2 Overview of Molecular Spectroscopy

When discussing molecular spectroscopy we will use the results that we have obtained from quantum chemistry quite frequently. I will start by giving you an overview of the field of molecular spectroscopy, dealing with issues that are common to all types of spectra. For this I will mostly use diatomic molecules as an example. We will then become more specific and consider particular types of spectroscopy (*i.e.*, transitions between different types of energy levels). Occasionally I will need to introduce new concepts related to quantum chemistry.

Because molecular spectroscopy involves making light-induced transitions between quantum states of a molecule, you can see how the basis of molecular spectroscopy would be quantum chemistry. One needs to know both the energy levels of molecules and their wave functions to be able to predict their spectra. However, the spectra themselves provide the most powerful means to investigate the energy levels and wave functions of molecules.

The approach of spectroscopy is to cause molecules to absorb and emit light and then measure the frequencies at which those transitions occur. The energy or frequency of each transition corresponds to a difference in energy levels. Recall that the separations of energy levels depends upon the potential energy term in the Hamiltonian for the system. We saw this in the simple one-dimensional problems such as the particle in a box and harmonic oscillator. For polyatomic molecules, this function is multidimensional. One of the primary goals of spectroscopy is to determine the multidimensional potential energy function, also called a potential energy surface, for a molecule from measuring these levels. Recall that the bottom of the potential well in a simple one-dimensional potential (*i.e.*, for a diatomic molecule) gives us the bond length. In a polyatomic case, the global minimum of the potential energy surface gives the geometry of the molecule.

After measuring the energy levels of a molecule, we can compare them to those predicted from calculated potential energy surfaces. This allows us to go back and refine the techniques used to calculate the surface. The goal would be to calculate these potential functions accurately enough to determine accurate molecular geometries and predict exactly where all the levels would be. This would allow us to predict at which frequencies molecules would absorb and emit light.

2.1 Starting Point: The Born-Oppenheimer Approximation

At the end of the Quantum Chemistry course we were discussing ways of solving the Schrödinger Equation for simple molecules. Although I didn't make it so clear at the time, this is only one part of the Schrödinger Equation, *i.e.*, the electronic part. As you will soon see, the Born-Oppenheimer approximation divides the Schrödinger equation into two parts.

Solving the electronic part of the Schrödinger Equation determines the potential energy curves (or surfaces) for the nuclei, *i.e.*, the potential function in which the nuclei move. Hence we get the electronic (potential) energy as a function of the nuclear coordinates, the electronic wave functions, and, by analysis of the potential energy function, the geometry. This, however, does not solve for the total energy of the molecule, since we have neglected the nuclear kinetic energy. We need to take the result of our solution of the electronic part (the potential energy as a function of the position of the nuclei) and insert it into the nuclear part of the Schrödinger Equation (together with the nuclear kinetic energy) and solve this equation. The solutions of the nuclear Schrödinger Equation will give us the eigenvalues for the total energy. It is these eigenvalues that we measure in a spectroscopic experiment.

Thus, the Born-Oppenheimer approximation divides quantum chemistry (the electronic Schrödinger Equation) from molecular spectroscopy (the nuclear Schrödinger Equation) and hence lies at the foundation of the latter.

Because of its importance, I would like to go back and look at the Born-Oppenheimer approximation in a slightly more general way. After doing this, we will come back and focus once again on the case of a simple diatomic molecule, using it to display many of the general principles about spectroscopy.

Let's write down (using atomic units) the Hamiltonian for a molecule neglecting relativistic interactions.

$$\hat{H} = -\frac{1}{2}\sum_{\alpha}\frac{1}{m_{\alpha}}\nabla_{\alpha}^{2} - \frac{1}{2}\sum_{i}\nabla_{i}^{2} + \sum_{\alpha}\sum_{\beta>\alpha}\frac{Z_{\alpha}Z_{\beta}}{r_{\alpha\beta}} - \sum_{\alpha}\sum_{i}\frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{j}\sum_{i>j}\frac{1}{r_{ij}}$$

α, β denote nuclei; *i,j* denote electrons.
$r_{\alpha\beta}$ is the distance between nucleus α and nucleus β
$r_{i\alpha}$ is the distance between electron *i* and nucleus α
r_{ij} is the distance between electron *i* and electron *j*

For understanding spectroscopy, we need to find both the wave functions and energies of a molecule.

These are found from the Schrödinger Equation

$$\hat{H}\psi(q_i, q_{\alpha}) = E\psi(q_i, q_{\alpha})$$

where q_i represents the electron coordinates and q_{α} the nuclei coordinates

You can see how things are getting pretty complicated for atoms with more than two electrons. Solving the Schrödinger Equation for a molecule with more than *two atoms* might appear hopeless. However, the Born-Oppenheimer approximation greatly simplifies the problem and is quite accurate. It essentially allows us to separate both the Hamiltonian and its eigenfunctions into electronic and nuclear parts.

Recall that the physical basis of the Born-Oppenheimer approximation lies in the fact that the masses of the nuclei are much greater than that of the electrons. The ratio of the rest mass of the proton to that of electron is

$$\frac{m_p}{m_e} \approx 1835$$

The ratio of the mass of a nucleus containing several protons and neutrons to that of an electron is even higher. As a result of this difference in mass, for the same coulombic forces between the nuclei and the electrons, the ***electrons move much faster than the nuclei.*** To a very good approximation, the nuclei can be considered to be fixed while the electrons carry out their motions. Making this approximation amounts to neglecting the nuclear kinetic energy term from the Hamiltonian for electronic motion.

We can then write the Schrödinger Equation for the electronic motion:

$$\left(\hat{H}_{el} + V_{nucl}\right)\psi_{el} = U\psi_{el}$$

where

$$\hat{H}_{el} = -\frac{1}{2}\sum_{i}\nabla_{i}^{2} - \sum_{\alpha}\sum_{i}\frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{j}\sum_{i>j}\frac{1}{r_{ij}}$$

and

$$V_{nucl} = \sum_{\alpha}\sum_{\beta>\alpha}\frac{Z_{\alpha}Z_{\beta}}{r_{\alpha\beta}}$$

The energy *U* is the electronic energy including nuclear repulsion. Remember that we only neglected nuclear kinetic energy, not the repulsion of the nuclei.

Note that since we make the approximation that the nuclei don't move, then $r_{\alpha\beta}$ aren't really variables but parameters. That is, we fix them and solve the electronic problem for fixed values of $r_{\alpha\beta}$. We choose values for the $r_{\alpha\beta}$ (designated more generally by q_{α}), evaluate V_{nuc}, and then solve our electronic Schrödinger Equation. *We must repeat this process for many values of the nuclear coordinates,* q_{α}.

Since the Hamiltonian depends on q_α, the energy we get will also depend parametrically on q_α.

$$U = U(q_\alpha)$$

So for each set of q_α we get a different Schrödinger equation, different energies U, and different electronic wavefunctions.

$$\psi_{el} = \psi_{el,n}(q_i;q_\alpha)$$

where n is the electronic quantum number, q_i are the electron positions and the ; signifies that the q_α are parameters.

Now, once we pick our q_α, the nuclear potential term V_{nuc} is constant.

$$\left(\hat{H}_{el} + V_{nucl}\right)\psi_{el} = U\psi_{el}$$

We can write this like:

$$\left(\hat{H}_{el} + V_{nucl}\right)\psi_{el} = \left(E_{el} + V_{nucl}\right)\psi_{el}$$

where E_{el} is simply the eigenvalue of $\hat{H}_{el}$:

$$\hat{H}_{el}\psi_{el} = E_{el}\psi_{el}$$

We often call this equation the electronic Schrödinger equation.

The total electronic energy, U, (including nuclear repulsion terms) is then given by

$$U = E_{el} + V_{nucl}$$

So we can leave out V_{nuc} from our Schrödinger equation and simply add it to E_{el} after solving the electronic Schrödinger equation.

Note that $\hat{H}_{el}$ still contains inter-electronic repulsion and attraction to the nucleus.

Let's say for the moment we know how to solve the electronic Schrödinger Equation using some of the techniques we discussed in our treatment of quantum chemistry.

$$\hat{H}_{el}\psi_{el} = E_{el}\psi_{el}$$

In practice, this is not trivial, but assume we can find a way to do this, for example using the Hartree-Fock method. Let us think about the procedure one would take in solving the full problem.

Consider the case of a diatomic molecule.

E_{el} and ψ_{el} depend on $r_{\alpha\beta}$

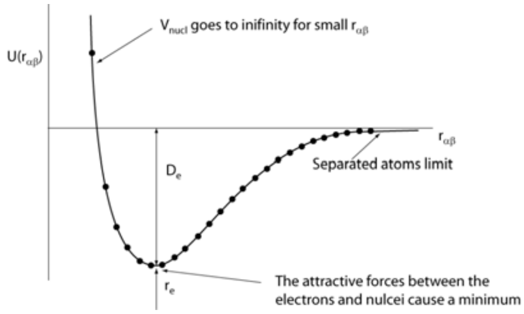
First fix $r_{\alpha\beta}$ at some value and solve this equation for E_{el}. We will get a whole set of solutions $\psi_{el,n}$, $E_{el,n}$. Let's now look only at the lowest energy state.

U, the total electronic energy (including nuclear repulsion) is

$$U = E_{el} + V_{nucl} = E_{el} + \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}$$

We then go through this procedure for a series of different $r_{\alpha\beta}$, each time finding a different value of E_{el} and hence another value for U. It is important to realize that every time we change the nuclear coordinates, we must resolve the electronic Schrödinger Equation.

If we plot U vs. $r_{\alpha\beta}$ we get something like this:



Once calls this plot a potential energy curve, since it represents the potential energy of interaction between the two nuclei. At each point along the curve (that is, each value of r) we have solved the electronic Schrödinger equation and then added the nuclear repulsion to get the total electronic energy U.

The fact that the electronic energy U has a minimum *vs*. r indicates that there is some equilibrium internuclear separation that corresponds to a state in which the two nuclei are bound and stable.

One usually denotes the $r_{\alpha\beta}$ at the minimum as r_e, and the difference between U at r_e and U at ∞ as D_e.

$$D_e = U(\infty) - U(r_e)$$

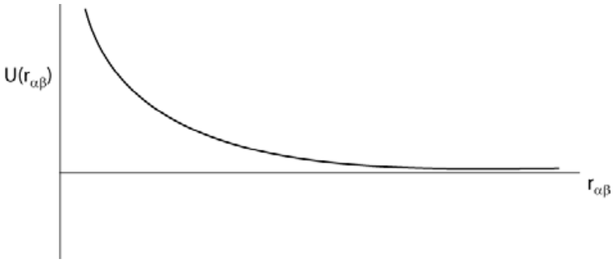
D_e is the energy needed to separate the two atoms of the diatomic, or in other words the binding energy or bond energy.

Notice that our nuclear term is purely repulsive:

$$V_{nucl} = +\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}$$

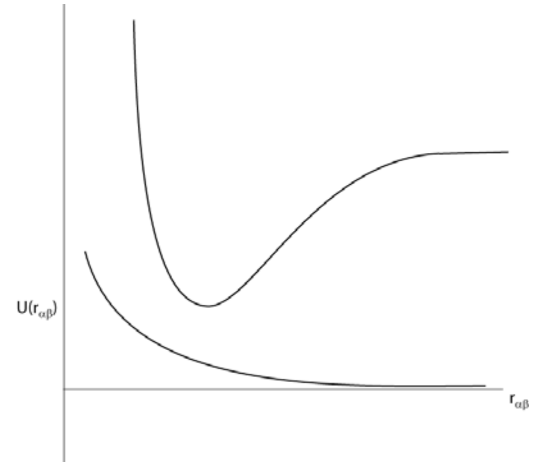
Thus it is electronic energy, E_{el}, which gives you the minimum in the potential.

There doesn't have to be a minimum in the potential. One can have an electronic state in which the potential energy curve looks like the following:



This is a purely dissociative electronic state since it has no stable minimum (no value of $r_e < \infty$ where the nuclei are at their lowest energy). This is the case for He_2 for example.

Molecules will in general have both bound and dissociative states. For stable molecules, obviously the ground state is bound. However, in the He dimer, He_2, the first two potential curves look something like that shown below (we already saw this when we discussed molecular last semester):



For this molecule, the lowest state is dissociative and first excited state is bound. A molecule that is bound in the excited state but dissociative in the ground state is called an ***excimer*** (or ***exciplex*** in the case where the two atoms are different).

Each one of these curves represents an electronic state, in the same way that each energy of the particle in box represents a quantum mechanical state. There is therefore an entire ladder of electronic states. However, we have added an additional coordinate that the electronic energy depends upon, *i.e.*, the internuclear separation. If we take a cut along the axis representing the internuclear separation, we get a series of energy levels corresponding to increasing values of the quantum numbers for electronic degrees of freedom. When I refer to an electronic state of a diatomic, I am speaking of the entire potential energy curve representing the electronic energy as a function of the internuclear coordinates. Most of the time I will only consider the lowest or the lowest few potential curves (*i.e.*, electronic states).

Solving the electronic part of the Schrödinger equation represents a field one would call ***chemical bonding***, since it is the electronic part of the Schrödinger equation that results in stable minima between the atoms and hence a chemical bond. I will say more about this in a moment.

The electronic part of the Schrödinger equation is only half the problem, however. We haven't yet considered nuclear motion.

Since electrons move much faster than the nuclei, they are able to immediately readjust as the nuclei move. In the diatomic case, if the nuclei move from $r_{\alpha\beta}$ to $r_{\alpha\beta'}$, the electronic wave function changes from $\psi_{el}(q_i;r_{\alpha\beta})$ to $\psi_{el}(q_i;r_{\alpha\beta'})$. The electronic energy changes smoothly from $U(r_{\alpha\beta})$ to $U(r_{\alpha\beta})$ as one moves along the potential curve. In effect, $U(r_{\alpha\beta})$ (or in the general case $U(q_\alpha)$) becomes the potential in which the nuclei move. One solves the electronic Schrödinger equation for different q_α and then fits the results to some functional form (one dimensional if diatomic; higher dimensional if more than two nuclei).

