Fundamentals of Spectroscopy

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Lecture-21
Origin of the Rotational Selection Rule

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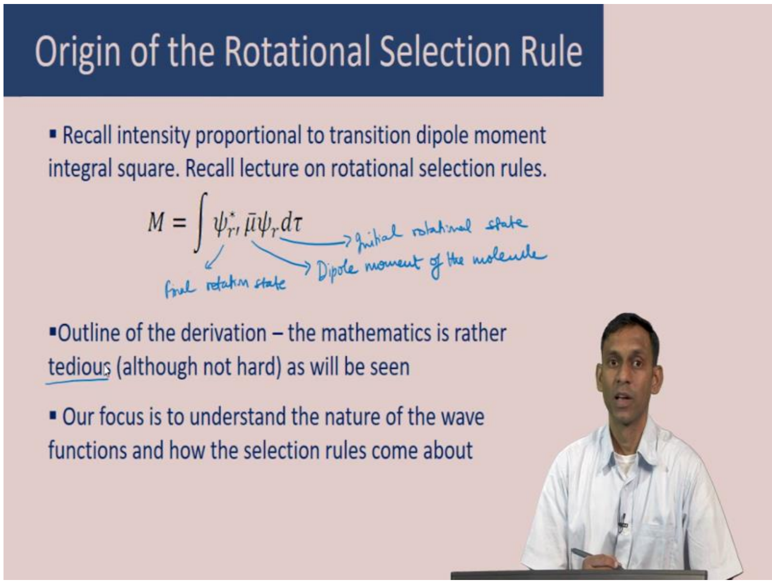

Origin of the Rotational Selection Rule

- Recall intensity proportional to transition dipole moment integral square. Recall lecture on rotational selection rules.

$$M = \int \psi_{r'}^{*} \bar{\mu} \psi_r d\tau$$

Initial rotational state

Dipole moment of the molecule

Final rotation state

- Outline of the derivation – the mathematics is rather tedious (although not hard) as will be seen
- Our focus is to understand the nature of the wave functions and how the selection rules come about

In this lecture we will discuss the origin of the rotational selection rule. You will recall that the intensity of a transition is proportional to the square of the transition dipole moment integral. You will also recall that in an earlier lecture on rotational spectroscopy my colleague has mentioned that the intensity of a rotational transition depends on the rotational transition dipole moment integral which is given here where this is the final rotational state this Psi r is the initial rotational state and mu is the dipole moment of the molecule.

We will now outline the derivation of this selection rule and keep in mind that the mathematics is rather tedious. By tedious I mean that it is not really hard but there are a lot of steps and it will take a long time to go through all the steps, so in the interest of time I will show you how the derivation works and not go through every step of it. Our focus is to understand the nature of the wave function and understand how the rotational selection rule comes about. We consider the simplest rotating chemical system namely a rotating diatomic molecule.

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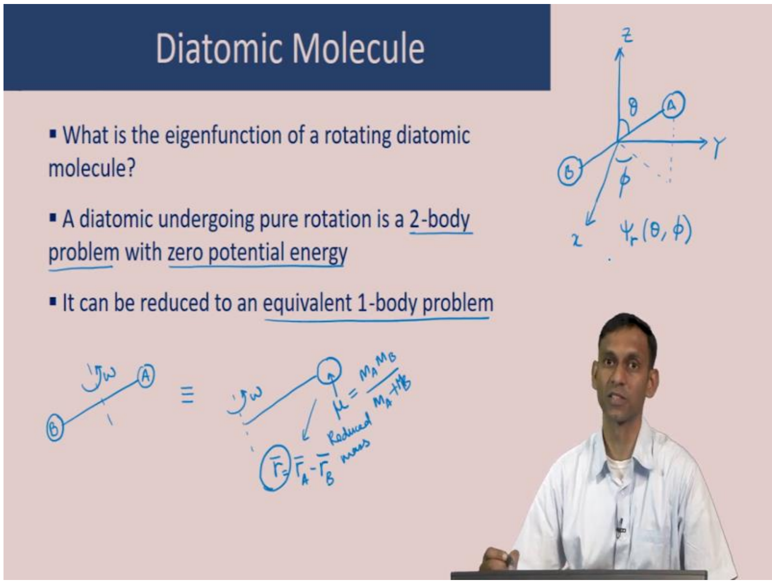

