

**Quantum Mechanics and Molecular Spectroscopy**  
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**Lecture No -27**  
**Molecular Rotations (Part-3)**

Hello welcome to the lecture number 27 of the course quantum mechanics and molecular spectroscopy. In the last class we were looking at the rotational Hamiltonian. The rotational Hamiltonian.

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$\hat{H}_{rot} = \frac{\hat{L}^2}{2\mu R_e^2} = \frac{\hat{L}^2}{2I_c}$   
 $I_c = \mu R_e^2$   
 $\Rightarrow$  moment of inertia  
 $\hat{L}^2 \Rightarrow$  Total angular momentum operator  
 $\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$   
 $\hat{L}_z = z$ -component of the angular momentum operator.  
 (  $R_e \equiv R_0 = r_e$  )  
 Rigid The bond (A-B) is fixed length. Rigid Rotor approximation.  
 $\theta$  and  $\phi$  are angular coordinates as part of spherical polar coordinates.

H rotation is given by  $L^2$  by  $2\mu R_e^2$ . I have used several you know  $R_e$  is identically  $= R_0$  is  $R = R$ . So that is nothing but the length of the A B bond, equilibrium length so that is  $R_0$  or  $R_e$ . And this is rigid that means it is not changing. So the bond of A B is fixed length. That is also so this gives you what is known as rigid rotor approximation. Now if that is the case this can slightly be written as  $R^2$  by sorry  $L^2$  by  $2I_e$  where  $I_e = \mu R_e^2$  and this is called moment of inertia.

And the operator  $L^2$  is the total angular momentum operator. Now this value will be equal to  $L^2$  operator actually  $L^2$  should be an operator. This will be equal to  $-\hbar^2$  into  $\frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{d}{d\theta} \right) + \frac{1}{\sin^2\theta} \frac{d^2}{d\phi^2}$  where  $\theta$  and  $\phi$  are angular coordinates as part of spherical polar coordinates. Now

there is also something called L z operator that will be equal to z component of the angular momentum.

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Solutions of the angular momentum problem

- ↳ Particle on a surface of a sphere
- ↳ particle in a central force problem.

$$\hat{H}_{rot} = \frac{L^2}{2I_e}$$

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

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

$$\hat{H}_{rot} Y_J^m(\theta, \phi) = \frac{\hbar^2 J(J+1)}{2I_e} Y_J^m(\theta, \phi)$$

$$\hat{E}_{rot}(J, m) = \frac{\hbar^2 J(J+1)}{2I_e}$$

$$\hat{E}_{rot}(J, m) = \frac{\hbar^2}{2I_e} J(J+1) = h B_e J(J+1)$$

$B_e = \frac{h}{8\pi^2 I_e} \Rightarrow$  Rotational Constant

Now it turns out that the solutions of the angular momentum problem. By the way one can imagine this as particle on a surface of a sphere or it can also where is called as particle in a central force problem. Then what we have is the L square operator will have wave function Y J M of theta and phi = h bar square J into J + 1 Y J M theta and phi and L z operator acting on Y J M theta and phi will give you M h bar Y J M theta and phi.

Now using this one can write H rotation = H rotation Y J M theta and phi will be = now H rotation had 2, 1 over 2 I as a additional this is so if you go back H rotation was = L square by 2 I e. So we already know the wave functions of this L square operator so only you multiply by this 2 I, 1 over 2 I so that will be = h bar square by 2 I e J into J + 1 Y J M theta and phi. So now you can look at your, so E rotation will now we depend on two quantum numbers J and m that = h bar square by 2 I e J into J + 1.

Even though the wave function depends on m and J the energy depends only on J. So that is your E rotation. This E rotation is all sometimes also written as E rotation J m = h bar square by 2 I e J into J + 1 or = h times B e J into J + 1 where B e is given by h by 8 pi square I e and this is called rotational constant.

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$$T_{MI} = \langle f | \mu \cdot \hat{\epsilon} | i \rangle$$

$$T_{MI} = \langle f | \left( \mu_0 + \frac{\partial \mu}{\partial r} \Big|_{r=r_0} \cdot r + \frac{1}{2} \frac{\partial^2 \mu}{\partial r^2} \Big|_{r=r_0} \cdot r^2 + \dots \right) \cdot \hat{\epsilon} | i \rangle$$
 if we have Rigid rotor.  
 $r_0$  is a fixed value.  