The Schrödinger equation for nuclear motion can be written.

$$\hat{H}_{nuc}\psi_{nuc} = E_{Tot}\,\psi_{nuc}$$

where

$$\hat{H}_{nuc} = -\frac{1}{2}\sum_{\alpha}\frac{1}{m_{\alpha}}\nabla_{\alpha}^{2} + U(q_{\alpha})$$

***E_{Tot}* is the total energy**, electronic + nuclear, since we are including electronic terms in the Hamiltonian though the potential, $U(q_\alpha)$.

For a diatomic, the potential, $U(q_\alpha)$, is a one-dimensional curve and can be treated like our simple model quantum mechanical systems.

So you can see that we have incorporated the solution to the electronic problem (*i.e.*, the electronic energy) into the nuclear problem through this quantity *U*. The solution to the nuclear Schrödinger equation, which has the nuclear kinetic energy added back in, will give us the total energy eigenvalues for the molecule. If the potential has a global minimum, these eigenvalues will be quantized.

Remember that quantization of energy occurs upon application of the boundary conditions to the Schrödinger equations. For energies below the asymptote, the energy will therefore be quantized. For higher energies (above the asymptote), there are no bound states (*i.e.*, no quantized energies). The same holds for purely dissociative electronic states, here also there are no bound levels.

Potential curves like this (or in many dimensions, potential energy surfaces) are called ***Born Oppenheimer potential surfaces***, since in deriving them the Born-Oppenheimer approximation is assumed. They allow us to solve each problem separately, using the eigenvalues from solving the electronic problem as the potential for the nuclear problem.

So there are basically two sides of the Born-Oppenheimer approximation.

Electronic Part:

$$\hat{H}_{el}\psi_{el} = E_{el}\,\psi_{el}$$

$$U(q_{\alpha}) = E_{el} + V_{nuc}$$

Chemical Bonding
Electronic Structure Calculations

Nuclear Part:

$$\hat{H}_{nuc}\psi_{nuc} = E_{Tot}\,\psi_{nuc}$$

$$\hat{H}_{nuc} = -\frac{1}{2}\sum_{\alpha}\frac{1}{m_{\alpha}}\nabla_{\alpha}^{2} + U(q_{\alpha})$$

Molecular Spectroscopy

The connection between the two sides is the function *U*.

The electronic part is what one would call *chemical bonding*, and people who do research in methods for solving this part of the Schrödinger equation are called *Electronic Structure Theoreticians* or *Quantum Chemists*. The people who work on electronic structure calculations try to determine accurate potential energy surfaces, *U*, using *ab initio* methods, like for example Hartree-Fock calculations.

The field of research that investigates the nuclear part of the Schrödinger equation is what we would call *Molecular Spectroscopy* and people who work in this field are called *molecular spectroscopists*. Molecular spectroscopists measure energy levels (among other things) and from their experimental data can provide potential energy functions to test the theoretical calculations. (Many spectroscopists also do electronic structure calculations, but there is a real art to these calculations, and those who do it at the highest level, usually specialize in the field.)

Thus, you can see that the Born-Oppenheimer approximation serves as a dividing point in quantum chemistry between electronic structure calculations (chemical bonding) and molecular spectroscopy. It is clear that the two branches must closely interact as they are connected to each other by $U(q_\alpha)$.

I will spend most of this semester discussing the nuclear side of the Born-Oppenheimer approximation. Towards the end of the course I will go back and say more about the electronic part of the Schrödinger equation when we need to treat electronic spectroscopy of polyatomic molecules.

2.2 Nuclear Side of the Born-Oppenheimer Approximation

2.2.1 General Treatment

We had reduced our nuclear problem to:

$$\hat{H}_{nuc}\psi_{nuc} = E_{Tot}\,\psi_{nuc}$$

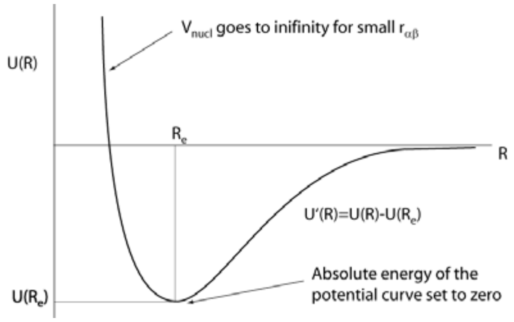
and

$$\hat{H}_{nuc} = -\frac{1}{2}\sum_{\alpha}\frac{1}{m_\alpha}\nabla_\alpha^2 + U(q_\alpha)$$

Let us confine our discussion to diatomics for the moment, realizing that we could generalize the result to larger molecules. For a diatomic, $U(q_\alpha)$ simply becomes $U(R)$.

Up to now we haven't considered the center of mass motion explicitly. If we are going to use relative (internal coordinates), we must separate the center of mass part of the Hamiltonian. We know, however, that we can always do this, we simply get an additional (kinetic energy) term added to the internal energy. Let us assume that we have separated off the center of mass motion. In this case the translational energy will not be included in our expression for the total energy. To signify that we use relative coordinates we will denote the corresponding wavefunction as ψ_{Int}

The function $U(R)$ will consist of a constant part and a part which varies with R. Call the constant part $U(R_e)$ and the variable part $U'(R)$



Thus we write: $U(R) = U'(R) + U(R_e)$

We can easily evaluate $U(R_e)$ by our definition of U

$$U = E_{el} + \frac{Z_\alpha Z_\beta}{R}$$

$U(R_e)$ is simply $U(R)$ evaluated at the minimum.

Solving $\hat{H}_{nuc}\psi_{Int} = E_{Tot}\,\psi_{Int}$

with

$$\hat{H}_{nuc} = \hat{H}_{KE} + U(R)$$

$$= \hat{H}_{KE} + U'(R) + U(R_e)$$

gives $$\left(\hat{H}_{KE} + U'(R) + U(R_e)\right)\psi_{Int} = E_{Tot}\psi_{Int}$$

and

$$\left(\hat{H}_{KE} + U'(R)\right)\psi_{int} = \left(E_{Tot} - U(R_e)\right)\psi_{Int}$$

$$= E_{Int}\psi_{Int}$$

where $$E_{Int} = E_{Tot} - U(R_e)$$

One can then see that the total energy E_{Tot} can be written

$$E_{Tot} = E_{Int} + U(R_e)$$

E_{Int} is therefore found from the Hamiltonian

$$\hat{H}_{KE} + U'(R)$$

So the net result is that we separated the wave function into

$$\psi = \psi_{el}\psi_{Int}$$

and the eigenvalues are

$$E_{Tot} = E_{Int} + U(R_e)$$

where $U(R_e)$ is the constant part of the electronic energy (the absolute offset of the curve).

Note that we have included some of the electronic energy in E_{Int} in the sense that we used the part that varied with R as the potential for nuclear motion. One typically talks about the electronic energy as being that at the bottom of the potential well (*i.e.*, the constant part $U(R_e)$). The part that varies with R is considered the nuclear potential energy. This essentially says that the electronic and internal energies are separable. This allows us to draw potential curves and draw in energy levels which are solutions to the internal or nuclear motion problem, adding the electronic energy as a constant offset for all the vibrational levels.

The nuclear Schrödinger equation for a diatomic in internal or relative coordinates (assuming we have separated the center of mass motion) is given by:

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + U'(R)\right]\psi_{Int}(R,\theta,\varphi) = E_{Int}\psi_{Int}(R,\theta,\varphi)$$

where μ is the reduced mass.

We want to be able to solve this equation to get the values of E_{Int}, and after doing so, we can add $U(R_e)$ to get the total energies.

2.2.2 Separation of Rotational Motion

Starting with the Schrödinger equation for the nuclear motion as shown above we find:

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + U'(R)\right]\psi_{Int}(R,\theta,\varphi) = E_{Int}\psi_{Int}(R,\theta,\varphi)$$

Recall that in Cartesian coordinates, the operator ∇^2 is given by

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

Converting this operator to spherical polar coordinates gives

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

If we now substitute for ∇^2 in spherical polar coordinates into the Schrödinger equation for nuclear motion we get

$$\left[-\frac{\hbar^2}{2\mu R^2}\left(\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)\right) + U'(R)\right]\psi_{Int}(R,\theta,\varphi) = E_{Int}\psi_{Int}(R,\theta,\varphi)$$

Notice that all the angular dependence is contained in the second and third terms. If you look back in your lecture notes of Quantum Chemistry, you will see that the $\hat{L}^2$ operator in spherical polar coordinates equals:

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

Using this, one can write the Schrödinger equation as

$$-\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial\psi_{int}(R,\theta,\varphi)}{\partial R}\right) + \frac{\hat{L}^2}{2\mu R^2}\psi_{int}(R,\theta,\varphi) + U'(R)\psi_{int}(R,\theta,\varphi) = E_{int}\psi_{int}(R,\theta,\varphi)$$

Note that the potential is only a function of R, and thus falls into the category of a *spherically symmetric potential*. Recall that whenever the potential is of this type (such as the rigid rotor or the hydrogen atom problem), the solution to the angular part will always be the spherical harmonic functions.

We can see this more clearly if we rearrange the above equation.

$$-\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial\psi_{Int}(R,\theta,\varphi)}{\partial R}\right) + \frac{\hat{L}^2}{2\mu R^2}\psi_{Int}(R,\theta,\varphi) + \left(U'(R) - E_{Int}\right)\psi_{Int}(R,\theta,\varphi) = 0$$

If we multiply through by $2\mu R^2$ and rearrange, we get

$$-\hbar^2\frac{\partial}{\partial R}\left(R^2\frac{\partial\psi_{Int}(R,\theta,\varphi)}{\partial R}\right) + \hat{L}^2\psi_{Int}(R,\theta,\varphi) + 2\mu R^2\left(U'(R) - E_{int}\right)\psi_{Int}(R,\theta,\varphi) = 0$$

You can see the only part of the operator that has angular dependence is the $\hat{L}^2$ term. We can therefore use the separation of variables and assume wave functions $\psi_{Int}(R,\theta,\varphi)$ of the form

$$\psi_{Int}(R,\theta,\varphi)=\psi_{vib}(R)Y_J^m(\theta,\varphi)$$

where the $Y_J^m(\theta,\varphi)$ are the spherical harmonics. We chose the spherical harmonics because they are eigenfunctions of the $\hat{L}^2$ operator. Please note that in spectroscopy often the quantum number *J* is used to describe angular momentum.

$$\hat{L}^2 Y_J^m(\theta,\varphi)=\hbar^2 J\left(J+1\right)Y_J^m(\theta,\varphi)$$

The part of the Hamiltonian that has derivatives with respect to *R* will do nothing to the angular part of the wave function.

Substituting for ψ_{int} and rearranging yields:

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+\frac{\hbar^2 J\left(J+1\right)}{2\mu R^2}\psi_{vib}(R)+U'(R)\psi_{vib}(R)=E_{int}\psi_{vib}(R)$$

↑	↑	↑
This term is the radial KE	This term is simply the rotational KE	Potential Energy

Note that we have made no other approximations other than the Born-Oppenheimer to get to this point, and that one is very accurate.

Since the rotational kinetic energy term depends on $1/R^2$, we cannot completely separate vibrational motion and rotational motion. To separate the vibrational and rotational motion, we have to make another approximation. This one isn't particularly accurate, but it can give a pretty good physical picture of diatomic energy levels. We will use it as a first order approximation.

If we recognize that the vibrational amplitudes of most diatomic molecules are very small, one can replace the *R* in the denominator of the rotational kinetic energy by R_e, the equilibrium internuclear distance. We can see that the rotational kinetic energy term now becomes

$$E_{rot}=\frac{\hbar^2 J\left(J+1\right)}{2\mu R_e^2}$$

where this term is now independent of *R*.

We can rewrite our equation:

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+U'(R)\psi_{vib}(R)=\left(E_{Int}-E_{rot}\right)\psi_{vib}(R)$$

or

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+U'(R)\psi_{vib}(R)=E_{vib}\psi_{vib}(R)$$

where

$$E_{Int}=E_{vib}+E_{rot}$$

This leaves us with

$$E_{Tot}=U(R_e)+E_{Int}=U(R_e)+E_{vib}+E_{rot} \text{ (neglecting translation, as usual)}$$

and

$$\psi_{Tot} = \psi_{el}\psi_{Int} = \psi_{el}\psi_{vib}\psi_{rot}$$

So to a first level of approximation, we can consider the electronic, vibrational and rotational motions of a molecule separately and write the total wave function as a product and the total energy as a sum. We can then solve each problem separately.

Note that from this treatment, we found the rotational energy to be

$$E_{rot} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2}$$

and the rotational part of the wave functions to be the spherical harmonics:

$$\psi_{rot} = Y_J^m(\theta,\varphi)$$

Our only approximation was to assume that the bond length R was constant. This is *the Rigid Rotor approximation* that we have already seen. We have already have solved the quantum mechanics of the Rigid Rotor model.

Before we go on to the vibrational part of the nuclear Schrödinger Equation, I would like to review the quantum mechanics of the Rigid Rotor.

2.2.2.1 REVIEW OF THE RIGID ROTOR MODEL

We first wrote down the classical expression for the rotational kinetic energy

$$KE_{classical} = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$$

and then found the Hamiltonian by substituting the $\hat{L}^2$ operator.

The Schrödinger equation for rotational motion is then

$$\hat{H}\psi_{rot}(\theta,\varphi) = E_{rot}\psi_{rot}(\theta,\varphi)$$
$$\frac{\hat{L}^2}{2\mu R^2}\psi_{rot}(\theta,\varphi) = E_{rot}\psi_{rot}(\theta,\varphi)$$

where there is no R dependence of the wave function since R is fixed. The solutions to this are the eigenfunctions of $\hat{L}^2$, which are the spherical harmonics, $Y_J^m(\theta,\varphi)$.