Diatomic Molecule

- What is the eigenfunction of a rotating diatomic molecule?
- A diatomic undergoing pure rotation is a 2-body problem with zero potential energy
- It can be reduced to an equivalent 1-body problem

The question then is what are the eigen functions of a rotating diatomic molecule we have to keep in mind that a diatomic undergoing pure rotation is a two body problem which is in motion but there is 0 potential energy. So, the only energy of this two bodies is the kinetic energy of rotation. Now you can reduce this to body problem where there is no translation of the center of mass and there is only kinetic energy you can reduce it to an equivalent one body problem where there is a rotation of only one mass which has a different mass which is called the reduced mass which I will discuss and that undergoes rotation with the same angular velocity as that of the diatomic molecule.

So consider the diatomic molecule to be something like this that you have the two atoms A and B and let us say that this molecule is undergoing rotation like this. We can show using some mathematics that this is equivalent to a single mass rotating in the same direction with the same angular velocity but the mass of this is M A M B divided by M A + M B this is called the reduced mass of the system. The position of this reduced mass is given by the position vector r is equal to r of A - r of B.

So, the system that we have to equivalently consider while thinking of a rotating diatomic is that of a mass with that this reduced mass and the position vector given by the r here. For the ease of the mathematics we consider the system in spherical coordinates. So, in spherical coordinates you can think of this as the diatomic having the spherical coordinate system at its center of mass and here are the axis z axis x and y axis.

And the orientation of this diatomic depends on the angles theta and Phi which are the angles associated with the spherical coordinates. The angles theta and Phi completely specify the orientation of this diatomic molecule and so the wave function of the system the rotational wave function is some function of theta and Phi. Our goal is to find the eigen functions of the Hamiltonian associated with the rotation of this diatomic system.

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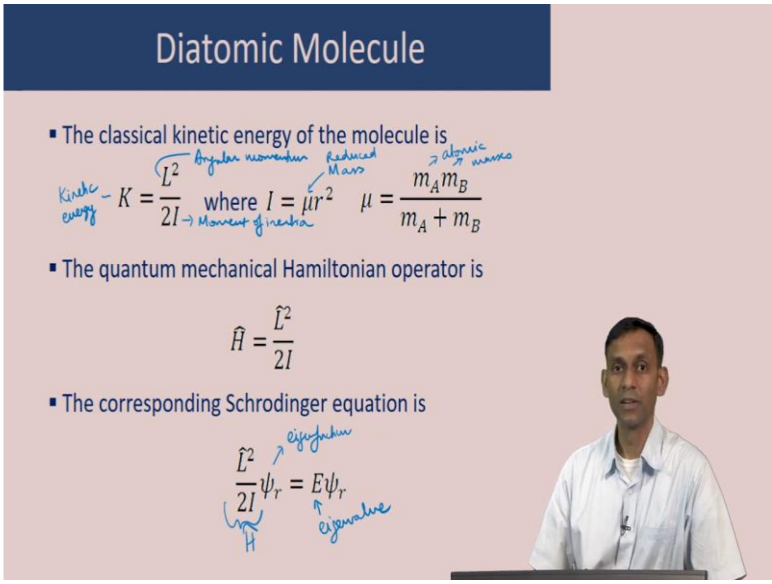

Diatomic Molecule

- The classical kinetic energy of the molecule is

$$\text{Kinetic energy} - K = \frac{\overset{\text{Angular momentum}}{L^2}}{2I} \rightarrow \text{Moment of inertia} \quad \text{where } I = \overset{\text{Reduced Mass}}{\mu} r^2 \quad \mu = \frac{\overset{\text{atomic masses}}{m_A m_B}}{m_A + m_B}$$

