**Quantum Chemistry of Atoms and Molecules**
**Prof. Anindya Datta**
**Department of Chemistry**
**Indian Institute of Technology – Bombay**

**Lecture-18**
**Rigid Rotor: Part 1**

Having performed a thorough discussion of harmonic oscillator now we move on to another system rigid rotor. Now rigid rotor will become to the rigid part later on but rotational dynamics is something that once again all of us would have studied in class 11 physics using classical mechanics. What we do is? We use the same concepts of classical mechanics but rewrite it in the language of quantum mechanics to develop a treatment of a rigid rotor.

Rigid rotor means whose length does not change while it rotates and the reason why it is interesting?

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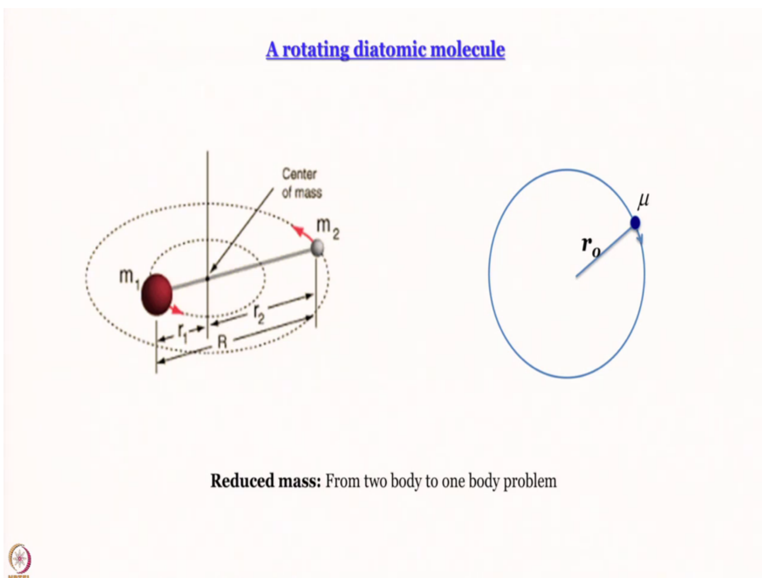


In our course is that a rigid rotor is a good model for a diatomic molecule that is rotating let us say I have two molecules something like HCl. Let us say H has mass m 2 CL has mass M 1 the distance of m 1 from center of mass let us say is r 1 distance of H from center of mass is r 2 and let us say that inter nuclear separation is capital R. So, capital R essentially will be small r 1 plus small r 2. So, let us consider this molecule rotating.

How do we; what kind of equations do we write, of course is we are using we are talking about molecules we have to use quantum mechanics? When you use quantum mechanics we have to talk about wave functions and we have to use operator that is what we learn in this next couple of modules. Now the first thing to do here and this is something that we do in classical mechanics as well is to reduce this two body problem to a 1 body problem.

Because if you want to write the equations of motions of two bodies moving around each other then the equation has too many terms. It is much simpler if we consider one body of mass equal to reduced mass I am not writing the expression of reduced mass here I think I have it somewhere later on but in any case I am sure everybody knows it. The way I remember it very well is that 1 by mu is equal to 1 by m1 plus 1 by m 2 and then you can simplify it.

So we can consider this reduced mass to rotate around a center with a radius of orbit of r 0 and this r 0 is essentially the radius of gyration. Exactly the same treatment as what we have done in one in classical mechanical treatment of rotational dynamics right reduced mass is used to go from a little more complicated two body problem to a one body problem right. So, that is where we start with so whenever we write mu in the subsequent discussion all I mean is reduced mass.

