Quantum Mechanics and Molecular Spectroscopy
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Lecture – 25
Molecular Rotations – Part 1

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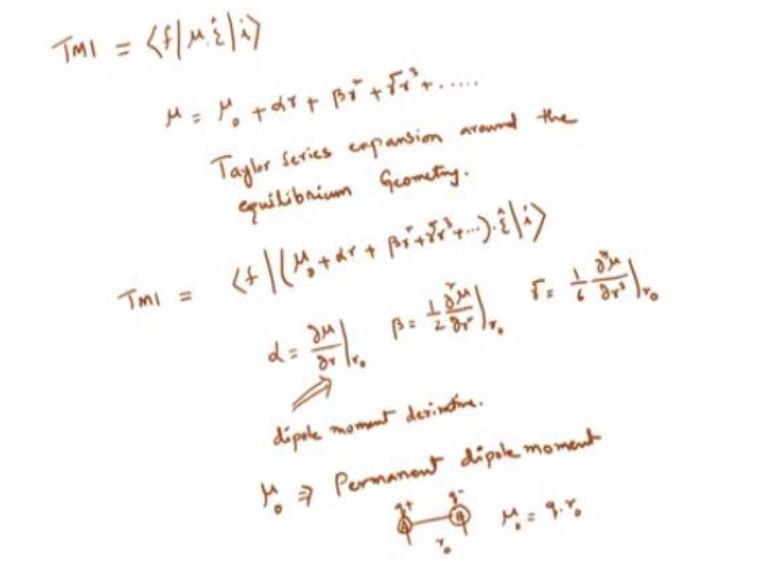

$TMI = \langle f | \mu \cdot \hat{\varepsilon} | i \rangle$

$\mu = \mu_0 + \alpha r + \beta r^2 + \gamma r^3 + \ldots\ldots$

Taylor series expansion around the equilibrium Geometry.

$TMI = \langle f | (\mu_0 + \alpha r + \beta r^2 + \gamma r^3 + \ldots) \cdot \hat{\varepsilon} | i \rangle$

$\alpha = \left.\frac{\partial \mu}{\partial r}\right|_{r_0}$ $\beta = \left.\frac{1}{2}\frac{\partial^2 \mu}{\partial r^2}\right|_{r_0}$ $\gamma = \left.\frac{1}{6}\frac{\partial^3 \mu}{\partial r^3}\right|_{r_0}$

dipole moment derivative.

$\mu_0 \Rightarrow$ Permanent dipole moment

$\mu_0 = q \cdot r_0$

Hello, welcome to the lecture number 25 of the course quantum mechanics and molecular spectroscopy. Towards the end of the last lecture, we were looking at the transition moment integral which is nothing but f mu dot e over i okay. Now we wrote that mu as an expansion of mu 0 not + alpha r + beta r square + gamma r cube + etc. okay. This is a Taylor series expansion around the equilibrium geometry.

Therefore, your TMI will now become f mu 0 + alpha r + beta r square + gamma r cube + etc dot epsilon i okay where alpha is nothing but d mu by dr evaluated at r0 and beta is nothing but half d square mu by dr square evaluated at r0 and gamma will be nothing but 1 over 6 d cube mu by dr cube evaluated at r0 okay. These are the coefficients okay. So this is nothing but dipole moment derivative okay.

We will come to the usage of dipole derivative later in this course okay. Now in this case what mu 0 is called permanent dipole moment, which is nothing but the dipole moment when the molecule is at equilibrium geometry. So simply for example, if you have a molecule A B okay because of the electronegativity difference if there is a partial charge q+ on A and q- on

B and this distance is r0 that is the equilibrium geometry. Then your mu 0 will be nothing but equal to q times r0 okay.