- The quantum mechanical Hamiltonian operator is

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

- The corresponding Schrodinger equation is

$$\underbrace{\frac{\hat{L}^2}{2I}}_{H}\overset{\text{eigenfunction}}{\psi_r} = \underset{\text{eigenvalue}}{E}\psi_r$$

To obtain the Eigen functions of this molecule we first need to write its Hamiltonian and for that we start with the classical energy of the system. Now the classical energy only has kinetic energy because as we have said there is no potential energy and this is the rotation of a molecule in the absence of any other forces. So, the kinetic energy which we have written here K kinetic energy of this rotating system is the square of the angular momentum, angular momentum square divided by two times the moment of inertia.

And the moment of inertia has the following expression r is equal to mu r squared mu is the reduced mass which has the expression given here where MA and MB are the two atomic masses. The corresponding quantum mechanical Hamiltonian operator is H hat is equal to L hat squared operator divided by 2I, we solve the Schrodinger equation for this system which is essentially the Eigen value equation of the Hamiltonian.

So, this is the Hamiltonian and these are the Eigen functions and this is the corresponding Eigen value. Let us look at the nature of the Eigen functions and the Eigen value

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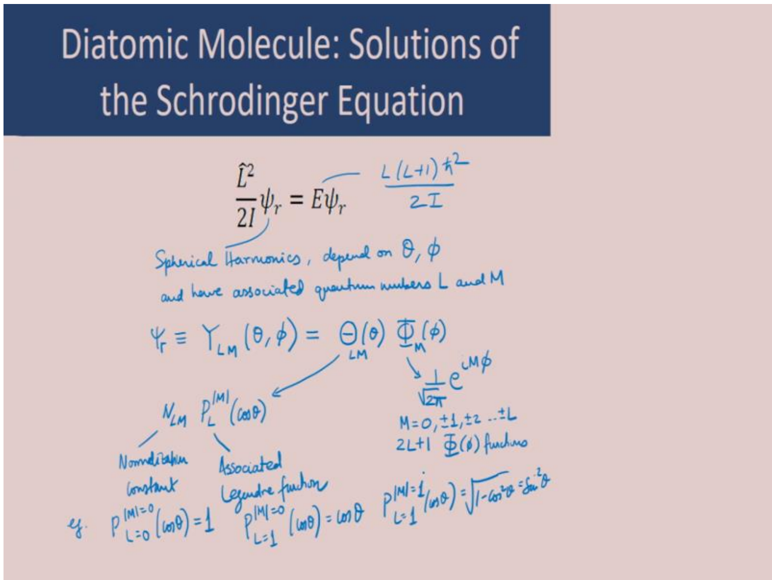

Diatomic Molecule: Solutions of the Schrodinger Equation

$$\frac{\hat{L}^2}{2I}\psi_r = E\psi_r \qquad \frac{L(L+1)\hbar^2}{2I}$$

Spherical Harmonics, depend on θ, ϕ and have associated quantum numbers L and M

$$\psi_r \equiv Y_{LM}(\theta,\phi) = \Theta_{LM}(\theta)\,\Phi_M(\phi)$$

$N_{LM}\, P_L^{|M|}(\cos\theta)$

Normalization constant

Associated Legendre function

$\frac{1}{\sqrt{2\pi}} e^{iM\phi}$

$M = 0, \pm 1, \pm 2 \ldots \pm L$

$2L+1$ $\Phi(\phi)$ functions

eg. $P_{L=0}^{|M|=0}(\cos\theta) = 1$ $\quad P_{L=1}^{|M|=0}(\cos\theta) = \cos\theta$ $\quad P_{L=1}^{|M|=1}(\cos\theta) = \sqrt{1-\cos^2\theta} = \sin^2\theta$

Here is the Schrodinger equation for the rotating diatomic system and on solving this we find that the energy has the expression L times L + 1 H bar squared by 2I and these rotational Eigen functions are called spherical harmonics they depend on theta and Phi the 2 variables and have associated quantum numbers you l and M. so, this Psi r is usually written as the spherical harmonic symbol which is a y LM and this is a function of theta and Phi.