Because the eigenvalues of $\hat{L}^2$ are $\hbar^2 J(J+1)$, we can write

$$\frac{\hat{L}^2}{2\mu R^2}\psi_{rot}(\theta,\varphi) = \frac{\hbar^2 J(J+1)}{2\mu R^2}\psi_{rot}(\theta,\varphi)$$

and thus

$$E_{rot} = \frac{\hbar^2 J(J+1)}{2\mu R^2} = \frac{\hbar^2 J(J+1)}{2I}$$

Where $I = 2\mu R^2$

This is the same expression we obtained for our more general treatment when we assumed the bond length of a diatomic molecule to be fixed at $R=R_e$.

If we define the *rotational constant* as*,*

$$B=\frac{h}{8\pi^2 cI} \qquad \text{(note the conversion to units of cm}^{-1}\text{)}$$

We can write for the rotational energy expressed in cm^{-1}:

$$E_{rot}=BJ\left(J+1\right) \qquad J=0,1,2,\ldots$$

Recall that the spherical harmonics can be written:

$$Y_J^m(\theta,\varphi)=\left[\frac{(2J+1)}{4\pi}\frac{\left(J-|m|\right)!}{\left(J+|m|\right)!}\right]^{\frac{1}{2}}P_J^{|m|}(\cos\theta)e^{im\varphi}$$

where the $P_J^{|m|}$ are the Associated Legendre functions.

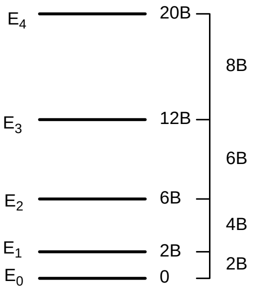
The first few spherical harmonics are:

$$\begin{aligned}
Y_0^0 &= \frac{1}{\sqrt{4\pi}}\\
Y_1^0 &= \sqrt{\frac{3}{4\pi}}\cos\theta\\
Y_1^1 &= \sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}\\
Y_1^{-1} &= \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}
\end{aligned}$$

Let's now recall the implications of the energy expression:

$$E_{rot}=BJ\left(J+1\right) \qquad J=0,1,2,\ldots$$

The first level (J=0) occurs at an energy of 0. The second level occurs at 2*B*. The next at 6*B*. This is shown in the figure below.



Energy Levels

Because the energy levels are spaced by *BJ*(*J*+1), the spacings between adjacent levels starts at 2*B* and increase by 2*B* for each successively higher level. We will use this result extensively when we begin to discuss rotational spectra.

To understand the transitions between these states (*i.e.*, upon the absorption of light), we must consider how light interacts with molecules and in particular we must discuss the subject of selection rules. I will do this shortly.

2.2.3 The Vibrational Problem

Once we separated off rotational motion by making the rigid rotor approximation, we were left with the following equation for the vibrational part of the wave function:

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+U'(R)\psi_{vib}(R)=E_{vib}\psi_{vib}(R)$$

To simplify this, let us expand the derivatives in the first term

$$\frac{1}{R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)=\frac{1}{R^2}\left(2R\frac{d\psi_{vib}(R)}{dR}+R^2\frac{d^2\psi_{vib}(R)}{dR^2}\right)$$

$$=\frac{2}{R}\frac{d\psi_{vib}(R)}{dR}+\frac{d^2\psi_{vib}(R)}{dR^2}$$

So we can write for the Schrödinger Equation

$$-\frac{\hbar^2}{2\mu}\left(\frac{2}{R}\frac{d\psi_{vib}(R)}{dR}+\frac{d^2\psi_{vib}(R)}{dR^2}\right)+U'(R)\psi_{vib}(R)=E_{vib}\psi_{vib}(R)$$

To simplify this a bit further, let us define a new function $\chi(R)=R\psi_{vib}(R)$. If we can find the function $\chi(R)$ then we can go back and get the original function $\psi_{vib}(R)$ by dividing by *R*.

We can put this equation in terms of $\chi(R)$ by substituting for the derivatives of $\psi_{vib}(R)$ in terms of $\chi(R)$.

Since $\chi(R)=R\psi_{vib}(R)$

and thus $\psi_{vib}(R)=\frac{\chi(R)}{R}$

we find for the first derivative:

$$\frac{d\psi_{vib}(R)}{dR}=\frac{1}{R}\frac{d\chi(R)}{dR}-\frac{1}{R^2}\chi(R)$$

For the second derivative:

$$\frac{d^2\psi_{vib}(R)}{dR^2}=-\frac{1}{R^2}\frac{d\chi(R)}{dR}+\frac{1}{R}\frac{d^2\chi(R)}{dR^2}+\frac{2}{R^3}\chi(R)-\frac{1}{R^2}\frac{d\chi(R)}{dR}$$

$$=\frac{1}{R}\frac{d^2\chi(R)}{dR^2}-\frac{2}{R^2}\frac{d\chi(R)}{dR}+\frac{2}{R^3}\chi(R)$$

Substituting these back into the Schrödinger equation one gets:

$$-\frac{\hbar^2}{2\mu}\left(\frac{2}{R}\left[\frac{1}{R}\frac{d\chi(R)}{dR}-\frac{1}{R^2}\chi(R)\right]+\left[\frac{1}{R}\frac{d^2\chi(R)}{dR^2}-\frac{2}{R^2}\frac{d\chi(R)}{dR}+\frac{2}{R^3}\chi(R)\right]\right)+U'(R)\frac{\chi(R)}{R}=E_{vib}\frac{\chi(R)}{R}$$

After canceling a few terms, one gets

$$-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{d^2\chi(R)}{dR^2}+U'(R)\frac{\chi(R)}{R}=E_{vib}\frac{\chi(R)}{R}$$

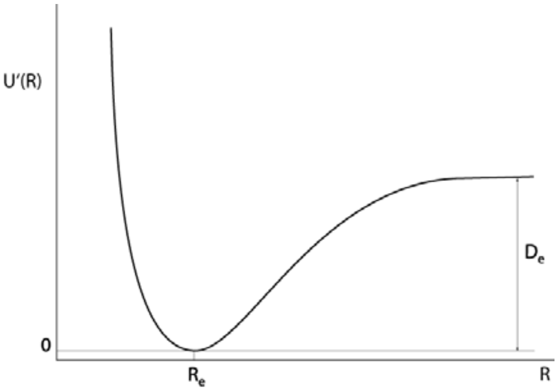
Finally, multiplying both sides by *R* gives

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(R)}{dR^2}+U'(R)\,\chi(R)=E_{vib}\chi(R)$$

This looks like a simple one-dimensional problem where the first term represents the kinetic energy, and the second term is the potential energy. Both the internal kinetic energy (*i.e.*, with the center of mass separated) and the potential energy depend only upon the separation of the nuclei, *R*.

Remember where the potential *U*'(*R*) comes from. It is the potential that results from solving the electronic part of the Schrödinger equation at a series of points (*i.e.*, a number of values for the internuclear separation *R*). I distinguish *U*(*R*) from *U*'(*R*) in that the latter has the electronic energy at the minimum of the curve, *U*(R_e), subtracted off.

Because *U*'(*R*) is a parametric function of *R*, no simple analytical form exists. Instead, one typically uses empirical forms for *U*'(*R*).



Let us use a Taylor series expansion for the potential *U'*(*R*) about the position *R*=R_e, and then we can keep only as many terms as we like.

$$U'(R)=U'(R_e)+\left.\frac{dU'(R)}{dR}\right|_{R=R_e}\left(R-R_e\right)+\frac{1}{2!}\left.\frac{d^2U'(R)}{dR^2}\right|_{R=R_e}\left(R-R_e\right)^2+\frac{1}{3!}\left.\frac{d^3U'(R)}{dR^3}\right|_{R=R_e}\left(R-R_e\right)^3+\frac{1}{4!}\left.\frac{d^4U'(R)}{dR^4}\right|_{R=R_e}\left(R-R_e\right)^4+\ldots$$

Remember how we defined *U*'(*R*). We introduced the prime when we subtracted off the electronic energy at the minimum in the potential, *U*'(R_e). By definition therefore, *U*'(R_e) = 0.

Also, because we expanded the potential about the minimum, the first derivative

$$\left.\frac{dU'(R)}{dR}\right|_{R=R_e}=0$$

We are then left with

$$U'(R)=\frac{1}{2!}\left.\frac{d^2U'(R)}{dR^2}\right|_{R=R_e}\left(R-R_e\right)^2+\frac{1}{3!}\left.\frac{d^3U'(R)}{dR^3}\right|_{R=R_e}\left(R-R_e\right)^3+\frac{1}{4!}\left.\frac{d^4U'(R)}{dR^4}\right|_{R=R_e}\left(R-R_e\right)^4+\ldots$$

We haven't introduced any additional approximations to this point. If the amplitude of the vibrational motion is sufficiently small, the $(R\text{-}R_e)^2$ term will be larger than the terms involving higher powers of $(R\text{-}R_e)$ (*i.e.*, cubic, quartic, etc.). As a first approximation, we can neglect these higher terms. We are then left with

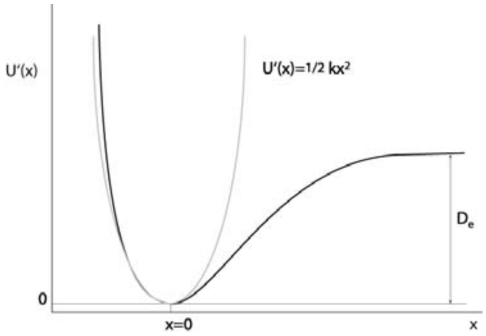
$$U'(R) = \frac{1}{2!}\left.\frac{d^2U'(R)}{dR^2}\right|_{R=R_e}\left(R-R_e\right)^2$$

If we define $x = R - R_e$ and $k = \left.\dfrac{d^2U'(R)}{dR^2}\right|_{R=R_e}$

We can then write:

$$U'(x) = \frac{1}{2}kx^2$$

This is the equation for a parabola. What we are doing in neglecting higher order terms is to say that near the bottom of the well, the potential is well approximated by a parabola.



This expression for the potential energy is the potential for a simple harmonic oscillator. To a first approximation, the *quantum mechanical* harmonic oscillator is a reasonable model for molecular vibrational motion.

2.2.3.1 REVIEW OF THE HARMONIC OSCILLATOR MODEL

I will briefly review the solutions (*i.e.*, the eigenvalues and wave functions) to the Schrödinger equation for the harmonic oscillator:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]\chi(x) = E_{vib}\chi(x)$$

Eigenvalues of the Quantum Mechanical Harmonic Oscillator

The eigenvalues are given by:

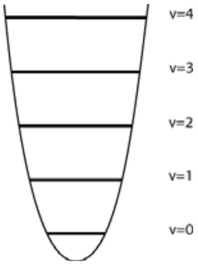
$$E_{\mathrm{v}} = h\nu\left(\mathrm{v} + \frac{1}{2}\right) \qquad \mathrm{v} = 0,1,2,3,\ldots$$

where

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Note that ν is the same as the frequency of the classical harmonic oscillator.

If we superimpose these levels on the potential curve, they look as follows:



There are several important things to note about the Harmonic Oscillator energy levels:

1) The energy levels are equally spaced in integral units of the classical frequency.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Remember that *k* is related to the width of the potential (which is a parabola):

$$U'(x) = \frac{1}{2}kx^2$$

2) The second point to notice is that even when the quantum number v=0, there is still energy in the amount of *h*⍰/2. This is called **zero point energy.**

Eigenfunctions of the Quantum Mechanical Harmonic Oscillator

Recall that wave functions corresponding to the eigenvalues E_v are non-degenerate and are given by

$$\chi_n(x) = N_n H_n(\alpha^{\frac{1}{2}}x)e^{-\frac{1}{2}\alpha x^2}$$

where

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

The normalization constant N_n is

$$N_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$$

and the $H_n(\alpha^{\frac{1}{2}}x)$ are polynomials called Hermite polynomials

The first few Hermite polynomials are:

$$H_0(\xi) = 1$$

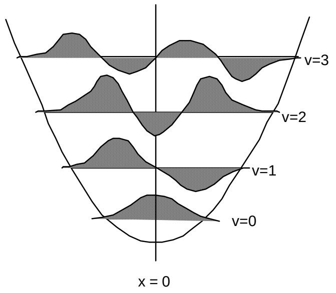
$$H_1(\xi) = 2\xi$$

Note: $\xi = \alpha^{\frac{1}{2}}x$

$$H_2(\xi) = 4\xi^2 - 2$$

$$H_3(\xi) = 8\xi^3 - 12\xi$$

The full harmonic oscillator wave functions look something like this:



2.2.4 Vibration-Rotation Interaction

If one makes spectroscopic measurements with any reasonable degree of accuracy, one finds that these simple models for vibration and rotation are not very good.

Thus, one must solve the coupled vibration-rotation problem to account for the experimental observations. I will not do this in class, but I will outline how it is done and give you the result.

If you go back to the Schrödinger equation:

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+\left[U'(R)+\frac{\hbar^2 J\left(J+1\right)}{2\mu R^2}\right]\psi_{vib}(R)=E_{Int}\psi_{vib}(R)$$

As before, we can make the substitution

$$\psi_{vib}(R)=\frac{\chi(R)}{R}$$

to simplify the kinetic energy term and find a new equation for $\chi(R)$.

