Quantum Mechanics and Molecular Spectroscopy
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Lecture No -26
Molecular Rotations (Part-2)

Welcome to lecture number 26 of the course Quantum Mechanics and molecular spectroscopy. We will have a quick recap of the previous lecture before proceeding.

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In the last lecture we looked at the total Hamiltonian H is divided in two parts which is H nuclear and H electronic and the H electronic will consist of terms K E of electrons, potential energy of electrons and nuclei and potential energy of nuclear repulsion and potential energy of electron repulsion. All this put together one call it as a U relative, and the energy that comes out of this and this H nuclear will consist of K E of nuclei.

Now that means your H internal that is the motion of the nuclei can be written as H N + U relative and I told you for a given nuclear configuration, U relative = constant and we can always measure energies with respect to some constant that is U relative therefore one can treat U relative = 0, that means measurement of energies relative to U, so what you get is H nuclear = H internal.

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$r_0 = fixed$

A-B Nuclear configuration in rigid

$$KE \text{ of } AB = -\frac{\hbar^2}{2m_A}\nabla^2_A - \frac{\hbar^2}{2m_B}\nabla^2_B$$

Center of Mass Transformation:

(x_a, y_a, z_a)

(x_b, y_b, z_b)

$$-\frac{\hbar^2}{2M}\nabla^2_{cm} - \frac{\hbar^2}{2\mu}\nabla^2_{int}$$

$$M = m_A + m_B \Rightarrow \text{Total mass}$$

$$\mu = \frac{m_A m_B}{m_A + m_B} \Rightarrow \text{Reduced Mass}$$

$$r_0 = \sqrt{(x_a-x_b)^2 + (y_a-y_b)^2 + (z_a-z_b)^2}$$
$$= \sqrt{x^2 + y^2 + z^2}$$

$x = x_a - x_b$
$y = y_a - y_b$
$z = z_a - z_b$

Now if you had two atoms A and B separated by distance r0 and which is fixed so which means the A B nuclear configuration is rigid, that means A and B are not moving with respect to each other. In such scenario the kinetic energy of A B which is nothing but, - h bar square by 2mA into del square A - h bar square by 2 m B into del square B, can be written as - h bar square by 2 capital M del square C M - h bar square by two mu del square internal.

Now, where M = m A + m B and mu = m A m B divided by m A + m B, this is the total mass, this is the reduced mass and this transformation is called center of mass transformation. So one can think of it like this if you have an axis A and B and distance is r A, this is r B, you can have center of mass somewhere here which I will call as r center of mass and then there is a r0, which is the distance between A and B. If the coordinates of A are x A, y A, z A and coordinates of B are x B, y B, z B.

Then one can tell r0 is equal to square root of x a – x b whole square + y a – y b whole square + z a – z b whole square, this I will also write it as x square + y square + z square root of where x is equal to x a – x b, y is equal to y a – y b, z is equal to z a – z b.

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$$\hat{H}_N = -\frac{\hbar^2}{2M}\nabla^2_{CM} - \frac{\hbar^2}{2\mu}\nabla^2_{int}$$

motion of Center of mass

$$\left(-\frac{\hbar^2}{2M}\nabla^2_{CM}\right)\chi_N = E_N\chi_N \Rightarrow \text{free particle.}$$

$$E_N = \boxed{\frac{\hbar^2 k^2}{2M}} \Rightarrow \text{not quantized.}$$

$$\Rightarrow \text{Translation energy of the AB molecule.}$$

$$\hat{H}_{int} = -\frac{\hbar^2}{2\mu}\nabla^2_{int} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

So what you have your Hamiltonian H will now be equal to or the nuclear Hamiltonian will now be equal to - h bar square by 2 capital M del square center of mass - h bar square by two mu del square internal. Now this is nothing but motion of center of mass, what is the motion of center of mass? Motion of center of mass simply means that the whole object A B is moving in some direction and that will not contribute to the internal structure.

Therefore one can write - h bar square by 2 m del square C M if this multiplied by chi n is equal to E N chi N, this is free particle because it has no potential energy term so this is a free particle, when you have free particle your energy is E N is equal to h square k square by 2, and we know this E N is not quantized. So the energy of the free particle of course is not quantized, that corresponds to the translation.

So this essentially corresponds to translation energy of the A B molecule, now one need to deal with this your H internal will now be - h bar square by 2 mu del square internal, so that will be nothing but - h bar square by 2 mu d square by d x square + d square by d y square + d square by d sub square. So this is the Hamiltonian that we need to solve.