The spherical harmonics further are a product of two functions one which is a function of theta which I will denote as capital theta as a function of theta multiplied by capital Phi which is a function of Phi. The function of theta depends on the quantum numbers L and M and the function of Phi depends on the quantum number M. The function Phi of M this one has a fairly straightforward form which is 1 over square root of 2 pi e to the power of i M Phi where the values of M are 0 + - 1 + - 2 and so on up to + or – L.

So the range of M is from - L to + L in integral increments. There are 2L + 1 values Phi M functions which implies that for a given L the degeneracy of a spherical harmonic is 2l + 1. Now let us look at the function of theta this is a little more complicated and it has the following form this has a normalization constant N of LM multiplied by a function which depends on L and only the magnitude of M and it is a function of the variable cosine theta.

This is the normalization constant as I said and this function is called The Associated Legendre function. Form of these Associated Legendre functions can be easily found in any physical chemistry textbook or spectroscopy textbook and I will just list a few of them to give you a feel for how these functions look. So, for example P when capital M is equal to 0 L is equal to 0 cosine of theta is equal to 1 and when capital P the Associated Legendre function when M is equal to 0 and L is equal to one cosine of theta is equal to cosine theta.

And another one when M is equal to 1, l is equal to 1 cosine theta this is equal to 1 over cosine squared theta which is equal to sine squared theta. So, clearly this spherical harmonic here has a functional form which depends on theta and Phi and for every theta and Phi there is a particular value of the function. The Phi part is always e to the power of i M Phi as we have seen and the theta part depends on the Associated Legendre functions. Now the Associated Legendre functions can always be looked up in a book but there is also a recursion relation which connects these Associated Legendre functions.

So let us look at this recursion relation because as we will see this will help us derive the selection rule for rotational spectroscopy.

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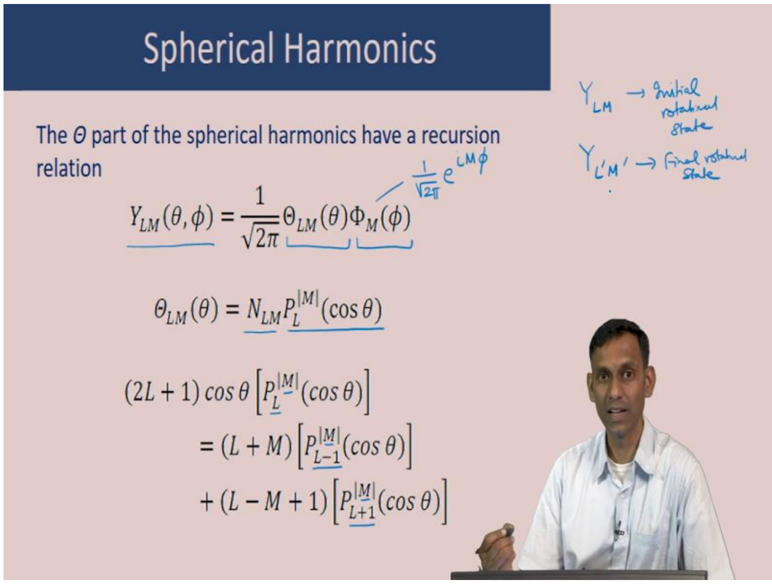

Spherical Harmonics

The Θ part of the spherical harmonics have a recursion relation

$$\underline{Y_{LM}(\theta,\phi)} = \frac{1}{\sqrt{2\pi}}\underbrace{\Theta_{LM}(\theta)}\underbrace{\Phi_M(\phi)}_{}$$

$\frac{1}{\sqrt{2\pi}}e^{iM\phi}$

$$\Theta_{LM}(\theta) = \underline{N_{LM}}\underline{P_L^{|M|}(\cos\theta)}$$

$$(2L+1)\cos\theta\left[P_{\underline{L}}^{|\underline{M}|}(\cos\theta)\right] = (L+M)\left[P_{\underline{L-1}}^{|\underline{M}|}(\cos\theta)\right] + (L-M+1)\left[P_{\underline{L+1}}^{|\underline{M}|}(\cos\theta)\right]$$