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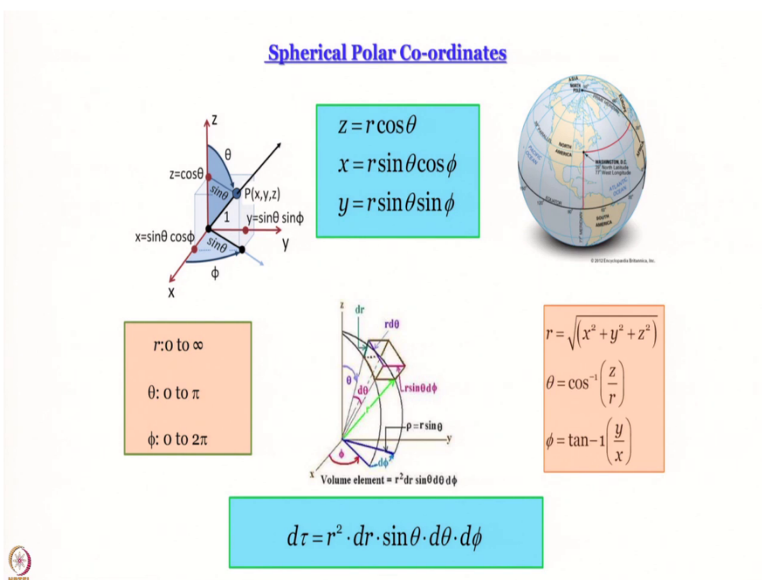


Another thing that we need to use here is spherical polar coordinates that is a departure from what we have been doing so far, we have been talking about XYZ coordinates. Now since the route we are talking about rotation, rotation is essentially a change of angle it is more convenient if we describe the same three-dimensional space which we are more familiar describing as XY and Z by r theta and phi ok.

But please do not forget it is the same space we are talking about for the benefit of those who might be a little rusty or might not have studied spherical polar coordinates we will just go through it quickly. So, please look at this diagram here what I have drawn is I have drawn the three Cartesian axes X Y and Z. And now we will define the three coordinates r theta and Phi. First of all let us say this is the point we are talking about this point has let us say coordinates of X Y and Z. Now if I join a line from the origin to that point we are talking about that line when drawn outwards from the origin represents the position vector of the point and it is called r remember r is really a vector.

For now we will work only with the magnitude so r is going to be ranging from 0 to infinity so r equal to 0 to infinity is not very difficult to understand where can the point be it can be at the origin or it can be on y axis or it can be on well X axis or Y axis or Z axis for which one of the coordinates will be 0. But then when it moves away from the origin then the length of r will increase and it is not very difficult to see what the relationship between r and X, Y and Z is.

To start with we can say y square equal to X square plus y square plus Z square but as we will see there are simpler relations. So, the first coordinate is actually a linear coordinate r the distance from the origin of the point we are talking about. Next we talk about the angle between the z axis and the position vector. Position vector remember is the line joining the origin with the point right when you draw it outwards that is a position vector.

So the first question is what is the angle between the z axis and the position vector that angle is called the azimuthal angle or theta right. This terms as azimuthal angle and all these are ancient they come from ancient trigonometry they have been used in a astronomy so this do not think that they are used only here ok. So, first of all we have theta, so what is theta? Let us say this is Z axis and let us say this is the position vector then the angle made between the Z-axis and the position vector this angle is theta all right. So that is what it is.

Now the reason why we have the picture of a globe here is this something we are very familiar with from our childhood we have studied maps in geography and we have talked about latitude and longitude. Can you tell me if theta is related to one of these two latitude or longitude? And give you a moment to come up with the answer. It is theta latitude or is theta longitude? Actually theta is sort of latitude the only difference is latitude is measured from equator up and theta is measured from the pole down.

So that is the only difference, difference in convention but that's the azimuthal angle right. So, this is theta. What is the range of theta? Theta goes from 0 to PI now you can think that I start from here ok we go down go down all the way to PI who is stopping me from going the other way? Nobody is stopping you but then there is a third coordinate which takes care of what happens when theta the vector goes the other way that is why the convention is to limit theta to the range 0 to PI, r of course can go to infinity.

