INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

CDEEP IIT BOMBAY

MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

PROF. ANINDYA DATTA
DEPARTMENT OF CHEMISTRY,
IIT BOMBAY

LECTURE NO. – 08
Conditions for Microwave Activity – 1

So now we are going to discuss the conditions in which a diatomic molecule let's say can absorb microwave radiation of the correct frequency, okay. I started off writing selection rules but then I remember that there is something beyond selection rules as well, so it is better to say conditions or microwave activity, okay.

You might know the conditions already, it's just that we are going to arrive at the conditions in a little more formal manner, okay, and when we do that we start from what we had retained in the previous discussion, we start from your transition moment integral, okay.

What is the transition moment integral for a rigid rotor for transition from say J to J dash, I'm talking about J to J dash and M to M dash kind of transition. Is the problem clear what we are trying to do? We're saying that we are going to discuss,
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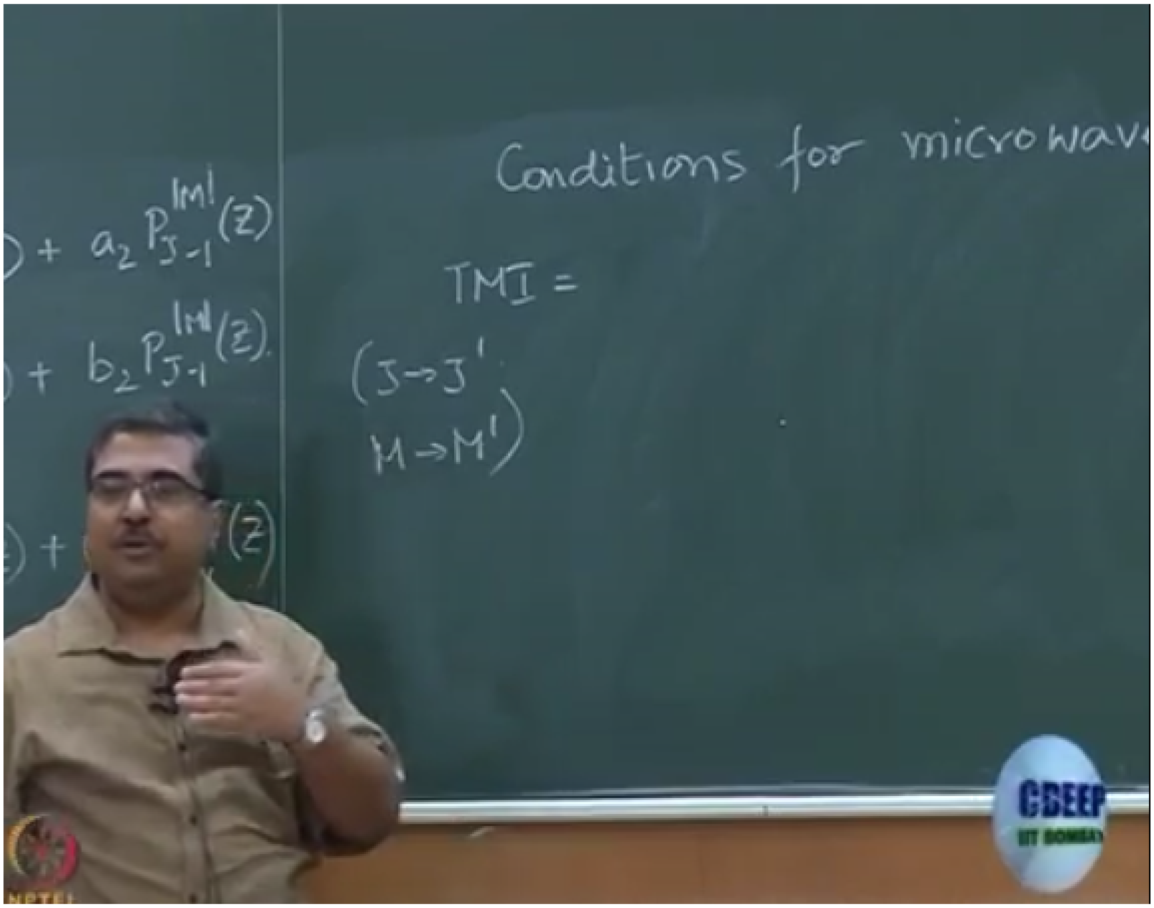

a transition of a rigid rotor from quantum number JM combination to the combination of quantum numbers J dash and M dash, okay. What do I have to do? I have to write the integral.

