INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

CDEEP IIT BOMBAY

MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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LECTURE NO. – 07
Recapitulation of Quantum Mechanics

So in the last couple of classes we have introduced the concept of the use of the rigid rotor model to understand rotation of diatomic molecules. And we have kind of told you without explaining too much what the spectrum would look like.

So today what we intend to do is to try and understand what the origin of that selection rule delta J = + - is, to do that first thing we need to do is recapitulate a little bit of the quantum mechanics of a rigid rotor.

Well we've already discussed some part of it, but I think we should recapitulate to start with the quantum mechanics of the rigid rotor is exactly the same as the treatment of the angular part of the wave function for hydrogen atom, right, even before that what we do essentially when we have a two body problem like a rigid rotor we reduce it to a one body problem, how do we do it? By considering one particle of reduce mass rotating around a mass less center with a radius = radius of gyration, for diatomic molecule this radius of gyration is equal to the bond length, alright.

And when we do that we understand that the only parameters that can change if you think in spherical polar coordinates at the angular parameters, R is fixed, right, R is equal to your length of the molecule. So this is the problem which you can express if you take the two angular coordinates theta and phi, accha I hope all of us remember what theta is, what phi is? Yeah, what is theta? Let us say your X, Y, and Z axis, and let us say this is the position vector or sum vector, than what is theta? The angle between Z axis and this vector, right, and what is phi? If you drop a perpendicular on the XY plane, than the angle between X axis and the projection on the XY plane of the vector that is phi, okay, so if the length of this vector let us say is mu, I say mu because we are going to use angular, sorry, the rapper moment vector in no time, if the length is mu, then what is the Z component of mu? Mu Z that is equal to what? That's equal to shake of the head. Let us say this is X axis, Y axis, Z axis, this year let us talk about the angular moment, dipole moment vector since we are going to talk about it anyway, mu, what we are saying is this angle between the Z axis and mu is your theta,

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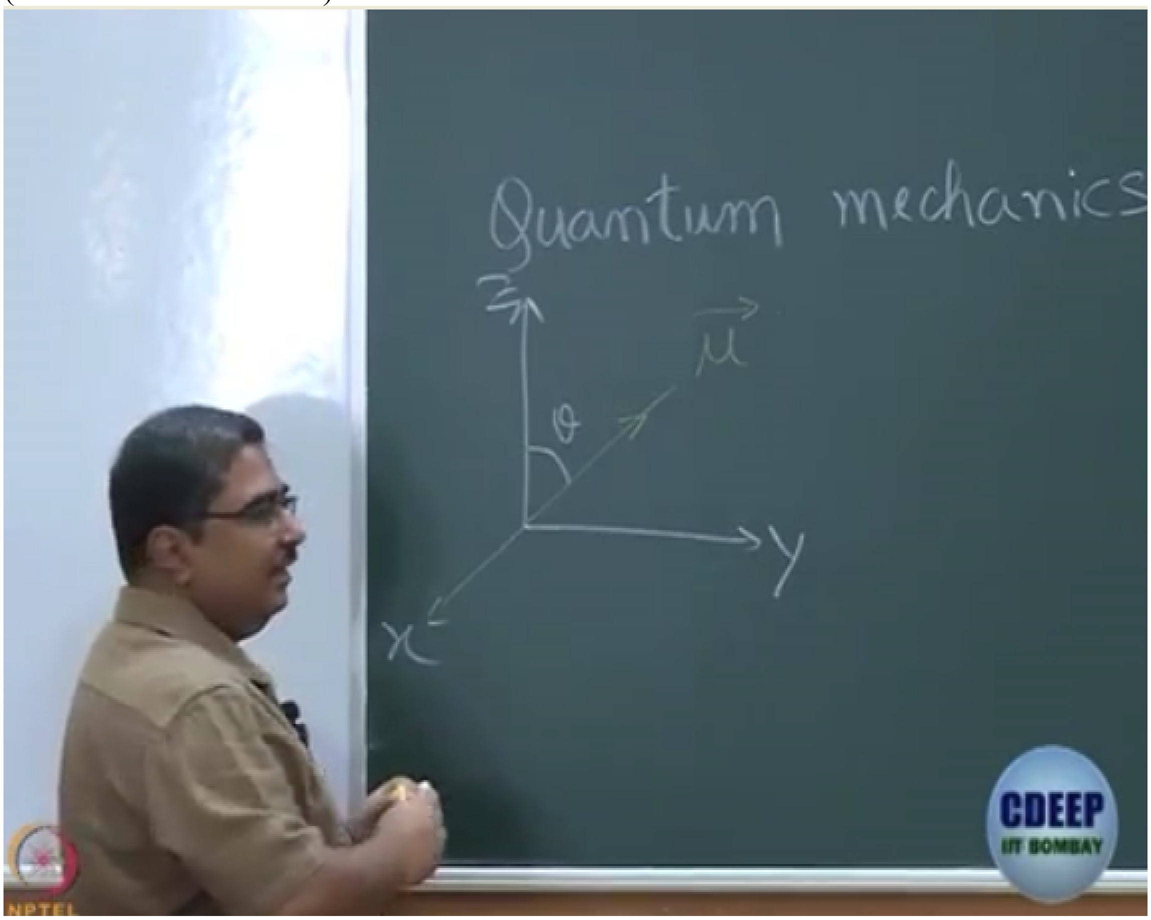

so if you drop a perpendicular here, what is Z component? This is mu cos theta, right, that essentially is mu Z,

