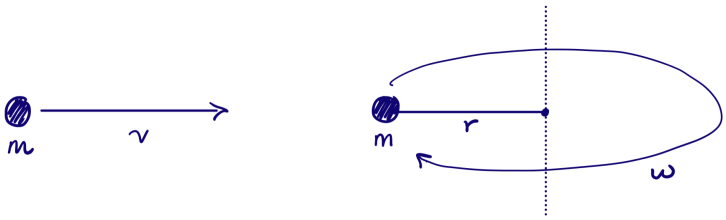
CHM 305 - Lecture 11 - Angular Momentum

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Today we will discuss angular momentum. We will first review the classical concept of angular momentum, then consider how it crops up in quantum mechanics in the context of molecular rotation. The material in today's lecture is covered in Section 1.7 and Chapter 6 of McQuarrie.

1 Classical Angular Momentum

Let's start by reviewing how rotating objects behave classically, and what we mean by angular momentum. By this point we should be familiar with the concept of linear momentum, which for a mass m moving with velocity v is given by $p = mv$. Now, consider instead a mass m on a string of length r that is being spun around a fixed point in space.



Let's define the following quantities for this rotating mass:

- ν_{rot} = the frequency of rotation in cycles/sec, e.g. the number of times the mass circles the central point per second.
- $\omega = 2\pi\nu_{rot}$ = the angular velocity in radians/sec, e.g. what angle in radians the mass covers per second.
- $v = (2\pi r) \cdot \nu_{rot} = r \cdot (2\pi\nu_{rot}) = r \cdot \omega =$ the velocity of the mass, calculated by multiplying the distance traveled in one cycle (one circumference) times the frequency of rotation.

We can now use these quantities to write down expressions for the kinetic energy, linear momentum, and angular momentum of this mass.

First, we can write the kinetic energy as:

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}m(r\omega)^2 = \frac{1}{2}(mr^2)\omega^2 \equiv \frac{1}{2}I\omega^2 \tag{1}$$

where we have defined the *moment of inertia*, $I = mr^2$, which behaves like mass and captures how difficult it is to get something spinning.

In Eqn. 1 the quantity $\frac{1}{2}I\omega^2$ is clearly analogous to $\frac{1}{2}mv^2$ in terms of kinetic energy. We can imagine making a similar comparison to linear momentum $p = mv$ by defining:

$$\ell \equiv I\omega = (mr^2)\omega = mr \cdot (r\omega) = mrv = r \cdot (mv) = r \cdot p \tag{2}$$

Where we will define ℓ as the *angular momentum*. We can also write the kinetic energy in terms of ℓ as:

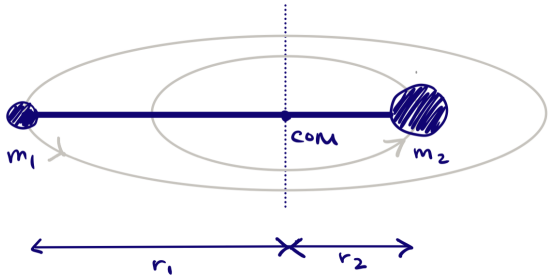
$$KE = \frac{p^2}{2m} = \left(\frac{\ell}{r}\right)^2 \cdot \frac{1}{2m} = \frac{1}{2}\frac{\ell^2}{mr^2} = \frac{\ell^2}{2I} \tag{3}$$

Let's summarize what we've covered here with a table of analogous quantities in linear and angular motion.

linear	angular
m	I
v	ω
$p = mv$	$\ell = I\omega$
$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$	$KE = \frac{1}{2}I\omega^2 = \frac{\ell^2}{2I}$

2 The Classical Rigid Rotor

Instead of a single mass on a string, let's now consider two connected masses, m_1 and m_2, spinning about their center of mass (COM). The COM is defined as the location where $m_1 r_1 = m_2 r_2$ where $r_{1,2}$ is the distance of $m_{1,2}$ from the COM.



