\pi^2 cI}$$

transition energy
in wave numbers,
cm⁻¹

rotational constant of the
molecule in cm⁻¹
(unique for every molecule)

transition involved	frequency of peak
$\ell = 0 \quad \rightarrow \quad \ell' = 1$	$\tilde{\nu} = 2\tilde{B}$
$\ell = 1 \quad \rightarrow \quad \ell' = 2$	$\tilde{\nu} = 4\tilde{B}$
$\ell = 2 \quad \rightarrow \quad \ell' = 3$	$\tilde{\nu} = 6\tilde{B}$
$\ell = 3 \quad \rightarrow \quad \ell' = 4$	$\tilde{\nu} = 8\tilde{B}$
$\vdots$	$\vdots$

The rigid rotor model predicts that the microwave spectrum of a diatomic molecule should consist of a series of equally spaced lines with a separation of $2\tilde{B}$
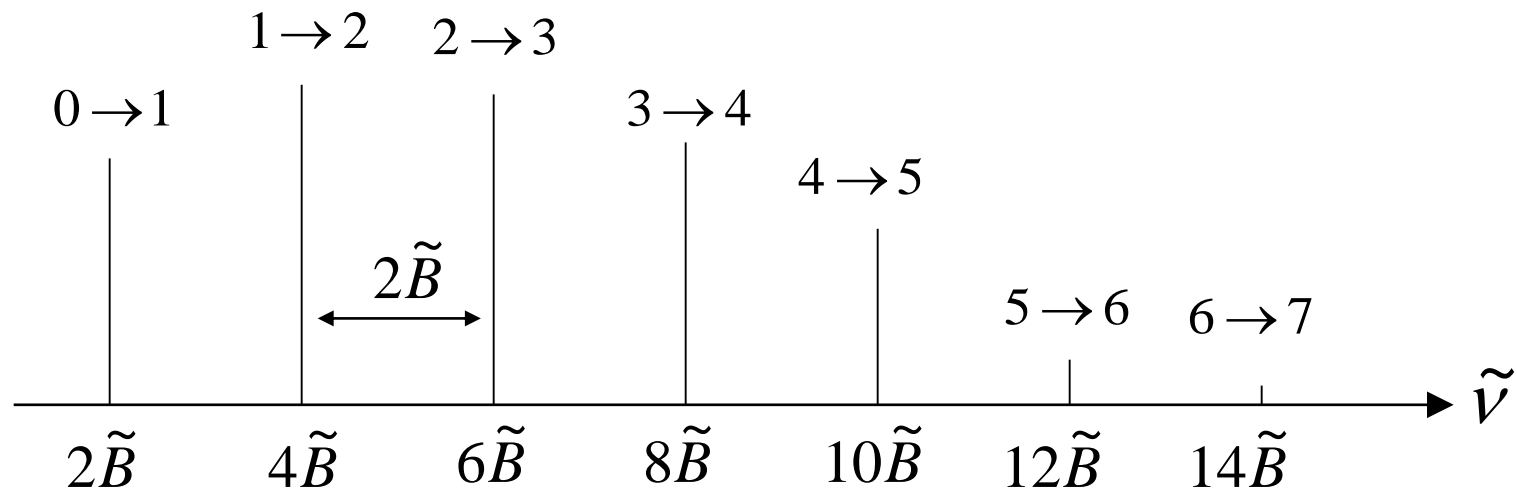
The intensity of the lines is given by the thermal distribution of the rotational states.

WHY?

Rotational spectra can be a used to determine accurate bond lengths. The pure rotational spectra of $H^{35}Cl$ is composed of a series of lines separated by 20.9 cm^{-1}. What is the bond length?

(0.129 nm)

Several unstable species can be recognized spectroscopically by their pure rotational spectrum. Compute the rotational spacings, 2B, for the OH radical (r = 0.97 Å) and for the OD radical.

2B for OH· is 37.5 cm^{-1} 2B for OD· is 20.0 cm^{-1}

So these two isotopomers can be distinguished by their pure rotational spectra.