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$$\left(-\frac{\hbar^2}{2\mu}\nabla_{int}^2\right)\phi = E\phi$$

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\right]\phi = E\phi$$

without changing the center-of-mass

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

⇓ Co-ordinate transformation.

$$\nabla_{int}^2 = \frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}-\frac{L^2}{R^2\hbar^2}$$

So the corresponding Schrodinger equation would be - h bar square by 2 mu del square internal into some wave function, I will call it as phi is equal to E phi, - h bar square by 2 mu d square by d x square + d square by d y square + d square by d z square, whole thing acting on phi is equal to E phi. So this is the equation that we need to solve Schrodinger equation, now to solve this Schrodinger equation we have to look at one important point that is the following.

If you have A B and this is called capital R, and of course this can rotate in the plane of this board and also perpendicular to plane of this board. So essentially what we are looking at is that without changing the center of mass, center of mass remains fix. Now that means we have a rotating particle, a particle that can rotate in x, y, z directions. So now your del square internal was nothing but in Cartesian coordinates d square by d x square + d square by d y square + d square by d z square.

We have only the center of mass is fixed so we have only the rotating particle, we look and transform this into spherical polar coordinates, so we do another coordinate transformation where in the del square internal can be written as d square by d R square + 2 times by R, d by d R - L square by R square h bar square. This is the transformation in spherical polar coordinates.

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$$\vec{\nabla}^2_{int} = \left[\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R}\right] - \frac{L^2}{R^2\hbar^2}$$

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

If R is fixed.

$$\vec{\nabla}^2_{int} = \frac{-L^2}{R^2\hbar^2}$$

$$\hat{H}_{Rot} \text{ (Rigid - Rotor)}$$

$$\hat{H}_{Rot} = \frac{-L^2}{R^2\hbar^2} \cdot \frac{-\hbar^2}{2\mu}$$

$$\hat{H}_{Rot} = \frac{L^2}{2\mu R^2} = \frac{L^2}{2I_e} \qquad I_e = \mu R^2 \quad \text{is moment of Inertia}$$

Now I will come back to what L is so del square internal will be d square by d R square + 2 by R, d by d R - L square by R square h bar square, and where your L square operator is given by - h bar square into 1 over sine theta d by d theta sine theta d by d theta + 1 by sine square theta d square by d phi square. Let me tell what these terms are, now we had the Cartesian coordinates x, y, z to begin with so let us suppose you have a Cartesian coordinates x, y, z.

There is a point here which is represented by x, y and z, so I will call it as a this as a z axis and this is x and this is y, now this distance is R and this angle along z axis is theta and the projection of this on to the x y plane, this is the angle phi. So that is how you define x, y, r theta and phi. So initially you had x, y, z there are three independent coordinate that describe this point, now you have similarly 3 independent point that is r theta and phi 3 independent variables.
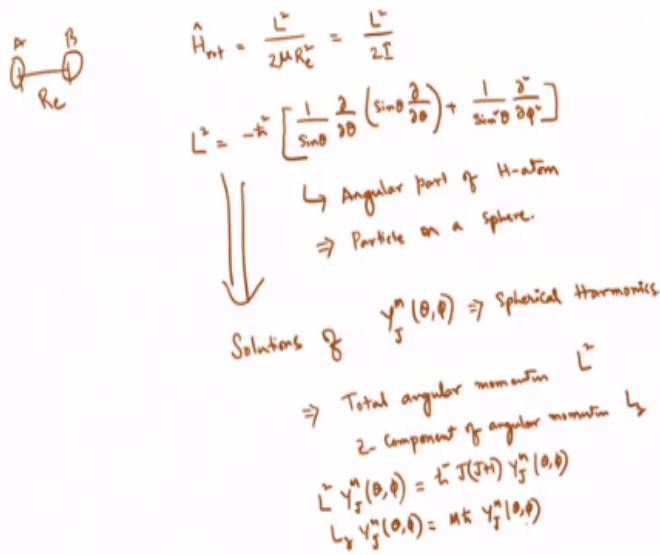
So essentially you are going from one coordinate to the other coordinate, now your del square internal will be nothing but if you ignore R or if R is fixed, why am I fixing R? I am fixing R because, I am considering the molecule A B has a fixed radius r0 or capital R, does not matter. If R is fixed then of course you cannot have a derivative with respect to a constant, you can only have a derivative with respect to variable, so you can ignore these two terms.

And all you are left out with this, so that will be equal to - L square by R square h bar square or this I will call it as a rotational Hamiltonian, H rotational under rigid rotor approximation. So my

H rot now will be equal to L square by R square h bar square into this minus, this is your del square so h bar square by 2 mu. So when I rearrange this will be h bar square this is all will cancel, negative sign will also cancel.

