

Lecture 13, February 17, 2006**Solved Homework** (*Homework for grading is also due today*)

We are asked to demonstrate the orthogonality of the functions  $\Phi(\phi)$  that are the  $\phi$ -dependent components of the spherical harmonics. We know that they are eigenfunctions of  $L_z$ , and thus, since they are non-degenerate eigenfunctions of a Hermitian operator, that they *must* be orthogonal, but demonstrating this point explicitly serves as a check on our accuracy, if you like.

So, the question is, given two eigenfunctions  $\Phi$  characterized by different eigenvalues  $m_l$  and  $m_l'$ , is it true that

$$\langle \Phi_{m_l}(\phi) | \Phi_{m_l'}(\phi) \rangle = 0?$$

The variable  $\phi$  ranges from 0 to  $2\pi$ . So, we evaluate the above integral as

$$\begin{aligned} \langle \Phi_{m_l}(\phi) | \Phi_{m_l'}(\phi) \rangle &= \int_0^{2\pi} (e^{im_l\phi})^* (e^{im_l'\phi}) d\phi \\ &= \int_0^{2\pi} (e^{-im_l\phi}) (e^{im_l'\phi}) d\phi \\ &= \int_0^{2\pi} e^{i(m_l'-m_l)\phi} d\phi \\ &= \frac{1}{i(m_l'-m_l)} e^{i(m_l'-m_l)\phi} \Big|_0^{2\pi} \\ &= \frac{e^{2\pi i(m_l'-m_l)}}{i(m_l'-m_l)} - \frac{1}{i(m_l'-m_l)} \end{aligned}$$

We may use the relationship

$$e^{2\pi i(m_l'-m_l)} = \cos[2\pi(m_l'-m_l)] + i \sin[2\pi(m_l'-m_l)]$$

to evaluate the first part of the solved integral. Since  $m_l$  and  $m_l'$  are integers, their difference is also an integer. The cosine of an integral multiple of  $2\pi$  is 1 and the sine of an integral multiple of  $2\pi$  is 0. Substituting this simplification into the eqs. above provides

$$\begin{aligned}
\langle \Phi_{m_l}(\phi) | \Phi_{m_l'}(\phi) \rangle &= \frac{e^{2\pi i(m_l' - m_l)}}{i(m_l' - m_l)} - \frac{1}{i(m_l' - m_l)} \\
&= \frac{1}{i(m_l' - m_l)} - \frac{1}{i(m_l' - m_l)} \\
&= 0
\end{aligned}$$

Thus proving the orthogonality of the eigenfunctions. Note that if  $m_l$  and  $m_l'$  had been equal to one another, the original integrand would have simplified to  $e^0 d\phi = d\phi$ , the integral for which would be  $2\pi$ , and as we've already seen, this gives rise to the normalization constant  $(2\pi)^{-1/2}$  included in  $\Phi$ .

### The Rigid Rotator

We've previously considered two masses connected by a spring in solving the vibrational Schrödinger equation. The solutions were the quantum mechanical harmonic oscillator wave functions. Now, if we replace the spring with a solid rod (no vibration) and permit the system to rotate about an axis perpendicular to the rod, it will rotate about its center of mass.

As we discussed in lecture 3, the kinetic energy for a rotating system is

$$T = \frac{l^2}{2I} \quad (13-1)$$

where  $l$  is the angular momentum and  $I$  is the moment of inertia. Although our original discussion considered only a single particle orbiting a fixed position, the moment of inertia generalizes to multiple particles as

$$I = \sum_{i=1}^N m_i r_i^2 \quad (13-2)$$

where there are  $N$  total particles each having a distinct mass  $m$  and distance from the center of mass  $r$ . When there are only two particles, one can show with some straightforward algebra that

$$I = \mu R^2 \quad (13-3)$$

where  $\mu$  is the reduced mass defined by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (13-4)$$

and  $R$  is the length of the rigid rod connecting them. It would behoove you to memorize eqs. 13-3 and 13-4.

