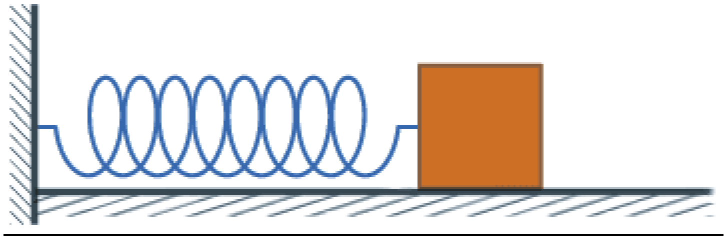
Lecture 10

The one and three-dimensional particle in a box are prototypes of **bound systems**. As we move on in our study of quantum chemistry, we'll be considering bound systems that are more and more complex and which represent more and more complex chemical systems. Another system that is important in chemistry is the **harmonic oscillator**. This problem is important because the harmonic oscillator is the most basic model with which we treat the vibrations of molecules. The properties of these vibrations are critical in interpreting infrared and Raman spectra, for the understanding of chemical dynamics and understanding the heat capacities of gas phase and liquid phase systems.

One feature of quantum mechanics that we've learned is that in order to properly set up a problem we need to know how the analogous classical problem is set up. So we'll begin our study of the harmonic oscillator by considering the classical case. The **classical harmonic oscillator** is usually represented by a mass m suspended from a wall by a massless spring. In this problem we ignore the effect of gravity.



Initially, the spring is at some length at which no force is exerted on the mass. We call this position 0. As the mass is moved from this position, the spring is distorted and a force is exerted on the mass by the spring. The **force is given by**

$$F = -kx$$

The negative sign means that the force is exerted in the direction opposite from the initial displacement, i.e., when the spring is stretched, the force is in a direction to compress the spring to its initial length, while if the spring is compressed, the force is in a direction to stretch the spring back to position 0. Such a force is called a restoring force. The constant **k is called the force constant**. If a spring is weak the force constant will be small, while if the spring is stiff the force constant will be large.

According to Newton's second law,

$$F = ma = m\frac{d^2x}{dt^2}$$

but F is also given by

$$F = -kx$$

Combining these gives us a second order differential equation for the position of the mass m as a function of time (a second order differential equation is one that contains a second derivative)

,

$$m\frac{d^2x}{dt^2} = -kx \quad or \quad \frac{d^2x}{dt^2} = -\frac{k}{m}x$$

Note that this latter form is almost identical to the differential equation we solved for the particle in a box, and will therefore have the same type of solution,

$$x(t) = A\sin\omega t + B\cos\omega t,$$

where $\omega = (\frac{k}{m})^{1/2}$ **is the fundamental vibrational frequency** in units of radians/s. ω is related to the frequency ν, by $\nu = \frac{\omega}{2\pi}$.

To complete the solution of this problem we need to specify the values of the terms A and B. To determine the value of the constants A and B in this problem, we need to specify a set of initial conditions, i.e., boundary values. For this problem the conditions usually specified are the initial displacement x_0 and the initial velocity, $\frac{dx}{dt}$ or x'. A common case is that where we stretch the spring to some initial displacement x_0 and release it. For this case the initial displacement $x(0) = x_0$, while the initial velocity, $x'(0) = 0$. If we apply the first boundary condition by setting t to 0 and x to x_0 we get

$$x(0) = x_0 = A\sin 0 + B\cos 0 \Rightarrow B = x_0.$$

The second boundary condition tells us that

$$x'(0) = 0 = \omega A\cos 0 - \omega B\sin 0 \Rightarrow A = 0$$

Together these give us

$$x(t) = x_0 \cos \omega t$$

as the solution for our harmonic oscillator. In other words, when we pull our mass out to an initial position x_0, it oscillates back and forth between x_0 and $-x_0$, $\omega/2\pi$ times a second.

In order to solve the quantum mechanical harmonic oscillator we need the Hamiltonian, and to write down the Hamiltonian, we need the potential energy, V(x). Classical mechanics tells us that for a conservative system the potential energy and force are related by

$$F_x = -\frac{\partial V}{\partial x} \quad or \quad V(x) = -\int F(x)dx.$$

Since for the harmonic oscillator, $F = -kx$, $V = 1/2\ kx^2 + C$. For the harmonic oscillator, c is taken to be 0, so $V = 1/2\ kx^2$.

We can use this result to show that the harmonic oscillator is a conservative system, i.e., that E = T + V is a constant.

$$V = \frac{1}{2}kx^2 = \frac{1}{2}kx_0^{\ 2}\cos^2\omega t$$

$$T = \frac{1}{2}m(\frac{dx}{dt})^2 = \frac{1}{2}kx_0^{\ 2}\sin^2\omega t$$

Therefore

$$E = T + V = \frac{1}{2}kx_0^{\ 2}(\sin^2\omega t + \cos^2\omega t) = \frac{1}{2}kx_0^{\ 2}$$

a constant.