So what I am getting is L square by 2 mu R square this one is H rot. Now this is written as L square by 2 I e, where I e is = mu R square and this is called moment of inertia.

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So and then what I have is my H rotational is equal to L square by 2 mu R e square, why am I writing R e or R? Because I want looking at the equilibrium distance, so A B this distances I will call it as Re equilibrium distance between the 2 A and B and it is not changing its a rigid order approximation that means, A and B are fixed at one place. So this is nothing but L square by 2 I, now what is my L square? L square is equal to - h bar square into 1 over sine theta d by d theta sine theta d by d theta + 1 over sine square theta d square by d phi square.

And one can quickly look at this is nothing but your angular part of H hydrogen atom or this is also nothing but particle on a sphere and the solutions of these are given by Y J M theta phi these are called spherical harmonics. You can look up any elementary quantum chemistry text book or quantum mechanics test books to look at the spherical harmonics. Now in spherical harmonics you have 2 important notion, one is the total angular momentum given by L square operator.

And there is a z component of angular momentum it is given by L z. Now we know that your L square operator is your Y L M is a Eigen function of the L square of h bar square into J into J + 1 into Y J M theta and phi and your L z operator acting on Y J M theta and phi will give you M h bar Y J M theta and phi.

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

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

$$[\hat{L}^2, \hat{L}_z] = 0$$

$\hat{L}^2, \hat{L}_z$ commute with each other.

$$\hat{H}_{rot} = \frac{\hat{L}^2}{2\mu R_e^2} = \frac{\hat{L}^2}{2I_e} \rightarrow \text{Constant}$$

$$\hat{H}_{rot} Y_J^m(\theta,\phi) = \boxed{\frac{\hbar^2}{2\mu R_e} J(J+1)} Y_J^m(\theta,\phi) \rightarrow \text{Eigen Value.}$$

$$E_{J,Rot} = \frac{\hbar^2}{2\mu R_e} J(J+1) = \frac{\hbar^2}{2I_e} J(J+1) \quad B_e$$

$$= \hbar B_e J(J+1) \qquad \boxed{\frac{h^2}{8\pi^2 I_e}} J(J+1)$$

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

Now let me quickly write once more, so essentially your Y J M theta and phi are Eigen functions of the operator L square will give you Eigen value of h bar square into J into J + 1 Y J M theta and phi and other is L z operator is also has Eigen function of Y J M theta and phi which will give you M h bar Y J M theta and phi, now there is one important thing you must realize that, if there are two operators have common Eigen functions, then the operators must commute with respect to each other.

Which means the commutator L square L z must be equal to 0, so operators L square and L z commute with each other. Now let us go back to our Hamiltonian, your H rotation was nothing but operator L square by 2 mu R e or same as L square by 2 I e, now you can see 2 mu R e or this part and this part is just a constant. So if you multiply a constant, the wave function is not going to change. We have this Hamiltonian and because this Hamiltonian consists of the operator L square.

This Hamiltonian will have same Eigen functions of L square, except that you know now they will be multiplied by different constants. You have H rotational acting on Y J M theta and phi will give you h bar square divided by 2 mu Re J into J + 1 Y J M theta and phi, and this is your Eigen value. Therefore your E J, now you have a that is rotation with quantum number J will be equal to h bar square by 2 mu Re J into J + 1 which is same as h bar square by 2 I e J into J + 1.

Somehow this is written as h B e J into J + 1, therefore if I write like this. Now what I have got h bar square is h square divided by 8 pi square I e J into J + 1, now if I remove h then I am left with instead of h square I can write h into 8 pi square, so if I take this as B e then i will get this one, so your B e is equal to h by 8 pi square I e.

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The E rotation that will depend on value J will be equal to h bar square by 2 I e J into J + 1 this is also equal to h B e J into J + 1, where B e is equal to h by 8 pi square I e and has a unit of second inverse, because you see energy is joules and h is joule second and J s are just quantum number. So this must be joule second this has to be multiplied by second inverse and so this should give me joules, so B has a units of second inverse.

So finally what you have? We have the following your H Y J M theta and phi or H rotation is equal to E rotation J Y J M theta and phi and your E rotation J is given by h B e J into J + 1, so this is your energy and this is your wave function, so we can now look at transition now they are

quantum numbers. So you will have rotational states that are J = 0, J = 1, J = 2 etcetera and we can look at the transitions between this in the next lecture, I am going to stop it here, thank you.