Now well writing the integral we have to remember something, it is not a simple integral, right, how many variables are there? Two, theta and phi, so the integral has to be over theta as well as over phi, so I don't know two, but when I was your age I use to get extremely scared whenever anybody wrote something like this, one integral is bad enough, say somebody writes two integrals one beside the other then that would scare me, but I am sure you're braver and you're better in mathematics then what I used to be or I am, so I hope this will not scare you, okay, all I mean is that first we are going to integrate this and then whatever we get we integrate that with respect to the second parable, and we don't even have to do that,

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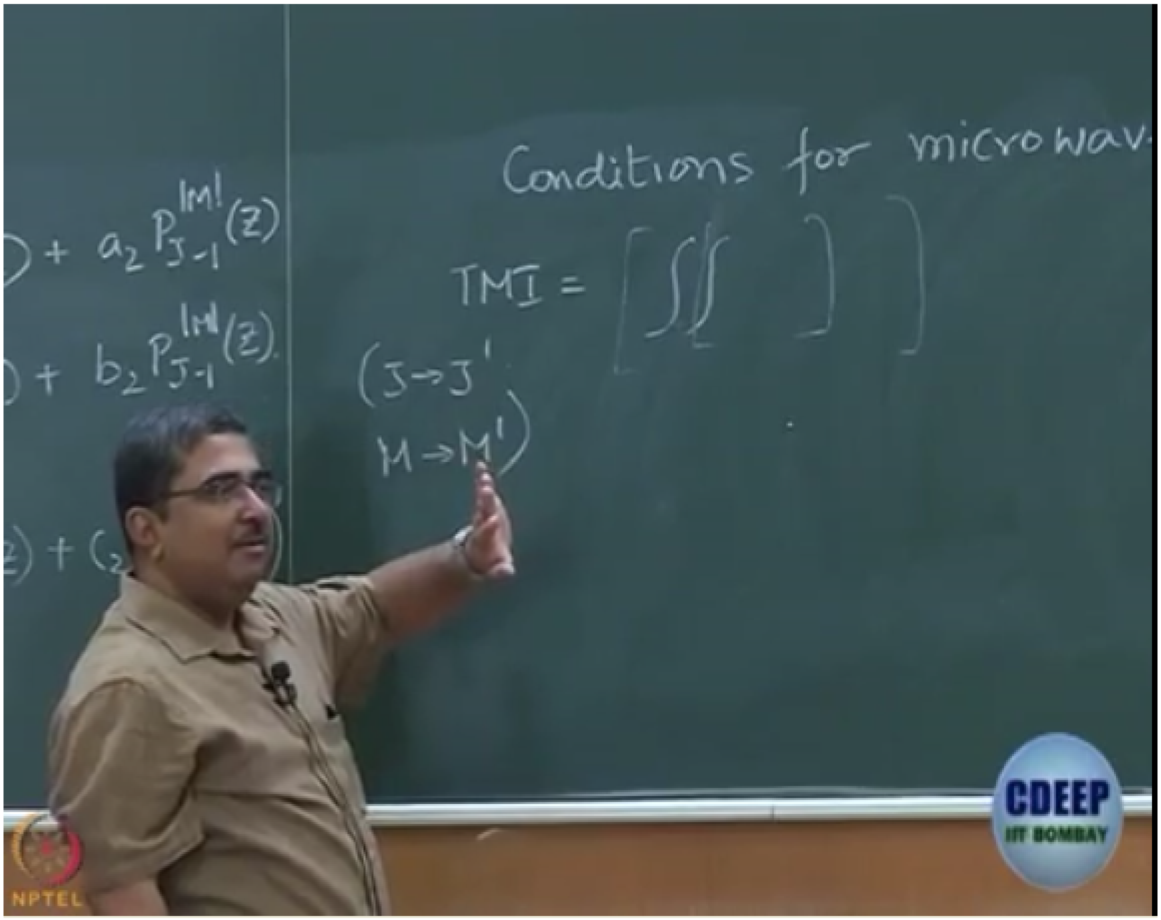

as you know we are going to be able to write this as a product of two integrals.