So far we've discussed the harmonic oscillator as a single mass hanging from a wall. [Draw] The simplest model of a vibrating molecule is two masses, m_1 and m_2, connected by a spring. [Draw] It turns out that this is completely equivalent to the problem we have just solved if we replace the mass m by the **reduced mass** $\mu = \frac{m_1 m_2}{m_1 + m_2}$. We can do this because the diatomic molecule is another example of two particles linked by a central force. Let's do three quick examples of calculating a reduced mass. The reduced mass in AMU of $H^{35}Cl$ is given by $\mu = \frac{1*35}{1+35} = .9722$ AMU. The reduced mass of $H^{79}Br$ in AMU is $\mu = \frac{1*79}{1+79} = .9875$ AMU. You can see from this that if we have a light atom bonded to a heavy atom, that changing the mass of the heavy atom doesn't change the reduced mass very much. Here's an example with two heavy atoms: the reduced mass of $^{79}Br^{35}Cl$ is $\mu = \frac{35*79}{35+79} = 24.25AMU.$ It is important to note that if k is in SI units, N m^{-1}, the reduced mass must be in kg rather than in AMU in order to obtain intelligible values for the frequency. We convert between kg and AMU by multiplying with the conversion factor 1 AMU = 1.66053×10^{-27} kg.

For diatomic molecules our differential equation for the motion of a harmonic oscillator now becomes

$$\mu \frac{d^2x}{dt^2} = -kx$$

and the vibrational frequency $\nu = \frac{1}{2\pi}(\frac{k}{\mu})^{1/2}$.

These are the basics of the classical harmonic oscillator. Let's turn now to the quantum mechanical case. To determine the wavefunction and energies of the quantum mechanical harmonic oscillator, we need to solve the Schrödinger equation, $\hat{H}\,\psi = E\psi$. To do this we need to write down our Hamiltonian $\hat{H}$. Remember that for a single dimension, the Hamiltonian is given by

$$\hat{\mathrm{H}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

For the harmonic oscillator, we replace the mass m with the reduced mass μ, and the potential V(x) with 1/2 kx^2. This yields

$$\hat{\mathrm{H}} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

as our Hamiltonian. Even adding so simple a potential as 1/2 kx^2 makes this Schrödinger equation much harder to solve, in fact hard enough that we won't attempt it. I'll just present and analyze the solutions. First, the **eigenvalues of the Hamiltonian** are

$$E_{\mathrm{v}} = (\mathrm{v} + \frac{1}{2})h\nu,\ \mathrm{v} = 0,1,2,3,....$$

where **the frequency ν is given by** $\nu = \frac{1}{2\pi}(\frac{k}{\mu})^{1/2}$**, just as in the classical case**. **The integers v are called vibrational quantum numbers**. Note that the energies are quantized, and that like the case of the particle in a box, we have a potential energy function that corresponds to a bound system. The lowest energy, for v=0, is called the **zero point energy** and is equal to 1/2hν. Note that as was the case for the particle in a box, this lowest energy is greater than zero. The next energy is for v = 1 and equals 3/2 hν. The next energy is for v = 2 and equals 5/2 hν. **Notice that for the harmonic oscillator, the spacing between energy levels is constant at hν.**

The **wavefunction for the harmonic oscillator** has the formula

$$\psi_{\mathrm{v}}(x) = N_{\mathrm{v}} H_{\mathrm{v}}(\alpha^{1/2} x) e^{-\alpha x^2/2}$$

This equation has three parts. N_v is a normalization factor, which varies as v varies. Its formula is

$$N_{\mathrm{v}} = \frac{1}{\sqrt{2^{\mathrm{v}}\mathrm{v}!\pi^{1/2}}}$$

The second factor is a group of functions $H_v(\alpha^{1/2}x)$, where $\alpha = (\frac{k\mu}{\hbar^2})^{1/2}$. In this equation the term $\alpha^{1/2}x$ is the argument of the function H_v, much the same as x is the argument of f(x). This set of functions is called the **Hermite polynomials**. They are a group of polynomials of order v, where v is the vibrational quantum number. The first few of these are

$$H_0(\alpha^{1/2}x) = 1$$

$$H_1(\alpha^{1/2}x) = 2\alpha^{1/2}x$$

$$H_2(\alpha^{1/2}x) = 4\alpha x^2 - 2$$

Remember that the order of a polynomial tells you how many solutions give y = 0. A first order polynomial has one zero, a second order polynomial has two and so on . The order of the Hermite polynomial tells us the number of oscillations of our wave function and the number of nodes in our probability density.