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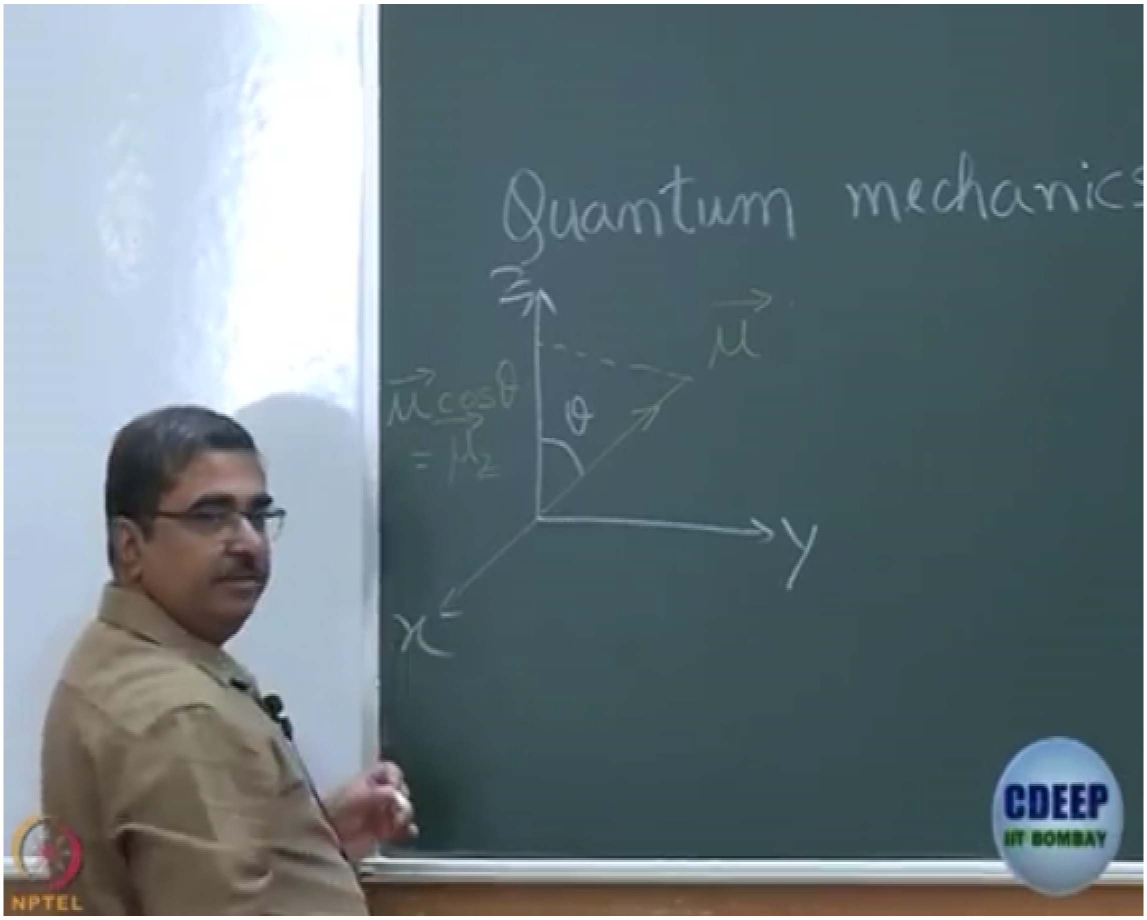

alright, to get the X and Y components we drop a perpendicular on the XY plane.

What is the length of this vector? Mu sin theta, of course, okay.
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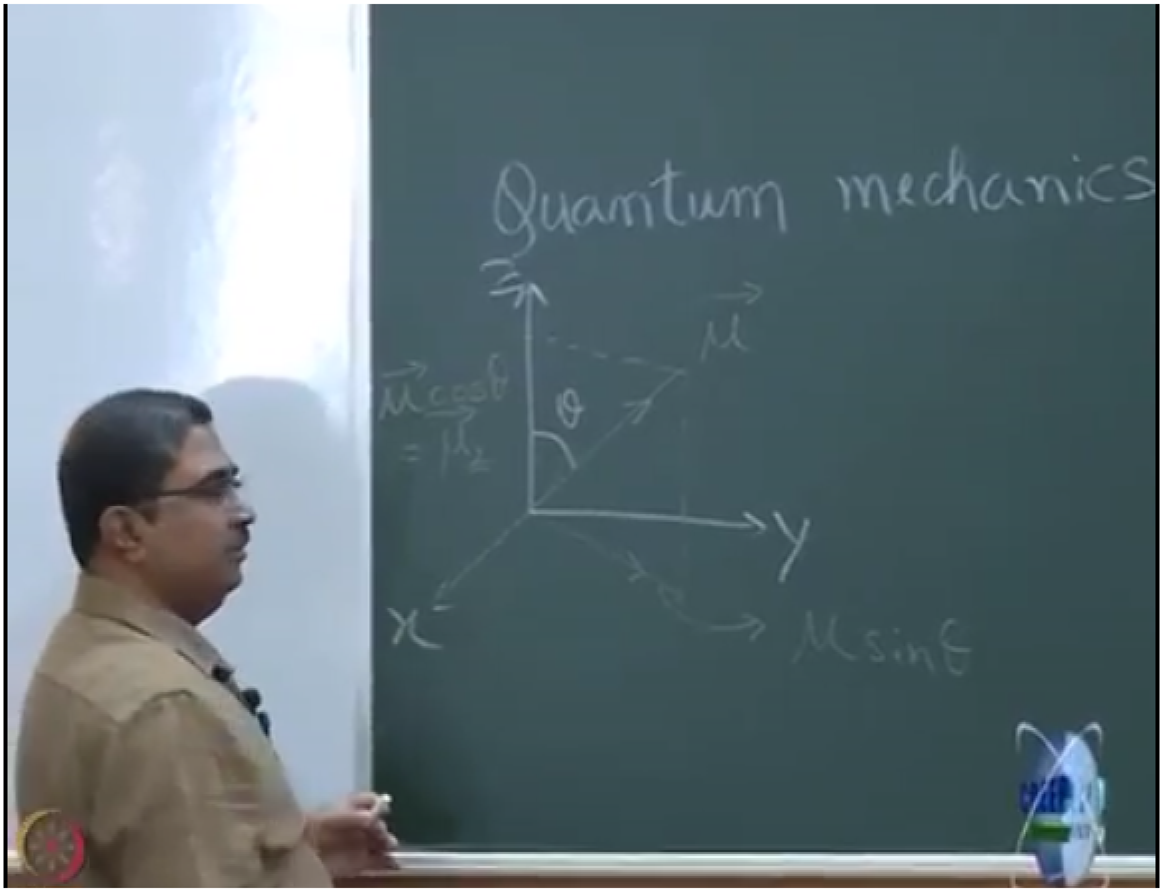

Let us call this mu 0, so then this becomes mu 0 cos theta, I don't even have to write the arrow, this is mu 0 sin theta, and then if this angle is phi, then what is this X coordinate? Length is mu 0 sin theta multiplied by cos phi or sin phi? Cos phi, very good.