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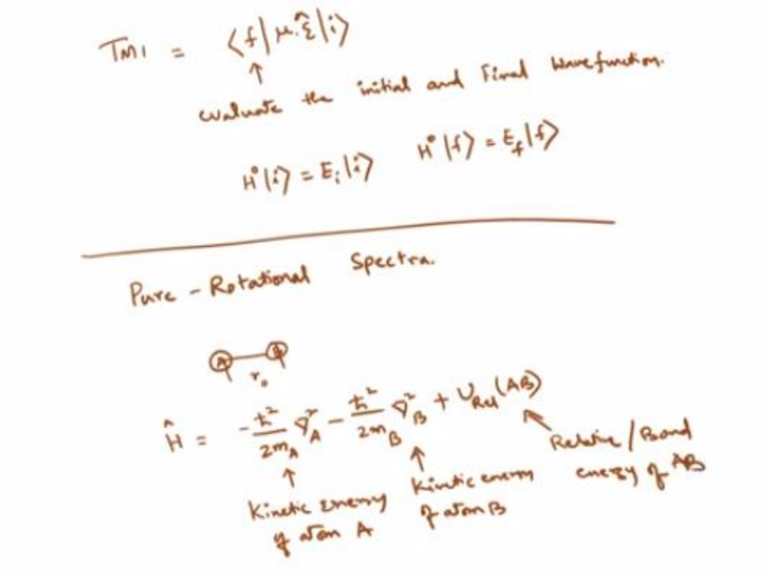

$$\text{TMI} = \langle f|\hat{\mu}\cdot\hat{\varepsilon}|i\rangle$$

evaluate the initial and final wavefunction.

$$\hat{H}^0|i\rangle = E_i|i\rangle \qquad \hat{H}^0|f\rangle = E_f|f\rangle$$

Pure - Rotational Spectra.

$$\hat{H} = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 + U_{Rel}(AB)$$

Now, one of the interesting thing that we will still need to evaluate in your transition moment integral when you write TMI this is equal to f mu dot epsilon i is the fact that we still have to evaluate the initial and final wave functions. In the beginning of the course or throughout the course up till now, what we have assumed that we have a Hamiltonian H0, we still do not know what that exactly is, into i = Ei i and H0 f = Ef f.

So this we have assumed all while, but we still do not know what is H0 precisely okay. Now what I am going to do is that let us start with a very simple problem that is the rotational state. So what we look at is pure rotational spectra okay. We look at the pure rotation spectra okay. Now if you take if you have a molecule A B okay and this is your r0 okay. One can write a Hamiltonian H = -h bar square by 2 mA del square A – h bar square by 2 mB del square B + URel AB okay.

Now one can write such a Hamiltonian H okay. Now this is what? This is the kinetic energy of atom A and this is nothing but kinetic energy of atom B and this is the relative or bond energy of AB okay.

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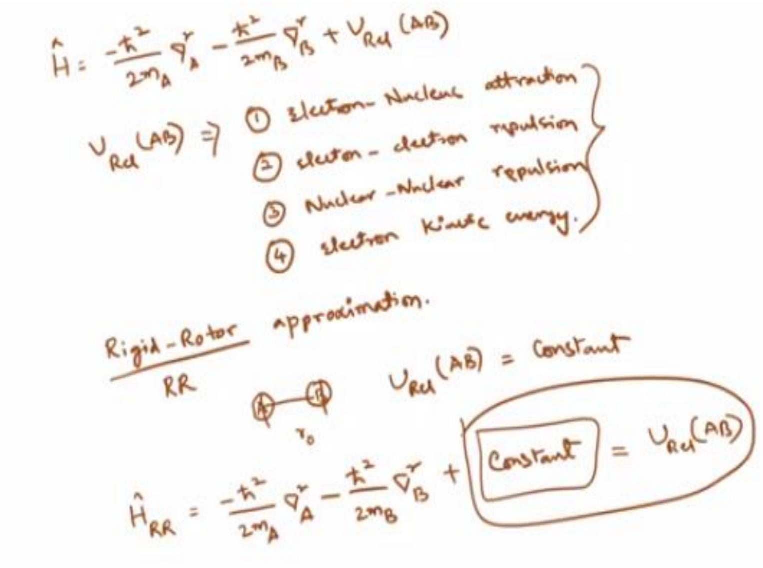

$$\hat{H} = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 + U_{Rel}(AB)$$

$U_{Rel}(AB) \Rightarrow$
① Electron- Nucleus attraction
② electron - electron repulsion
③ Nuclear -Nuclear repulsion
④ electron kinetic energy.