Just like we did for the single mass, let's imagine that this system rotates with frequency ν_{rot} and angular frequency $\omega = 2\pi\nu_{rot}$. Both masses rotate about the COM with the same frequencies. However, their velocities will be different, as m_1 and m_2 traverse circular trajectories with different radii (and thus different circumferences) in the same period of time. So:

$$v_1 = (2\pi r_1)\nu_{rot} = r_1\omega \tag{4}$$

$$v_2 = (2\pi r_2)\nu_{rot} = r_2\omega \tag{5}$$

We can write down the kinetic energy of this combined system, which is just the sum of the kinetic energies of the two masses:

$$KE = \frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2 \tag{6}$$

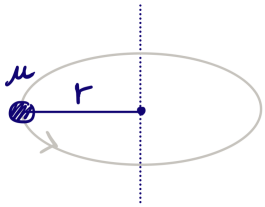
$$= \frac{1}{2}m_1 (r_1\omega)^2 + \frac{1}{2}m_2 (r_2\omega)^2 \tag{7}$$

$$= \frac{1}{2}\left(m_1 r_1^2 + m_2 r_2^2\right)\omega^2 \tag{8}$$

$$\equiv \frac{1}{2}I\omega^2 \tag{9}$$

where here, the moment of intertia $I \equiv m_1 r_1^2 + m_2 r_2^2$.

Another convenient simplification we can include here is to use the *reduced mass*, which we introduced in our treatment of the harmonic oscillator. The reduced mass allows us to treat our two-mass system as an effective single body with mass μ rotating about a fixed origin.



For a two-mass system, μ is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{10}$$

It also turns out that we can express the moment of inertia for this system as:

$$I = \mu r^2 \tag{11}$$

where $r = r_1 + r_2$.

3 The Quantum Rigid Rotor

Let's now take a step into the quantum mechanical. If we are thinking about describing the rotational behavior of a rigid diatomic molecule, the masses and length scales involved are small enough that the classical model will not suffice. Instead, we will have to solve the problem of a quantum rigid rotor. In a classical system, the energy and angular momentum associated with rotation have continuously allowed values. In a quantum system, the energies and angular momenta we can measure in our system take on discrete values.

As always, we will start by writing down the time-independent Schrödinger equation, which we will solve to find the eigenfunctions and energy eigenvalues of this system. In three dimensions, the Schrödinger equation is:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + \cancel{V(x,y,z)} \tag{12}$$

where we have used the reduced mass μ. Note that the rigid rotor has $V(x, y, z) = 0$ for all space. In fact, we can conceive of this system as a free particle constrained to explore the surface of a sphere.

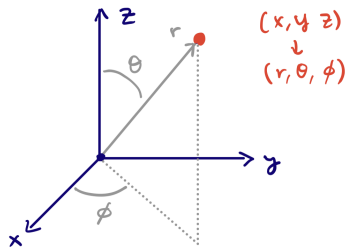
Another step we can take here is to define an operator called the Laplacian operator:

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{13}$$

So we can write our Hamiltonian in a very compact way:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 \tag{14}$$

Because our "particle" of reduced mass μ is constrained to explore a rigid spherical surface of distance r from the origin, it actually becomes much simpler to solve the Schrödinger equation and express its eigenfunctions in terms of spherical coordinates (r, θ, ϕ) rather than Cartesian coordinates (x, y, z). The spherical coordinate system is shown below:



The coordinate transformation we would have to use here is:

$$r = \sqrt{x^2 + y^2 + z^2} \tag{15}$$

$$\theta = \arccos\left(\frac{z}{r}\right) \tag{16}$$

$$\phi = \arctan\left(\frac{y}{x}\right) \tag{17}$$

We will not derive the Laplacian operator in terms of spherical coordinates here, but it can be written as:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{18}$$

For our rigid rotor, r is fixed, so we can treat it as a constant and the derivatives with respect to r disappear. We can therefore write:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{19}$$

$$= -\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{20}$$

$$= -\frac{\hbar^2}{2I}\left[\cdots\right] \tag{21}$$

It's also worth pointing out here that since $\hat{H} = \hat{KE} = \frac{\ell^2}{2I}$, we can express the square of the angular momentum operator, $\hat{\ell}^2$, as:

$$\hat{\ell}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left[\sin\theta \frac{\partial}{\partial\theta} \right] + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \tag{22}$$

We can find the rigid rotor solutions by using the Hamiltonian in Eqn. 20 and solving:

$$\hat{H}\psi(\theta,\phi) = E\psi(\theta,\phi) \tag{23}$$

where $\psi(\theta,\phi)$ will encode the probability distribution for how we expect our rotor to be oriented in 3D space at any given moment in time.