The final term is the exponential, $e^{-\alpha x^2/2}$. This type of exponential is so important in math, physics, and statistics that it has its own name, the **gaussian function**. A plot of the gaussian yields a bell shaped curve. The function of the gaussian in this wavefunction is to determine the overall shape and width of the wavefunction, sometimes called the envelope of the function. Let's draw the wavefunctions and probability densities for the first few vibrational states. [Draw]

Note that in the lowest state the most probable position for the oscillator is at the minimum of the potential energy curve. For a molecule, this position corresponds to a **bond length**. Because this is the bond length that the molecule will be spending most of its time in when the molecule is in its vibrational ground state, this bond length is called the **equilibrium bond length**, and is symbolized by r_e. This quantum result that the molecule in v = 0 spends most of its time at r_e is in direct contradiction to our classical result, which says that the molecule will spend most of its time at the bond lengths corresponding to the classical turning points, the points where the kinetic energy is zero. However, notice that as the energy increases, the probability density moves out toward the edges of the potential curve. Once again, we see that as the quantum number increases, we approach the classical limit.

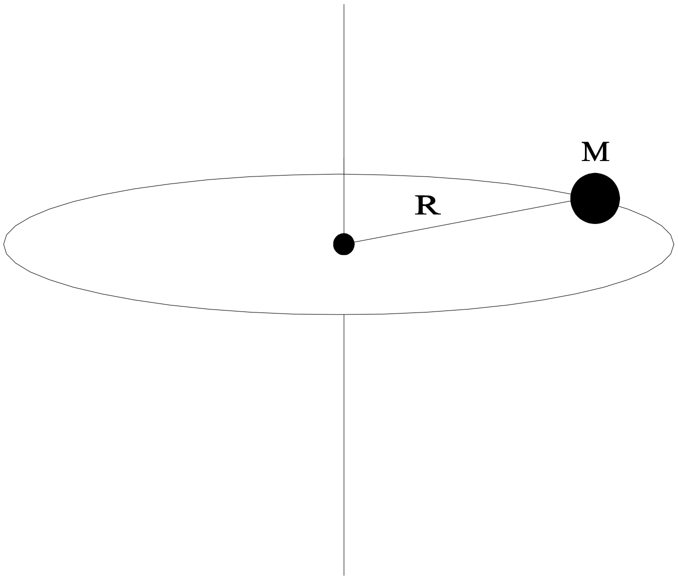
Note also that when we plot the probability density vs. r, **for all states there is some probability that the molecule will be found at positions outside of the classical turning points**. The probability is greatest for v= 0, where the molecule spends fully 16% of its time outside of the turning points. This would be impossible classically, since the kinetic energy would have to be negative. This phenomenon, in which a particle is in a state that is energetically forbidden, is called quantum mechanical tunneling. It is very important in the understanding of many chemical phenomena, including electron transfer reactions, and the rates of chemical reactions, especially chemical reactions involving the transfer or rearrangement of hydrogen atoms.

Let's end this discussion by calculating the vibrational frequencies of two molecules. Note that for this we need only know the reduced mass and the force constant. Let's do this for HI and HCl. Our formula is $\nu = \frac{1}{2\pi}(\frac{k}{\mu})^{1/2}$. For HCl we've already shown that $\mu = 0.9722$ AMU, but for the purposes of our calculations we need μ in kg. The conversion is 1.66×10^{-27} kg/AMU, so $\mu = 1.613 \times 10^{-27}$ kg. The force constant k for HCl = 515.7 N m^{-1}, so $\nu = \frac{1}{2\pi}(\frac{515.7}{1.613x\,10^{-27}})^{1/2} = 8.993 \times 10^{13}$ s^{-1}. As noted earlier, in spectroscopy we more commonly use units of wavenumbers, cm^{-1}, instead of frequency units. We calculate wavenumbers from frequency by using $\bar{\nu} = \frac{\nu}{c}$, where c is the speed of light in cm/s, so for this case, $\bar{\nu} = \frac{8.993x10^{13}s^{-1}}{3x10^{10}cm/s} = 2998\,cm^{-1}$. For HI, $\mu = \frac{1*127}{1+127}x1.66x10^{-27} = 1.647x10^{-27}kg$. The force constant for HI is 293 N m^{-1}. Plugging these into our formula for μ yields $\nu = 6.71 \times 10^{13}$ s^{-1} or $\bar{\nu} = 2237$ cm^{-1}. So we see that even though the reduced masses are very similar, the difference in force constants results in a substantially different vibrational frequency. We will find as well that when two molecules have similar force constants but different reduced masses, the vibrational frequencies will differ as well. Thus observed **vibrational frequencies depend on both reduced mass and force constant**.

Lecture 11

A new problem but one of fundamental interest is the **rigid rotator**. The rigid rotator is important in its own right, because it is the **simplest model for the rotation of a molecule**. However, it is also important because it is the first of many problems of importance in quantum mechanics in which the motion is circular, i.e., problems with **spherical symmetry**. Of course this includes all problems involving atoms. Two unique features of problems with spherical symmetry are that it is more convenient to treat them in **spherical coordinates**, and that different dynamical variables, like the moment of inertia and the angular momentum, are more useful than their linear counterparts in expressing the dynamics of the system.