Rigid-Rotor approximation.
RR

A—B, r_0

$U_{Rel}(AB) = \text{Constant}$

$$\hat{H}_{RR} = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 + \boxed{\text{Constant}} = U_{Rel}(AB)$$

So we will go back to the same thing. So your H is –h bar square by 2 mA del square A – h bar square by 2 mB del square B + URel AB. Now what does URel AB consist of? If URel AB b will consist of okay will consist of 3 terms. One is electron-nucleus attraction, two consist of electron-electron repulsion, three nuclear-nuclear repulsion and four because of electron kinetic energy okay.

Now I want to make one approximation called rigid-rotor approximation. Now what am I saying when I say rigid-rotor approximation, very simply it means the following. If I have A and B and they are separated by distance r0 okay, the distance is fixed that means the nuclei are no longer moving okay. So the nuclear at the fixed positions in this case. When you have such a scenario, then the sum of URel AB will be equal to a constant okay.

So the nuclear fixed and in the AB molecule the nuclear fix, they are not vibrating, they are just fixed okay. When such are fixed, when the 2 nuclei are fixed, then okay electron-nucleus attraction will not change, the electron-electron repulsion will not change, the nuclear-nuclear repulsion will not change, electron kinetic energy will not change, all of them will be some constant numbers and when you add all the 4 constants you will get one more constant.

So your U relative AB will be equal to constant, so which means your Hamiltonian HRR okay, RR because rigid-rotor okay, I will call rigid-rotor as RR okay. HRR will be now be equal to –h bar square by 2 mA del square A – h bar square by 2 mB del square B + some constant okay. Now one of the interesting things of you know energy measurements is that you can always measure energy with respect to some value okay.

For example in thermodynamics, we only measure delta g's because we always think that the delta g of the standard states is 0 okay and we measure delta g with respect to a standard state. Similarly, in this case one can think that one can measure energy with respect to this constant which is nothing but U relative AB okay. So means I am measuring with respect to this constant, I can ignore it.

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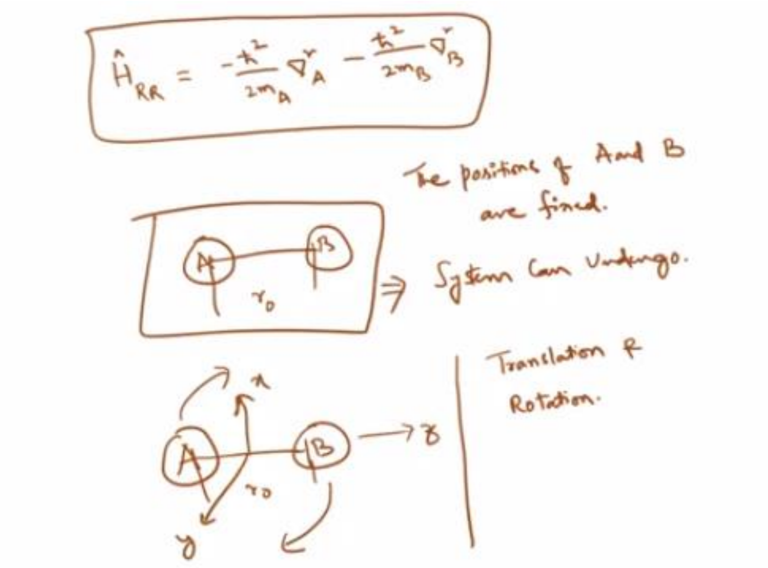

So my HRR will be now be equal to – h bar square by 2m A del square A – h bar square by 2m B del square B, there was a constant which I ignored because I am measuring energy with respect to that. So this is my Hamiltonian okay. Now if you think of it, so what I have is the following okay. I have A and A is connected to B by a stick that has length r0 and that is not changing that is what I said rigid-rotor okay.

So the positions of A and B are fixed okay. Now let us for a time being think that what all the possible motions that this particular system can undergo okay. Now I told you the r0 is fixed okay. So when the r0 is fixed, this can only undergo 2 motions. One is that if you have A and B okay attached by r0, then of course it can move along say z direction, it can move along x direction and it can move along the y direction.