Now the third calm third coordinate might look a little more complicated but it is really very simple once you understand it. Let us see what it is? So of course it has to be the angular deviation from either X-axis or Y-axis but angular deviation of what? When we work with the position vector we had this advantage that we had only two lines right Z axis and position vector and we could define theta.

Now if you want to draw Phi between say x-axis and the same position vector that Phi will not be unique anymore right because theta is already there, so, we should not go beyond XY plane theta is what tells us about angular deviation from Z axis. So, we should only focus on X and Y plane well XY plane when we talk try to define the third and third coordinate the second angular coordinate to do that what is done is to draw a perpendicular from the point to the XY plane.

And then draw a line from the origin to that perpendicular of course that line is going to be in the XY plane right. So, in other words what we have done is we have taken a projection of the position vector in XY plane and the angle between the X-axis and the projection is called Phi.

Now Phi is allowed to go from 0 to 2 Pi, now you understand there is no need for theta to also go from 0 to 2 Pi it is enough if theta goes up 2 Pi.

Anything that goes well beyond Pi is taken care of by the Phi value because Phi goes a full circle. We return to our globe is Phi related to latitude or longitude? Of course the answer is very easy to give now because latitude is taken the only thing that is left is longitude. So, this is sort of longitude okay. Phi is the same as what you have studied in geography as longitude okay. So, it goes from 0 to 2 Pi. Now let us talk about the relationship between XYZ Cartesian coordinates and r Theta Phi the spherical polar coordinates.

First one is very simple Z equal to r cos theta, r is the length of the position vector if you drop a perpendicular from there this angle is theta you can see very easily that this Z is nothing but hypotenuse r multiplied by cos theta right because theta is this angle using the properties of a right angle triangle you find out that Z equal to cos theta or you might not even have to go that far back you can figure out very easily from your understanding of components and all okay.

What about X and what about Y for that we need the length of this projection of the position vector that we had drawn in the XY plane. So, see the length of the projection I hope is not very difficult to understand is r sine theta because what we have done essentially is you have drawn a rectangle is not it. Starting from this point we had earlier dropped a perpendicular to Z axis and from there we got this Z equal to r cos theta.

Now from here we are draw a perpendicular here so what will be this length yeah so the length of the projection is r sine theta I hope that is not very difficult to see this hypotenuse is r this angle is theta. So, the opposite side of course has to be r sine theta. Now what is X? X will be the component of this projection along X axis length of this projection is r sine theta angle with x-axis is Phi. So, I hope it is not very difficult to understand that X is going to be r sine theta cos Phi.

Similarly Y is going to be r sine theta sine Phi these are extremely useful relationships that we use all the time when we keep switching between Cartesian and spherical polar coordinates. The other inverse relationships are I already told you r square equal to X square + Y square + Z square. So, r will be equal to square root of that. Now Z equal to r cos theta so Z by r equal to cos theta and I say theta is cos inverse Z by r.

And how do you define Phi? Well you define this by dividing X by Y or Y by X, Y by X is a little better because then you get sine Phi by cos Phi that is tan Phi. So, Phi is naturally tan inverse Y by X. So, if you know XYZ you can figure out r theta Phi if you know r theta Phi you can figure out XYZ there are two different ways of looking at the same space essentially right the same space in two different languages you can think okay.

Now since we are talking about quantum mechanics the other quantity that we will need is the volume element. We have you know we have done normalization, we have found out the probability and all. So, what is the volume element? If you work in X Y Z the volume element is very simple dx dy dz. When we work in spherical polar coordinates then what we have to do is we have to work with a volume element like this where you increase r by a small amount dr that is simple.

Now increase theta by a small amount theta for that what you need to know is what is the length of this arc? what would the length of this r would be? This length is r as we know and this small angle is d theta so the length of the R we can say is our d theta right rd theta. So, this volume element the straight side is dr this curved side is rd theta. Similarly the third curved side you can work out from the projection in the XY plane what is this?