For a rigid rotator in free space, there is no potential energy affecting the system, and the Hamiltonian operator is simply the kinetic energy operator. Thus, the time-independent, rigid rotator Schrödinger equation for a diatomic molecule is

$$\begin{aligned} H\Psi &= (T + V)\Psi \\ &= T\Psi \\ &= \frac{L^2}{2I}\Psi = E\Psi \end{aligned} \quad (13-5)$$

where  $L^2$  is the total angular momentum squared operator with which we've just spent much time. We already know its eigenfunctions and eigenvalues, so we may rewrite eq. 13-5 as

$$\frac{L^2}{2I} Y_{l,m_l} = \frac{l(l+1)\hbar^2}{2I} Y_{l,m_l} = E_l Y_{l,m_l} \quad (13-6)$$

Thus, we see that the allowed energies of the rigid rotator are quantized by the total angular momentum quantum number  $l$ , and depend inversely on the moment of inertia. The energies are independent of  $m_l$ . We already know that  $m_l$  can take on  $2l + 1$  different values depending on  $l$ , so each energy level of the rigid rotator is  $2l + 1$  degenerate.

In discussing the rigid rotator for *molecular* rotation, it is traditional to replace the notation  $l$  with  $J$  for the total angular momentum quantum number. It is also traditional to define a rotational constant  $B$  according to

$$B = \frac{\hbar^2}{2I} \quad (13-7)$$

In that case, the allowed energy levels for the rigid rotator may be compactly written as

$$E_J = J(J + 1)B \quad (13-8)$$

Note that the separation between allowed energy levels depends on  $B$ , which is itself a function of the atomic masses and  $R$ , the distance between them. If we know the identity of our molecule, say CO (carbon monoxide), we know the masses and the only unknown is the bond distance. So, if we can measure the separation between rotational energy levels (and know which levels are which), we can determine the bond length. This is indeed a standard protocol for determining molecular structure.

## Microwave Spectroscopy of the Rigid Rotator

Consider the energy levels of the rigid rotator. The ground state, for which  $J = 0$ , has zero rotational energy according to eq. 13-8. Thus, *there is no zero-point energy*. This does not violate the uncertainty principle because, although we know the angular momentum exactly, we don't know anything about the angular "position" (how the molecule is oriented in space, if you will). The ground state has no degeneracy, since, given that the total angular momentum is zero, the only allowed value for the  $z$  component of the angular momentum is zero.

The next higher energy levels correspond to  $J = 1, 2, 3$ , etc., and have energies according to eq. 13-8 of  $E_J = 2B, 6B, 12B$ , etc. with degeneracies of 3, 5, 7, etc. The degeneracies may be thought of as reflecting the different angles that are allowed between the axis of rotation and the  $z$  axis of the system. When the two axes are orthogonal, the  $z$  component of the angular momentum is zero. With higher total angular momenta, there are more deflections allowed from  $m_J = 0$ , but it can never get to the point where the  $z$  axis corresponds to the rotation axis, because then the  $z$  component of the angular momentum would be the total angular momentum, and we would know that the other two components must be zero, and *this* would violate the uncertainty principle.

In any case, we now know the separation in energy between levels, but we do not know the selection rules for what transitions are allowed (and may therefore be observed spectroscopically). Remember that to observe a transition, it must be true that the integral

$$\langle \Psi_m | \mu | \Psi_n \rangle = \int \Psi_m^*(\mathbf{r}) e \mathbf{r} \Psi_n(\mathbf{r}) d\mathbf{r} \quad (13-9)$$

is not zero. Some playing around with the relevant integrals in spherical polar coordinates allows one to prove that spectroscopic transitions will only be observed between two rotational states  $m$  and  $n$  if

$$\Delta J = \pm 1 \quad \text{and} \quad \Delta m_J = 0 \text{ or } \pm 1 \quad (13-10)$$

Thus, we can only observe transitions between adjacent rotational states, and those transitions cannot change the  $z$  component by more than one quantum number (one h-bar), although they *are* allowed to leave it unchanged.