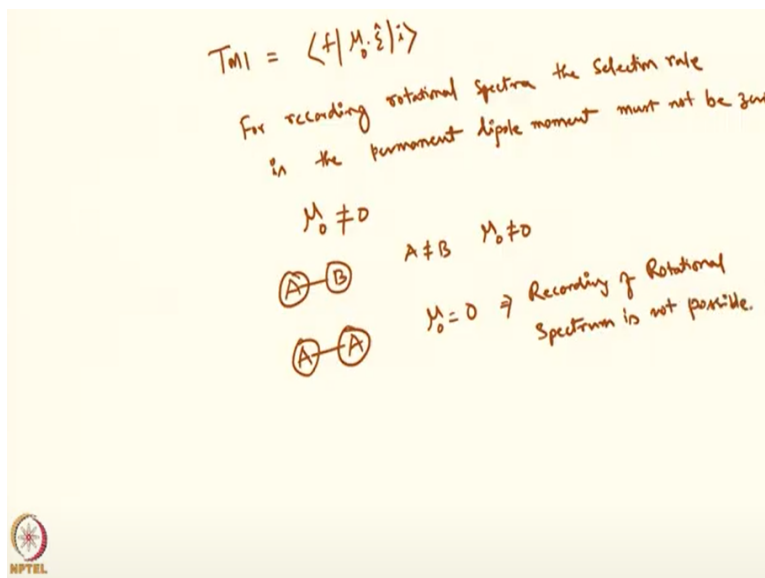
$$T_{MI}(\text{Rigid Rotor}) = \langle f | \mu_0 \hat{\epsilon} | i \rangle$$
 $\mu_0 \Rightarrow$  Permanent dipole moment  
 For Rigid Rotor  $T_{MI} = \langle f | \mu_0 \hat{\epsilon} | i \rangle \neq 0$   
 $\mu_0 \neq 0$   
 Have rotational transitions if  $\mu_0 \neq 0$

So now we know the wave functions and we know the energies. Now let us go back to the transition moment integral. A transition moment integral is given by  $\int \mu \cdot \epsilon \, i$ . Now but your  $\mu$  itself is written as  $\mu$  is written as  $\mu_0 + \frac{d\mu}{dr} \Big|_{r=r_0} \cdot r + \frac{1}{2} \frac{d^2\mu}{dr^2} \Big|_{r=r_0} \cdot r^2 + \dots$  evaluated  $r_0$  into  $r^2$  plus etcetera whole thing  $\epsilon \cdot i$ . Now if you take rigid rotor  $T_{MI}$ , if we have rigid rotor then of course the  $r_0$  is a fixed value.

Therefore the derivatives with respect to  $r$  will not exist therefore for rigid rotor,  $T_{MI}$  for rigid rotor will be  $= \int \mu_0 \cdot \epsilon \, i$  because this will go to 0 and this will also go to 0 all the other terms will go to 0 what you have is  $\mu_0 \cdot \epsilon \, i$  where  $\mu_0$  is called permanent dipole moment. Now your  $T_{MI}$  is given by this so you have to have  $\mu_0$ , you have to have  $\mu_0$  so under rigid rotor approximation for rigid rotor if  $T_{MI}$  has to be non-zero  $T_{MI}$  that  $= \int \mu_0 \cdot \epsilon \, i$ .

This has to be non-zero then  $\mu_0$  has to be non-zero that is the initial if that is a minimum condition if  $\mu_0$  becomes 0 of course this entire integral becomes 0 so the  $\mu_0$  must be not = 0. That means you can only have rotational transitions if  $\mu_0$  is not equal to 0 that means the permanent dipole moment of molecules must be non-zero to record rotational spectra.