So the whole molecule can move in some direction okay along x, y and z okay. Now what else can it do? Because A and B cannot move, then what can it do? It can rotate, AB can rotate like that without changing the distance or it can rotate like this okay. So AB can rotate and AB can translate. So only possible motions are translation and rotation okay.

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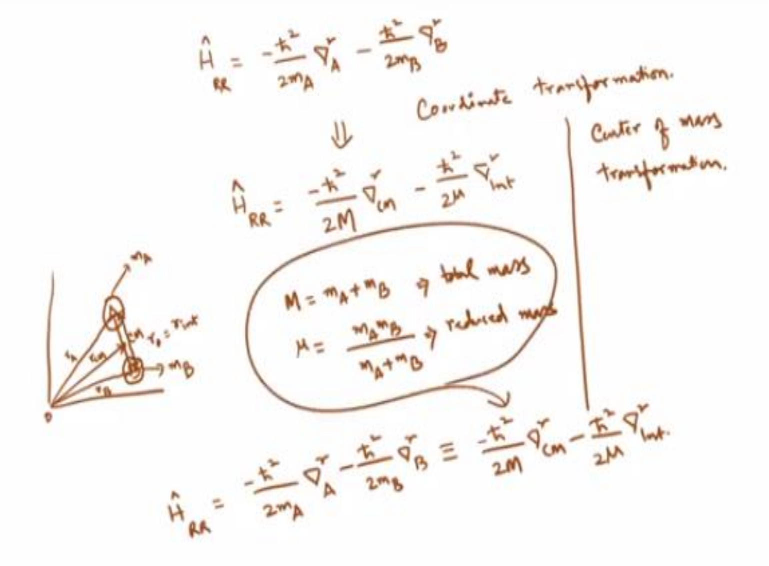

Now what did I say, so we had this Hamiltonian which was nothing but H okay is equal to = –h bar square by 2m A del square A – h bar square by 2m B del square B okay. Now we have two of them. So there are two possible motions, one is the motion of A atom and other is motion of atom B. However, they are stuck to each other. So A and B cannot move independently.

So in that scenario, this equation can be written as –h bar square by 2 capital M del square CM – h bar square by two mu del square internal okay. So this is something called coordinate transformation okay. I will not go to the mathematics of it, but I will tell you what. So if I have a quantity A and B okay, that is my body A and B, so what you have is the coordinates of A and B okay.

And there is a mass of this is mA and the mass of this is mB and there are some coordinates okay and what we are going to call it as rA and rB. So the center of mass will lie somewhere here. So this is center of mass okay. So this will have r center of mass. Similarly you have another distance called this as r0 which is nothing but r internal. So there are two things that one can do is that instead having rA and rB, there are the vectors from the origin going to A and B.

There are 2 vectors that are representing this system rA and rB, instead of that you could choose an alternate description that is r center of mass and r0. So it is an equivalent description of it and one can do the math okay, there is something called center of mass transformation okay. One can look it up in some text books okay and it will clean found out that one can make such a transformation in the Hamiltonian without making any approximations.

But there is only one thing that I need to define where your capital M = mA + mB okay and small mu is mA mB divided by mA + mB and this is called reduced mass and this is total mass okay. Now, these 2 Hamiltonians, so HRR = – h bar square by 2 mA del square A – h bar square by 2 mB del square B is identically equal to – h bar square by 2m del square centre of mass – h bar square by 2 mu del square internal okay.

So instead of having two coordinates representing A and B, now you have an alternate description in terms of coordinates representing centre of mass in an internal motion okay and this is of course valid only when these are valid under this okay.