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(R)}{dR^2}+\left[U'(R)+\frac{\hbar^2 J\left(J+1\right)}{2\mu R^2}\right]\chi(R)=E_{int}\chi(R)$$

Then, rather than assuming that the potential is harmonic, we can expand $U'(R)$ in a Taylor series in the displacement from R_e, $x=R-R_e$.

$$U'(x)=U'(0)+\left.\frac{dU'(x)}{dx}\right|_{x=0}x+\frac{1}{2!}\left.\frac{d^2U'(x)}{dx^2}\right|_{x=0}x^2+\frac{1}{3!}\left.\frac{d^3U'(x)}{dx^3}\right|_{x=0}x^3+\frac{1}{4!}\left.\frac{d^4U'(x)}{dx^4}\right|_{x=0}x^4+\ldots$$

The first term is zero by definition, and the second is zero because we are expanding about the bottom of the well.

We are then left with

$$U'(x)=\frac{1}{2}kx^2+\frac{1}{6}ax^3+\frac{1}{24}bx^4+\ldots$$

where we have simplified the coefficients of x

One can also expand the $1/R^2$ term in a Taylor series in x.

$$\frac{\hbar^2 J(J+1)}{2\mu R^2} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2\left(1+\frac{x}{R_e}\right)^2} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2}\left(1+\frac{x}{R_e}\right)^{-2}$$

Note that

$$(1+y)^s = 1 + sy + \frac{s(s-1)}{2!}y^2 + \frac{s(s-1)(s-2)}{3!}y^3 + \ldots$$

We can therefore write

$$\frac{\hbar^2 J(J+1)}{2\mu R_e^2}\left(1+\frac{x}{R_e}\right)^{-2} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2}\left[1 - 2\left(\frac{x}{R_e}\right) + \frac{(-2)(-3)}{2!}\left(\frac{x}{R_e}\right)^2 + \frac{(-2)(-3)(-4)}{3!}\left(\frac{x}{R_e}\right)^3 + \ldots\right]$$

$$= \frac{\hbar^2 J(J+1)}{2\mu R_e^2} - \frac{\hbar^2 J(J+1)}{\mu R_e^3}x + \frac{3\hbar^2 J(J+1)}{2\mu R_e^4}x^2 + \ldots$$

Putting it all together, we get something that looks like:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(x)}{dx^2} + \left[\frac{1}{2}kx^2 + \frac{1}{6}ax^3 + \frac{1}{24}bx^4 + \ldots \frac{\hbar^2 J(J+1)}{2\mu R_e^2} - \frac{\hbar^2 J(J+1)}{\mu R_e^3}x + \frac{3\hbar^2 J(J+1)}{2\mu R_e^4}x^2 + \ldots\right]\chi(x) = E_{Int}\chi(x)$$

where the constants *k*, *a*, *b* come from the expansion of *U*, and the $1/R_e$ terms come from the expansion of the $1/R^2$ term.

After rearranging we get:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(x)}{dx^2} + \left[-\frac{\hbar^2 J(J+1)}{\mu R_e^3}x + \frac{1}{2}\left(k + \frac{3\hbar^2 J(J+1)}{\mu R_e^4}\right)x^2 + \frac{1}{6}ax^3 + \frac{1}{24}bx^4 + \ldots\right]\chi(x) = \left(E_{Int} - \frac{\hbar^2 J(J+1)}{2\mu R_e^2}\right)\chi(x)$$

We can simplify this expression by including the Rigid Rotor term (first term in expansion of the $1/R^2$ term) into the energy by defining

$$E'_{Int} = E_{Int} - E_{RigidRotor}$$

and defining an effective force constant

$$k' = k + \frac{3\hbar^2 J(J+1)}{\mu R_e^4}$$

This yields then

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(x)}{dx^2} + \left[\frac{1}{2}k'x^2 - \frac{\hbar^2 J(J+1)}{\mu R_e^3}x + \frac{1}{6}ax^3 + \frac{1}{24}bx^4 + \ldots\right]\chi(x) = E'_{int}\chi(x)$$

You can see that this looks like a perturbed Harmonic Oscillator (a harmonic oscillator with a few extra small terms added into the potential). We can use perturbation theory to solve this problem. I will not go through the details of the perturbation theory solution to this problem, but using the tools that we already have developed (particularly the raising and lowering operators), it is not difficult.

The result for the energy E_{Int} (now also called E_{vJ}) is as follows:

$$F(\mathrm{v},J)=\frac{E_{\mathrm{v}J}}{hc}=\underset{\overset{\uparrow}{\text{HO}}}{\omega_e\left(\mathrm{v}+\frac{1}{2}\right)}+\underset{\overset{\uparrow}{\substack{\text{rigid}\\\text{rotor}}}}{B_eJ(J+1)}-\underset{\overset{\uparrow}{\text{anharmonicity}}}{\omega_e x_e\left(\mathrm{v}+\frac{1}{2}\right)^2}-\underset{\overset{\uparrow}{\substack{\text{vib-rot}\\\text{interaction}}}}{\alpha\left(\mathrm{v}+\frac{1}{2}\right)J(J+1)}-\underset{\overset{\uparrow}{\substack{\text{centrifugal}\\\text{distortion}}}}{DJ^2(J+1)^2}+\ldots$$

where the constants are given in units of cm^{-1}.

The constants ω_e, B_e, $\omega_e x_e$, α, and D can be simply related to the coefficients in our Taylor series expansion of the potential and centrifugal term, a, b, k, R_e. (*i.e.* related to the potential)

This expression results from taking a certain number of terms in $\hat{H}'$ in the perturbation theory treatment. If we were to take more terms, our energy expression would also contain more terms. You can see that the energy expression looks like a power series in the quantum numbers v and $J(J+1)$, and one can take it to higher order.

The terms that I have included here give a reasonably accurate expression for the energy levels of a diatomic molecule. How accurate you need to be depends upon how precisely you measure. However, the higher order terms begin to lose their physical significance.

I would like you to have a good feel what these constants in the E_{vJ} formula mean physically.

1) $\omega_e\left(\mathrm{v}+\frac{1}{2}\right)$

This term represents the vibrational energy. We know that

$$\omega_e=\frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

is the frequency of the classical harmonic oscillator (expressed in units of cm^{-1}). Remember that k is the width of the parabola, the force constant of vibration. Small k means that it is a wide parabola and a "loose" vibration. The wider the parabola the more closely spaced the levels. A thin parabola (large k) results in wide spacing and a "stiff" vibration.

2) $B_eJ(J+1)$

This term gives the rotational energy. Remember that

$$B_e=\frac{h}{8\pi^2 cI} \qquad \text{(in units of cm}^{-1}\text{)}$$

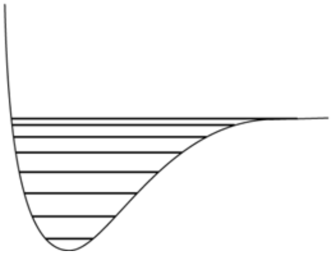
where I is the moment of inertia $I=\mu R_e^2$. Remember the rigid rotor energy levels are given by:

$$E_{rot}=BJ(J+1).$$

Consequently larger B_e means more widely spaced levels. This corresponds to smaller R_e or smaller μ. Light atoms ⍰ large B_e. H_2 has the largest B_e.

3) $-\omega_e x_e \left(\mathrm{v} + \frac{1}{2} \right)^2$

This term is due to the anharmonicity of the potential. It accounts for lowering of the energy levels due to the widening of the parabola:



As the bond weakens as *R* increases, the potential gets looser and the level spacing decreases. The negative sign in front of the term accounts for this decrease of the level spacings.

4) $-DJ^2 \left(J+1 \right)^2$

This term is named the centrifugal distortion term. Remember that

$$B = \frac{h}{8\pi^2 cI} \qquad \text{(in units of cm}^{-1}\text{)}$$

As *R* increases due to rotation, *B* will decrease. So *B* will be smaller than B_e , and the level spacings will be smaller than rigid rotor spacings. The minus sign in front of this term is responsible for reducing the level spacings with increasing rotation.

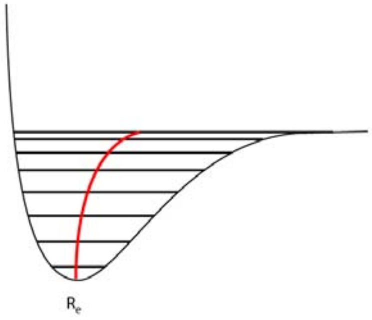
One could show that

$$D = \frac{h^3}{32\pi^4 I^2 ckR_0^2} = \frac{4B_e^3}{\omega_e^2}$$

5) $-\alpha \left(\mathrm{v} + \frac{1}{2} \right) J \left(J+1 \right)$

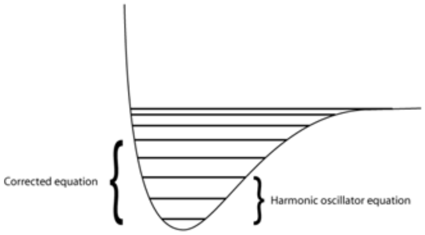
This term describes the vibration-rotation interaction. The rotational spacing depends on *B* which in turn depends on *R*. Up to now we considered a rigid molecule with *R* fixed.

But the <u>vibrational state</u> affects the average value of *R*.



$\langle R \rangle$ changes with vibrational state. This results from the anharmonicity of the vibration. (If the potential were a parabola, $\langle R \rangle$ wouldn't change.) You can see that the anharmonicity and the vibration-rotation interaction are related. They both are related to the "*a*" constant in the power series expansion of *U*'(*R*).

The best evidence for the fact that we solved the problem correctly is that it works. Using this expression for the energy levels, one can account reasonably well for the measured energy spacings.



One can measure these spacings very well using modern spectroscopic techniques.

2.3 What is a Spectrum?

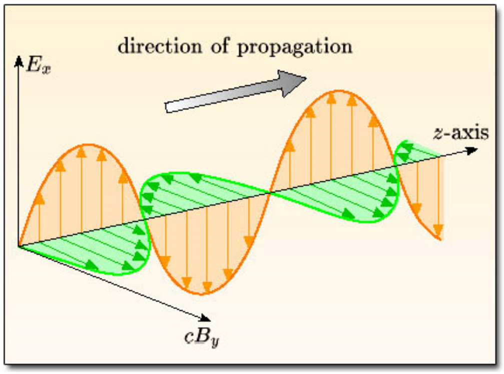
Up to this point I have reviewed much of the important quantum mechanical background. All I have talked about, however, is spacings of energy levels. I have said little about spectroscopic transitions. The field of molecular spectroscopy involves causing molecules to make transitions from one state to another, and we must consider the details of how this occurs.

Before I go any further, however, I want to define some of the ***terminology*** that we will be using. Much of the difficulty in understanding a subject is often simply understanding what the different terms mean. I will start by addressing the questions:

What is a spectral line or spectral transition? and What is a spectrum?
I will then go on to define what we mean by **spectral intensity** or **transition strength** and the **linewidth** of a transition.

Before I answer these questions, I need to remind you of a few things about the nature of electromagnetic radiation or light. Light usually refers to only visible wavelengths, but I will often use it in the more general sense meaning all electromagnetic radiation.

In a wave picture, electromagnetic radiation contains, as its name implies, oscillating electric and magnetic fields. These fields are oriented perpendicular to each other and perpendicular to the direction of propagation. This is best shown in the figure below, by considering linearly polarized light.



The magnitude of the electric and magnetic field vectors can be given by:

$$E(z,t) = E_{x0}\sin(2\pi\nu t + kz + \phi) \qquad B(z,t) = B_{y0}\sin(2\pi\nu t + kz + \phi)$$

with

E_{x0}, B_{y0} the electric and magnetic field amplitudes, respectively ($B_{y0} = E_{x0}/c$)

$\nu = \dfrac{c}{\lambda}$ is the frequency of the light, given by the speed of light, c, divided by the wavelength of the light, λ.

$k = \dfrac{2\pi}{\lambda}$ is called the wave vector

ϕ is the relative phase

Recall that light can be treated either as a wave or as a particle. In the particle picture, light consists of photons with energy:

$$E = h\nu$$

When light shines on a molecule in a particular quantum state, it is *possible* for that molecule to absorb a photon. If the energy of the photon, defined by the expression $E = h\nu$, corresponds precisely to the difference in energy between the quantum state that the molecule is in and some other quantum state, then it is possible for the molecule to absorb a photon and make a transition from the initial quantum state to the final quantum state.

The frequency or energy of the photon must be such that

$$E_{photon} = h\nu_0 = \Delta E = E_{final} - E_{initial}$$

or

$$\nu_0 = \frac{E_{final} - E_{initial}}{h}$$

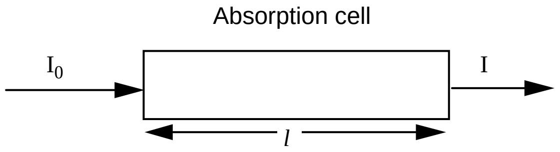
This expression is called the *Bohr frequency condition*

Note that I said it was *possible* for the molecule to absorb the radiation. Whether it does or not depends upon several factors that we will consider shortly.

A ***spectral line*** is what one calls a plot of the absorption of light by a molecule or atom as a function of the frequency of that light. This is also referred to simply as a ***transition***, although this latter term is used more generally to refer to the act of going from one state to the other.

The ***intensity*** or ***strength*** of a transition is related to the probability that the molecule or atom will undergo the transition when illuminated by light at the proper frequency.

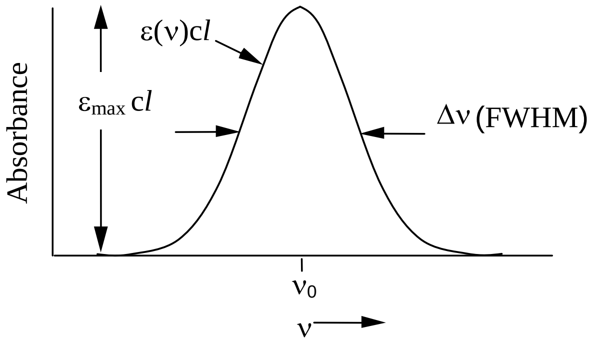
To be more specific, assume we have an absorption cell of length l containing a sample of the material which we are studying at concentration c in moles per liter. Let I_0 be the intensity of light going into the cell (*i.e.* the number of photons per unit time per unit area) and I be the intensity of the light coming out.