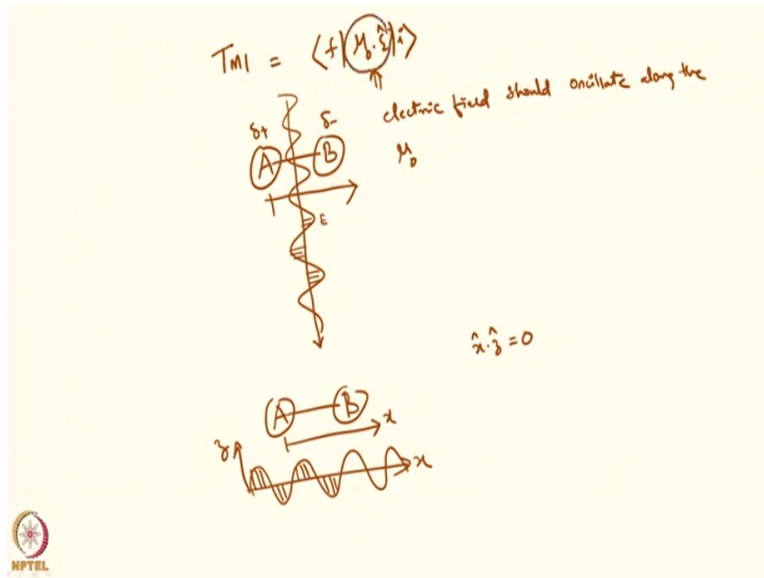
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So  $TMI = \int f \mu_0 \cdot \hat{\epsilon}$  so for recording rotational spectrum the selection rule is the permanent dipole moment must not be 0. So only  $\mu_0 \neq 0$  transitions will be allowed. So for example if you have a  $AB$  diatomic molecule where  $A$  is not equal to  $B$  then this molecule will have permanent dipole moment  $\mu_0 \neq 0$  but if you have a homodiatomics like  $AA$  then of course  $\mu_0 = 0$ .

So which means you cannot record recording of rotational spectra is not possible. So one of the selection rules for the recording rotation spectra is that the transition moment integral will go to 0 when  $\mu_0$  becomes 0. So we can only record rotation spectra of molecules that are that have permanent dipole moment. Now let us look at the  $TMI$  little more carefully

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$T_{MI} = f \mu_0$  and one thing that you must remember that when I have this that means if you take a molecule A B and your dipole moment is in this direction let us suppose so this is delta plus and delta minus then the dipole moment will be in the direction. So the propagation should be in this direction and the electric field should be so your E should be along the dipole moment that is the selection rule.

So this says that the electric field should oscillate along the because you are taking a dot product of course you can come at an angle because you can always have a the projection along that axis however if you have A and B and if a direction of propagation is like this and your electric field is like this and your dipole moment is like this so dipole moment is along let us say x axis and the propagation of light is along x axis then your electric field will be along z axis.


Let us assume so this is my z axis then of course  $x \cdot z$  will be  $= 0$  therefore the transitions will not take place. So it is not only that you know the  $\mu_0$  must be 0 but the electric field must be aligned along the permanent dipole moment to have the transitions that is the this TMI. So now once I assume

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① Molecule has permanent dipole moment  
 ② The electric field vector of the light has non-zero projection along the dipole moment.

$$T_{MI} = \langle f | \mu_0 \cdot \hat{\epsilon} | i \rangle$$

Necessary conditions for recording the rotational spectrum.



That becomes non-zero that means the molecule has dipole moment so two things one is molecule has permanent dipole moment and two the electric field vector of the light has non-zero projection along the dipole moment only then the transition moment integral can become non-zero. So T M I will be =  $f \mu_0 \cdot \epsilon$  so I am only looking at this part. This part needs two conditions one is the dipole moment must be non-zero or the permanent dipole moment must be non zero.

And the electric field vector must be aligned or projected have a projection along the dipole moment. If these two conditions are satisfied then we can look at the following the f and i so these are what are known as necessary conditions so these two are for recording the rotational spectra. Necessary condition without these conditions of course one cannot record the rotational spectrum.

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$$T_{fi} = \langle f | \hat{M} \cdot \hat{\epsilon} | i \rangle$$

$$|i\rangle = \psi_{el} \chi_N$$

$$|f\rangle = \psi_{el'} \chi_{N'}$$

$$\chi_N = \phi_{int} \cdot \phi_{trans}$$

$$|i\rangle = \psi_{el} \phi_{int} \phi_{trans}$$

$$|f\rangle = \psi_{el'} \phi_{int'} \phi_{trans'}$$

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

KE of electrons  
 PE of electrons - nuclei - attraction  
 PE of electron - repulsion  
 PE of nuclei  $\rightarrow$  repulsion.

Now if you are now what we have now we have  $T_{fi} = \langle f | \hat{M} \cdot \hat{\epsilon} | i \rangle$ . So we have already taken care of this. Now let us look at the wave functions. Now your wave function  $i$  will be equal to now this will be the total wave function  $i$  so what will a total wave function  $i$  will consist of that will consist of electronic part  $\psi_{el}$  and the nuclear part while  $i$  will call it as a  $\chi_N$ . And similarly there is a notation always the ground state is given by double dash and the excited state is given by single dash so  $f = \psi_{el'} \chi_{N'}$ .