Two integrals, one over theta, one over phi, I'm going to write the limits soon, okay, so let's write this, remember what transition moment integral is, integral sai star mu sai, right, sai F star mu sai I, what is sai F star here? Well, I can write the normalization constants out already, let's say I write the normalization constant of the destination level as N dash, alright, N dash then you have P J dash M dash in cos theta, ideally I should have written P star,

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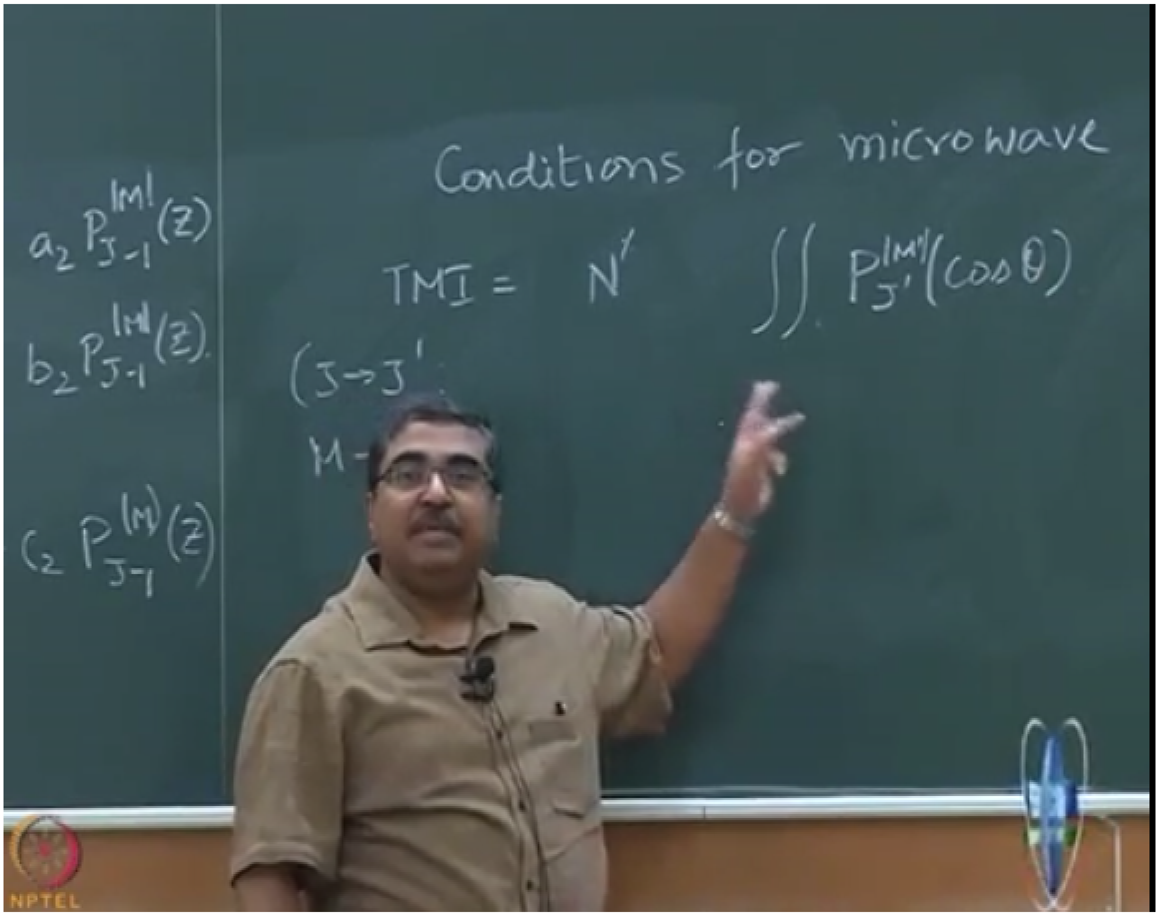

but as you, I hope you know these polynomials in cos theta are actually all real, so star does not arise here, but the next part, the phi part, what is the phi part? E to the power IM dash phi, isn't it? But since I am writing it in the,