And what about the Y component, so this is what, this is equal to mu X, and what about this? What is mu I? Length once again is mu 0 sin theta, right, multiplied by sin theta? Sin phi,
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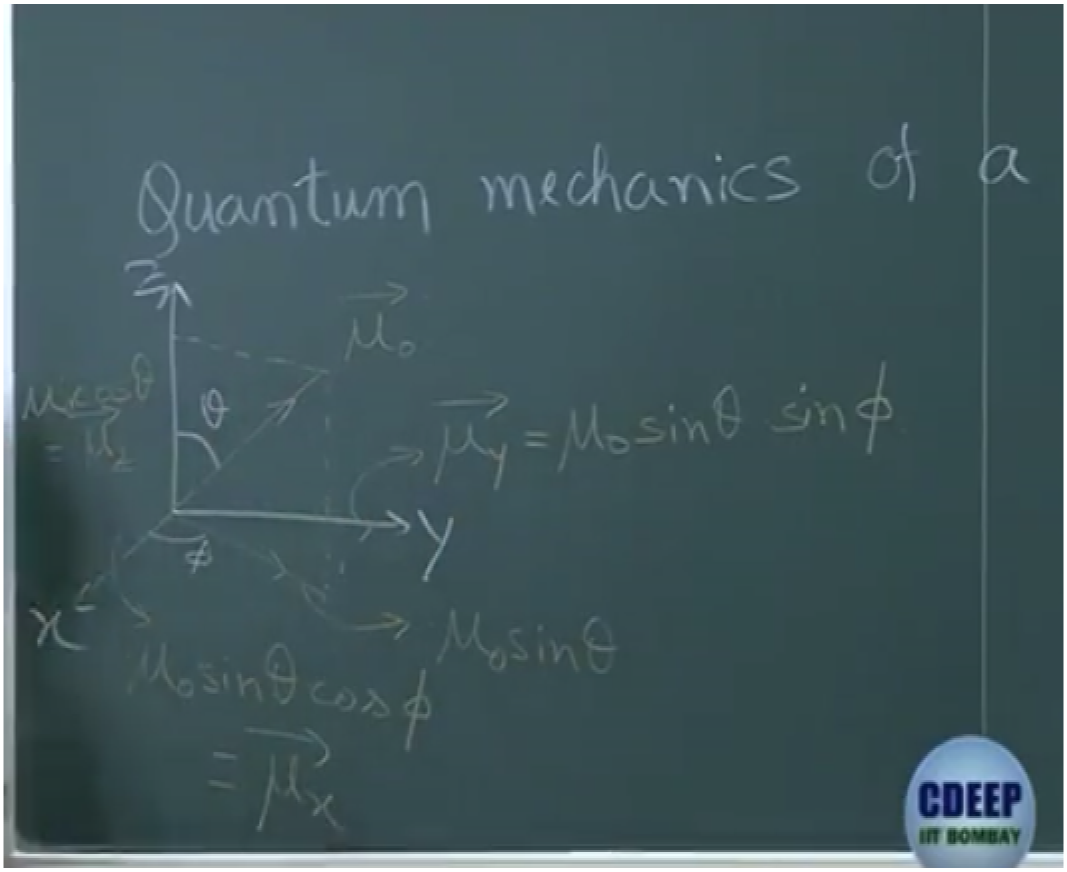

so you know right away what are the X, Y and Z components, you know this already but sometimes you forget so I thought it is better to recapitulate once. Why mu we'll see in a moment, okay.

Now coming back to the rigid rotor, the wave function is a function of the two angular coordinates theta and phi is given by, I'm not going to write the entire expression, you do not need to remember this, right, I'll write it in little cryptic notation, it is enough if you can understand that, okay, some constant that I am going to write as N is actually something like J+mod M + 1/J – mod M, you do not need to remember such long expressions. So I'll just write like this, this is the normalization constant, and as we know how many quantum are associated with rotational motion? Two, what are the two? J and M right? What does J stands for? Total angular momentum, right?

And what does M stands for? Yeah, Z component of the angular momentum.
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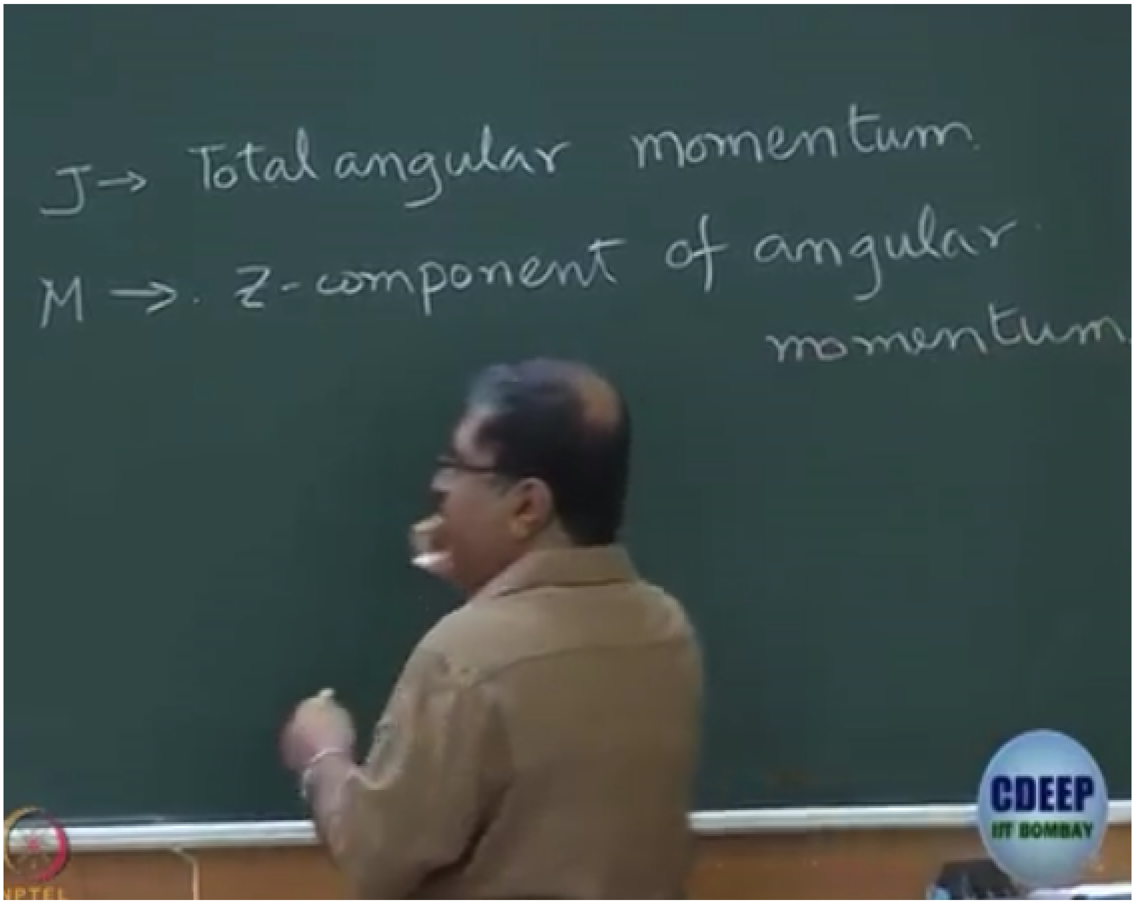

Of course as you know, one term numbers arise out of solution of different parts of Schrodinger equation. Here Schrodinger equation would be described in terms of two coordinates, theta and phi, so does J comes from theta part or phi part, does M comes from phi part or theta part? What, you don't know this? Are you sure we don't know this? Go back to hydrogen atom problem from the phi part, I've heard you, wait, let's see if others can respond. In hydrogen atom problem, where did the magnetic quantum numbers small m come from? Theta part or phi part? Phi part, so this capital M is the same as small m, we are just writing it differently because it is not hydrogen atom problem it is a rigid rotor problem, okay, so this also comes from the phi part. This comes from the theta part. J if you remember is equivalent to small l for hydrogen atom, okay.

And when we talk about change in phi, what does it mean? Change in phi means, let's say this is Z, X, Y, phi means this angle right? If you've rotational motion in like this, what will be the reduction of the result in angular momentum? If this is the reduction of rotational motion, like this, right? Right, I hope you remember this, perpendicular to the plane of the orbit, okay, so J and M.