I briefly discussed **angular momentum** in the course of our treatment of the Bohr atom, but I'd like to go over it again, since it is a concept which some find difficult. Consider a particle of mass m, rotating around a fixed axis, and whose motion is restricted to a single plane. We can treat its energy in terms of the linear velocity, v, but this can be inconvenient since in angular motion, the velocity is always changing. It is more convenient to express the energy in terms of the **angular velocity** **ω**, which doesn't change for a particle moving at constant speed around a circle of radius r. The angular velocity is defined as $\omega = \frac{d\theta}{dt}$, where θ is measured in radians. It is related to the frequency

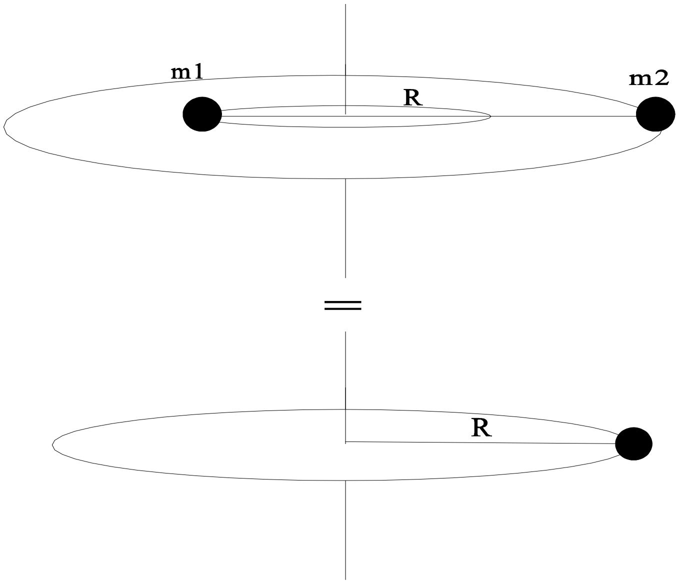


by $\omega = 2\pi\nu$. It is related to linear velocity by $v = r\omega$. If we substitute this in our definition for kinetic energy, we find that

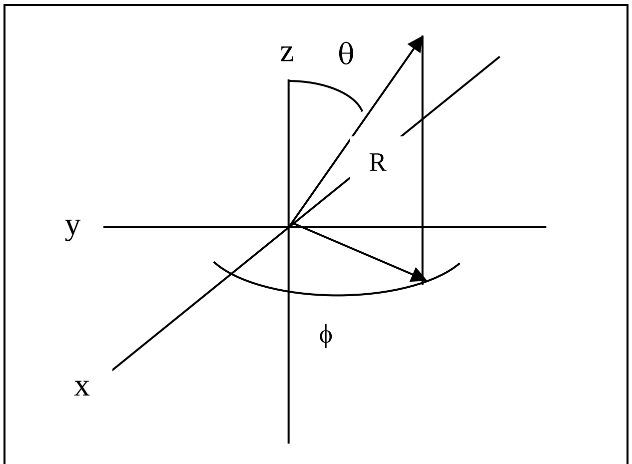
$$T = \frac{1}{2}m\mathrm{v}^2 = \frac{1}{2}mr^2\omega^2.$$

Since the angular velocity ω is analogous to the linear velocity, it is logical that the term mr^2 serves a function similar to the mass for circular motion, i.e., just as mass represents the tendency to resist linear acceleration, the quantity mr^2 represents the tendency to resist angular acceleration. We call this quantity **the moment of inertia**, and for this simple case define it by $I = mr^2$. Thus we can now express the kinetic energy with $T = \frac{1}{2}m\mathrm{v}^2 = \frac{1}{2}I\omega^2$. Since there is a circular analog for the velocity and a circular analog for the mass, it seems logical that there should be a circular analog for the linear momentum, $p = mv$. This circular analog, **the angular momentum**, is constructed by taking the product of the angular velocity and the moment of inertia, $L = I\omega$, just as the linear momentum is the product of mass and velocity. Thus we can express the kinetic energy for the rotation of a mass around a fixed axis in terms of the angular velocity or in terms of the angular momentum, $T = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$. The quantities I, ω and L are fundamental quantities for the dynamics of angular motion.

A rotating molecule can be represented by two masses bound by a rigid massless rod of length R rotating around the center of mass of the system. While this system may appear more complicated than a single mass rotating around a fixed axis, it turns out not to be. To treat our rotating molecule, we need only replace the mass of the single particle by the reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ of the diatomic molecule. The only change in our results on circular motion is that the definition of the moment of inertia becomes I = μr^2. Of course anywhere else where we refer to the mass it will be replaced by the reduced mass as well.



To treat the rigid rotator quantum mechanically, we need to write down our Hamiltonian. WHAT ARE THE TWO TERMS IN EVERY HAMILTONIAN OPERATOR? The potential energy function is simple. A molecule rotating in a vacuum encounters no resistance, so our potential is 0. Thus the Hamiltonian is simply $\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2$. However, for a problem with rotational symmetry it is most useful to express the Hamiltonian in terms of **spherical coordinates**.