This angle would be d Phi and this length would be r sine theta remember r sine theta so r sine theta multiplied by d Phi. So, what is the volume element d r multiplied by r d theta multiplied by r sine theta d Phi. So, finally we get d tau is equal to r Square d r sine theta d theta d Phi this is something that will be very, very useful when we talk about hydrogen atom especially we are going to revisit it at that time for now let this be a preview okay.

So spherical polar coordinate is introduced, now we want to work with spherical polar coordinates, why do we want to do it? Remember because we are talking about a rotating diatomic molecule a rigid rotor. So, in a rotation length does not change. If it is a rigid rotor what changes is angle and we are not talking about rotation in a particular plane any rotation. So, any rotation means rotation will change in theta change in Phi both has to be accounted for.

So what we now need to do is we need to rewrite the rewrite Schrodinger equation in terms of r theta and Phi okay. We are not going to do all of it whoever is interested can go through the math what we will do is we will just show you the final result we have to remember the final result not really okay will tell you what you need to remember in fact you will see it for yourself that part is not so difficult to remember also.

But remember well I am saying remember too many times but I say it once more the emphasis of this of this course is not on remembering things but rather on understanding. Let us not lose that focus okay. Let us go ahead.

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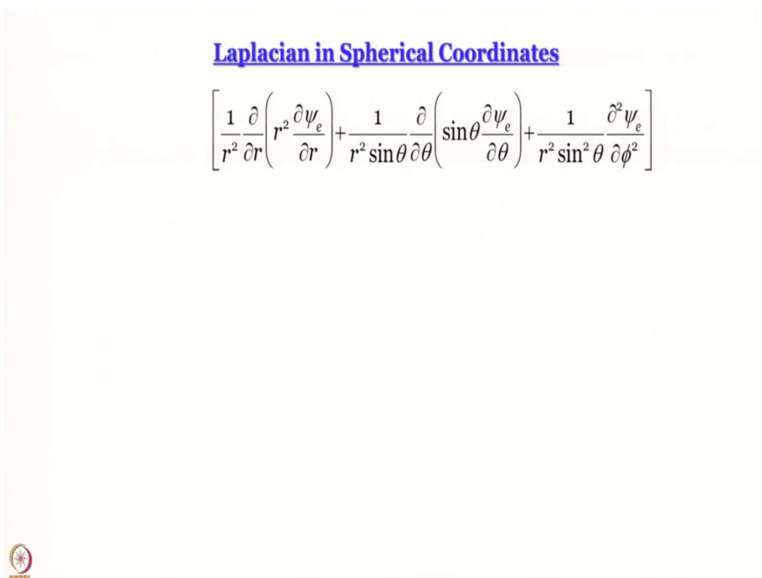


So, what we will do is we know that in Schrodinger equation it is all about the Hamiltonian operator and Hamiltonian operator consists of two terms the Laplacian and the potential energy term Laplacian multiplied by some constant. So, let us show you what the Laplacian looks like in spherical coordinates. Shall we work it out? No we shall not why not because if you start from the relationship between well it is written in appendix two because I have copied it from some other presentation of ours and I was too lazy to change appendix too in many slides.

So please bear with me on that but if you start from here and you keep on differentiating and try to change bases then this is what you have to do something that we have summarized in 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13 slides only in the 13 slide you get the result that is what we will work with. Please believe me right now that the Laplacian in spherical polar coordinates looks like this and whoever is mathematically inclined is welcome to work it out great.

But let is have a look at what we have in the Laplacian we have three terms the first term is purely in r 1 by r square del del r of Psi r square del del r of sy okay well this is not really the Laplacian because I have included Psi also it is Laplacian operating on Psi okay. So, you can just neglect the Psi in the subsequent discussion. What is the second term? In the second term we have r we have theta 2 coordinates mixed and in the third term it is a worst we have 1 by r square you have sine square theta we also have del 2 del Phi 2.