So what I will do is, I'll erase this, and write this expression, this N will be a function of J as well as M, that will be multiplied by the theta part, then it will be multiplied by the phi part, as we have discussed earlier theta part is this polynomial in cos theta,

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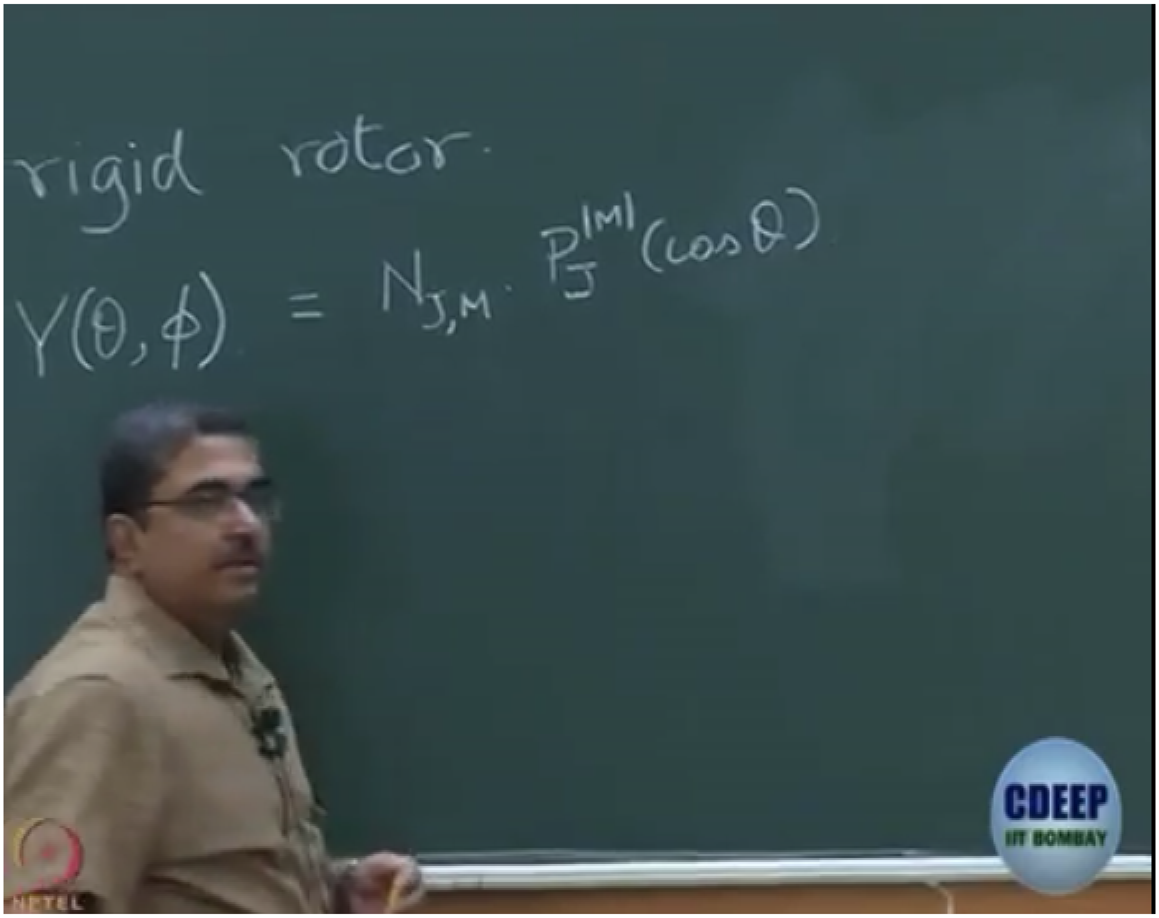

this polynomial as we have discussed in the previous class is called associated legendry polynomial, and the point to note is that the polynomial is in cos theta and naught theta, point number 1. Point number 2 is that what the polynomial will look like determines not only on J, but also on mod M, mod M multiplied by E to the power IM phi, we are going to need this.

So for a given value of J, how many different wave functions am I going to have? For a given value of J, how many different wave functions will I have? Will I have one wave function per J or will I have many? Will have many, how many? 2J+1, and where does this 2J+1 comes from? It comes from the number of values of capital M, okay.

Will this 2J+1 levels have same energy or different energy? Same energy, what is energy? Epsilon J if I write in centimeter inverse is given by BJ(J+1), is that right? What is B? H/8 pi square mu R0 square C, this mu is reduced mass, that's why I wanted to write mu 0 there, otherwise this mu and that mu would have created some problem, so this is B.
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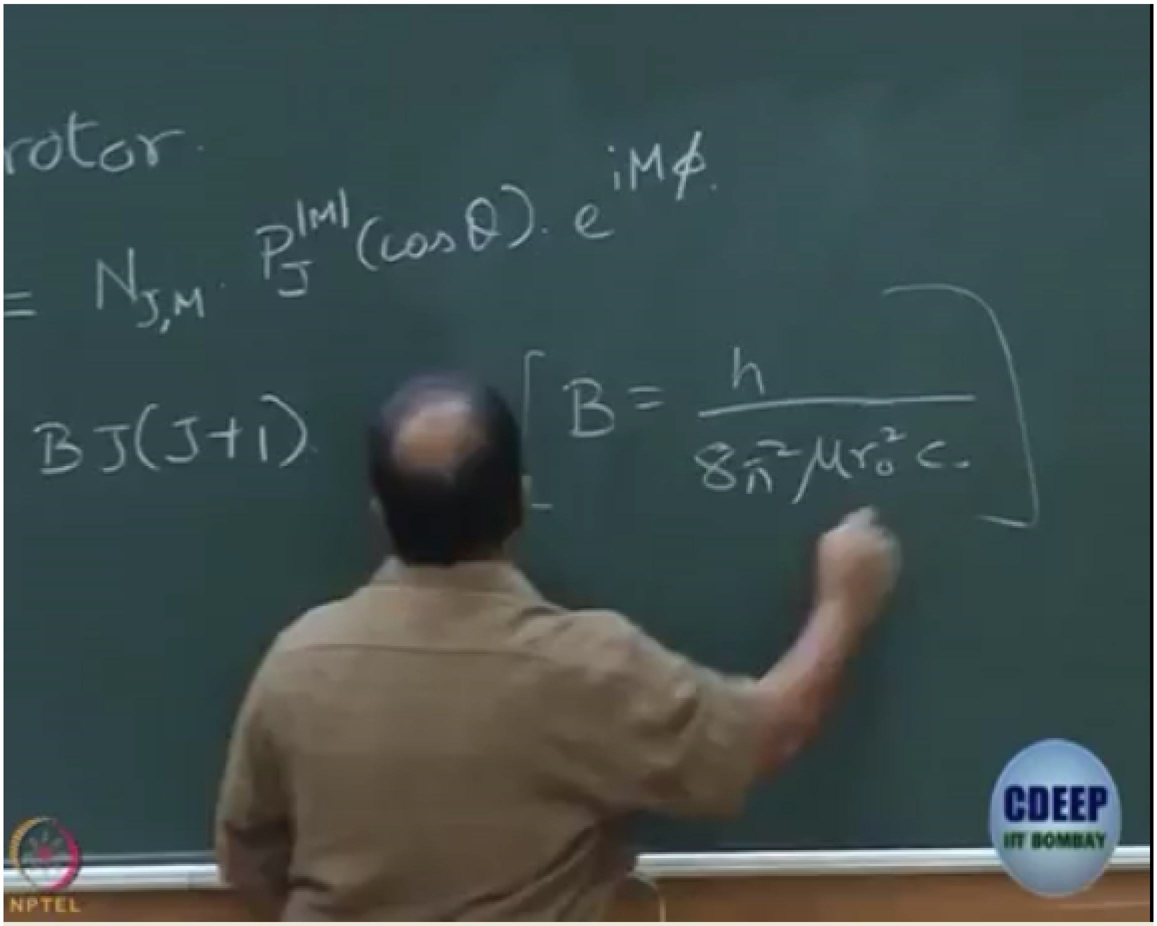

In this expression there is no contribution of capital M, isn't it? No contribution of capital M, so energy is determined only by capital J, as we know each J is associated with 2J+1 values of capital M, so all this levels are going to be of some energy, so each J level is 2J+1 whole degenerate, alright.