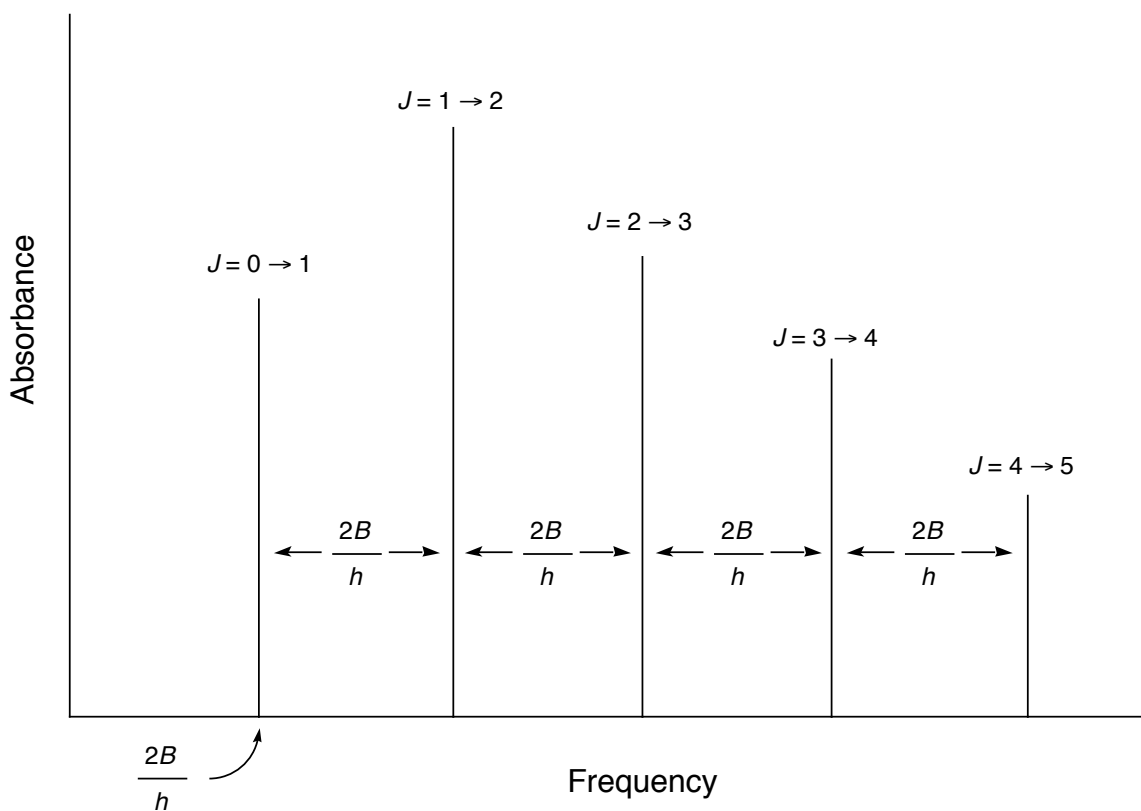
The restrictions of transitions to only the next higher or lower quantum number is a delightful simplification for spectroscopic purposes. Let's consider absorption spectroscopy. For any state  $J$  being excited to state  $J + 1$ , we have

$$\begin{aligned} \Delta E_{J \rightarrow J+1} &= E_{J+1} - E_J \\ &= (J+1)[(J+1)+1]B - J(J+1)B \\ &= 2(J+1)B \end{aligned} \quad (13-11)$$

The Bohr hypothesis says that photons of energy  $E = h\nu$  will be absorbed at these characteristic energies, so we expect to see absorptions at frequencies

$$\begin{aligned} \nu &= \frac{2(J+1)B}{h} \\ &= \frac{2B}{h}, \frac{4B}{h}, \frac{6B}{h}, \text{etc.} \end{aligned} \quad (13-12)$$