According to the Beer-Lambert Law, the absorbance A is given by

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon(\nu)cl$$

$\varepsilon(\nu)$ is a function of the frequency ν and is called the *molar absorption coefficient, c* is the concentration and l the length of the cell.
Often what we are plotting when we show a spectral line is the absorbance as a function of the frequency or sometimes the molar absorption coefficient as a function of frequency.



One usually plots the absorption coefficient as a function of the frequency, since it is proportional to the absorbance and independent of c and l. It is a property of the molecule alone.

This is what we would call a ***spectral line***. The term comes from early experiments observing the emission from excited atoms. If I showed this spectral feature on a wide enough frequency scale, it would appear as a spike or a line.

Strictly speaking, the **intensity** of a transition or the **transition strength** is proportional to the integral of the function ⍰⍰⍰⍰ across the entire profile

$$\text{Transition strength} \propto \int_{\nu_1}^{\nu_2} \varepsilon(\nu)\,d\nu$$

I will not be so concerned with the units that we use for the intensity of a transition.

As we will as the course progresses, the intensity of the transitions is related to the wavefunctions corresponding to the energy levels involved in the transition.

The **linewidth**, $\Delta\nu$, of a transition is usually defined as the width at half the height of the maximum of the curve (Full Width Half Maximum or FWHM). We will see later that the linewidth can provides us information on the dynamics or kinetics of the molecules.

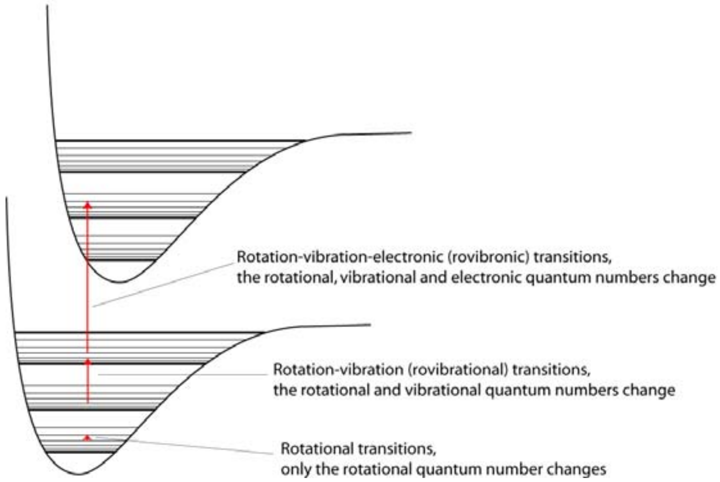
The **<u>frequency of the line center</u>**, ν_0, provides information on the energy levels of the atom or molecule, and as we have seen to some degree already and will see more later, this can tell us things like the geometry of a molecule, the vibrational force constants, etc.

I still haven't defined the term **spectrum**.

A ***spectrum*** is a collection of many spectral lines that results when one measures the absorption of a molecule as a function of frequency. As you will see, spectral lines tend to be clumped together in certain frequency regions and a spectrum is usually a measurement of an entire clump. However, one *could* call even a single spectral line a spectrum.
We will consider 3 types of spectroscopic transitions (indicated on the figure below):

1. pure rotational → microwave
2. rotational-vibrational → infrared
3. rotational-vibrational-electronic → Visible-UV

Spectroscopic transitions occur at frequencies (energies) corresponding to the difference between two energy levels. For the most part, energy level spacing for different types of motion are sufficiently different that it is straightforward to tell what type of transition one is observing given the frequency.



It is important to have a good physical feel for the relative magnitudes of the transition frequencies (energies).

Molecular process	**Wavelength (m)**	**Wave number (cm^{-1})**	**Region**
polyatomic rotation	0.3 - 0.003	0.033 - 3.3	Microwave
rotation of small molecules	$3x10^{-3}$ - $3x10^{-5}$	3.3 - 330	Far infrared
vibrational motion	$3x10^{-5}$ - $3x10^{-6}$	330 - 3300	Infrared
electronic transitions	$3x10^{-6}$ - $3x10^{-8}$	3300 - 3.3 $x10^{5}$	Visible and Ultraviolet

You should be able to look at a spectrum and immediately tell if it is a pure rotational, rovibrational, or rovibronic (rotational-vibrational-electronic) spectrum.

We will spend much time later in the semester discussing the expected frequencies for different types of transitions. This is simply a question of where the different energy levels occur. It will be specific to each type of motion and will have different patterns for different classes of molecules.

In the present chapter, which is meant as an overview of molecular spectroscopy, I will discuss the subject of spectroscopic intensities and linewidths. There are a number of different factors that determine the intensity and linewidth of a spectral line. I will discuss them in a general sense now, and then we will apply these general concepts later to different types of spectroscopic transitions.

2.4 Spectroscopic Intensities

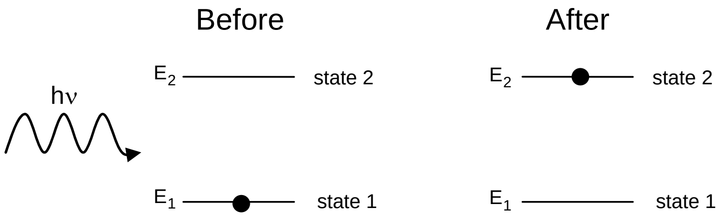
2.4.1 Kinetics of Optical Absorption

Not all transitions occur with equal intensity. In fact, many transitions are completely forbidden. If this weren't the case, it would be much more difficult to interpret molecular spectra.

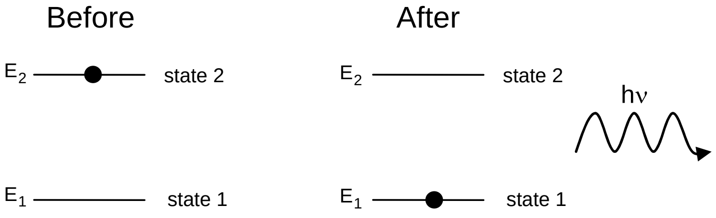
To fully understand the intensities of transitions between discrete states in an atom or molecule, one must have some understanding of the interaction of radiation with matter. In particular, we must consider the rates of transitions from one state to another induced by electromagnetic radiation.

In 1916, Einstein published a treatment of a quantum mechanical system (*i.e.*, a system with discrete energy levels) in a classical radiation field. The following discussion follows his treatment.

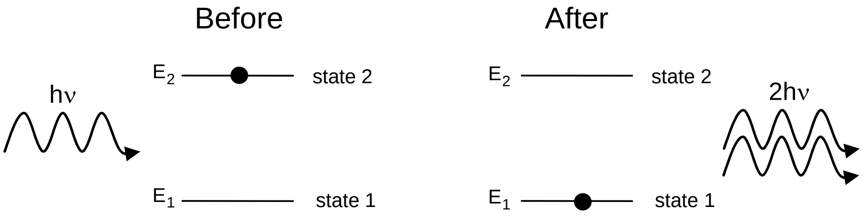
Let us start by considering a few of the processes that could occur when light interacts with an atom or molecule (or any two level quantum mechanical system). I have already introduced to you the process that we call ***absorption***. In this process, a photon with energy $E = h\nu$, which is equal to the difference in energy between state 1 and state 2, causes the system to make a transition from state 1 to state 2. During this process, the photon is absorbed.



Now consider the case in which the molecule is *initially in the upper state* rather than starting in the lower state.One process that can occur in this situation is that the molecule can spontaneously make a transition from the upper state to the lower state, giving off a photon of energy $E=h\nu$ where this energy is equal to the difference in energy between the two levels. This process is called ***spontaneous emission.*** The term spontaneous comes from the fact that it happens without any external influence (*i.e.*, not initiated by a photon).



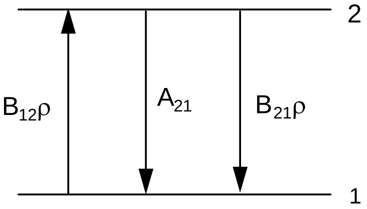
In a third type of process, the molecule initially in the excited state encounters a photon with energy equal to the separation between states 1 and 2. In this case, the photon can induce or stimulate a downward transition from state 2 to state 1.



In this case, the original photon remains and is accompanied by the emission of a second photon of the same frequency. This process is called ***stimulated emission*** because the emission of the second photon is *stimulated* by the presence of the first. Stimulated emission is essentially the inverse process of absorption. Both are induced by the radiation field (*i.e.*, the photon). In one case a photon is destroyed, in the other a photon is created. You can see from the conservation of energy that stimulated emission must be accompanied by the creation of a photon.

With these three processes in mind, consider the following:

Let's say we have a collection of *N* two level systems with lower level 1 and upper level 2. The energies of these states are given by W_1 and W_2 respectively (I use *W* rather than *E* because we will use *E* for electric field). Assume that these systems are all at the temperature *T* and are put in a bath of ambient radiation of density $\rho(\nu)$ (the energy of radiation between frequencies ν and $\nu + d\nu$ in unit volume being $\rho(\nu)d\nu$). The system is at equilibrium (*i.e.*, no net change in the populations of levels 1 and 2). We will denote the populations of levels 1 and 2 by N_1 and N_2. Consider the rates of transitions between these states due to absorption, spontaneous emission, and stimulated emission.



Absorption:

The rate at which the systems are promoted from level 1 to level 2 due to absorption of radiation of the proper frequency must be proportional to

1. the radiation density, $\rho(\nu_{12})$
2. the number of molecules in state 1 (clearly, if there were no molecules in state 1 there would be no transitions from 1 to 2.).

Thus we can write the rate of change of the population of state 2 due to absorption as

$$\frac{dN_2}{dt} = B_{12}\rho(\nu_{12})N_1$$

where B_{12} is simply the rate constant or proportionality constant. This constant is called the Einstein *B* coefficient.

Spontaneous Emission:

Spontaneous emission takes the systems initially in state 2 and brings them down to state 1.

1. This process is independent of the radiation density, since it is spontaneous.
2. It will be proportional to the number of systems in state 2 (clearly, if there were no systems in state 2, there would be no spontaneous transitions from 2 to 1).

We can therefore write:

$$\frac{dN_2}{dt} = -A_{21}N_2$$

where A_{21} is the proportionality constant or **rate constant for spontaneous emission**. This is called the Einstein A coefficient. The negative sign arises from the fact that state 2 is being *depopulated* by this process.

Note that since the rate of spontaneous emission is proportional to the Einstein *A* coefficient and not the radiation density, the *lifetime* of a molecule in a particular state in the absence of radiation is given by

$$\tau = \frac{1}{A_{21}}$$

Thus, the *A* coefficient is the inverse of the lifetime.

Stimulated Emission:

Finally, stimulated emission will induce transitions from state 2 to state 1.

1. As in the case of absorption, it will be proportional to the radiation density.
2. It will also be proportional to the number of systems in state 2.

We can write:

$$\frac{dN_2}{dt} = -B_{21}\rho(\nu_{12})N_2$$

where B_{21} is the Einstein coefficient for stimulated emission.

If the system is at equilibrium, the populations in systems 1 and 2 must not be changing. This means that the rate of transitions from 1 to 2 must be equal to the rate of transitions from 2 to 1. Another way to say this is that the net rate $\frac{dN_2}{dt}$ (or $\frac{dN_1}{dt}$) must equal zero. Thus we can sum all the contributions to $\frac{dN_2}{dt}$ and set them equal to zero.

We then have:

$$B_{12}\rho(\nu_{12})N_1 - A_{21}N_2 - B_{21}\rho(\nu_{12})N_2 = 0$$

Rearranging, one gets:

$$\begin{aligned} B_{12}\rho(\nu_{12})N_1 &= A_{21}N_2 + B_{21}\rho(\nu_{12})N_2 \\ &= \left[A_{21} + B_{21}\rho(\nu_{12})\right]N_2 \end{aligned}$$

or

$$\frac{N_2}{N_1} = \frac{B_{12}\rho(\nu_{12})}{A_{21} + B_{21}\rho(\nu_{12})}$$

We know from statistical thermodynamics that the equilibrium populations of states 1 and 2 are related by the Boltzmann distribution law:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1}e^{-\frac{(W_2 - W_1)}{k_b T}} = \frac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_b T}}$$

where k_b is the Boltzmann constant and g_1 and g_2 are the degeneracies of states 1 and 2.

Thus, we can write

$$\frac{B_{12}\rho(\nu_{12})}{A_{21}+B_{21}\rho(\nu_{12})}=\frac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_bT}}$$

or solving for ρ

$$\rho(\nu_{12})=\frac{A_{21}\frac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_bT}}}{B_{12}-B_{21}\frac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_bT}}}$$

$$=\frac{A_{21}}{B_{12}\frac{g_1}{g_2}e^{\frac{h\nu_{12}}{k_bT}}-B_{21}}$$

There is one more thing that we know. I originally stated that the system was bathed in radiation density $\rho(\nu)$. We know from *Planck's law of black body radiation* that:

$$\rho(\nu_{12})=\frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{k_bT}}-1}$$

Setting the two expressions for ρ equal gives:

$$\frac{8\pi h\nu_{12}^3}{c^3}\frac{1}{e^{\frac{h\nu_{12}}{k_bT}}-1}=\frac{A_{21}}{B_{12}\frac{g_1}{g_2}e^{\frac{h\nu_{12}}{k_bT}}-B_{21}}$$

You can see that there are two conditions that must be met for this equality to hold:

1. $B_{12}\frac{g_1}{g_2}=B_{21}$ (note that if $g_1 = g_2$ then $B_{21} = B_{12}$)
   this will always be true for non-degenerate states since $g_1 = g_2 = 1$
2. $A_{21}=\frac{8\pi h\nu_{12}^3 B_{21}}{c^3}$

The first tells us that for non-degenerate states, the strength of the upward transition is equal to the strength of the downward transition.