$Y_{LM} \rightarrow$ Initial rotational State

$Y_{L'M'} \rightarrow$ Final rotational State

So here I have written out the spherical harmonic one more time which depends on a function of theta and a function of Phi. The function of Phi is 1 over square root of 2 pi e to the power of i M Phi as we have seen and the function of theta is the normalization constant multiplied by the Associated Legendre function. The recursion relation for The Associated Legendre function looks like this so you note here that you have a Legendre function P which depends on L and M and that is related to the Legendre function which depends on L - 1 and M and L + 1 and M.

So given a particular Legendre function with L is equal to 0 you can find all the other ones for a given M. Using this we can get expressions for Phi L M which is let us say the initial rotational state and Psi of L prime M prime which is the final rotational state and then using these 2 and the expression for the dipole moment of the molecule we can find the transition dipole moment integral and from there the selection rule for the intensity of a rotational transition.

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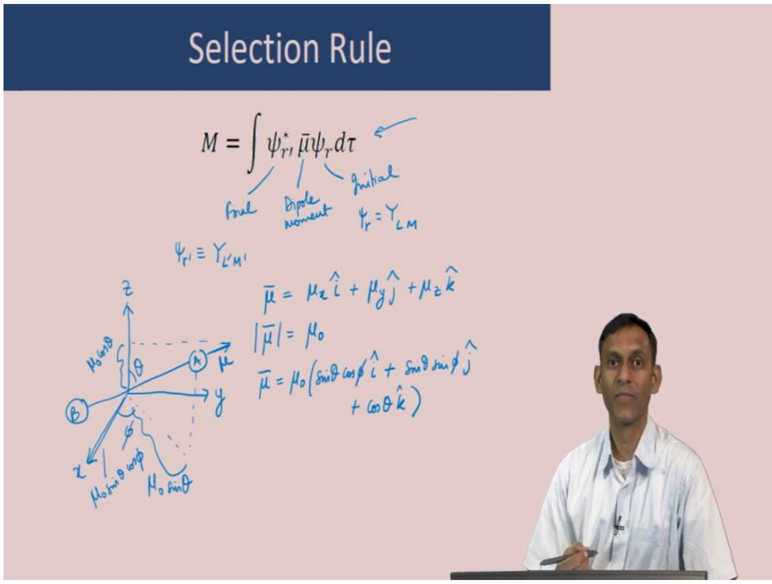

Selection Rule

$$M = \int \psi^*_{r'} \bar{\mu} \psi_r d\tau$$

Final Dipole moment Initial

$\psi_r = Y_{LM}$

$\psi_{r'} \equiv Y_{L'M'}$

$\bar{\mu} = \mu_x \hat{i} + \mu_y \hat{j} + \mu_z \hat{k}$

$|\bar{\mu}| = \mu_0$

$\bar{\mu} = \mu_0 (\sin\theta \cos\phi \hat{i} + \sin\theta \sin\phi \hat{j} + \cos\theta \hat{k})$

We have here the expression for the rotational transition dipole moment integral where the Psi r prime is the final rotational state Psi r is the initial rotational state and mu is the dipole moment of the molecule. We have seen what the form of the initial and final states are those are the spherical harmonics having different quantum numbers. So, for example Phi r prime could be denoted as the spherical harmonic L prime M prime and this Psi of r the initial state can be denoted as y of L M.

And we have seen that these spherical harmonics have Associated Legendre functions with them and they have a recursion relation. So, in principle we can write out the expressions for these rotational functions which would be functions of theta and Phi. Let us now write the expression for the dipole moment and then we can evaluate the entire integral. For this we have to realize that for a diatomic molecule the dipole moment is along the molecule or along the bond and if we go back to our picture of the coordinates where the molecule was like this A and B where it made an angle theta with the z axis.