Molecular rotational frequencies are in the microwave region of the spectrum, so a typical rotational spectrum for a diatomic will appear very simple, namely



Note that the first absorption corresponds to the ground state to first excited state transition and occurs at  $2B/h$ . Typically, however, it may be rather hard to decide exactly what line in a spectrum corresponds to the  $0 \rightarrow 1$  transition. A much better way to determine  $2B/h$  is to notice that the separation between every pair of adjacent lines is *also* equal to this value. So, if we have a nice spectrum like that above, and we know the masses of our two atoms, it is trivial to measure  $2B/h$  and solve for  $R$ , the interatomic distance, which is the only unknown in  $B$ .

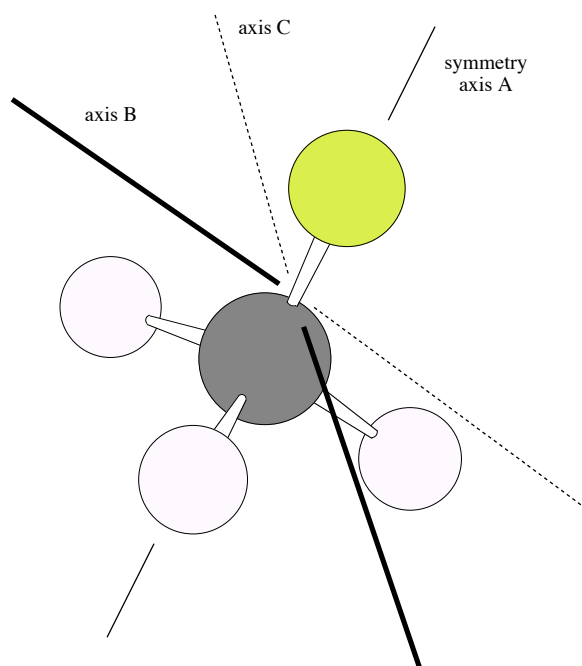
Note that the intensities of the absorptions depend on how many molecules are in the starting state, and that depends on the temperature (this is one of the reasons why it may be hard to see the  $0 \rightarrow 1$  transition; the Boltzmann distribution may have very few

molecules in the ground state). Thus, this kind of spectroscopy can also be used to determine the temperature of a sample!

While we've considered thus far only a diatomic system, the approach outlined above works for any *linear* molecule. Non-linear molecules are more complicated than linear ones because they are characterized by three separate moments of inertia (one about each cartesian axis). In highly symmetric cases, however, relatively simple solutions of the correct rotational Schrödinger equation continue to exist. For instance, in molecules possessing an axis of rotation that is 3-fold or higher in symmetry, the two moments of inertia for rotation about the two axes perpendicular to the high-symmetry axis will be equal. For example, in fluoromethane (shown below), which is  $C_{3v}$ , there is one moment of inertia,  $I_A$ , about the symmetry axis A, and there are two equal moments of inertia,  $I_B$  and  $I_C$ , about the axes perpendicular to axis A. In this particular case, the magnitude of the latter two moments is larger than that of the former moment because the heavy atoms C and F have displacements of 0 from axis A but not from the other two, and such a molecule is called a prolate top. In the case of a prolate top, the rotational eigenvalues are given by

$$E_J^K = \frac{J(J+1)\hbar^2}{2I_B} + K^2 \left( \frac{1}{I_A} - \frac{1}{I_B} \right) \frac{\hbar^2}{2} \quad (13-13)$$

where  $K$  is the quantum number corresponding to  $m_l$ , running over  $-J, -J+1, \dots, J-1, J$ , and expressing the component of the angular momentum along the highest symmetry axis. The selection rules for a rotational transition in this case are  $\Delta J = \pm 1$  and  $\Delta K = 0$ , and thus eqs. 13-11 and 13-12 continue to be valid for absorption frequencies using  $I = I_B$  in the rotational constant  $B$ .