The second gives us a relationship between the strength of a transitions and the lifetime of the state, since $A = 1/\tau$. Also, note the ν^3 factor in the numerator. This says that as the frequency increases, the rate of spontaneous emission increases rapidly compared to stimulated emission.

One could show that the Einstein *B* coefficient for absorption, B_{12} is directly related to the integrated band intensity:

$$B_{12}=\frac{\ln 10}{1000N_A h\nu_{12}}\int\varepsilon(\nu)d\nu$$

where ε is defined by

$$\frac{I}{I_0} = 10^{-\varepsilon(\nu)cl}$$

c is the concentration in moles per liter. N_A is Avogadro's number.

I will demonstrate shortly how the Einstein coefficient is directly related to properties of the molecular wave function.

2.4.2 Time Dependent Perturbation Theory

We now need to understand *which* levels can be connected by a spectroscopic transition. Up to now we have only considered the interaction between radiation and matter in a general way. We have not at all considered the nature of the quantum mechanical levels (*i.e.*, the wave functions). We now need to connect the expression for the band strength to properties of the wave functions. This will allow us to determine *selection rules* for spectroscopic transitions (*i.e.,* the rules that tell us which transitions can occur).

In order to do this, we need to use *time dependent perturbation theory*.

The very nature of a spectroscopic transition implies a time-dependent phenomenon, and so we must consider the time-dependent Schrödinger equation.

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

If the Hamiltonian does not explicitly depend upon time, we know that

$$\Psi_n(\mathbf{r},t) = \psi_n(\mathbf{r})e^{-\frac{iW_n t}{\hbar}}$$

where $\psi_n(\mathbf{r})$ is the solution to the Time Independent Schrödinger Equation (*i.e.*, is an eigenfunction of the Hamiltonian) and is called a stationery state (since $\Psi_n^*(\mathbf{r},t)\Psi_n(\mathbf{r},t) = \psi_n^*(\mathbf{r})\psi_n(\mathbf{r})$)

When we consider the interaction of matter with radiation, we must take into account the fact that electromagnetic field depends upon time:

$$\mathbf{E} = \mathbf{E}_0\cos(2\pi\nu t)$$

In all the types of spectroscopy that we will consider, the electric field interacts with the molecule through its electric dipole moment. There are other types of interactions between a radiation field and a molecule, but these are much weaker in general. We will only consider electric dipole induced transitions. The electric dipole moment is defined as:

$$\boldsymbol{\mu} = \sum_j q_j\mathbf{r}_j$$

where q_j is the charge of particle *j* and $\mathbf{r}_j$ its position.

Knowing the charge of the electrons and of the nuclei this can also be written as:

$$\boldsymbol{\mu} = \sum_i -e\mathbf{r}_i + \sum_\alpha Z_\alpha e\mathbf{r}_\alpha$$

where $\mathbf{r}_j$ is the position of electron *i* and Z▯ and $\mathbf{r}_\alpha$ are the charge and position, respectively, of nucleus α.

If $\boldsymbol{\mu}$ is the dipole moment of the molecule, the interaction energy between the field and the molecule is

$$\hat{H}' = -\boldsymbol{\mu}\cdot\mathbf{E} = -\boldsymbol{\mu}\cdot\mathbf{E}_0\cos(2\pi\nu t)$$

We therefore need to solve

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

Where:

$$\hat{H} = \hat{H}_0 - \boldsymbol{\mu}\cdot\mathbf{E}_0\cos(2\pi\nu t) = \hat{H}_0 + \hat{H}'$$

This looks like a problem for perturbation theory if the second term on the right is sufficiently small.

Recall that in Time Independent Perturbation Theory, we expressed the first order correction to the wave function as a linear combination of the zeroth-order wave functions (since they form a complete orthonormal set).

$$\psi_n^{(1)} = \sum_{m\neq n}\frac{H'_{mn}}{\left(E_n^{(0)} - E_m^{(0)}\right)}\psi_m^{(0)} = \sum_{m\neq n} a_m\psi_m^{(0)}$$

We can do the same thing here, but because the perturbation depends upon time, *the expansion coefficients will also depend upon time* in a manner more complex than the simple exponential time dependence we have discussed earlier. You can see how this might lead to transitions between zeroth-order states.

To simplify matters, let us consider a system in which the unperturbed problem has only two states. (The development for a real molecule which has an infinite number of states is analogous to this simple case).

For such a system:

$$\hat{H}_0\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

The stationery state solutions are

$$\Psi_1(\mathbf{r},t) = \psi_1(\mathbf{r})e^{-\frac{iW_1t}{\hbar}} \qquad \text{and} \qquad \Psi_2(\mathbf{r},t) = \psi_2(\mathbf{r})e^{-\frac{iW_2t}{\hbar}}$$

We will assume that the wave function at any time *t* can be written as a linear combination of the zeroth-order wave functions:

$$\Psi(\mathbf{r},t) = a_1(t)\Psi_1(\mathbf{r},t) + a_2(t)\Psi_2(\mathbf{r},t)$$

where the expansion coefficient are time dependent. This is essentially saying that although the wave function is changing in time, at any instant it can be written as a linear combination of the zeroth-order eigenfunctions.

Assume that the system starts at *t*=0 in state 1 (*i.e*. in the ground state).

This means that:

$$a_1(t=0) = 1 \qquad \text{and} \qquad a_2(t=0) = 0$$

To determine the time dependence of the expansion coefficients, we need to substitute $\Psi(\mathbf{r},t)$ into the Time dependent Schrödinger equation:

$$a_1(t)\hat{H}_0\Psi_1(\mathbf{r},t)+a_2(t)\hat{H}_0\Psi_2(\mathbf{r},t)+a_1(t)\hat{H}'\Psi_1(\mathbf{r},t)+a_2(t)\hat{H}'\Psi_2(\mathbf{r},t)=$$

$$i\hbar\Psi_1(\mathbf{r},t)\frac{\partial a_1(t)}{\partial t}+i\hbar\Psi_2(\mathbf{r},t)\frac{\partial a_2(t)}{\partial t}+i\hbar a_1(t)\frac{\partial\Psi_1(\mathbf{r},t)}{\partial t}+i\hbar a_2(t)\frac{\partial\Psi_2(\mathbf{r},t)}{\partial t}$$

Note that the first and second terms on the left hand side cancel with the third and fourth terms on the right hand side.
This leaves:

$$a_1(t)\hat{H}'\Psi_1(\mathbf{r},t)+a_2(t)\hat{H}'\Psi_2(\mathbf{r},t)=i\hbar\Psi_1(\mathbf{r},t)\frac{\partial a_1(t)}{\partial t}+i\hbar\Psi_2(\mathbf{r},t)\frac{\partial a_2(t)}{\partial t}$$

If we now multiply by ψ_2^* and integrate over spatial coordinates and use the fact that ⍰$_1$ and ⍰$_2$ are orthogonal we get (after some rearranging):

$$i\hbar\frac{\partial a_2(t)}{\partial t}=a_1(t)e^{-\frac{i(W_1-W_2)t}{\hbar}}\int\psi_2^*(\mathbf{r})\hat{H}'\psi_1(\mathbf{r})d\mathbf{r}+a_2(t)\int\psi_2^*(\mathbf{r})\hat{H}'\psi_2(\mathbf{r})d\mathbf{r}$$

Note that I have separated the wave functions ψ_1 and ψ_2 into the spatial parts and the exponential time dependent part.

Since $\hat{H}'$ is a small perturbation, there are not enough transitions out of state 1 that a_1 and a_2 differ significantly from their initial values. This approximation is called the "weak field limit".

Thus we can assume $a_1 \approx 1$ and $a_2 \approx 0$ at all times. This gives

$$i\hbar\frac{\partial a_2(t)}{\partial t}=e^{-\frac{i(W_1-W_2)t}{\hbar}}\int\psi_2^*(\mathbf{r})\hat{H}'\psi_1(\mathbf{r})d\mathbf{r}$$

Now, let us take the electric field to be in the *z*-direction. (We need not do this, but it is easy to generalize to isotropic radiation).

We then have

$$\hat{H}'=-\hat{\mu}_z E_{0z}\cos(2\pi\nu t)$$

$$=-\frac{1}{2}\hat{\mu}_z E_{0z}\left(e^{i2\pi\nu t}+e^{-i2\pi\nu t}\right)$$

If we substitute this into the above equation we get the instantaneous transition rate:

$$\frac{\partial a_2(t)}{\partial t}=\frac{i}{2\hbar}\left(\mu_z\right)_{21}E_{0z}\left[e^{\frac{i(W_2-W_1+h\nu)t}{\hbar}}+e^{\frac{i(W_2-W_1-h\nu)t}{\hbar}}\right]$$

where

$$\left(\mu_z\right)_{21}=\int\psi_2^*(\mathbf{r})\hat{\mu}_z\psi_1(\mathbf{r})d\mathbf{r}$$

This quantity, $\left(\mu_z\right)_{21}$, is the *z*-component of the ***dipole moment matrix element*** (otherwise known as the ***transition moment***) between states 1 and 2. The rate of transitions out of state 1 into state 2 is proportional to $\left(\mu_z\right)_{21}$. If this term is zero, transitions will not occur.

It is this term that gives rise to the selection rules for transitions induced by electromagnetic radiation. We will show this more explicitly in a moment. However, first I will integrate the preceding equation for the duration of the perturbation (*i.e*. the finite time the molecule interacts with the field). This gives

$$a_2(t) = -\frac{1}{2}(\mu_z)_{21} E_{0z} \left[\frac{1 - e^{\frac{i(W_2 - W_1 + h\nu)t}{\hbar}}}{W_2 - W_1 + h\nu} + \frac{1 - e^{\frac{i(W_2 - W_1 - h\nu)t}{\hbar}}}{W_2 - W_1 - h\nu} \right]$$

Note that in each term within the brackets, the complex exponential can only vary between 1 and -1 (since a complex exponential is simply sines and cosines). Thus, the numerator of each of these terms can only vary between 0 and 2. For either one of these two terms to get large, the denominator must become very small.

Because $W_2 > W_1$, the second term gets much larger than the first when $W_2 – W_1 = h\nu$. This occurs when the radiation is on resonance with an upward transition (*i.e.,* leading to absorption). In this case one could neglect the first term.

Note that the second term goes to infinity when the radiation is on resonance. This arises because we treated the field classically. Treating the electric field quantum mechanically will still give a resonance, but it won't go to infinity.

The magnitude of the coefficient a_2 depends strongly upon the frequency of the radiation, as $|a_2(t)|^2$ gives the probability that the system which started in state 1 will have made a transition to state 2 by time *t*. Thus, when the radiation is tuned to a resonance (*i.e.*, $W_2 – W_1 = h\nu$), the probability of making a transition is at a maximum.

If we neglect the first term and only consider the absorption process, we can obtain (after some rearrangement):

$$|a_2(t)|^2 = a_2^*(t)a_2(t) = (\mu_z)_{21}^2 E_{0z}^2 \frac{\sin^2\left(\frac{W_2 - W_1 - h\nu}{2\hbar}t\right)}{(W_2 - W_1 - h\nu)^2}$$

This expression has been derived assuming an oscillating electric field at only a single frequency. In practice we always deal with a range of frequencies, and we must integrate this expression over the range of frequencies near the resonance condition. Because the integrand will only be significant over the region of ν near ν_{12}, we can take E_{0z}^2 outside of the integral and evaluate it only at ν_{12}.

We then have:

$$|a_2(t)|^2 = (\mu_z)_{21}^2 E_{0z}^2(\nu_{12}) \int \frac{\sin^2\left(\frac{W_2 - W_1 - h\nu}{2\hbar}t\right)}{(W_2 - W_1 - h\nu)^2} d\nu$$

We can integrate this from -∞ to +∞ because the integrand will only be significant near resonance. We can then make use of the fact that

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi$$

This gives us

$$|a_2(t)|^2 = \frac{1}{4\hbar^2}(\mu_z)_{21}^2 E_{0z}^2(\nu_{12})t$$

One can easily show that for isotropic radiation, the *z*-component of the electric field is related to the radiation density by

$$E_{0z}^2(\nu) = \frac{2}{3\varepsilon_0}\rho(\nu)$$

The probability of finding the system at time *t* in level 2 is then given by:

$$|a_2(t)|^2 = \frac{1}{6\hbar^2\varepsilon_0}\left(\mu_z\right)_{21}^2 \rho\left(\nu_{12}\right)t$$

The average transition rate is the probability of making the transition during the time interval *t* during which the perturbation exists.

Thus we can write

$$\text{transition rate } = \frac{|a_2(t)|^2}{t} = \frac{1}{6\hbar^2\varepsilon_0}\left(\mu_z\right)_{21}^2 \rho\left(\nu_{12}\right)$$

But recall that the rate of making an upward transition is related to the Einstein B coefficient

$$\text{transition rate} = B_{12}\rho(\nu_{12}) = \frac{1}{6\hbar^2\varepsilon_0}\left(\mu_z\right)_{21}^2 \rho(\nu_{12})$$

Therefore

$$B_{12} = \frac{1}{6\hbar^2\varepsilon_0}\left(\mu_z\right)_{21}^2$$

Remember that we treated only polarized light in the *z*-direction. The expressions for the *x* and *y*-directions are completely analogous. We therefore have in general

$$B_{12} = \frac{1}{6\hbar^2\varepsilon_0}\left[\left(\mu_x\right)_{21}^2 + \left(\mu_y\right)_{21}^2 + \left(\mu_z\right)_{21}^2\right]$$

Thus, we have related the absorption strength directly to the dipole moment matrix elements (or transition moments)

$$\left(\mu_z\right)_{21} = \int \psi_2^*(\mathbf{r})\hat{\mu}_z \psi_1(\mathbf{r})d\mathbf{r}$$

and likewise for the *x* and *y* components. If we have an expression for the dipole moment of a molecule, we can calculate the intensity of its spectroscopic transitions. Selection rules arise because in certain situations, these integrals become identically zero.