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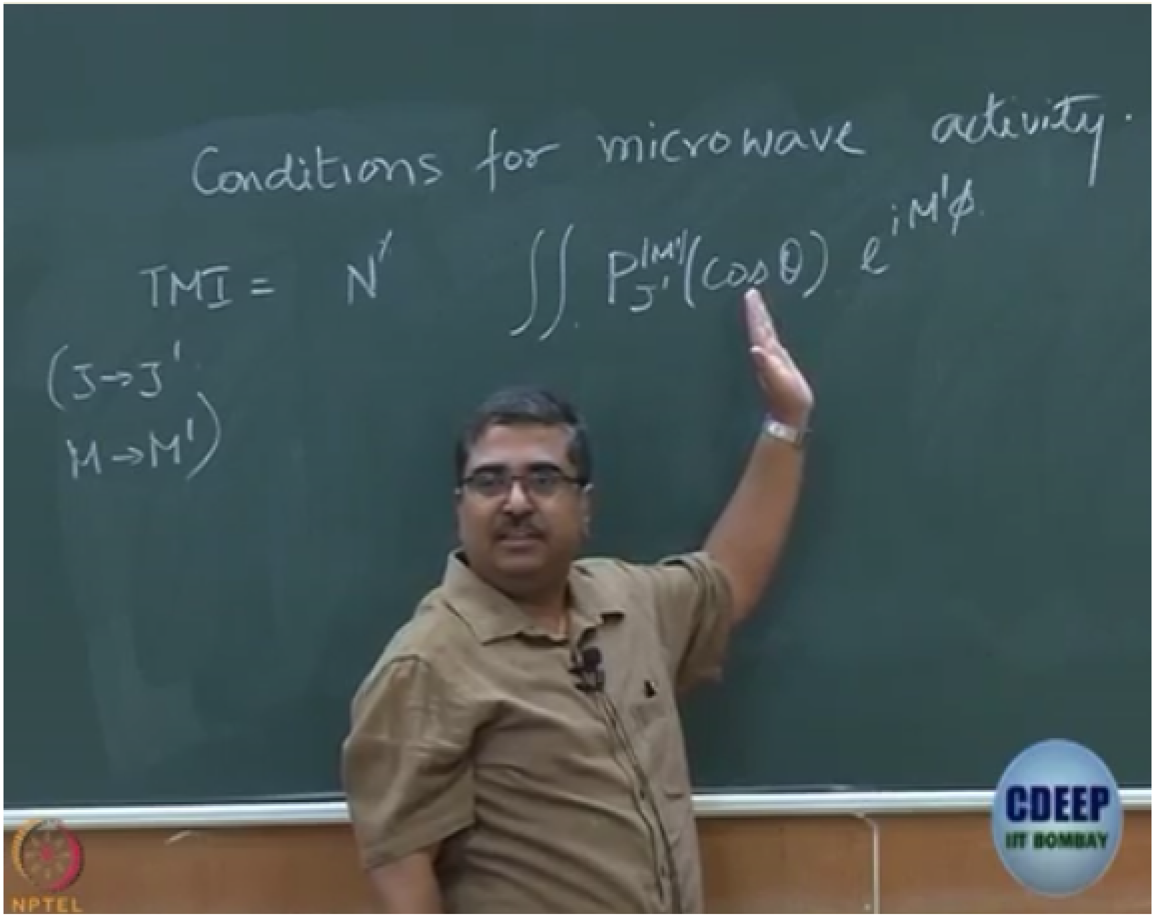

the first one has to be complex conjugate, right, so this I have to write the complex conjugate of it.

What is the complex conjugate of E to the power IM dash phi? Minus, that's very simple, E to the power –I M dash phi, right, what do I have to write next? I have to write the expression for mu, right? We'll come back to this in a minute mu, then I write the initial wave function that would be PJ mod M(cos theta), E to the power I capital M phi, now I don't have to write complex conjugate, right,