Now what are we trying to do here, why are we invoking so much of contra mechanics, what we are trying to do is, we are trying to understand which transitions in for this rigid rotor are going to be allowed? Which transitions for the rigid rotor are not going to be allowed? You already know the answer, delta J = +- 1, how do we get that? If I ask the mode general question, what is it that determines whether a transition is allowed or not? The answer is transition moment integral which is integral sai F star mu sai D tau that must be nonzero for the sai I to sai F transition to be allowed,

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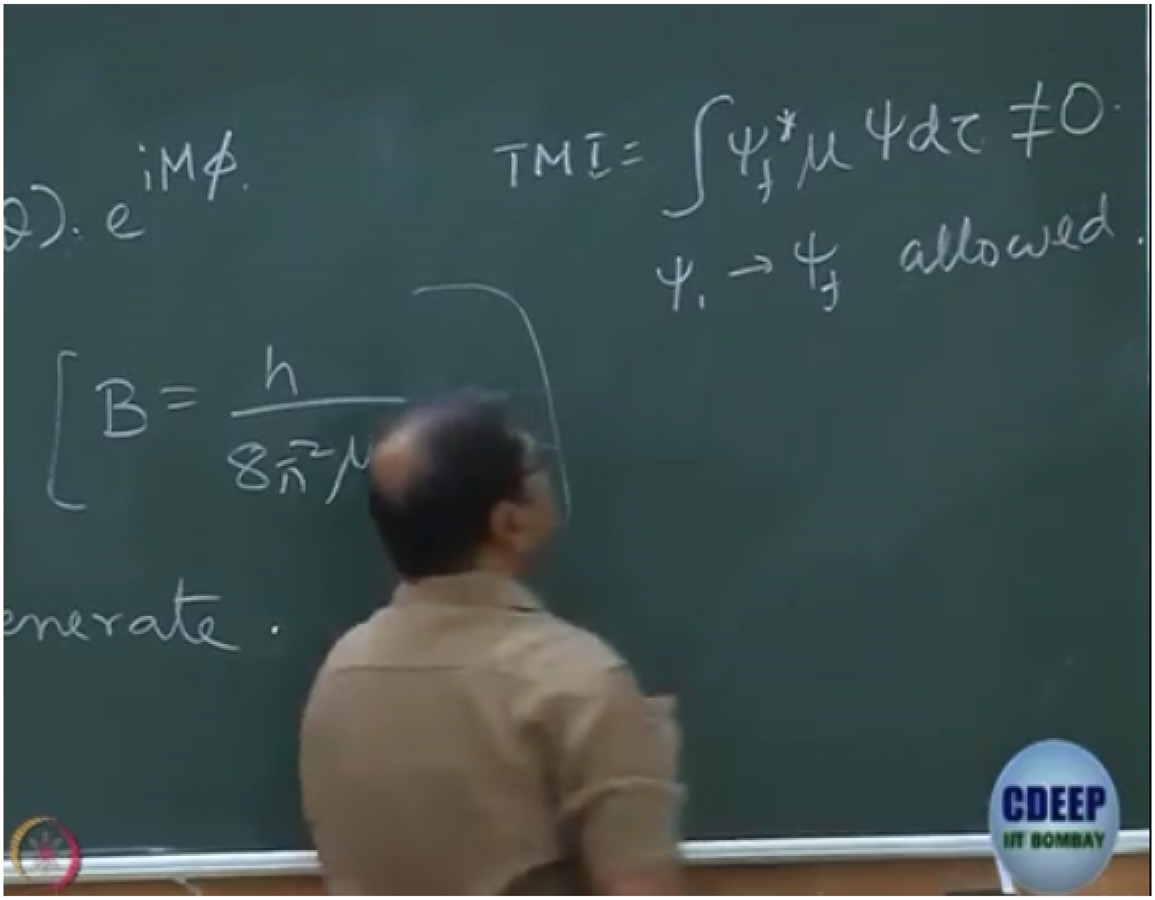

this integral here is called transition moment integral and in order for a transition from sai I to sai F, I for initial, F for final to be allowed this transition moment integral must be nonzero. Do you all know this?

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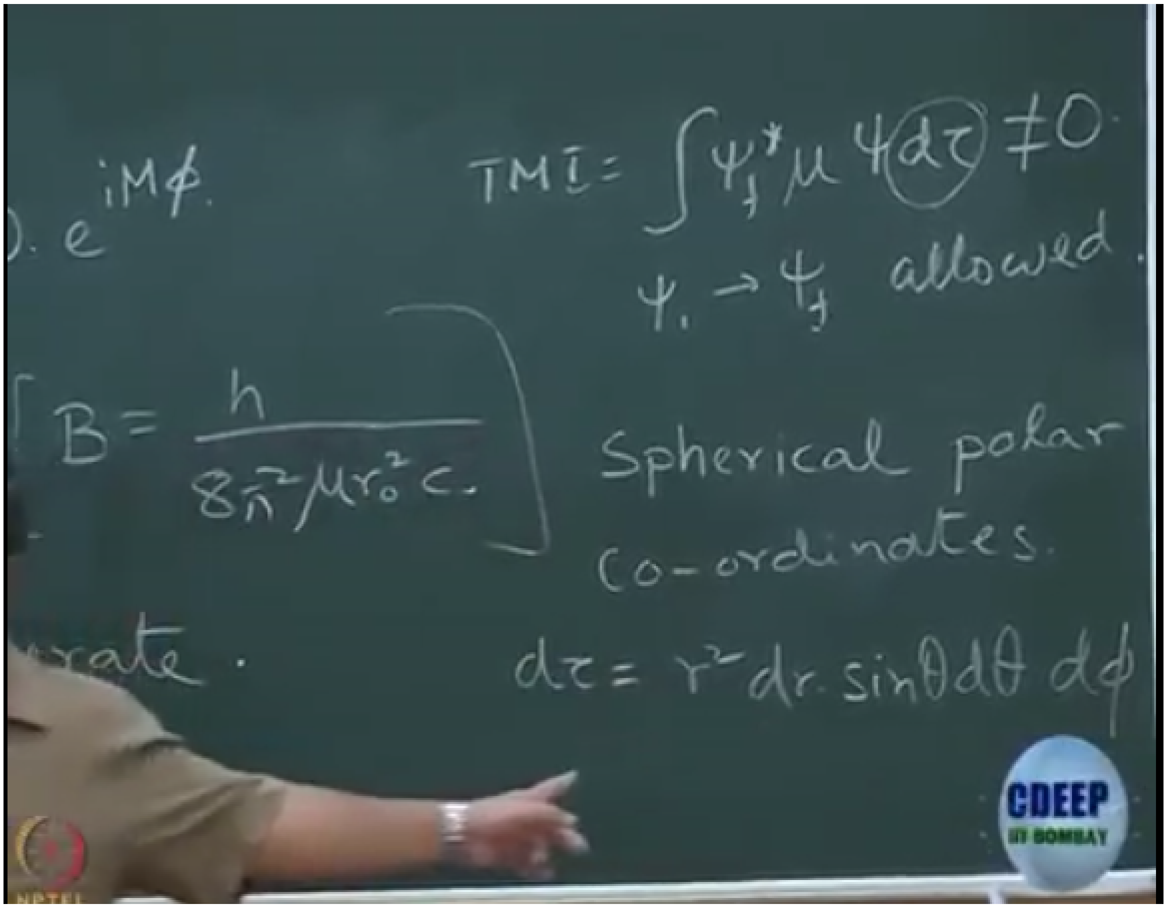