So what we have here is differential equation but it is a partial differential equation and see there is three variables. The way to go about solving this is to perform a what is called a separation of variables in hydrogen atom you have to start from here because r can change.

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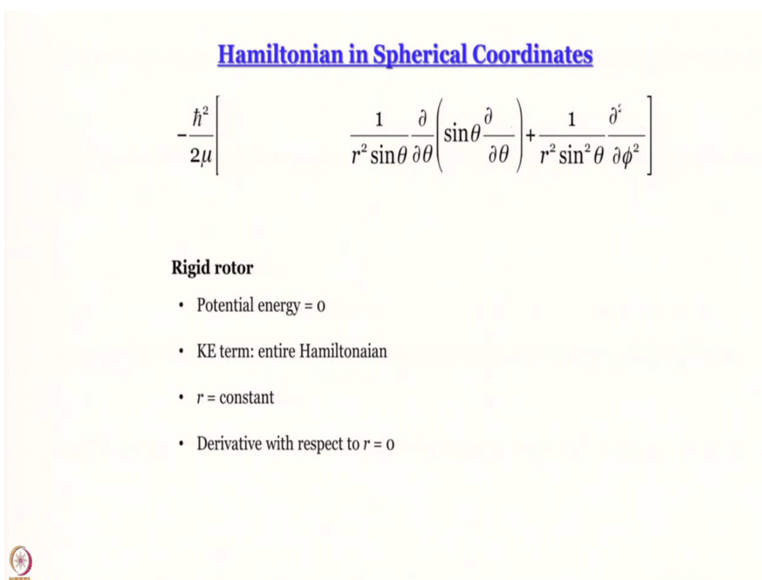


In rigid rotor the good thing is we have a little bit of advantage but before that let me just show you the kinetic energy operator if you remember kinetic energy operator is Laplacian multiplied by minus h cross square by in this case 2 mu why mu? Why not m? Because we have reduced a two-body problem into a one body problem so we have to use reduced mass. Now we are talking about a rigid rotor so one of these terms happily vanish to start with why because r is a constant remember and also we do not even have to worry about potential energy.

So this Laplacian is all that is there in the Hamiltonian potential energy is 0 we you have a reduced mass mu rotating about a mass less center. So, the all the energy that is there is kinetic energy alright and that has some implication that we are going to talk about later. So, potential energy is 0 and what I had started saying already jumping the gun is that r is a constant. So, what is the consequence of r being a constant?

We do not have to worry about the first term is not it. It is del del r that does not arise anymore because r does not even change. So, if r does not change, so we do not have to worry about how the wave function changes as a function of r that is what del del r is is not it so the derivative with respect to r vanishes you do not have to worry anymore about it anymore. Also what we have done in the next slides is that instead of r here we have written r 0 just to remind us that this r is a constant value, r 0 the bond length you can say or read radius of gyration for a rigid rotor okay.

So what could the Hamiltonian be in spherical coordinates? This is the Hamiltonian what we have written here minus h cross square by 2 mu multiplying 1 by r square sine theta del del theta of sine theta del del theta I think I miss this bracket outside sine theta r del del theta in the previous slides but this is a right thing plus 1 by r square sine theta del 2 del Phi 2 this is our Hamiltonian.