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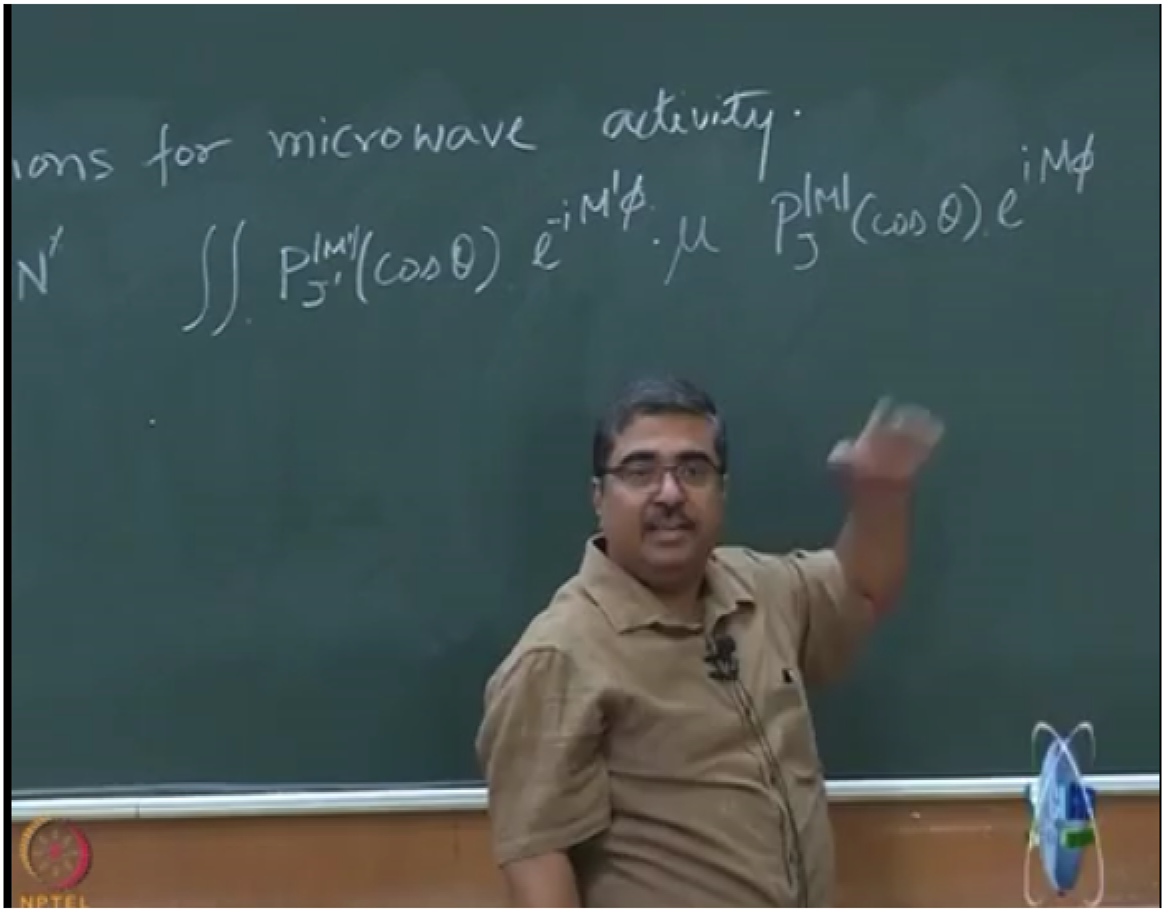

the second wave function we write just itself, multiplied by D tau, what did you tell me D tau was in the previous discussion? D tau is, Gurujot told us what? Sin theta D theta D phi, right, we don’t worry about DR because R is not changing, sin theta D theta D phi.

Now let us write the limits,
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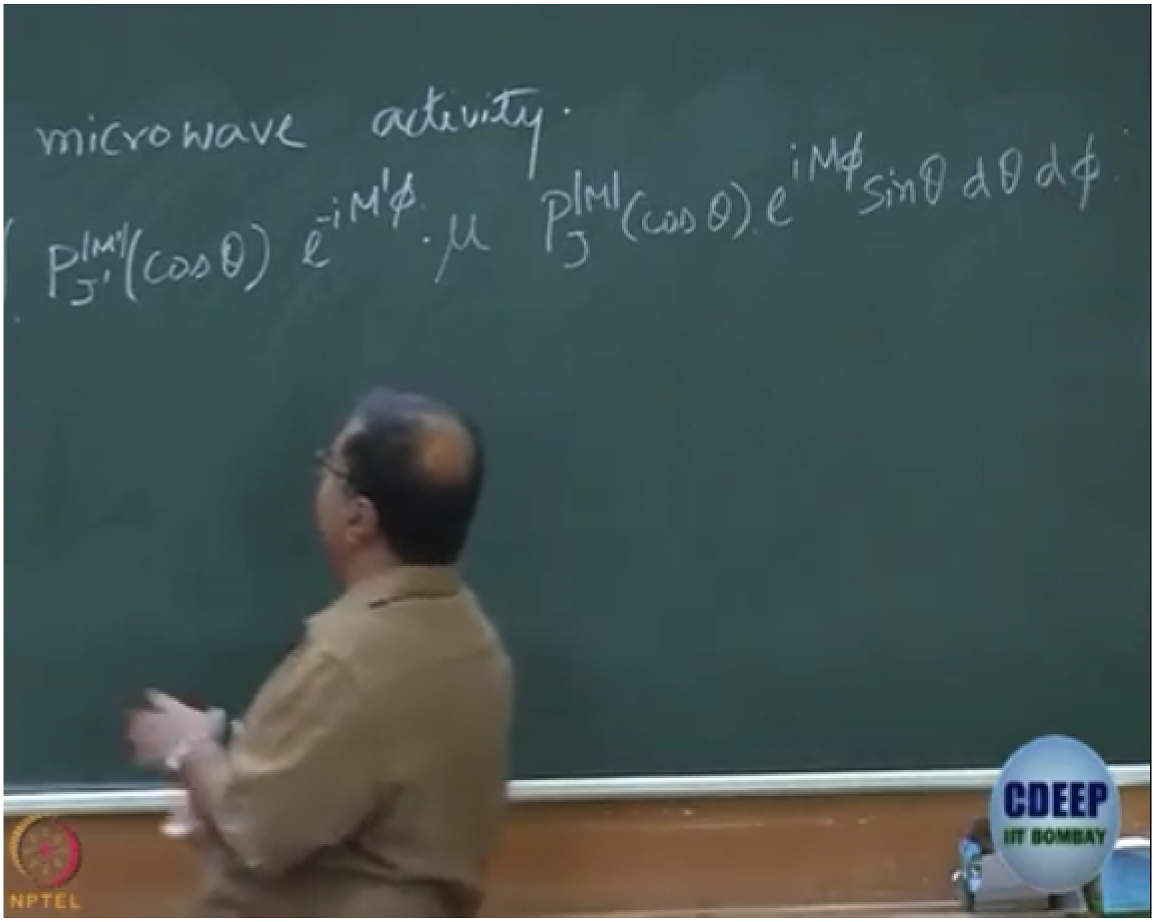