Practice Problem 1: The rigid rotor Hamiltonian has the form

$$\hat{H} = -\frac{\hbar^2}{2I} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left[\sin\theta \frac{\partial}{\partial\theta} \right] + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$

and can also be written as

$$\hat{H} = \frac{\hat{\ell}^2}{2I}$$

Do $\hat{H}$ and $\hat{\ell}^2$ commute? What does this tell you about their eigenfunctions? Can you draw an analogy to the energy and linear momentum of a free particle?

4 Eigenfunctions of the Quantum Rigid Rotor Hamiltonian

We will just write down the solutions to this Hamiltonian here. If you want to see how they are derived, the math is not terribly difficult. It is done out in McQuarrie Ch. 6, Sections 6.1 and 6.6, for those of you interested in learning more.

The rigid rotor eigenfunctions are called *spherical harmonics*. They factor neatly into components that are purely functions of θ and ϕ and are labeled with two quantum number indices J and m. By convention, the wavefunctions are denoted as $Y_J^m(\theta,\phi)$. They take the following form:

$$\psi(\theta,\phi) \equiv Y_J^m(\theta,\phi) = \Theta(\theta)\cdot\Phi(\phi) \tag{24}$$

$$\Phi(\phi) = \frac{1}{(2\pi)^{1/2}} \cdot e^{im\phi} \tag{25}$$

$$\Theta(\theta) = \left[\left(\frac{2J+1}{2} \right) \left(\frac{(J-|m|)!}{(J+|m|)!} \right) \right]^{1/2} \cdot P_J^{|m|}(\cos\theta) \tag{26}$$

$$J = \{0, 1, 2, \dots\} \tag{27}$$

$$m = \{0 \pm 1, \pm 2 \cdots \pm J\} \tag{28}$$

and where $P_J^{|m|}(\cos\theta)$ are Legendre polynomials, expressed as functions of $\cos\theta$. The Legendre polynomials are a special orthogonal set of polynomial functions that are solutions to a certain differential equation that falls out of our rigid rotor Hamiltonian.

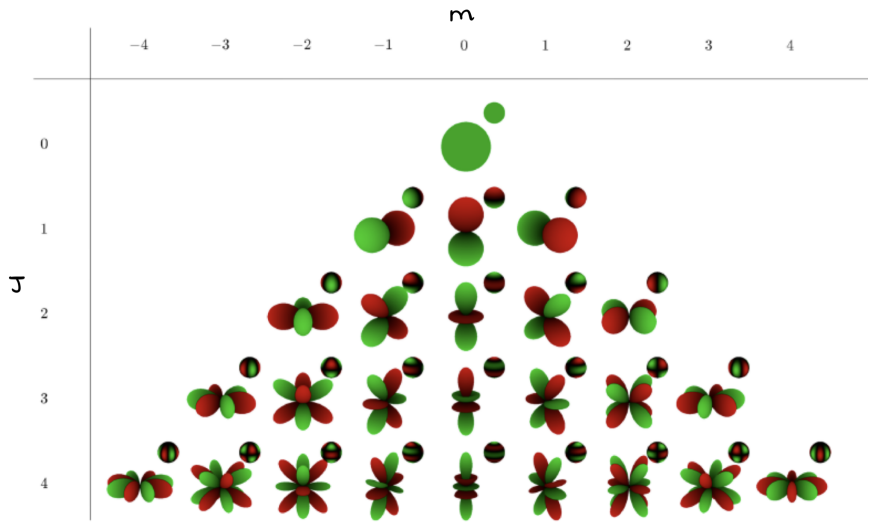
The first few Legendre polynomials $P_J^{|m|}(x)$ are:

$$P_0^0(x) = 1 \tag{29}$$
$$P_1^0(x) = x \tag{30}$$
$$P_1^1(x) = (1 - x^2)^{1/2} \tag{31}$$
$$P_2^0(x) = \frac{1}{2}(3x^2 - 1) \tag{32}$$
$$\dots$$