It is important to realize that dipole moment matrix elements such as these play an extremely important role in spectroscopy! The two most important features in a spectrum are the frequency and the intensity of the transitions. The frequencies tell us about the spacing of the energy levels and ultimately about the potential energy surface. The intensities are related to properties of the wave functions through this dipole moment integral.

I would now like to discuss some general considerations in evaluating the spectroscopic selection rules for different kinds of spectroscopy.

2.4.3 Spectroscopic Selection Rules

I have just shown that the transition probability or transition rate $B_{12}\rho$ is proportional to the square of the dipole moment matrix elements. This gives us a measure of the relative strength or intensity of a spectroscopic transition.

I have frequently used the term *selection rules* in discussing spectroscopic transitions but I haven't clearly defined what I mean. Selection rules are restrictions on the changes in quantum numbers between the initial and final state in a spectroscopic transition.

In other words, transitions are only allowed for certain changes in the quantum numbers. The origin of these rules can be clearly seen by considering the integral of the dipole moment operator that we had to perform to determine the Einstein coefficient.

That integral will be non-zero for only certain allowed changes in the quantum numbers during a transition. From a practical point of view, the fact that transitions are not allowed between all levels is extremely important. If all possibilities were allowed, it might be hopeless to understand the pattern of transitions that one observes in a spectrum. However, the fact that only a restricted number of transitions occur makes the pattern of lines simpler.

Let us go back and consider the transition moment integral and see how it gives rise to several different types of selection rules.

For plane polarized light in the z-direction,

$$B_{12} \propto \left(\mu_z\right)_{21}^2 = \left(\int \psi_2^* \hat{\mu}_z \psi_1 d\tau\right)^2$$

where $\hat{\mu}_z$ is the dipole moment operator.

For any kind of dipole-induced transition between two states (*i.e.*, rotational, vibrational, electronic) we can write to a first approximation:

$$\int \psi_2^* \hat{\mu}_z \psi_1 d\tau = \int \psi_{2el}^* \psi_{2vib}^* \psi_{2rot}^* \hat{\mu}_z \psi_{1el} \psi_{1vib} \psi_{1rot} d\tau_{el} d\tau_{vib} d\tau_{rot}$$

$\hat{\mu}_z$ is the dipole moment operator in the lab fixed frame.

From the point of view of intensities, the rigid rotor and harmonic oscillator wave functions are good enough to use in these integrals. However, the breakdown of these approximations will lead to certain “forbidden” transitions having small intensities.

When one thinks of dipole moments, one usually thinks in the molecular frame. For a diatomic molecule, we can relate the z component of the dipole moment in the lab fixed frame to that in the molecule fixed frame by:

$$\mu_z = \mu_\eta \cos\theta$$

where μ_η is the dipole moment in the molecule fixed frame and θ is the angle between the lab and molecule fixed z-axis (z and η axes)). The $\cos\theta$ is the direction cosine for the z-component. If we were to use the x or y component, this factor would be the corresponding direction cosine. (For x: $\sin\theta\cos\varphi$ and for y: $\sin\theta\cos\varphi$)

It is important to realize that μ_η depends on the position of the electrons and nuclei and therefore on the electronic and vibrational coordinates.

We can substitute the above expression for μ_z into the integral to get:

$$\left(\mu_z\right)_{21} = \int\int \psi_{2el}^* \psi_{2vib}^* \hat{\mu}_\eta \psi_{1el} \psi_{1vib} d\tau_{el} d\tau_{vib} \int \psi_{2rot}^* \cos\theta \psi_{1rot} d\tau_{rot}$$

The first integral of this expression will give us the selection rules for electronic and vibrational transitions. The second integral will give us the same rotational selection rules for all types of transitions (between rotational states, vibrational states, electronic states). We can evaluate this integral by putting in the eigenfunctions for the rigid rotor, *i.e*. the spherical harmonics.

You can see that to determine spectroscopic intensities one must evaluate these integrals for different types of molecules in particular quantum states.

As we discuss each type of spectroscopy in more detail, we will evaluate these integrals to determine the selection rules in a particular type of situation. We will also see that there are other factors that can determine whether the transition moment integral is non-zero or not. In particular, the symmetry of the integrand (and hence the symmetry of the wave functions) will often determine that the integral is equal to zero.

2.4.4 State Populations

An additional factor that clearly must affect the intensities of spectroscopic transitions is the number of molecules in the state from which the transition originates. In the limit that there are no molecules in the initial state, the number of molecules that absorb a photon and make a transition from that state to some higher state (and hence the intensity of the transition) must clearly equal zero.

Thus, we have to incorporate what we know about the populations of quantum states at a particular temperature into our analysis of molecular spectra.

The populations of quantized energy levels can be determined using ***statistical mechanics.*** I will only briefly discuss the results.

If we have a set of quantized energy levels of a molecule, we need to know how many molecules are in level 1, how many are in level 2, etc..., at a particular temperature.

This number of molecules in the i^{th} level is given by statistical mechanics to be:

$$N_i = cg_i e^{-\frac{E_i}{k_b T}}$$

where c is a proportionality constant, g_i is the degeneracy of the i^{th} level, E_i is the energy of the i^{th} level, k_b is the Boltzmann constant, and T is the temperature.

We can determine the proportionality constant by summing over both sides of this equation and noting that

$$\sum_i N_i = N$$

Thus

$$\sum_i N_i = N = c\sum_i g_i e^{-\frac{E_i}{k_b T}}$$

or

$$c = \frac{N}{\sum_i g_i e^{-\frac{E_i}{k_b T}}}$$

The result is

$$N_i = N\frac{g_i e^{-\frac{E_i}{k_b T}}}{\sum_i g_i e^{-\frac{E_i}{k_b T}}}$$

We can express the fraction of molecules in a particular state as

$$f_i = \frac{N_i}{N} = \frac{g_i e^{-\frac{E_i}{k_b T}}}{\sum_i g_i e^{-\frac{E_i}{k_b T}}}$$

The denominator of this expression, is called the ***partition function***, and is given the symbol Q

$$Q = \sum_i g_i e^{-\frac{E_i}{k_b T}}$$

The partition function is a constant for a molecule at a certain temperature. Thus, at a given temperature, the fractional population of the i^{th} state will decrease as the energy of that state increases.

To evaluate this expression, one must evaluate the partition function *Q* for the system of interest. You can see that if the energy of the system (molecule) can be written as a sum of energies (*e.g.*, electronic + vibrational + rotational), the total partition function will be a product of partition functions for each type of motion (since the exponential of a sum is a product of exponentials).

If you have an explicit expression for the energies, then one can evaluate the sum. Otherwise one can do it numerically.

Let me have a look at two examples in which I calculate the fraction of diatomic molecules in a particular vibrational state assuming harmonic oscillator energy levels and a particular rotational state assuming rigid rotor energy levels.

First for the vibrational level. The energy is given by:

$$E_{\mathrm{v}} = \left(\mathrm{v} + \frac{1}{2}\right) h\nu$$

Since it is a diatomic, the vibrational levels are non-degenerate. We can therefore write:

$$f_{\mathrm{v}} = \frac{e^{-\frac{\left(\mathrm{v}+\frac{1}{2}\right)h\nu}{k_b T}}}{\sum_{\mathrm{v}=0}^{\infty} e^{-\frac{\left(\mathrm{v}+\frac{1}{2}\right)h\nu}{k_b T}}} = \frac{e^{-\frac{\frac{1}{2}h\nu}{k_b T}}}{e^{-\frac{\frac{1}{2}h\nu}{k_b T}}} \frac{e^{-\frac{\mathrm{v}h\nu}{k_b T}}}{\sum_{\mathrm{v}=0}^{\infty} e^{-\frac{\mathrm{v}h\nu}{k_b T}}} = \frac{e^{-\frac{\mathrm{v}h\nu}{k_b T}}}{\sum_{\mathrm{v}=0}^{\infty} e^{-\frac{\mathrm{v}h\nu}{k_b T}}}$$

The denominator of this expression can be evaluated by recognizing it to be a geometric series

$$\sum_{\mathrm{v}=0}^{\infty} x^{\mathrm{v}} = \frac{1}{1-x}$$

where $x = e^{-\frac{h\nu}{k_b T}}$

We can therefore write

$$\sum_{\mathrm{v}=0}^{\infty} e^{-\frac{\mathrm{v}h\nu}{k_b T}} = \frac{1}{1 - e^{-\frac{h\nu}{k_b T}}}$$

Putting this into the expression for the fraction of molecules in the v^{th} state gives

$$f_{\mathrm{v}} = \left(1 - e^{-\frac{h\nu}{k_b T}}\right) e^{-\mathrm{v}\frac{h\nu}{k_b T}}$$

To find the fraction of molecules in the lowest level, we just let v=0.

$$f_0 = 1 - e^{-\frac{h\nu}{k_b T}}$$

A typical frequency for a diatomic molecule is 2000 cm^{-1}.

Note: Rather than using *h*⍰, if we express k_bT in cm^{-1}, we can just use the wavenumber in cm^{-1}·

$$k_b = 0.69509 \text{ cm}^{-1} \text{ K}^{-1}$$

so $$k_bT = (0.69509 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K}) = 207.1 \text{ cm}^{-1}$$

Thus we have: $f_0 = 1 - e^{-2000/207} = 0.99994$

Essentially, all the molecules will be in their lowest vibrational state at room temperature. This is usually the case unless either the vibrational frequency is very low or the temperature is very high.

Let us now do the same for the rotational levels. The energy of the rigid rotor is given by:

$$E_J = BJ(J+1)$$

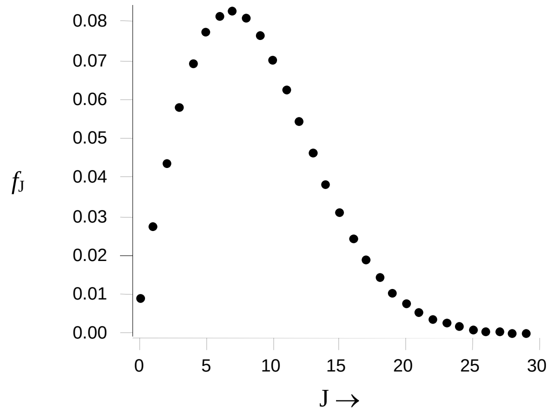
The fraction of molecules in a particular rotational state *J* given by

$$f_J = \frac{(2J+1)e^{-\frac{BJ(J+1)}{k_b T}}}{Q_{Rot}}$$

where

$$Q_{Rot} = \sum_J (2J+1) e^{-\frac{BJ(J+1)}{k_b T}} \approx \frac{k_b T}{B}$$

Note that the 2*J*+1 factor comes from the *m* degeneracy, as *m* can take values from *m*=-*J*, -*J*+1, …, 0,…,*J*-1, *J*
The probability distribution as a function of *J* is plotted below for the CO molecule (B = 1.9225 cm^{-1}) at 300K.



In contrast to vibrations, this function peaks away from zero. This is caused by the (2*J* + 1) degeneracy factor which is increasing with *J* and at low *J* it dominates. At higher *J*, the exponential factor wins and causes the probability to decrease with *J*.

As the energies for electronic states are in general much larger than the thermal energy only the lowest state electronic states will be populated at room temperature.

It is important to realize that the intensity of the transition depends on the difference in populations between the upper and lower states. This is because the probability of making a transition from the upper state down to the lower state is the same as the upward transition. The downward transition results in the emission of two photons (the original one and the one due to stimulated emission). If there were equal populations in both states, there would be no net absorption. Clearly, this will only be a problem for low energy transitions (*i.e.*, those in which the upper state is low enough in energy to be thermally populated). Thus, it will never be a problem in electronic or vibrational spectroscopy, but may be in rotational spectroscopy.

2.4.5 Nuclear Spin Statistics

There is one more factor that affects the intensities of spectroscopic transitions that I have not yet mentioned related to the degeneracy, g_I, in the expression for the state populations. It arises from the treatment of indistinguishable particles in quantum mechanics. During the Quantum chemistry course the topic of the Pauli Principle was extensively discussed. I will briefly review the major conclusions and then apply it to linear molecules. Similar arguments can be made for nonlinear polyatomics.

The interchange of identical particles cannot affect the properties of a molecule. Because all observable properties are related to the square of the wave function, $\psi\psi^*$ cannot change when identical particles are exchanged. This implies that the wave function ψ can either remain unchanged or change sign upon interchange of indistinguishable particles.

All known particles in nature can be divided into two groups:
- Particles whose wave functions are **symmetric**with respect to interchange (+ sign) are called **Bosons**.
- Particles whose wave functions are **antisymmetric** (- sign) are called **Fermions**.

According to the spin statistics theorem:
- half integral spin particles (electrons, positrons, neutrons, protons) are Fermions
- integral spin particles (photons, mesons) are Bosons

Now let us consider what effect this has on the intensities of spectroscopic transitions. Consider a homonuclear diatomic molecule. This discussion below is valid for any linear molecule with indistinguishable nuclei (*i.e.*, HCCH, OCO, etc.), but for simplicity, we will treat a diatomic.

Depending upon whether the indistinguishable particles are Fermions or Bosons, the wave functions must be either antisymmetric or symmetric with respect to interchange. Because rotation of a molecule can interchange two nuclei, one must consider the symmetry properties of the rotational wave functions.