Combined Rotational-Vibrational Spectra

Recall from our harmonic oscillator model of diatomic vibrations, we had the following **selection rules**:

$$\Delta n = \pm 1$$

Because the ground-vibrational state is mostly occupied and since the harmonic oscillator model predicts equally spaced energy levels, we predict one strong IR peak that we call the fundamental frequency:

$$\Delta E = E_{n+1} - E_n = \hbar\omega = \hbar\left(\frac{k}{\mu}\right)^{1/2}$$

For example, for $H^{35}Cl$ the harmonic oscillator model predicts a fundamental vibrational frequency at 2886 cm^{-1} with a force constant of k = 482 N/m.

With low resolution IR spectra, this is indeed what we observe, a single strong absorption peak. *But wait!* With high-resolution spectrometers, the band can be resolved into contributions from many individual transitions.

3000   2800

$\tilde{v}\,(\mathrm{cm}^{-1})$ *High Resolution IR spectrum of HCl*
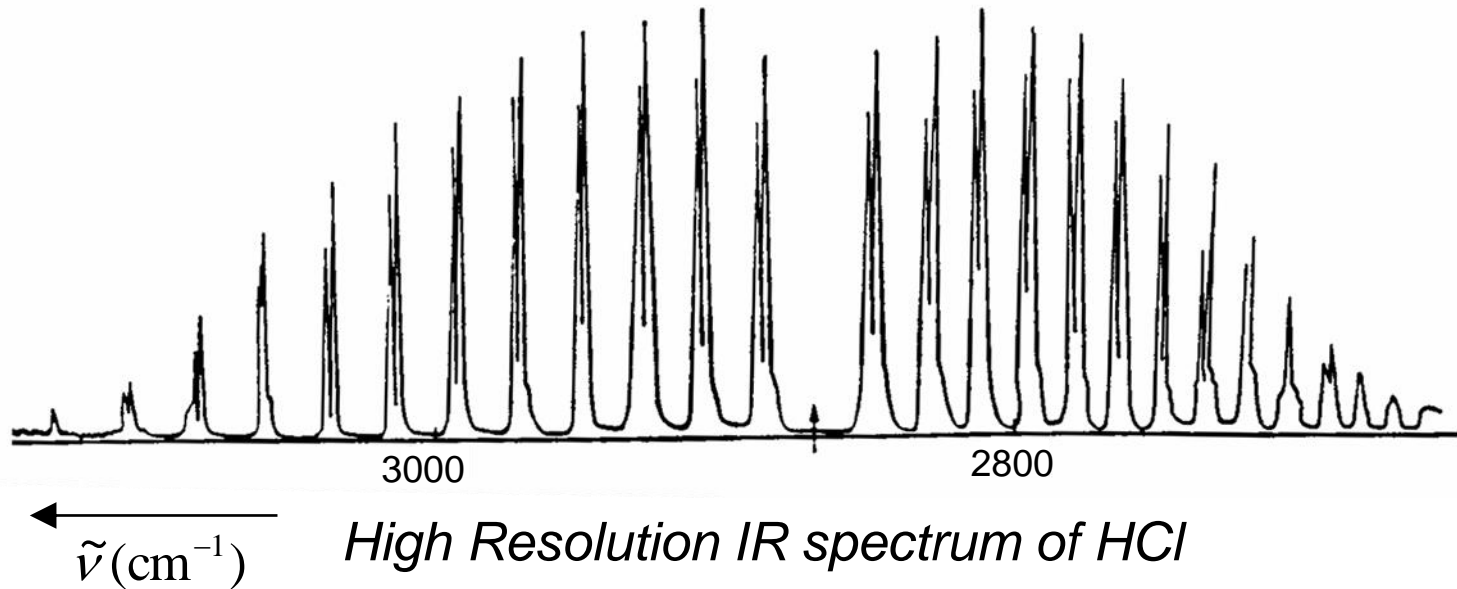
Notice the equally spaced peaks on either side of the fundamental frequency.