Well, I've said it just now so you know it now, even if you didn't know it earlier.

How do we get to this? For that we will need to wait a couple of weeks, for now please believe me that this is condition, but then we are going to derive this as well from time dependent perturbation theory. For now let us just take it extra somatically that condition for a transition sai I to sai F to be allowed is that this transition moment integral must be nonzero, okay.

Before we start working out the selection rule for rigid rotor, two more things need to be remembered first is what is D tau? For spherical polar coordinates, what is this volume element D tau? Gurujot? If I am working with X, Y, Z, Cartesian coordinates, then I know very well that this D tau or DV, whatever you want to call it is DX x DY x DZ, right, if I'm working with R theta phi, what is this D tau or DV? R square, let us finish writing the R terms first, R square DR, then sin theta D theta D phi, excellent, do we all know this? And do we know how we get this, it's not very difficult, right, so it's very easy to get it using geometry, relationship between Cartesian spherical polar coordinates, apparently it's easier if you use as Jacobean, but then I don't know what a Jacobean is so I cannot do it, some of you might be able to, alright, so this is what it is, we're going to need this expression for volume element in our subsequent discussion.

Now last point that we will need to use is this, this E to the power IM phi is pretty straight forward, right, but this polynomial looks a little intriguing to us,

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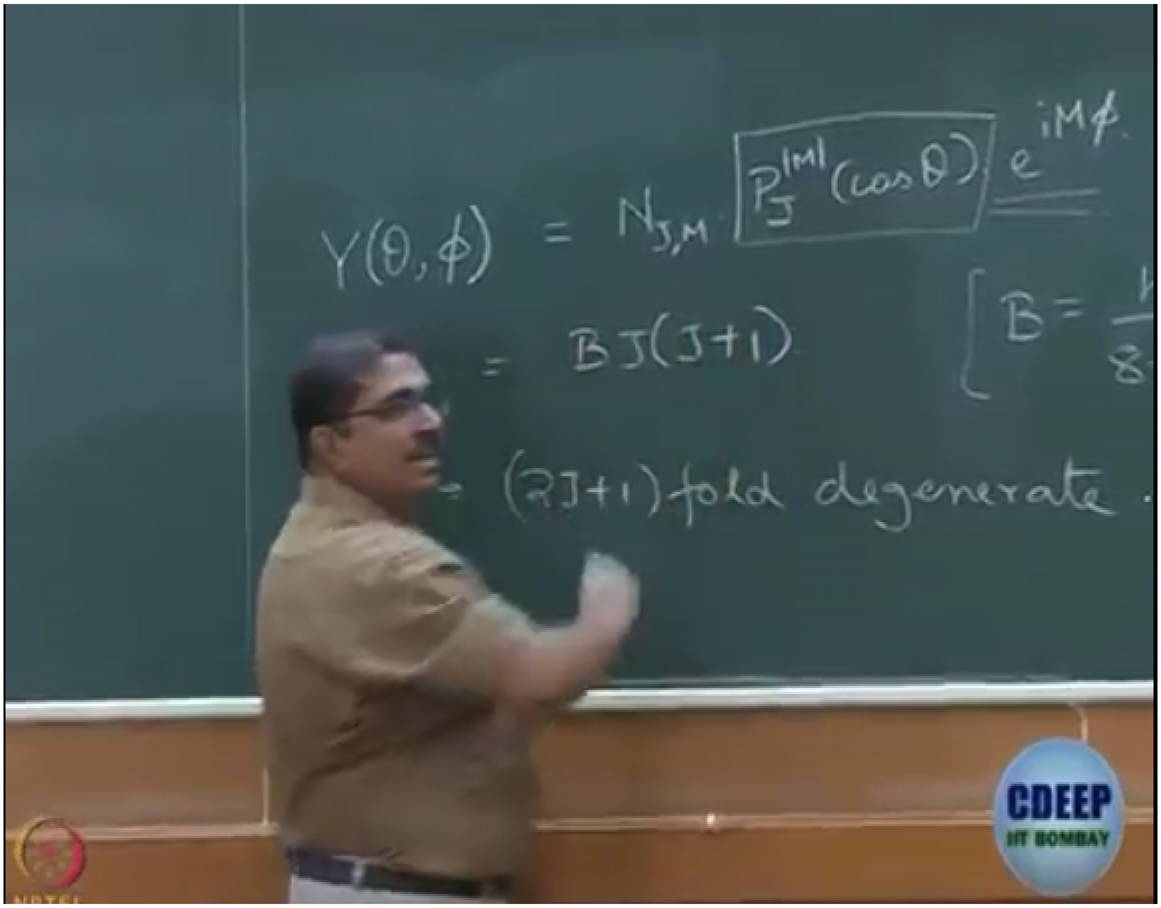

but the reason why we write it in this polynomial form is that this associated legendry polynomials are not unrelated to each other, they are related to each other in a very nice fashion, there are three different rules that relate polynomials of a series, right, and these are called recursion relations. A recursion relation means you can express a polynomial as a linear combination of the polynomial before it and the polynomial after it, so recursion relations for associated legendry polynomials go like this.