And therefore, the functional forms of the first few rigid rotor eigenfunctions $\{Y_J^m(\theta, \phi)\}$ are:

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}} \tag{33}$$
$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \tag{34}$$
$$Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \cdot e^{i\phi} \tag{35}$$
$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi} \tag{36}$$
$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \tag{37}$$
$$\dots$$

These functions are normalized and together form a complete orthonormal basis set. Spatial plots of these functions are additionally shown below.



A few things to note in these wavefunctions:

- Green regions represent locations where the wavefunction has positive amplitude; red regions represent negative amplitude.
- The small spherical graphics give the actual map of how the rigid rotor is expected to be oriented in θ and ϕ. The lobed graphics give a better picture of where the angular nodes are – which angles the particle will never found pointing towards in a given eigenstate.
- The quantum number J gives the number of spatial nodes. The quantum number m encodes the *orientation* of these nodes.
- Notice how the ground state Y_0^0 eigenfunction shows a uniform probability distribution on the surface of the sphere. This indicates that a rotor in state Y_0^0 is equally likely to be found pointing in any direction, since the expression for Y_0^0 is independent of θ and ϕ.

5 Rigid Rotor Energy Eigenvalues

The rigid rotor eigenfunctions have relatively complex forms, but it turns out the expression for their energy eigenvalues is very simple and depends only on J:

$$\hat{H}Y_J^m(\theta,\phi) = E_J Y_J^m(\theta,\phi) \tag{38}$$

$$E_J = \frac{\hbar^2}{2I}J(J+1) \equiv BJ(J+1) \tag{39}$$

where $B = \frac{\hbar^2}{2I}$ is defined as the *rotational constant* for a given system.

Since the energy eigenvalues depend only on J, all the levels with a given J quantum number have the same energy, regardless of m. Put another way, the energy of these states depends only on the total number of nodes in the wavefunction, not their orientation in space!

For a given J, there are $2J+1$ states with different $m = -J, -J+1, \ldots J-1, J$. The J^{th} energy level therefore has a *degeneracy* of $2J+1$.

The allowed angular momenta of this system are quantized just like the energies. Recall $KE = \frac{\ell^2}{2I}$, so $\ell^2 = 2I \cdot KE$. Therefore:

$$\ell^2 = \hbar^2 J(J+1), \quad J = 0, 1, 2, \cdots \tag{40}$$

Practice Problem 2: Show that

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

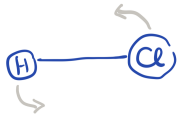
is a solution to the rigid rotor Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

and find its energy eigenvalue.

6 Rotational States of Diatomic Molecules

The rigid rotor model quite accurately describes the allowed energies and orientational probability distributions of a diatomic molecule freely tumbling in space, e.g. the HCl molecule as sketched below:



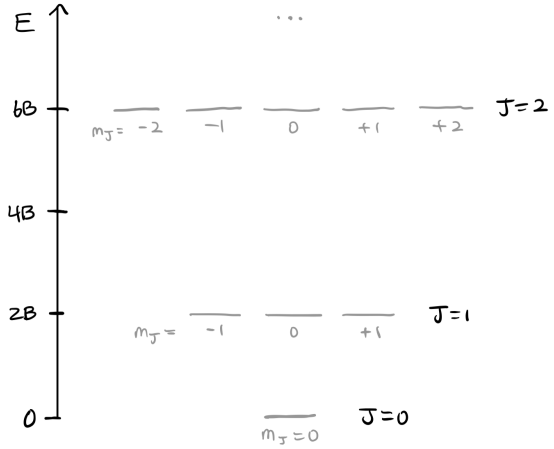
As we've already established, a given molecule has a rotational constant which sets the spacing of it's energy levels, and is quite easy to calculate:

$$B = \frac{\hbar^2}{2I} \tag{41}$$

$$I = \mu r^2 \tag{42}$$

where μ is the reduced mass and r is the bond length. We will work more with this quantity next class when we discuss molecular spectroscopy.