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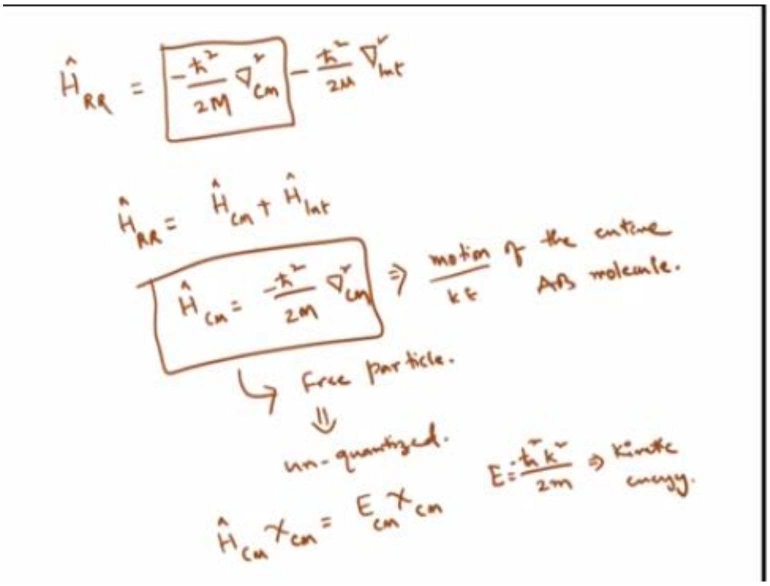

$$\hat{H}_{RR} = \boxed{-\frac{\hbar^2}{2M}\nabla^2_{cm}} - \frac{\hbar^2}{2\mu}\nabla^2_{int}$$

$$\hat{H}_{RR} = \hat{H}_{cm} + \hat{H}_{int}$$

$$\boxed{\hat{H}_{cm} = -\frac{\hbar^2}{2M}\nabla^2_{cm}} \Rightarrow \frac{\text{motion}}{\text{k.E}} \text{ of the entire AB molecule.}$$

↳ Free particle.

⇓

un-quantized.

$$\hat{H}_{cm}\chi_{cm} = E_{cm}\chi_{cm}$$

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow \text{Kinetic energy.}$$

Now there are 2 things that let us go to the Hamiltonian HRR = – h bar square by 2M del square center of mass – h bar square by 2M del square internal okay. Now there is one issue is the following is that this quantity is the center of mass portion that means the whole object is moving okay. So this is nothing but your, so you can now calculate your HRR as 2 quantities, one is H center of mass plus another is H internal.

Where H center of mass = – h bar square by 2M del square center of mass, so this represents the motion of the of the or k of the entire AB molecule okay. Now this is just a motion of the entire AB molecule in some direction x, y, z or a linear combination thereof and there is no potential acting on it, so essentially this leads to what is known as free particle okay and we know the free particle is unquantized okay.

So one can think of having this one as Hcm Chi cm = Ecm Chi cm where E = h bar square k square by 2m is the – h bar square k square by 2m that is the kinetic energy okay. So we do not have to worry about the Hamiltonian corresponding to centre of mass because that just represents the motion of the entire AB okay and just if you want to move a particle or a mass or AB molecule okay, of course it is not related to any spectroscopic transition, so we would not worry about it anymore in this course okay.

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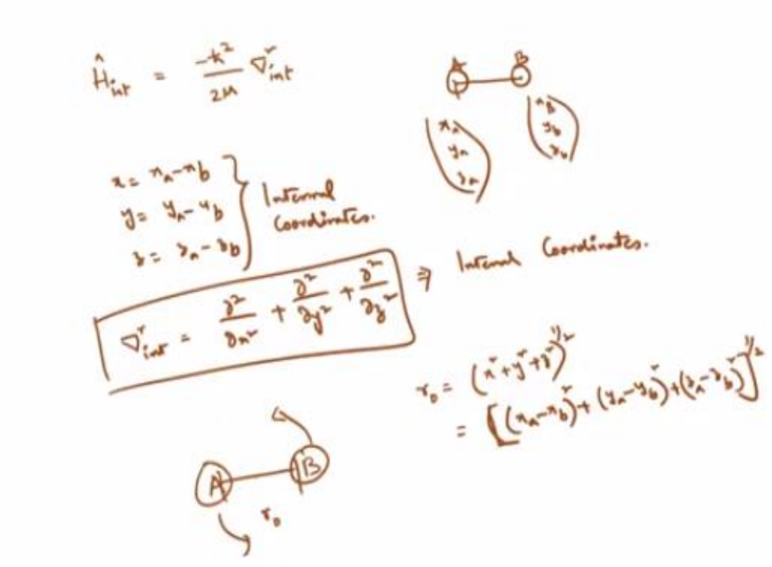