Spherical Coordinates

For those of you who are in need of refreshing about spherical coordinates, suppose we have a point at distance $r_1 = x_1, y_1, z_1$ from the origin. This point can also be represented by two angular variables, θ and ϕ, and the radius r from the origin. The angle θ is the angle from the z axis to the line between 0 and r, and the angle ϕ is the angle between the projection of the vector on the x-y plane and the x-axis. Two sets of equations are used to convert from Cartesian coordinates to spherical coordinates and back. To go **from Cartesian coordinates to spherical coordinates**, we use

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

$$\theta = \cos^{-1}\left(\frac{z}{(x^2 + y^2 + z^2)^{1/2}}\right)$$

$$\phi = \tan^{-1}\frac{y}{x}$$

The domain of r is from 0 to ∞, while θ can vary from 0 to π and ϕ can vary from 0 to 2π.

To convert from spherical coordinates to Cartesian coordinates we use

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

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

$$z = r\cos\theta.$$

It will turn out that for problems of spherical symmetry, like for example those involving atoms, it will be much easier to write the potential using spherical coordinates, and in fact, **spherical coordinates will be the only set of coordinates in which the problems will be separable**. The problem in spherical coordinates is writing the Laplacian, ∇^2, which takes on the rather imposing form,

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

Since the two particles in the rigid rotor are separated by a fixed distance, the term involving derivatives with respect to R will drop out and our Hamiltonian will take on the form

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

If we factor out the R^2, then our denominator contains the factor μR^2, which we replace with the moment of inertia, I, to get finally

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

The **solution to the Schrödinger equation for this problem is a function of both θ and ϕ**, and has the symbol **Y(θ,ϕ)**. The Schrödinger equation thus becomes

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

The solutions to this equation are called **spherical harmonics**. HOW MANY QUANTUM NUMBERS DO WE EXPECT TO BE A PART OF EACH EIGENFUNCTION? Each solution includes two quantum numbers called *l* and m, and the solutions are labeled $Y_l^m(\theta,\varphi)$. The values of the quantum numbers *l* and m are not independent, but are related. ***l* can take on any integer value from 0 to ∞. m can take on only integer values from -*l* to *l*.**

Some of the first few solutions are $Y_0^0 = (\frac{1}{4\pi})^{1/2}$, a spherical solution with no nodes, $Y_1^0 = (\frac{3}{4\pi})^{1/2}\cos\theta$, which has a single planar node, and $Y_2^0 = (\frac{5}{16\pi})^{1/2}(3\cos^2\theta - 1)$, which has two planar nodes. DO THESE LOOK FAMILIAR TO YOU? So you see that **the probability densities for the eigenfunctions of the rigid rotor are the same as the shapes**

of the s, p, d, f orbitals, etc, the angular portions of the hydrogen atom wavefunction that you learned about in general chemistry.

Even though the eigenfunctions depend on both the *l* and *m* quantum numbers, the **eigenvalues of the rigid rotor** depend only on the value of the quantum number *l* and are given by $E_l = \frac{l(l+1)\hbar^2}{2I}$. The first few eigenvalues are $E_0 = 0$, $E_1 = \frac{2\hbar^2}{2I}$, $E_2 = \frac{6\hbar^2}{2I}$ and $E_3 = \frac{12\hbar^2}{2I}$. Notice that **the spacing between the energy levels increases with increasing *l***. Note also that since the energy depends only on *l*, and since for each quantum number *l*, there are 2*l* + 1 wavefunctions with different values of m but the same *l*, we can conclude that **each energy level of the quantum mechanical rigid rotor is 2*l* + 1 fold degenerate**. For example, E_1 will be threefold degenerate, with wavefunctions Y_1^0, Y_1^1 and Y_1^{-1} having the same energy. E_2 will be fivefold degenerate with wavefunctions Y_2^{-2}, Y_2^{-1}, Y_2^0, Y_2^1, Y_2^2 having the same energy and so on. This will be important in interpreting the intensities of the infrared spectra of gas phase molecules.

Lecture 12

When we began our discussion of the rigid rotor, I emphasized the usefulness of the angular momentum and other dynamical variables of particular applicability to systems of spherical symmetry. So far the only one of these we've used is the moment of inertia. I'd like to turn now to **angular momentum**. While this may seem a somewhat esoteric topic, it is of critical importance in quantum chemistry, especially in spectroscopy, where the descriptions of the various electronic states of molecules and atoms are primarily in terms of the angular momenta. Angular momentum states are at the core of the form of spectroscopy that you are probably most familiar with, Nuclear Magnetic Resonance.