since I have written sin theta first, second one will have limits of sin theta, I'm so sorry, theta right? What are the limits of theta? 0 to pi or 2 pi? Pi, and what are the limits of phi? 0 to 2 pi, okay, and of course and I have to multiply it by the normalization constant of the first one as well, what I'll do is, the whole thing I'll write maybe as stylist normalization constant N, okay.

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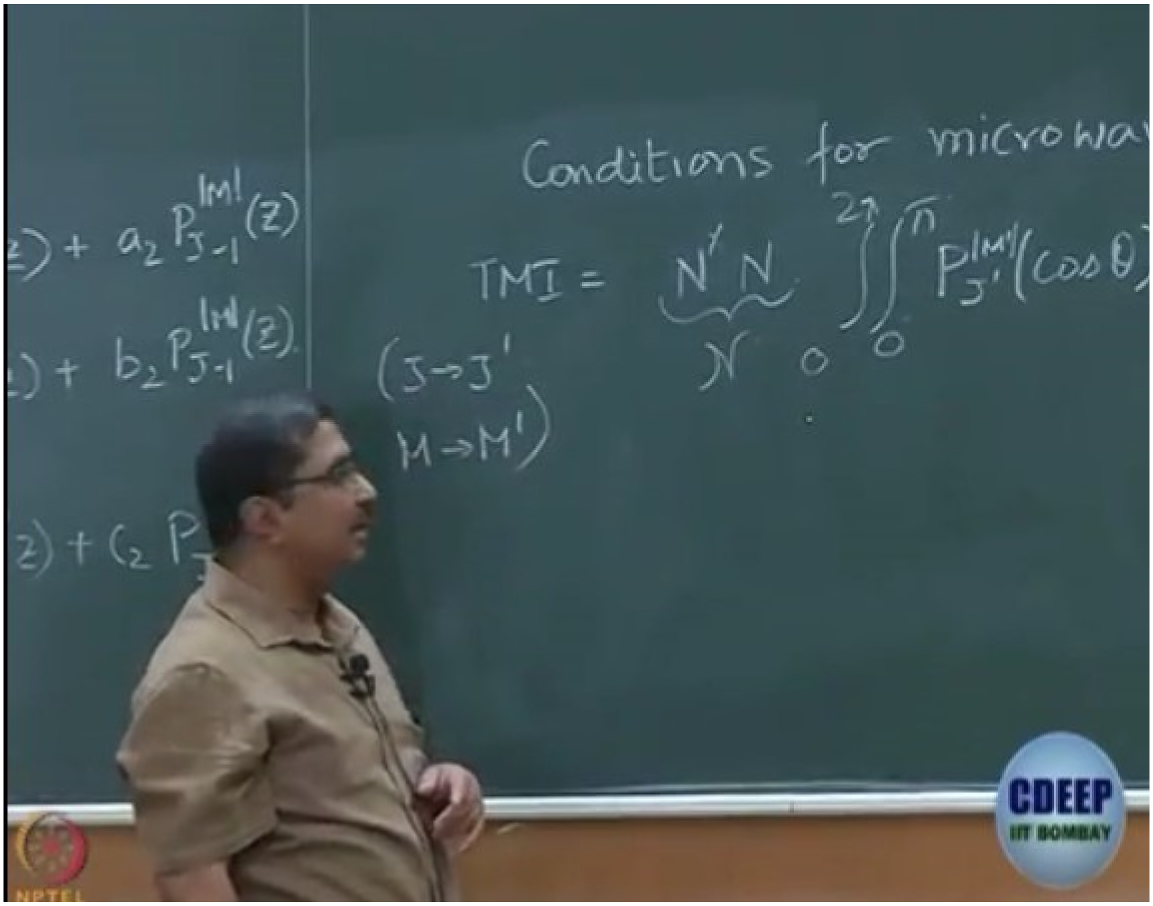