In the meantime, it's worth briefly sketching out the energy diagram for a molecule like HCl, showing the degeneracies and spacings for different rotational quantum states:



Where here:

$$E_0 = B \cdot J(J+1) = B \cdot 0(0+1) = 0 \tag{43}$$

$$E_1 = B \cdot 1(1+1) = 2B \tag{44}$$

$$E_2 = B \cdot 2(2+1) = 6B \tag{45}$$

$$\dots$$

There are a few interesting things to note here:

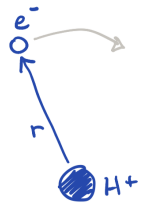
- When the atomic masses m_1 and m_2 are larger $\rightarrow$ μ is larger $\rightarrow$ I is larger $\rightarrow$ B is smaller. Heavier molecules therefore have more closely spaced rotational levels.

- When the bond length r is larger $\rightarrow$ I is larger $\rightarrow$ B is smaller. Larger molecules therefore have more closely spaced rotational levels.
- Therefore, as a molecule grows in mass or size, $B \rightarrow 0$. This represents the classical limit for macroscopic objects, where the spectrum of allowed rotational states become continuous and the values of their rotational energies and angular momenta are not quantized.

7 A Note About the Hydrogen Atom

If the spherical harmonic rotational wavefunctions looked familiar to you – perhaps evocative of atomic orbitals – you are totally correct! The electronic structure of the hydrogen atom is very closely related to the rigid rotor. Let's quickly lay out what the problem looks like. You will tackle this problem more explicitly in the second half of the course.

The H atom consists of one negatively charged electron orbiting one positively charged proton (the nucleus) in 3D space.



At first glance, this system looks very similar to a 2-mass rigid rotor. However, there are two key differences:

- Unlike the rigid rotor, the electron does not orbit the nucleus at a fixed radius r.
- Unlike the rigid rotor, the electron does not find itself in free space with $V(r, \theta, \phi) = 0$. Instead, the electron lies in a Coulomb potential, where its negative charge is attracted to the positively charged nucleus. So $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$.

The Hamiltonian for this system is therefore:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{46}$$

where ∇^2 is the full Laplacian operator in spherical coordinates.

This Hamiltonian is solved in Chapter 7 of McQuarrie. We can jot down the solutions here. They look exactly like the spherical harmonics that we already discussed, but with an additional quantum number n that describes the total number of nodes of the wavefunction, now including both angular *and radial* nodes:

$$\psi_{n,\ell,m}(r, \theta, \phi) = R_{n\ell}(r) \cdot Y_\ell^m(\theta, \phi) \tag{47}$$

where the $Y_\ell^m(\theta, \phi)$ are our old friends the spherical harmonics while $R_{n\ell}(r)$ are radial wavefunctions that capture both (a) the exponentially decaying probability that we find the electron at a large r

from the nucleus and (b) radial nodes in addition to angular nodes. The quantum number J which we use for rotations is relabeled as ℓ by convention when talking about electron orbitals.

The H-atom energy levels are simple to write down and are simply functions of the quantum number n, which again encodes the total number of spatial nodes:

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2}\frac{1}{n^2} \tag{48}$$

	s ($\ell = 0$)	p ($\ell = 1$)			d ($\ell = 2$)					f ($\ell = 3$)						
	$m = 0$	$m = 0$	$m = \pm 1$		$m = 0$	$m = \pm 1$		$m = \pm 2$		$m = 0$	$m = \pm 1$		$m = \pm 2$		$m = \pm 3$	
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	f_{z^3}	f_{xz^2}	f_{yz^2}	f_{xyz}	$f_{z(x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{y(3x^2-y^2)}$
$n = 1$																
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$n = 6$					...	...	...	...	...	...	...	...	...	...	...	...
$n = 7$		...	...	...	...	...	...	...	...	...	...	...	...	...	...	...