When I defined angular momentum earlier, I was not entirely accurate. My definition of angular momentum as $L = I\omega$ ignores the fact **that in three-dimensional systems angular momentum is a vector quantity**. It was only because we were dealing with motion restricted to a plane that we were able to use such a simple definition for the magnitude of the angular momentum. In the more general case where motion can occur in three dimensions, **the angular momentum L is a vector given by the cross product of the linear momentum p, given by the vector (p_x, p_y, p_z) and the radius r, given by the vector (x, y, z)**

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}.$$

Remember that **the cross product of two vectors** a and b is a new vector with magnitude $ab \sin \theta$, where θ is the angle between the two vectors, and pointing at right angles to the two component vectors.

The vectors r and p can be expressed in terms of their x, y, and z components and the three unit vectors, i, j, and k, which are vectors with magnitude 1 in the x, y and z directions respectively,

$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$$

$$\mathbf{p} = p_x\mathbf{i} + p_y\mathbf{j} + p_z\mathbf{k}.$$

These definitions lead to a convenient definition of the angular momentum in terms of the components of r and p,

$$\mathbf{L} = \mathbf{r} \text{ x } \mathbf{p} = (yp_z - zp_y)\mathbf{i} + (zp_x - xp_z)\mathbf{j} + (xp_y - yp_x)\mathbf{k}$$

These lead in turn to the concept of components of angular momentum, L_x, L_y and L_z. These are simply the amounts of the classical angular momentum in the x, y and z directions and are given by

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x.$$

Note that **even though angular momentum is a vector, the magnitudes of the x, y and z components are scalar quantities**.

In quantum mechanics we are interested in the operators that correspond to these observables, and since angular momentum is particularly important in systems of spherical or cylindrical symmetry, we will express the operators for these three components in spherical coordinates,

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

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

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

It is interesting to note that **the operators for the three components of the angular momentum do not commute with each other**. Remember that this means that the uncertainty principle applies to these quantities - we can measure one of them at a time with infinite precision, but not the other two. By convention, we usually say that L_z is the one that we can know with infinite precision, but not L_x or L_y. In the language of eigenfunctions and eigenvalues we say that if a wavefunction is an eigenfunction of L_z then it is not an eigenfunction of L_x or L_y. This has an important implication. Remember that $\mathbf{L} = L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k}$. But we've just said that we cannot measure the three quantities L_x, L_y and L_z with infinite precision at the same time. This means that **the angular momentum itself can never be known with infinite precision in quantum mechanics**. In other words, angular momentum is not an eigenvalue of any wavefunction.

We can, however, learn more about the angular momentum of a system than just L_z. It turns out that **even though L cannot be determined exactly, its square,** $L^2 = \overline{L} \cdot \overline{L}$ **, can be determined exactly**. We can figure out what the operator for the angular momentum squared is by looking at our Hamiltonian for the rigid rotor. Remember that this Hamiltonian is the same as the operator for the kinetic energy, since the potential is zero for this problem. The kinetic energy can be expressed in terms of the angular momentum, $T = \frac{L^2}{2I}$. If we compare this with the Hamiltonian,

$$\hat{\mathrm{H}} = \hat{T} = -\frac{\hbar^2}{2I}\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right).$$

we see that the operator for the angular momentum squared must be

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

The operators $\hat{L}^2$ and $\hat{L}_z$ commute, which means that the uncertainty principle does not apply to these two quantities. Again using the language of eigenfunctions and eigenvalues, this means that if a function is an eigenfunction of one of these operators it will also be an eigenfunction of the other.

In fact we have already found a set of functions that are eigenfunctions of both $\hat{L}^2$ and $\hat{L}_z$, the spherical harmonics, $Y_l^m(\theta,\phi)$. If we operate on the spherical harmonics with $\hat{L}^2$, we get

$$\hat{L}^2 Y_l^m(\theta,\phi) = l(l+1)\hbar^2 Y_l^m(\theta,\phi)$$

where $l = 0, 1, 2, \ldots$ as before. WHAT IS THE EIGENVALUE OF $\hat{L}^2$? WHAT OBSERVABLE DOES THIS CORRESPOND TO? This gives us a way to calculate the *magnitude* of the angular momentum, since $L^2 = l(l + 1)\hbar^2$, and therefore

$$L = \hbar(l\,(l + 1))^{1/2}.$$

Operating on the spherical harmonics with $\hat{L}_z$ gives

$$\hat{L}_z Y_l^m(\theta,\phi) = m\hbar Y_l^m(\theta,\phi)$$

where $-l \leq m \leq l$. This is the eigenvalue equation for the angular momentum in the z direction, and so we find that the angular momentum in the z direction is given by $L_z = m\hbar$.

We can draw some interesting conclusions from these results. Suppose we have a state with angular momentum quantum number l. Then the value of the overall angular momentum for that state is $L = \hbar(l\,(l + 1))^{1/2}$. WHAT IS THE MAXIMUM VALUE OF M FOR THIS STATE? WHAT IS THE MAXIMUM ANGULAR MOMENTUM IN THE Z DIRECTION? So we see that $L > L_{z,\,max}$, and **you can**

never have the entire angular momentum along the z-axis. In other words, the angular momentum always has to point at least a little bit away from the z-axis.