Now what we are left with is the remaining part H internal which is nothing but –h bar square by 2 mu del square internal. Now if I had a particle AB okay and this one was at xa, ya, za these are the coordinates of A and xb, yb, zb as internal coordinates of or coordinates of B. Then you can write x = xa – xb, y = ya – yb, z = za – zb and this represents internal. Therefore your del square internal will be equal to d square by dx square + d square by dy square + d square by dz square okay.

This is the internal coordinates okay. There is of course one problem okay. Now the problem is this is that when you want to, so I know I told you that AB is a rigid body okay and of course you must remember r0 will be equal to x square + y square + z square to the power of half which will be nothing but xa – xb whole square + ya – yb whole square + za – zb whole square to the power of half okay.

Now there is one thing that I told you is that of course this can move in the x, y, z direction the entire molecule AB, but I told you that we are not concerned with such a motion because it does not lead to any spectroscopic transitions okay. Now the thing that we are interested is in the rotational motion either in the plane of the board that I am writing or a plane that is perpendicular to the plane of the board okay.

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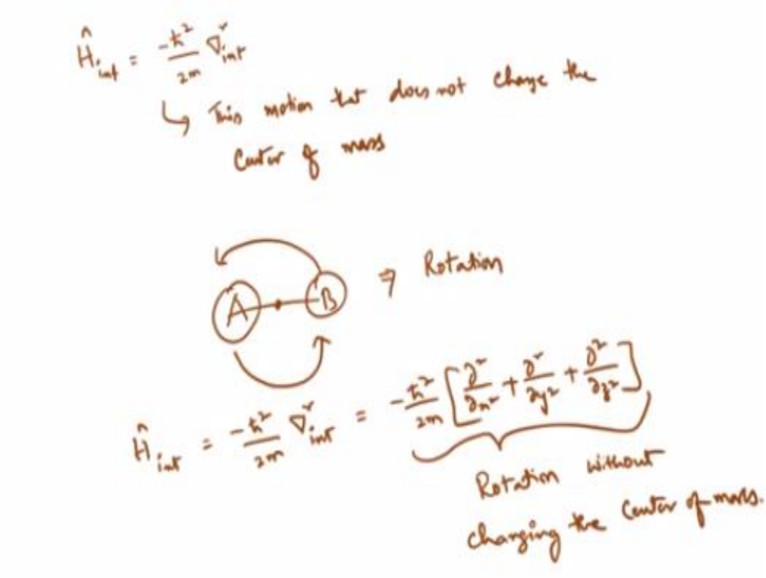

$$\hat{H}_{int} = -\frac{\hbar^2}{2m}\nabla^2_{int}$$

↳ This motion that does not change the Center of mass

$$\hat{H}_{int} = -\frac{\hbar^2}{2m}\nabla^2_{int} = \underbrace{-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]}_{\text{Rotation without changing the Center of mass.}}$$

When you have such motion, then you are talking about a motion of AB in a circular fashion. So that means you can think of your H internal = – h bar square by 2m del square internal and this internal motion is the motion of the molecule without moving the center of mass, so what is this? It says that this is motion that does not change the center of mass okay. So you have to keep your center of mass fixed and then move around okay.

So you have to rotate the body either in the plane of the board okay, so AB can rotate okay or rotate perpendicular the plane of the board okay while keeping its center of mass fixed because if there is a motion of the center of mass that is already gone into the other Hamiltonian of the free particle that I discussed little bit earlier okay. So now what we are concerned is just the motion of this AB molecule in a such a way that its centre of mass remains exactly in the same position.

So this will lead to rotation, so your H internal this is called –h bar square by 2m del square internal which is nothing but –h bar square by 2m d square by dx square + d square by dy square + d square by dz square. This should represent rotation without changing the center of mass okay. We will stop here and continue in the next class. Thank you.