The overall wave function for a molecule can be written as a product of electronic (spatial + spin), rotational, and nuclear spin parts.
Thus

$$\psi_{Total} = \psi_{el}\psi_{vib}\psi_{rot}\psi_{ns}$$

It is the overall wave function that must be symmetric or antisymmetric. Assume for the moment that the electronic part of the wave function is symmetric with respect to interchange of the nuclei. This need not be the case, but our conclusion will just be reversed for the case of an antisymmetric electronic wave function.

The vibrational part of the wave function will be symmetric since the potential only depends upon the absolute value of the internuclear separation.

For a given electronic state, the symmetry of the overall wave function will therefore be controlled by the rotational and nuclear spin parts.

Interchanging identical nuclei in a diatomic can be brought about by rotating the molecule by 180°. One can verify by examining the rigid rotor wave functions that changing θ and φ by 180° multiplies the function by $(-1)^J$.

This means that

- *for even J, the rotational wave function is symmetric* with respect to particle interchange
- *for odd J, the rotational wave function is antisymmetric* with respect to particle interchange

The general phenomenon holds true for any molecule with indistinguishable particles. Moreover, nuclear spin statistics affect <u>all types of spectroscopy</u> insofar as it <u>modifies the expected populations of states</u>.

Let us consider the simple case of the H_2 molecule.
A hydrogen atom has a nuclear spin I = 1/2. This makes it a Fermion. Thus, the overall wave functions of H_2 must be antisymmetric.

This introduces the requirement that even J levels (symmetric) must be paired with antisymmetric nuclear spin wave functions and odd J levels (antisymmetric) must be paired with symmetric wave functions.
Let us think about nuclear spin wave functions in the same way as we think about electronic spin wave functions. With I = 1/2, one has a possibility of one of two spin states for each nuclei, each representing different orientations of the angular momentum vector in space.

Each nucleus can have either spin up (M_I = 1/2) represented by α, or spin down M_I =-1/2) represented by β.

This leads to 4 possibilities for combination of the two, 3 of which are symmetric, and one antisymmetric:

$$\left.\begin{array}{c}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]\end{array}\right\}\quad \text{symmetric, 3 with odd } J\text{'s}$$

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\quad \text{antisymmetric, 1 with even } J\text{'s}$$

To result in an overall wave function that is antisymmetric, the odd J states must be paired with one of the three symmetric nuclear spin functions and the even J states must be paired with the antisymmetric wave function. You can see that there will be 3 times as many odd J states as there will be even J states. In the absence of a magnetic field, the nuclear spin doesn't affect the energy. So the odd states are 3-fold degenerate compared to the even states.

This means that the odd J states will have 3 times the statistical weight as even J states. This will be reflected in a spectrum as a 3:1 intensity alternation between even and odd states.

In general, the levels with the higher statistical weight are designated <u>***ortho***</u> and the states with the lower statistical weight is designated <u>***para***</u>.

Hydrogen comes in two forms: **ortho-Hydrogen** (odd *J* states) and **para-Hydrogen** (even *J* states).
The three nuclear spin states of ortho-hydrogen correspond to having both nuclear spins parallel. That would give a net nuclear spin of 1 with projections 1, 0, -1.

Para-hydrogen has the two nuclear spins anti parallel giving a net spin of 0.

It turns out that it is *very difficult to interchange between ortho and para forms*, not only spectroscopically, but by collisions or other means. If one starts out with pure para-hydrogen, for example, and leaves it in a bulb, it can take weeks or months for a significant amount to convert to ortho.

These two forms of hydrogen are basically *different molecules*. They have different heat capacities at low temperature and can be isolated. One method to convert ortho to para hydrogen is to use a charcoal catalyst at very low temperature. In this way one can produce pure para-hydrogen. Once taken off the catalyst, this will remain in the para form for a long time, and one can measure its properties.

Now consider the case of D_2:

Deuterium atoms have a nuclear spin *I*=1 and hence are Bosons. For the exchange of identical Bosons, the total wave function must be symmetric. Therefore, odd *J* states go with antisymmetric spin functions and even *J* states go with symmetric spin functions (the opposite of the case of H_2).

Because *I*=1, there are now three orientations of the angular momentum vector and three possible spin functions corresponding to M_I = -1, 0, 1

I will call the three spin functions α, β, and γ. There will be six symmetric spin functions and three antisymmetric functions.

symmetric	**antisymmetric**
$\alpha(1)\alpha(2)$	
$\beta(1)\beta(2)$	
$\gamma(1)\gamma(2)$	$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right]$
$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right]$	$\frac{1}{\sqrt{2}}\left[\alpha(1)\gamma(2)-\alpha(2)\gamma(1)\right]$
$\frac{1}{\sqrt{2}}\left[\alpha(1)\gamma(2)+\alpha(2)\gamma(1)\right]$	$\frac{1}{\sqrt{2}}\left[\beta(1)\gamma(2)-\beta(2)\gamma(1)\right]$
$\frac{1}{\sqrt{2}}\left[\beta(1)\gamma(2)+\beta(2)\gamma(1)\right]$	
6 with even *J*'s	**3 with odd *J*'s**

Thus, there are twice as many molecules in even *J* states as in odd *J* states. This will give rise to a 2:1 intensity alternation in the spectra.

General Case:

In general, the number of orientations, or spin wave functions, for a specific nucleus of spin *I* is $(2I+1)^2$.

- The number of symmetric spin functions for two particles will always be $(I+1)(2I+1)$
- The number of antisymmetric functions will be $I(2I+1)$.

The ratio of antisymmetric functions to symmetric functions is therefore: $\frac{I}{I+1}$

It is this factor that determines the intensity ratio.

Note what happens when I = 0. If I=0, the number of antisymmetric spin functions = 0. Since an I = 0 particle is a Boson, the total wave function must be symmetric. Since there are no antisymmetric spin functions to combine with the odd number J levels, which are antisymmetric, ***it is impossible to construct a satisfactory wave function with odd J values!!***

CO_2 is an example. Oxygen is an I = 0 particle. This means that there are no odd J values in CO_2. As we will see shortly, the vibration-rotation spectrum shows that ***all the odd J values are missing!!***

Nuclear spin statistics affect all kind of spectra, and are not limited to diatomic or linear molecules. For example, the hydrogen atoms in NH_3 are indistinguishable and give rise to certain levels having higher statistical weight than others.

I will not discuss these slightly more complicated situations, but I will refer to nuclear spin statistics and expect that you can appreciate the physical origin of these effects.

2.5 Spectral Line Broadening

There are several effects that give rise to a finite width in the spectral lines that one measures. I would like to briefly comment on three of them.

2.5.1 Natural Line Broadening

I pointed out previously that the lifetime of a molecule in a particular state (in the absence of radiation to cause stimulated emission) is inversely proportional to the Einstein A coefficient.

$$\tau = \frac{1}{A}$$

This is the average time that a molecule remains in a particular level before it undergoes spontaneous emission, making a transition to a lower energy state. For this reason it is called the ***radiative lifetime.***

Analogous to the position-momentum uncertainty principle there is also a time-energy uncertainty principle. Although the origin of this uncertainty principle is different from that of the position-momentum uncertainty principle, it has a similar form:

$$\Delta E \Delta t \geq \hbar$$

Because a molecule remains in a particular state for a finite amount of time, τ, there will be an uncertainty to the energy of that state. If we associate the lifetime, τ, with Δt, then we can write

$$\Delta E \tau \geq \hbar \qquad \text{or} \qquad \Delta E \geq \hbar A$$

This energy uncertainty will appear as a broadening of the spectral line that one measures.

If we write $\Delta E = h \Delta \nu$

then

$$h \Delta \nu \geq \frac{h}{2\pi} A \quad \rightarrow \quad \Delta \nu \geq \frac{1}{2\pi} A \quad \rightarrow \quad \Delta \nu \geq \frac{1}{2\pi \tau}$$

or in units of cm^{-1}

$$\Delta \tilde{\nu} \geq \frac{1}{2\pi c \tau}$$

This is a fundamental limit to the line width of a spectral transition and is called the **natural linewidth**. There is nothing one can do to remove or reduce it.

In practice, because vibrational and rotational levels have long lifetimes, the natural linewidth is often much smaller than one's ability to measure it.

However, recall that the Einstein A coefficient increases as ν^3. Electronically excited states, which are at much higher energies, have short lifetimes. In this case, transitions to these states can be significantly broadened.

This type of spectral broadening gives rise to a *Lorentzian* line shape:

$$g(\nu) = \frac{\Delta\nu}{(\nu-\nu_0)^2 + \left(\frac{\Delta\nu}{2}\right)^2}$$

2.5.2 Other Types of Lifetime Broadening

There are other mechanisms that can shorten the time a molecule remains in an particular quantum state, and each of these will give rise to *lifetime broadening* as determined by the time-energy uncertainty principle.

The expression $\Delta\nu \geq \frac{1}{2\pi\tau}$ holds in general, although the details of the proportionality constant may differ depending upon the form of the decay in time (*i.e.*, exponential, square wave, etc.)

For example, molecules can change quantum states as the result of a collision with another molecule or atom. If the frequency of collisions is sufficiently high, the average time between collisions can be short enough to broaden the energy levels. This type of spectral broadening is called ***pressure broadening*** since it increases with increasing pressure.

We saw before that

$$\Delta\nu \propto \frac{1}{\tau_{coll}}$$

And since

$$\tau_{coll} \propto \frac{1}{P}$$

We find

$$\Delta\nu = bP$$

where *b* is a pressure broadening coefficient and *P* is the pressure. The value of *b* can vary greatly, depending upon the type of molecule and the type of energy level. A typical value, assuming the collisions between molecules are like those of hard spheres, is about

b ~ 10 MHz per mBar

As in the case of natural line broadening, pressure broadening gives rise to a Lorentzian line shape.

Pressure broadening can be eliminated by working at low enough pressure to make the average time between collisions very long.

Another type of lifetime broadening is called ***power broadening***. If one uses an intense light source such as a laser, one can pump a molecule up to the excited state and then stimulate it back down to the ground state. The rate at which a molecule performs this cycle limits its lifetime in any one state and hence gives rise to spectral broadening.

A fourth type of lifetime broadening is ***transit time broadening***. This comes from the fact that a molecule may only be exposed to a light source for a finite amount of time due to its flight through the beam. In the reference frame of the molecule, the light source seems pulsed, and hence has a limited linewidth by the time-energy uncertainty principle.

In this case, the broadening is actually the broadening of the laser in the reference frame of the molecule and not actually a broadening of the levels. But the measured transition will be nonetheless broadened.

With reasonable molecular velocities, the amount of transit time broadening it is usually very small. However, it must be taken into account when performing very high-resolution measurements.

Other processes that shorten a molecule's lifetime can also give rise to broadening. If in the excited state the molecule dissociates (*i.e.*, breaks a chemical bond), this will also broaden the molecular energy levels.

Lifetime broadened line widths can often provide important information on the rates of certain processes such as chemical reactions and collisional energy transfer.
Natural line broadening, pressure broadening, power broadening, and transit time broadening are considered ***homogeneous*** types of broadening. This means that if you were to take the spectrum of different individual molecules, they would all show the same spectral width.

This is to be contrasted with ***inhomogeneous*** types of broadening which arise from different molecules having slightly different frequencies. Each individual transition may be sharp, but the collection together result in a broad spectral feature.

Doppler Broadening and Other Types of Inhomogeneous Broadening

The frequency at which radiation is absorbed or emitted depends upon the velocity of the atom or molecule relative to the source or detector. It is for this very same reason that a train whistle sounds to be at a higher pitch when it is approaching you and at a lower one as it moves away. This is known as the ***Doppler effect***.

If an atom or molecule is traveling towards the light source with a velocity v_a, then the frequency ν_a at which a transition is observed to occur is related to the frequency ν_0 in a stationary atom or molecule by

$$\nu_a = \nu_0 \left(1 - \frac{\mathrm{v}_a}{c}\right)^{-1}$$

where *c* is the speed of light.

Because there is usually a spread of molecular velocities v_a in a sample, there will be a corresponding spread in the absorption frequencies. At thermal equilibrium, the velocity distribution <u>in one dimension</u> is given by

$$P(\mathrm{v}) = \sqrt{\frac{m}{2\pi k_b T}}\, e^{-\frac{m\mathrm{v}^2}{2k_b T}}$$

This Gaussian velocity distribution gives rise to a Gaussian frequency distribution for the spectral transition

$$g_D(\nu) = \frac{1}{\nu_0}\sqrt{\frac{mc^2}{2\pi k_b T}}\, e^{-\frac{mc^2(\nu-\nu_0)^2}{2k_b T \nu_0^2}}$$

This is characteristically different than the Lorentzian that one obtains for lifetime broadening. One can easily show that the width of the transition is given by

$$\Delta\nu = \frac{2\nu_0}{c}\sqrt{\frac{2k_b T \ln 2}{m}}$$

where *m* is the mass of the atom or molecule.

We have

$$\Delta\nu = 7.1\cdot 10^{-7}\nu_0\sqrt{\frac{T}{M}}$$

where *M* is in amu and *T* in Kelvin.

Note the linear dependence on the frequency (or wavenumber). This means that microwave and infrared spectra will have much less Doppler broadening than electronic spectroscopy in the visible or UV region.

Doppler broadening is a major source of spectral broadening and is usually far greater than the natural line width.

This type of broadening is inhomogeneous, since not all atoms or molecules have the same spectrum. Doppler broadening can be greatly reduced using one of several clever experimental techniques.

If the molecules are not isolated, but rather solvated in a liquid or embedded in a solid (matrix) the transitions are often significantly broadened. This line broadening can be caused by several effects. For example due to the interaction of the molecule with the environment, the excited state lifetime might be significantly reduced, giving rise to homogeneous lifetime broadening. The transition frequencies are also weakly modified due to the interaction of the molecule with the environment. Since the environment seen by the molecule is not isotropic, especially in solids, inhomogeneous line broadening results. Of course, both effects are generally present. Which one is the most important depends on the system.