In addition to finding out the angular momentum and the angular momentum along the z-axis, we can find out something about the angular momentum along the x- and y-axes. Remember that we know L^2 and L_z, and that $L^2 = L_x^2 + L_y^2 + L_z^2$. This means that

$$L_x^2 + L_y^2 = L^2 - L_z^2.$$

What this equation tells us is that we can learn the magnitude of the vector $\mathbf{i}L_x + \mathbf{j}L_y$, but we can't know how the angular momentum is distributed between L_x and L_y.

As I said earlier, the rigid rotor is the **simplest model for the rotations of a molecule**. When we discuss the rotational energies of molecules we use the letter J rather than *l* as the quantum number for the total angular momentum. Thus **the energy of a rotating molecule is given by**

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

Similarly, if we wish to find other quantities like the square of the angular momentum or the angular momentum in the z direction, we simply substitute J for *l* in the equations we've already worked out.

At this point we've applied quantum mechanics to three simple physical systems, the particle in a box, the harmonic oscillator and the rigid rotor. Each of these allows us to take a measurement of a frequency or wavelength and extract information about the molecule. In the case of the particle in a box, we learn the length in which an electron can move freely in a linear conjugated system. In the case of the harmonic oscillator we can extract k, the force constant for the bond, which tells us how strong the bond is and how hard it is to distort the shape of a molecule.

The key thing that we learn from a rotational spectrum is the bond length of the molecule.

We can learn this because the energy of a given level depends only on $\hbar$, J and I. Once we know J, we can figure out I, and since I = μr^2, we can figure out the bond length R. For example, suppose we find that the rotational energy of HI in its J = 5 state is 8.952 x 10^{-21} J. What is its bond length?

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

Solving for I gives

$$I = J(J+1)\frac{\hbar^2}{2E_J} = \frac{5x6x(1.055x10^{-34}\,Js)^2}{2x8.95x10^{-21}\,J} = 1.865x10^{-47}\,kgm^2$$

I = μr^2, so $r = (\frac{I}{\mu})^{1/2}$. Now we need to calculate μ. The reduced mass of HI, which we calculated before, is given by,

$$\mu_{HI} = \frac{m_H m_I}{m_H + m_I} = \frac{(1)(127)}{(1+127)}x1.66x10^{-27} = 1.647x10^{-27}\,kg$$

Therefore r, the bond length of HI, is

$$r = (\frac{I}{\mu})^{1/2} = (\frac{1.865x10^{-47}}{1.647x10^{-27}})^{1/2} = 1.604x10^{-10}\,m$$

Lecture 13

So far all of our efforts have been concentrated on the spatial distributions of wavefunctions, and on calculating the so-called stationary states of systems. It is useful to ask about the **time dependence of quantum mechanics**, i.e., how wavefunctions and probability densities change with time. To answer this we need to introduce another postulate. This postulate states that **the time evolution of a wavefunction is given by the time dependent Schrödinger equation,**

$$\hat{H}\Psi(r,t) = -i\hbar\frac{\partial\Psi(r,t)}{\partial t}$$

Notice that **in the time dependent equation, our wavefunction is a function of both position and time.** In the most general case, the Hamiltonian for this equation is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r,t),$$

where the potential is a function not just of position, but of time, as well. This is the type of Hamiltonian one would use in rigorously calculating the energy states of a molecule interacting with light.

The **solution of Schrödinger equations with time dependent Hamiltonians** can be extremely involved, because it is usually not possible to apply the technique of separation of variables, so we'll pass on this for the moment (a semester-long moment. I.e, a moooooooooomeeeeeeent.). However, the solution of the time dependent Schrödinger equation is relatively easy when the potential is time independent, i.e., when the system is conservative. In this case our Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(r,t) + V(r)\Psi(r,t) = -i\hbar\frac{\partial\Psi(r,t)}{\partial t}.$$

We apply the technique of **separation of variables** by writing the wavefunction as a product of a function of position and a function of time,

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})f(t).$$

Substituting this for $\Psi(\mathbf{r},t)$ in our equation leads to separate equations for $\psi(r)$ and $f(t)$. The equation for $\psi(r)$ is

$$(-\frac{\hbar^2}{2m}\nabla^2 + V(r))\psi(r) = E\psi(r),$$

which is the time independent Schrödinger equation that we've been working with all along. The elements of the set $\psi(r)$ are the time independent eigenfunctions like the ones we've calculated for the particle in a box, or the rigid rotor.