Now the electronic is the, this comes from the electronic so what is electronic  $H_{el}$  electronic  $\psi_{el}$  electronic is  $E_{el}$  electronic  $\psi_{el}$ . So this is the Newtonian that one needs to solve and this  $H_{el}$  electronic wave function will  $H_{el}$  electronic Hamilton will consist of KE of electrons PE of electrons and nuclei and PE of electrons repulsion either this is attraction and PE of nuclei this is repulsion.

Now, so this is the  $H_{el}$  electronic that you have to use different techniques you have to do a quantum chemistry to solve that but in this course we will assume that we know that. Now the  $\chi_N$  nuclear will have so the  $\chi_N$  nuclear will have two parts; one is the what is known as  $\phi_{int}$  nuclear or  $\phi_{int}$  into  $\phi_{trans}$  into the other thing is the translation. So your  $i$  will now become  $\psi_{el} \phi_{int} \phi_{trans}$  and your  $f$  will be  $= \psi_{el'} \phi_{int'} \phi_{trans'}$ .

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$$T_{MI} = \langle \psi_{el}' \phi_{trans} \phi_{int'} | \mu_0 \hat{\epsilon} | \psi_{el}'' \phi_{trans} \phi_{int''} \rangle$$

$\psi_{el} \Rightarrow \text{remains unchanged.}$   
 $\psi_{el}'' = \psi_{el}' = \psi_{el}.$   
 $\phi_{trans}' = \phi_{trans}'' = \phi_{trans}$

$$T_{MI} = \langle \psi_{el} \phi_{trans} | \mu_0 \hat{\epsilon} | \psi_{el} \phi_{trans} \rangle \langle \phi_{int'} | \mu_0 \hat{\epsilon} | \phi_{int''} \rangle$$

$$= \langle \psi_{el} \phi_{trans} | \psi_{el} \phi_{trans} \rangle \langle \phi_{int'} | \mu_0 \hat{\epsilon} | \phi_{int''} \rangle$$

$$T_{MI} = \langle \phi_{int'} | \mu_0 \hat{\epsilon} | \phi_{int''} \rangle$$

|| (wavefunction are normalized)

So your T M I will be = psi electronic phi translation and phi internal dash mu 0 epsilon psi electronic phi trans and phi internal. Now if you are looking at rigid rotor approximation let us think of a molecule A B separated by distance r 0 or R e whatever some of them and then it is rotating so what will happen to electrons nothing will happen to electrons the electronic part of the wave function remains unchanged.

So psi el remains unchanged so which means psi el double prime should be = psi el single prime this = psi el. Now if it is rotating and it is translating so the rotation will not will assume that rotation is not going to affect the translation rotational degrees of freedom and translation degrees of freedom can be separated out so then what happens is that phi trans prime will be = phi trans and when you have the electronic degrees of freedom frozen your dipole moment is not going to change.

Similarly when you have translation if the A B molecule is translating its dipole moment is not going to change so I can write rewrite my T M I as psi electronic so this is now three integrals is not it? psi electronic phi trans phi internal mu 0 epsilon psi electronic phi trans phi internal. This is single prime and this is double prime so that is my so since the psi electronic and psi trans these two quantities are not going to depend on the this then I can bring them out.



That means I will have psi electronic phi trans psi electronic phi trans and what I will have is the phi internal prime mu 0 epsilon phi internal double front. Now if your electronic wave function and translation wave function are normalized then this will go to 0 or sorry this will go to 1. Wave functions are normalized therefore your TMI will become phi internal mu 0 epsilon phi internal.

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$$T_{MI} = \langle \phi_{rot} | M_0 \hat{\epsilon} | \phi_{rot} \rangle$$

$$T_{MI} = \langle Y_J^{m'}(\theta, \phi) | M_0 \hat{\epsilon} | Y_J^m(\theta, \phi) \rangle$$

Transition moment integral can be written in terms of  $Y_J^m(\theta, \phi) \Rightarrow$  Spherical harmonics

So for rotation the T M I will now become your phi internal is nothing but your rotational wave function so I will call it as a phi rotation in the sited state and mu 0. So now phi rotation in the ground state wave functions. Now we know this will be nothing but if you take rigid rotor approximation the phi rotation will nothing but Y J M J prime m prime theta and phi mu 0 epsilon Y J double prime M double prime theta and phi so that is going to be your T M I.

Your transient moment integral can now be written in terms of spherical harmonics so transition moment integral can be written in terms of Y J M theta and phi which is nothing but your spherical. I am going to stop here and will continue in the next lecture thank you.