First if you take a polynomial like this, a polynomial for J and the value of mod M is given,
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right, and let us say this polynomial is in terms of some variable Z. Take this polynomial and multiply it by Z, you get something like A1 P J+1 mod M(Z) + A2 P J-1 mod M(Z), A1 and A2 are constants,

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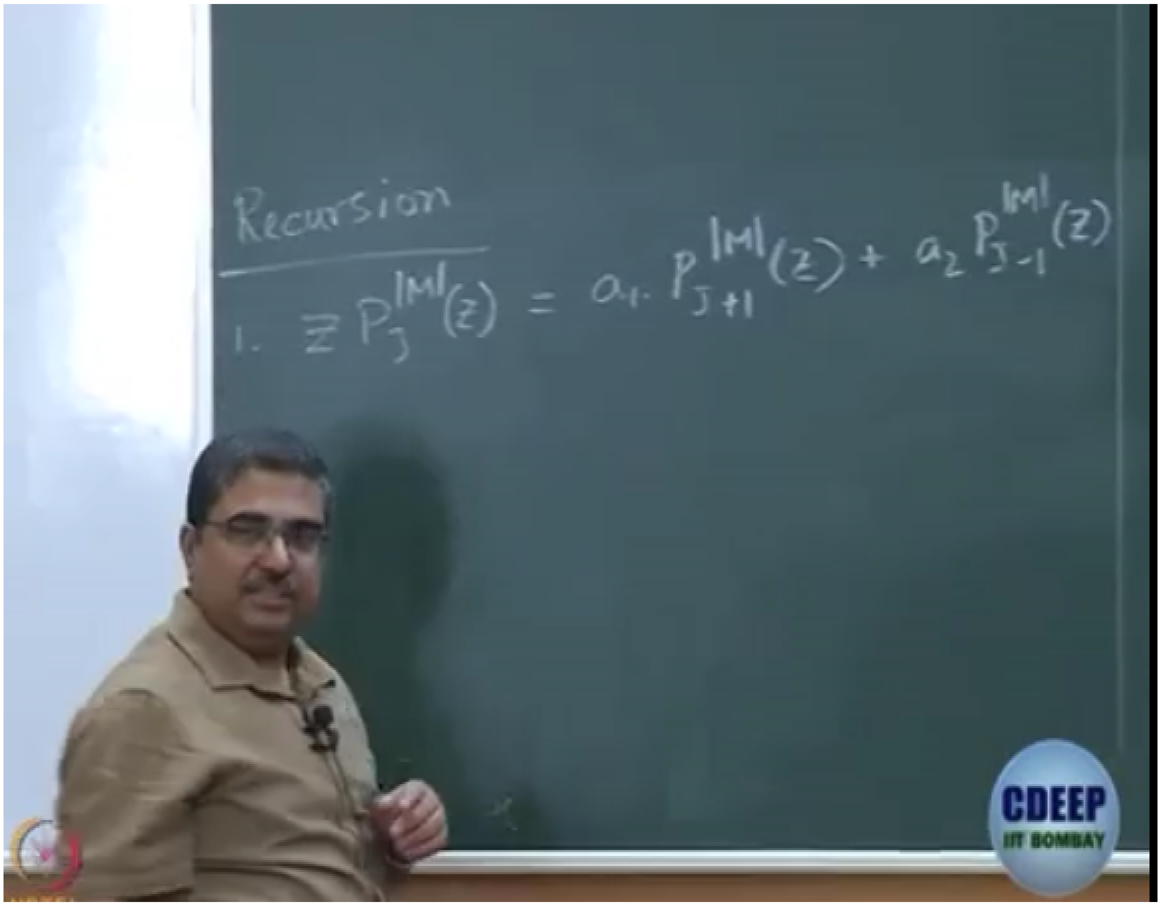

once again these are constants that are made up of, the values of J, M and some numbers, we do not need to know what A1 is, what A2 is? In the exam if I need to use the explicit value of A1, A2 or whatever is I'm going to write now then it will be provided, so please do not worry about mugging up the expressions, mugging up the expressions for the coefficients, it's not required, okay, if you need then they will be provided. But this is something that you'll need to know, but this is very straight forward right, it's not very difficult, okay.

Second one, are you aware of this recursion relations? Yes, what is the second one then? Yeah, I'll write the right hand side, B1 P J+1 mod M(Z) + B2 P J-1 mod M(Z),
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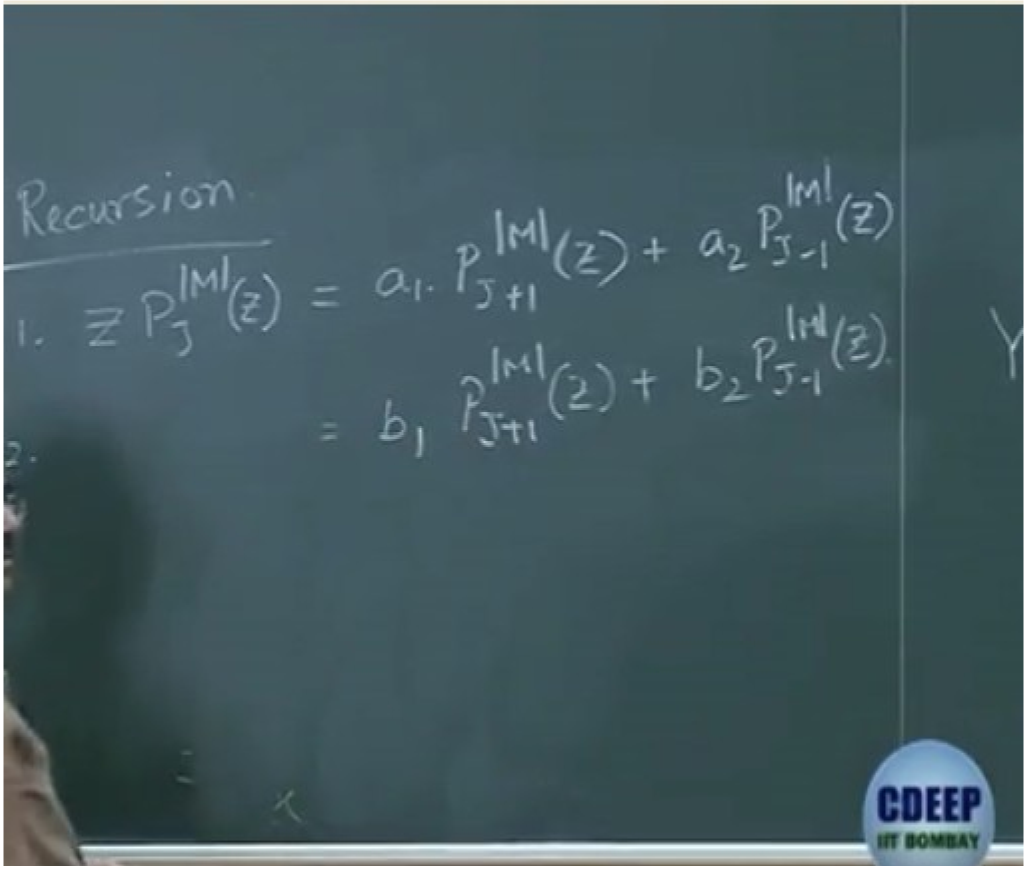

in fact there is a third one I'll write that as well C1 P J+1 mod M(Z) + C2 P J-1 mod M(Z), so right hand side is essentially the same, right, linear sum of the polynomial,