The equation for f(t) is

$$-i\hbar\frac{df(t)}{dt} = Ef(t)$$

Since this is a first order differential equation, this is pretty easy to solve. We just collect variables and integrate,

$$\int\frac{df(t)}{f(t)} = \int -\frac{iE}{\hbar}dt$$

Which yields the solution

$$f(t) = e^{-iEt/\hbar}.$$

Thus our overall solution is

$$\Psi(r,t) = \psi(r)e^{-iEt/\hbar}$$

We call the solutions $\psi(\mathbf{r})$ of the time independent Schrödinger equation **stationary states**. To see why this is let's take one of these eigenfunctions, $\psi_1(\mathbf{r})$, with energy eigenvalue E_1, and look at the time dependence of the probability density. The probability density of the time dependent wave function is given by

$$\Psi_1^*(r,t)\Psi_1(r,t) = \psi_1^*(r)e^{iE_1t/\hbar}\psi_1(r)e^{-iE_1t/\hbar} = \psi_1^*(r)\psi_1(r)$$

so we see that the **probability density of an eigenstate is independent of time.**

How does this compare to the **time dependence of the probability density of a wavefunction that is not an eigenfunction?** The simplest way to construct a wavefunction that is not an eigenfunction is to take the linear combination of two nondegenerate eigenfunctions. Thus if we have two eigenfunctions $\Psi_1(r,t) = \psi_1(r)e^{(-iE_1t)/\hbar}$ and $\Psi_2(r,t) = \psi_2(r)e^{-iE_2t/\hbar}$, then the sum $\Psi(r, t) = \Psi_1(r,t) + \Psi_2(r, t)$ is not an eigenfunction. I'd like you to prove this for yourselves as part of your homework. If we calculate the time dependence of the probability of this new wavefunction, we have

$$\Psi^*(r,t)\Psi(r,t) = (\psi_1^*(r)e^{iE_1t/h} + \psi_2^*(r)e^{iE_2t/\hbar})(\psi_1(r)e^{-iE_1t/h} + \psi_2(r)e^{-iE_2t/\hbar})$$

$$= \psi_1^*(r)\psi_1(r) + \psi_2^*(r)\psi_2(r) + \psi_1^*(r)\psi_2(r)e^{i(E_1-E_2)t/\hbar} + \psi_2^*(r)\psi_1(r)e^{i(E_2-E_1)t/\hbar}$$

so you see that when the wavefunction is not an eigenfunction that there are terms in the probability density which change with time. The meaning of these time dependent terms is that the system jumps between the two eigenstates with a frequency given by ΔE/h. This helps explain our observation that we always measure eigenvalues even when the state is not an eigenstate. Before the process of measurement, the system jumps between the eigenstates making up the wavefunction. At the moment of measurement, the measurement yields the eigenvalue corresponding to the eigenstate the system happened to be in at that moment. This is sometimes referred to as the collapse of a wavefunction at the moment of measurement – before the measurement the wavefunction contains the possibility of two (or more) states, but it is always reduced to a single state by the process of measurement.

At this point we've completed our introduction to quantum mechanics. We've introduced and begun to explore five of the six postulates of quantum mechanics. I'd like to review these five postulates and briefly mention the sixth.

Postulate 1

The state of a quantum mechanical system is completely specified by a function $\Psi(\mathbf{r}, t)$ that depends on the coordinates of the particle and on the time. This function, called the wave function or the state function, has the important property that $\Psi^*(\mathbf{r}, t)\ \Psi(\mathbf{r}, t)\ dx\ dy\ dz$ is the probability that the particle lies in the volume element dx dy dz, located at **r**, at the time t.

When we say that the state of a quantum mechanical system is completely specified by the wavefunction $\Psi(r,t)$, we mean that all of the information which we use to describe the state can be obtained from the wavefunction. WHAT ARE SOME OF THE THINGS THAT WE CAN LEARN FROM OUR WAVEFUNCTION?

Postulate 2

To every observable in classical mechanics there corresponds an operator in quantum mechanics.

Postulate 2'

To every observable in classical mechanics there corresponds a linear Hermitian operator in quantum mechanics.

This second version of postulate two poses additional requirements on the operator to ensure that all eigenvalues that we obtain will be real. WHAT ARE SOME OF THE OPERATORS WE'VE USED? HOW DO WE GENERATE THESE OPERATORS?

Postulate 3

In any measurement of the observable associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a, which satisfy the eigenvalue equation

$$\hat{A}\psi = a\psi \,.$$

GIVE ME AN EXAMPLE OF AN EIGENVALUE THAT WE'VE CALCULATED. HOW CAN WE TELL EXPERIMENTALLY THAT A SYSTEM IS IN AN EIGENSTATE?

Postulate 4

If a system is in a state described by a normalized wave function Ψ, then the average value of the observable corresponding to $\hat{A}$ is given by

$$< a > = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau.$$

WHAT ARE THE KINDS OF THINGS WE CAN CALCULATE ABOUT A WAVEFUNCTION USING THIS EQUATION?

Postulate 5

The wave function or state function of a system evolves in time according to the time-dependent Schrödinger equation

$$\hat{H}\Psi(x,t) = i\hbar \frac{\partial \Psi}{\partial t}$$

Postulate 6

The wavefunction of a system of electrons must be antisymmetric to the interchange of any two electrons.

This last postulate is one that we won't treat until the next chapter, but is included here for completeness. This postulate is one that you know in different words as the Pauli exclusion principle.