Why?   The vibrational energy level transitions are accompanied by changes in the rotational energy levels!   The selection rules for the combined transitions are also 'combined':

$$\Delta n = \pm 1 \quad \& \quad \Delta \ell = \pm 1$$

The energy change associated with the allowed transitions is therefore:

$$\Delta E = \Delta E_{vib} + \Delta E_{rot} = \hbar \omega + \frac{\hbar^2}{I}(\ell + 1)$$
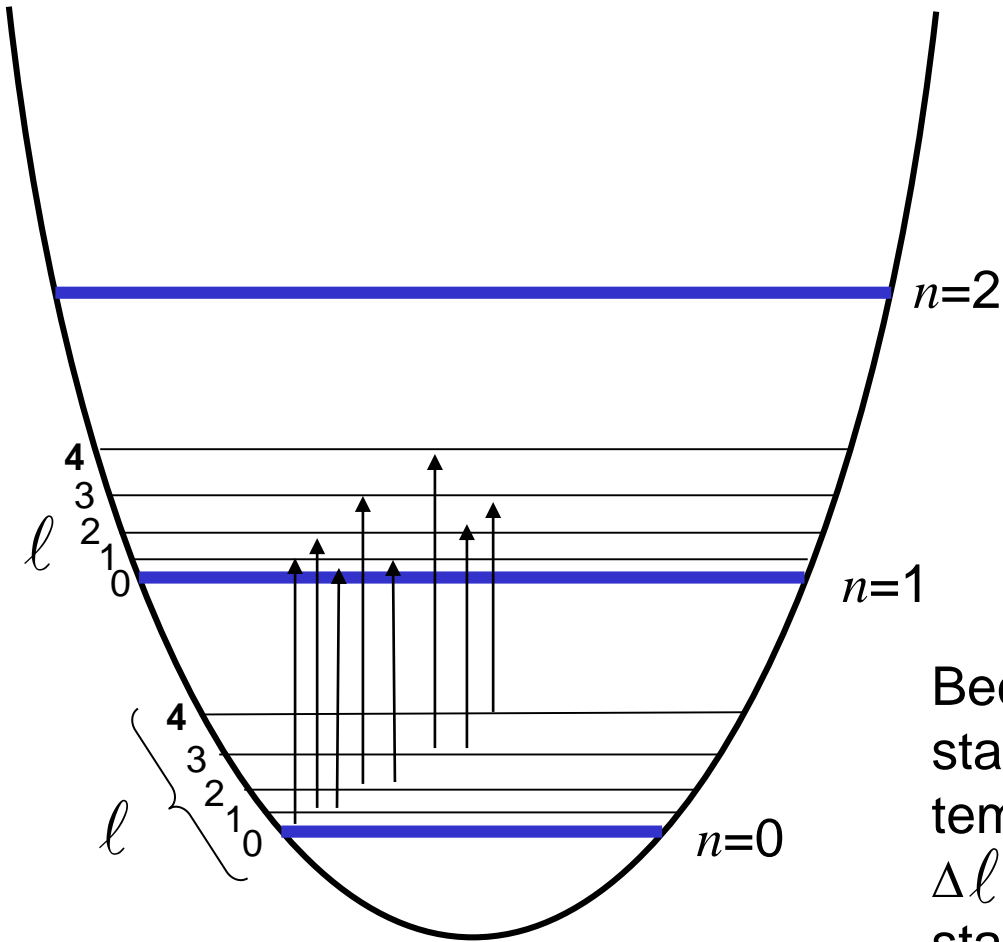
At room temperature, it is mostly the ground vibrational state that is populated, therefore, most vibrational transitions will be:
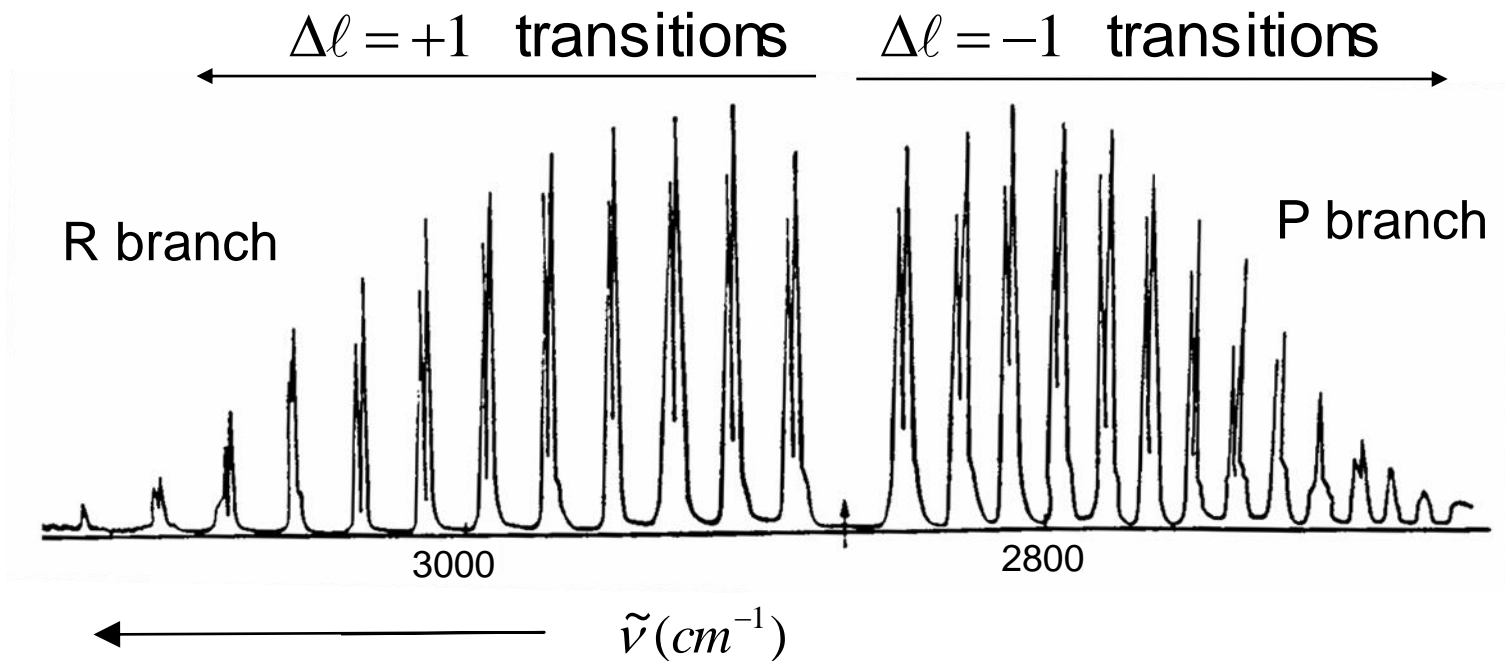
$$n = 0 \rightarrow n = 1$$