And the projection of this made an angle Phi with the x axis then the dipole moment vector which is in this direction the mu vector can be decomposed into components mu is equal to mu x of i which is the unit vector in the x direction + mu yj the unit vector in the y Direction + mu z K which is the unit vector in the z direction. Now if the magnitude of the dipole moment vector is mu 0 the x y and z components of this dipole moment can be obtained by recognizing the orientation of this dipole moment vector.

So, for example the z component would be mu 0 cosine of theta and the projection on the xy plane would be this distance here would be mu 0 sine theta and further the projection on the x axis would be mu 0 sine theta cosine of Phi. And similarly we can get the component on the y axis. So, the dipole moment vector is equal to mu 0 sine theta cosine of Phi i + sine theta sine of Phi j the z component + cosine of theta k which is the k component.

We need to substitute this expression for the dipole moment in this transition dipole moment integral which is here and that will give us the conditions for which this integral is nonzero and thereby it will give us the rotational selection rule.

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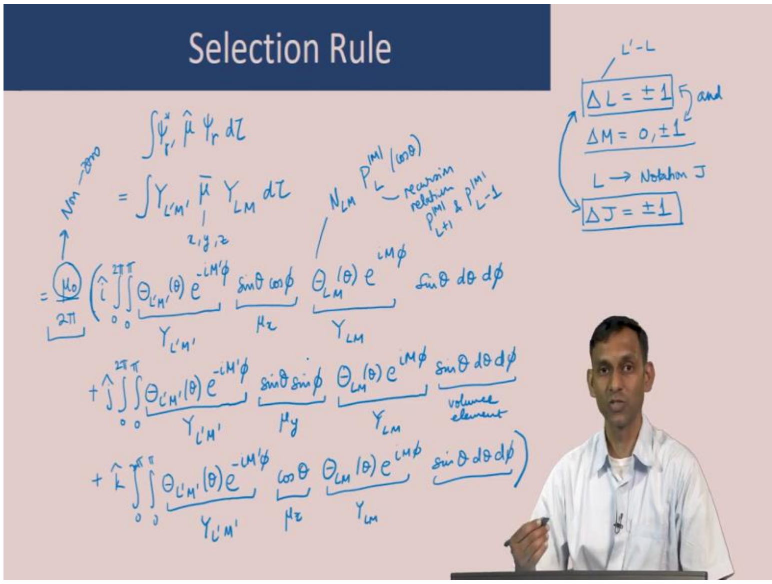

Selection Rule

$$\int \psi_{r'}^{*} \hat{\mu} \psi_r \, d\tau$$

$$= \int Y_{L'M'} \underset{x,y,z}{\bar{\mu}} Y_{LM} \, d\tau$$

$$= \underbrace{\frac{\mu_0}{2\pi}} \left(\hat{i} \int_0^{2\pi}\!\!\int_0^{\pi} \underbrace{\Theta_{L'M'}(\theta) e^{-iM'\phi}}_{Y_{L'M'}} \underbrace{\sin\theta \cos\phi}_{\mu_x} \underbrace{\Theta_{LM}(\theta) e^{iM\phi}}_{Y_{LM}} \sin\theta \, d\theta \, d\phi \right.$$

$$+ \hat{j} \int_0^{2\pi}\!\!\int_0^{\pi} \underbrace{\Theta_{L'M'}(\theta) e^{-iM'\phi}}_{Y_{L'M'}} \underbrace{\sin\theta \sin\phi}_{\mu_y} \underbrace{\Theta_{LM}(\theta) e^{iM\phi}}_{Y_{LM}} \underbrace{\sin\theta \, d\theta \, d\phi}_{\text{volume element}}$$

$$\left. + \hat{k} \int_0^{2\pi}\!\!\int_0^{\pi} \underbrace{\Theta_{L'M'}(\theta) e^{-iM'\phi}}_{Y_{L'M'}} \underbrace{\cos\theta}_{\mu_z} \underbrace{\Theta_{LM}(\theta) e^{iM\phi}}_{Y_{LM}} \underbrace{\sin\theta \, d\theta \, d\phi} \right)$$