Now before proceeding any further let me express it like this, N multiply it by, now see the two variables are independent of each other, so I can write this double integral as a product of the integral in theta and integral in phi, right, whatever is phi will become constant as far as theta is constant, is concerned and will come out of the integral, so I can write it like this, this N multiply it by 0 to 2 pi E to the power and I can simplify while writing this I(M-M dash), but hold on, before I can do that I should know what I'll write for mu, okay, what I'll write for mu. Now mu as you know is a vector sum of mu X + mu Y + mu Z, right, and you've told me in the previous discussion

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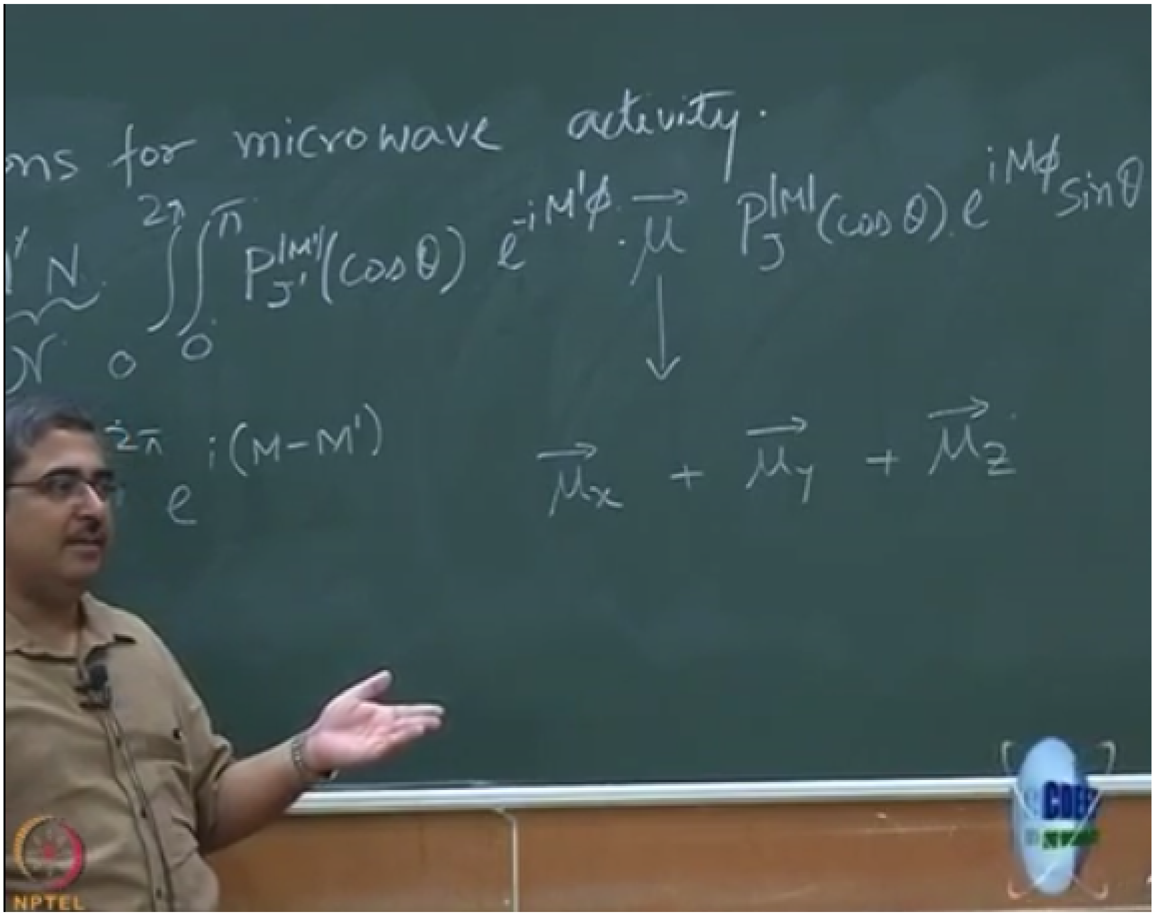

that mu Z = mu 0, okay again I'll write mu 0 here, mu 0 cos theta, this one is mu 0 sin theta, sin phi and this one is mu 0 sin theta cos phi, right.