Less symmetric molecules require a considerably more complicated treatment, which we will not go through here, but in the end their spectral transitions are functions of their 3 moments of inertia. From a spectroscopy standpoint, then, prediction of rotational spectral lines depends *only* on the moments of inertia, and hence only on the molecular geometry. Thus, rotational spectra provide a good way to measure molecular structure within the regime where the rigid-rotor approximation is valid. To further nail down structures, one often carries out the spectroscopy on many different isotopomers of the molecule in which one is interested, in order to be able to vary the different moments of inertia in alternative fashions and thus narrow down the possible ways in which the atoms may be arranged relative to one another and still give the observed spectra.

### **The Diffuse Interstellar Bands**

Let's leave the world of the tiny and change length scales by, oh, 25 orders of magnitude or so. And, let's ask a profound question: What is the molecular composition of the matter which is found in distant regions of space? It should be fairly clear that sending a spaceship out to collect the contents of a nebula 2000 light years away is probably not the best experimental option for answering this question.

So, astrophysicists use spectroscopy (it's still sort of a long experiment, since the light being observed takes 2000 years to reach Earth in the above example, but we'll settle for knowing about the composition of the matter 2000 years ago...) One approach is to find a nebula (a cloud of gas and dust) in which you are interested, to look at the spectrum of a star shining through it, and to observe what frequencies of light are depleted that you would otherwise *expect* to see from the star (based on having observed similar stars that aren't stuck behind nebulae). Something must be absorbing those frequencies, and given their magnitudes you may be able to decide what that something is. Such spectroscopy is usually done in the UV/Vis region, and corresponds to electronic absorptions, like those we've already considered for the H atom in the Bohr model for that atom.

But what if the nebula is so thick that *no* starlight comes through? In that case, you can't look at absorptions, you have to look for *emissions*. Why might there be emissions? Well, one way in which a molecule can be in an excited state is if it exchanged energy with another molecule that just bashed into it. If it takes some energy from the other molecule in the collision, it can be in an excited rotational state. Given a sufficient amount of time, it will ultimately radiate a photon (in the microwave region) to come back into thermal equilibrium.

Space is fantastically diffuse, so molecular collisions, even in nebulae, occur on the time scale of days to years (!). Nevertheless, if you consider that a receiver on Earth gets to sample a path length of at least half the width of the universe (longer if you are willing to believe that you are not, personally, the absolute center of the universe...), then you will perhaps not be surprised to learn that this microwave radiation can be detected by enormous radio antennae. This is one function of radioastronomy: to identify

molecular components of interstellar gas clouds based on their rotational emission spectra. These dominate the microwave region of what are called the diffuse interstellar bands (DIBs) in the universal spectrum. By observing changes in the DIBs as a function of what slice of sky is sampled, one can assign variations in signal to particular interstellar objects.

*None of this would be possible if the rotational spectra were not to be quantized!* If all values of angular momenta were allowed, we'd see no lines in spectra, only broad blurs that would be completely uninformative.

### Homework

To be solved in class:

The lowest microwave frequency absorbed by carbon monoxide (formed from the  $^{12}\text{C}$  and  $^{16}\text{O}$  isotopes) is 115.271 GHz. (a) Compute the moment of inertia of CO and the average value of the C–O bond distance. (b) Estimate the frequency at which the  $J = 1$  to  $J = 2$  transition occurs for this molecule in both GHz and  $\text{cm}^{-1}$ .

To be turned in for possible grading Feb. 24:

Consider a 2-dimensional so-called planar rigid rotator—a quantum mechanical compact disc, if you will. In this system, rotation is confined to a plane, so all of the angular momentum is along a single axis. The Schrödinger equation for this system is thus

$$\frac{L_z^2}{2I}\Psi = E\Psi$$

If the moment of inertia  $I$  is taken to be  $1/2$ , what are the eigenfunctions and eigenvalues for this system (use spherical polar coordinates)? Looking at the Schrödinger equation for the free particle may be helpful, but this case is quantized, while that for the free particle is not—why is there a difference? What are the lowest 3 possible energies? What degeneracies are associated with these energies?