$$\Delta E_{vib} = \hbar \omega$$

Because many rotationally excited states are occupied at room temperature, there will be both $\Delta \ell = +1$ and $\Delta \ell = -1$ transitions starting from various levels ℓ.

Thus, the total energy of the transitions can smaller or larger than that for the fundamental vibrational frequency.

$$\Delta E = \Delta E_{vib} \pm \Delta E_{rot}$$

$\Delta \ell = +1$ transitions $\Delta \ell = -1$ transitions

R branch

P branch

3000   2800

$\tilde{\nu}(cm^{-1})$

The shape of each of the branches is again due to the thermal populations of the rotational energy levels governed by Boltzmann's law.

Shoulders are due to natural abundance of $H^{37}Cl$, which has larger reduced mass than $H^{35}Cl$, and therefore a shift in the fundamental vibrational frequency.
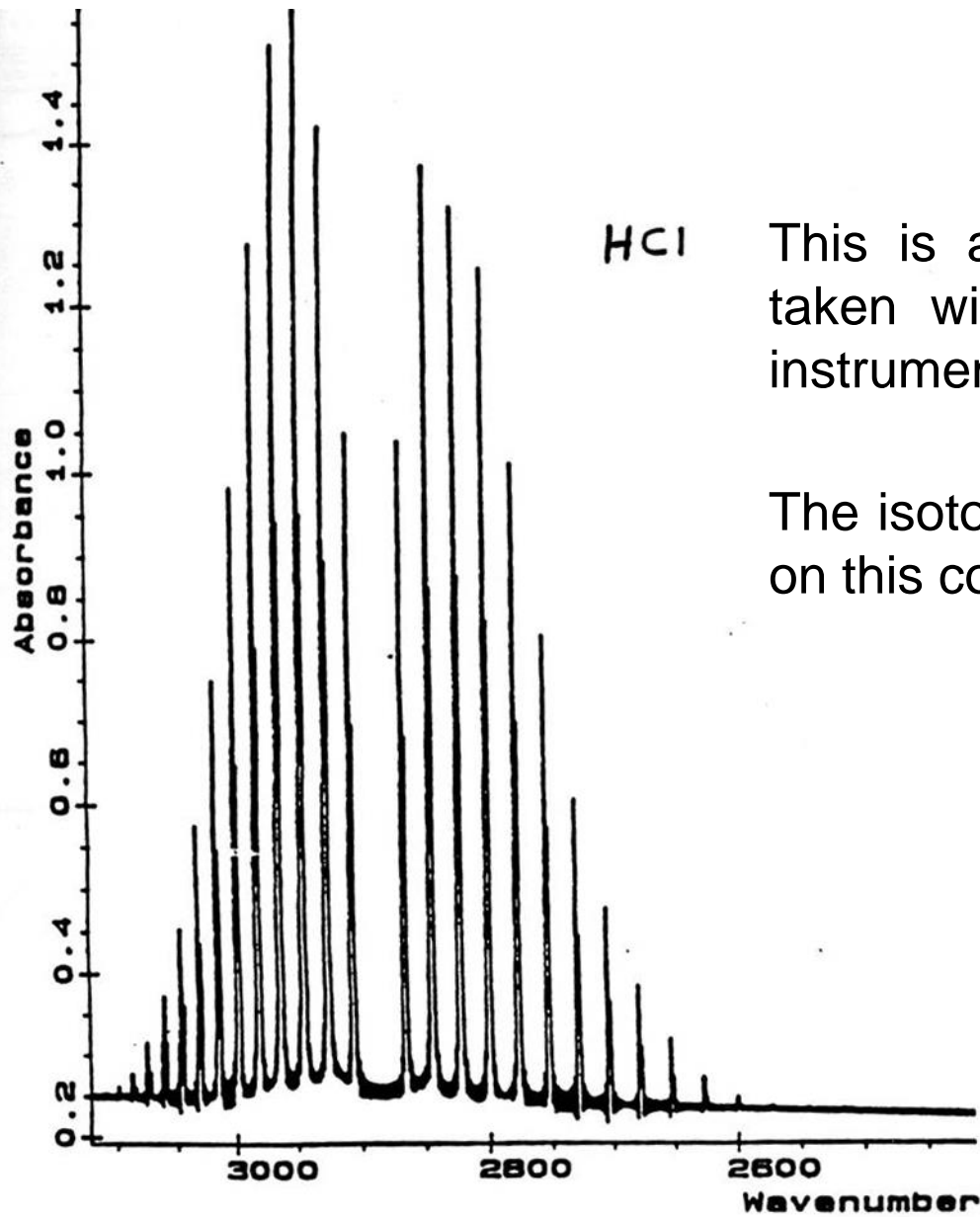
HCl

This is an actual spectrum of HCl taken with the departmental FT-IR instrument.

The isotopic splitting is barely visible on this compressed scale.