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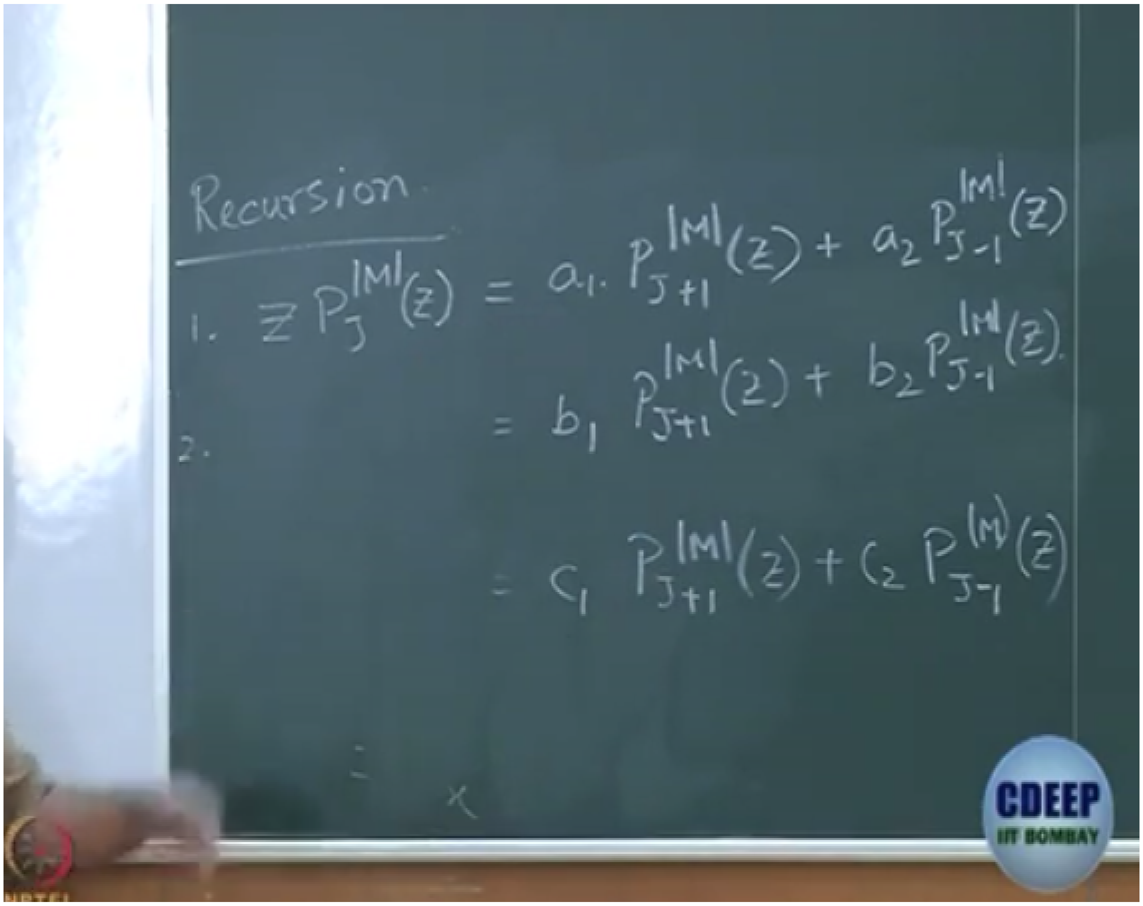

before polynomial after with no change in M.

What are the left hand sides? Do you know this or no? Say that I'll write it, it's okay, so left hand side what you have is in one case you have PJ mod M + 1(Z), in the other case you have PJ mod M – 1(Z), and it is multiplied by square root of 1 – Z square, this is also multiplied by square root of 1 – Z square,

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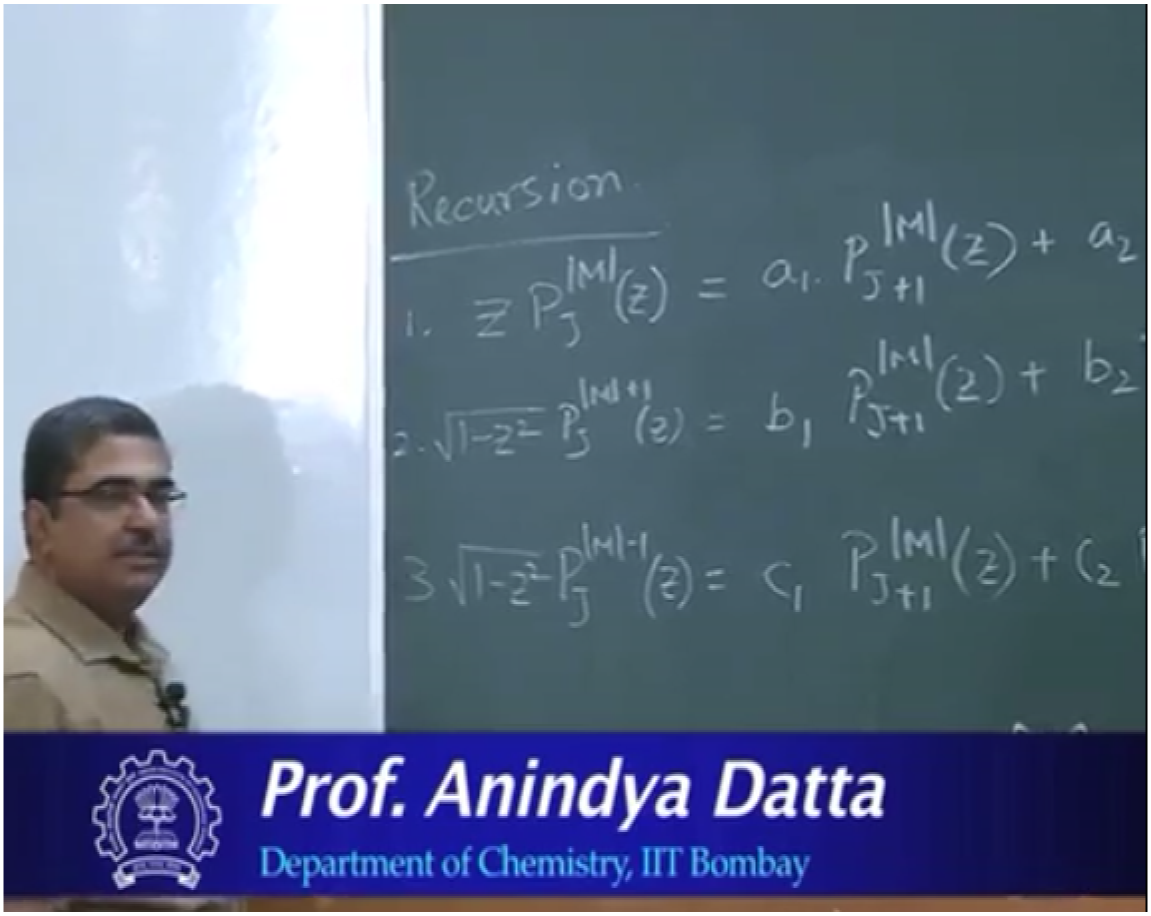

so this where little more complicated than the first one, but nothing that should actually scare us, alright.

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