Non-zero

$N_{LM} P_L^{|M|}(\cos\theta)$ — recursion relation $P_{L+1}^{|M|}$ & $P_{L-1}^{|M|}$

$L' - L$

$\boxed{\Delta L = \pm 1}$ and

$\Delta M = 0, \pm 1$

$L \rightarrow$ Notation J

$\boxed{\Delta J = \pm 1}$

So, a job is to obtain the value of this integral Psi rotational prime star mu psy of our d tau so that is the spherical harmonic L prime M prime multiplied by the dipole moment vector multiplied by Psi of L M d tau, let us now write the expression for this integral explicitly keeping in mind that the dipole moment 3 components x y and z so there will be 3 terms. So, this entire integral is equal to mu 0 the magnitude of the dipole moment divided by 2 pi the x component is 0 to 2 pi these are the range of integration for the Phi variable integral 0 to PI this is the range of integration for the theta and then the spherical harmonic corresponding to L prime M prime which is the function theta depending on L prime M prime.

Function of theta multiplied by the Phi part which is e to the power of - i M prime Phi multiplied by sine theta cosine of Phi which is the x component of the dipole moment comes from here this first part was y of L prime M prime and then we write y of L M which is the theta L M function of theta multiplied by e to the power of i M Phi. So, this is y of L M and finally the variable of integration and here in spherical coordinates for constant r the volume element is sine theta d theta d Phi.

And similarly we will have to write the y and z components of the dipole moment. So, we have then j 0 to 2pi 0 to PI these are the limits of integration for pi and theta respectively and again L prime M prime theta e to the power of - i M prime Phi and now the mu y component is sine theta sine Phi x j LM theta e to the power of i M Phi sine theta d theta d Phi again let us write these as y of L prime M prime this is mu of y this is y of L M and this is the volume element of integration.

And similarly we can write the z component which is k hat 0 to 2pi 0 to PI in prime theta e to the power of; where this is y L prime M prime this comes from the mu z and this comes from y L M and this is the volume element and the whole thing has a bracket which closes the bracket that we opened here which is multiplied by mu 0 divided by 2 pi. Now if we recall that the theta part of all the spherical harmonics say for example this one depends on the Associated Legendre functions. So, this theta is a normalization constant depending on L and M multiplied by an Associated Legendre function which depends on L and M.

And this has a recursion relation connecting it 2P M L + 1 and P M L - 1 now that we have expressions for all the terms here if we substitute the value of theta which depends on the quantum numbers LNM from the recursion relation and evaluate this integral which involves a little bit more tedious mathematics then we will see that the only time this entire integral is nonzero is when Delta L is equal to + or - 1 and by Delta L I mean L prime - L which is the difference in quantum numbers between the two rotational levels.

And Delta M should be 0 or + or - 1 sometimes the notation for L is J so L the notation J is sometimes used and then the rotational selection rule appears as Delta J is equal to + or - 1 but this is essentially the same as what we have seen here. So, the selection rule that we see for rotational transitions follows from quantum mechanics and it depends on the rotational Eigen functions and the dipole moment vector.

The selection rule Delta M is equal to 0 or + or - 1 is not discussed that often because both of these conditions this and this have to be satisfied for the transition dipole moment integral to be nonzero, so for therefore both of these together constitute the selection rule and the minimal selection rule is Delta L is equal to + or - 1 our Delta J is equal to + or - 1 and that therefore is the most important condition for the transition to occur.

Even more grossly the selection rule is that the total dipole moment of the molecule should be nonzero. So, the first level of the selection rule is simply that the molecule should have a permanent dipole moment so that mu 0 is nonzero and then Delta L or Delta J is equal to + or - 1 and then Delta M is equal to 0 + or – 1. So, in some sense these selection rules can be stated to be more general to going to be more specific.

You will now hopefully appreciate the origins of the rotational selection rules which comes to us from applying quantum mechanics to the rotating molecule.