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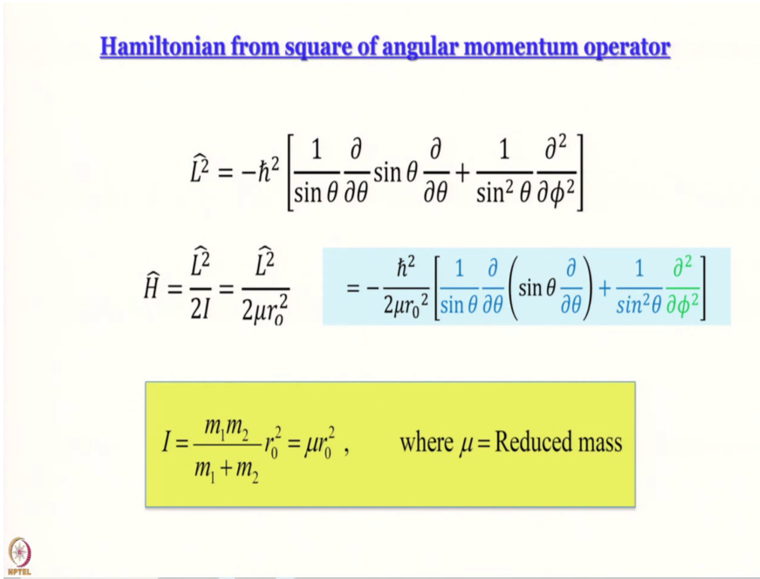


In fact we can arrive at the Hamiltonian from a different starting point. For now please take it axiomatically that the square of angular momentum operator is this we are. In the one of the next subsequent modules we are going to talk in a little more detail about angular momentum because there is one thing that we have been taking raincheck on and there is a bit of formalism of quantum mechanics. So, before going into hydrogen atom at least we should talk a little bit about formalism we should talk about commutativity and what happens when two operators commute and when they do not?

And we will also talk a little bit about angular momentum because it is a very, very interesting discussion and also the same angular momentum has got to do with spin as well okay. But right now we are talking about motion spherical well rotational motion. For that let us start with angular any rotational motion will be associated with angular momentum. So, just believe me when I say that the square of angular momentum operator is minus h cross square multiplying 1 by sine theta del del theta sine theta del del theta again the sine theta del Del theta is in brackets plus 1 by sine square theta multiplying del 2 del Phi 2 does that ring a bell?

Have you seen it, I mean it would better ring a bell because we saw it just now in the previous slide. It is just that this was multiplied by some constant right so this is L square. Now let us remember what we know already from classical mechanics. What is the relationship in classical mechanics between rotational kinetic energy and angular momentum? I think all of us would be able to say that the relationship is kinetic energy is equal to the square of angular momentum divided by 2 into I what is I is a moment of inertia.

So rotational motion is sort of similar to linear motion but the difference is moment of inertia always replaces mass and angular momentum always replaces momentum. Otherwise the relationship between energy and angular momentum kinetic energy and angular momentum in linear motion is similar to the relationship between kinetic energy of rotation and motion angular momentum right. So, kinetic energy is square of angular momentum divided by 2I knowing that and knowing the operator for L square is not difficult for us to construct the operator for kinetic energy.

That would just be L square operator divided by 2I yeah L square divided by 2 I that is L square by 2 mu r 0 square where now here I have written it this is a reduced mass m 1 m 2 by m 1 m + m 2 I is m 1 m 2 by m 1 + m 2 r 0 square we write it simply as mu r 0 square. So, all I have to do to get the Hamiltonian in this case is I have to divide this L square operator by 2 mu r 0 square it is as simple as that. let us do that. What do we get we get and now let us be careful and make sure that there is no mistake here minus h cross square divided by 2 mu r 0 square.

I am dividing by 2 mu R 0 square remember inside the bracket now let us be very, very careful 1 by sine theta del del theta on del del theta of sine theta del del theta that I should have written the bracket here plus 1 by sine square theta del 2 del Phi 2 this here is my Hamiltonian. Before trying to use this Hamiltonian let us try to make it a little simpler because a partial differential equation where you have more than one independent variable is always solved or solved wherever it is possible by separating it into individual differential equations in the different independent variables.

That is why what I have done is I have written the constants in black and I have written the terms in theta this should have been written in blue as well terms in theta r in blue and the term in Phi is in green okay. What we try to do is we'll try to separate the variables in other words we are going to try and write equations in which we will have only theta and no Phi, only Phi and no theta and those equations will be easy to solve. Let us take a break now we will come back and in the next module we will start from here.