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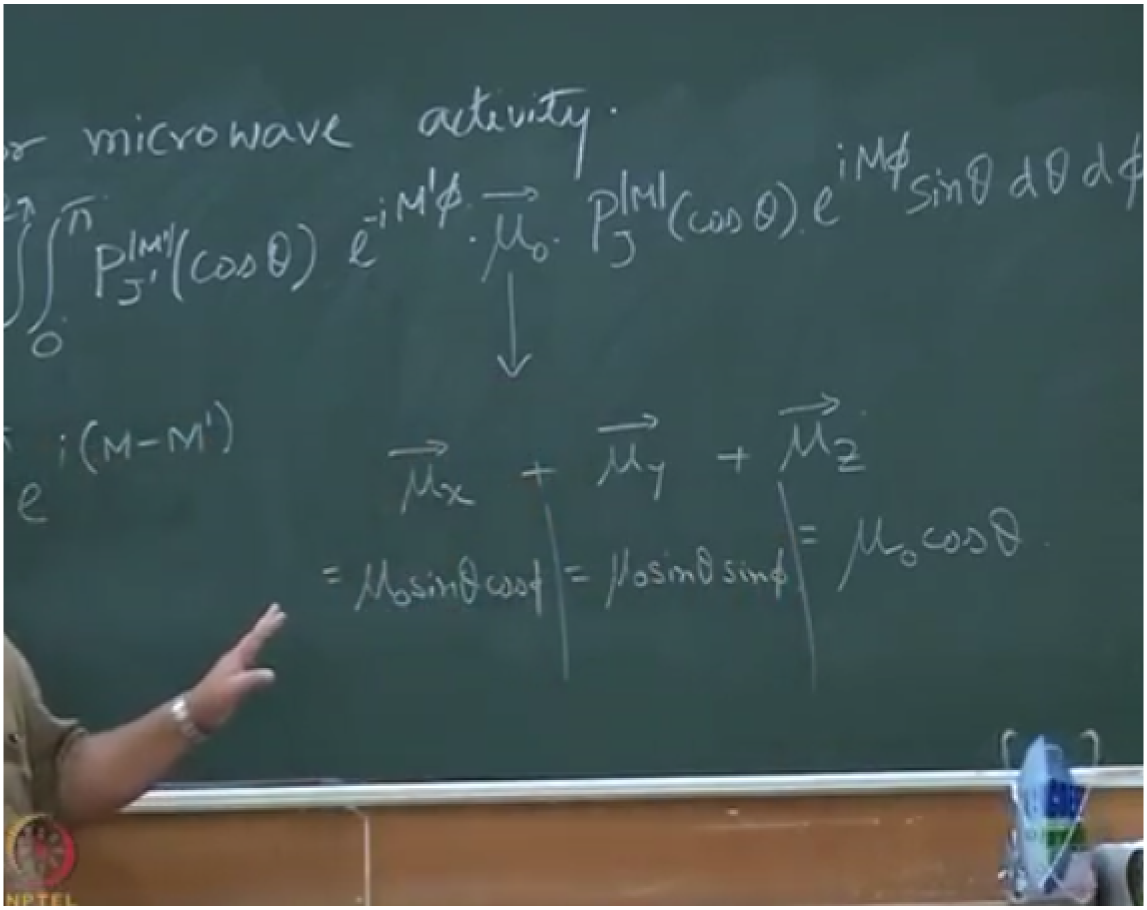

So instead of this mu 0 I should write this sum and the moment I write this sum it becomes apparent that I've to do it in three different steps. First I have to work with say mu X, then with mu Y, then with mu Z separately, okay. Since mu X and mu Y are very similar, what I'll do is I'll work with mu Z first, to start with let us only consider this mu Z, now I can go ahead and I can write this. From working with only mu Z, then what happens? I'll write mu 0 cos theta, right? So no component of phi here, so as far as the first integral is concerned it is complete. So that comes in the second integral which consists of your,

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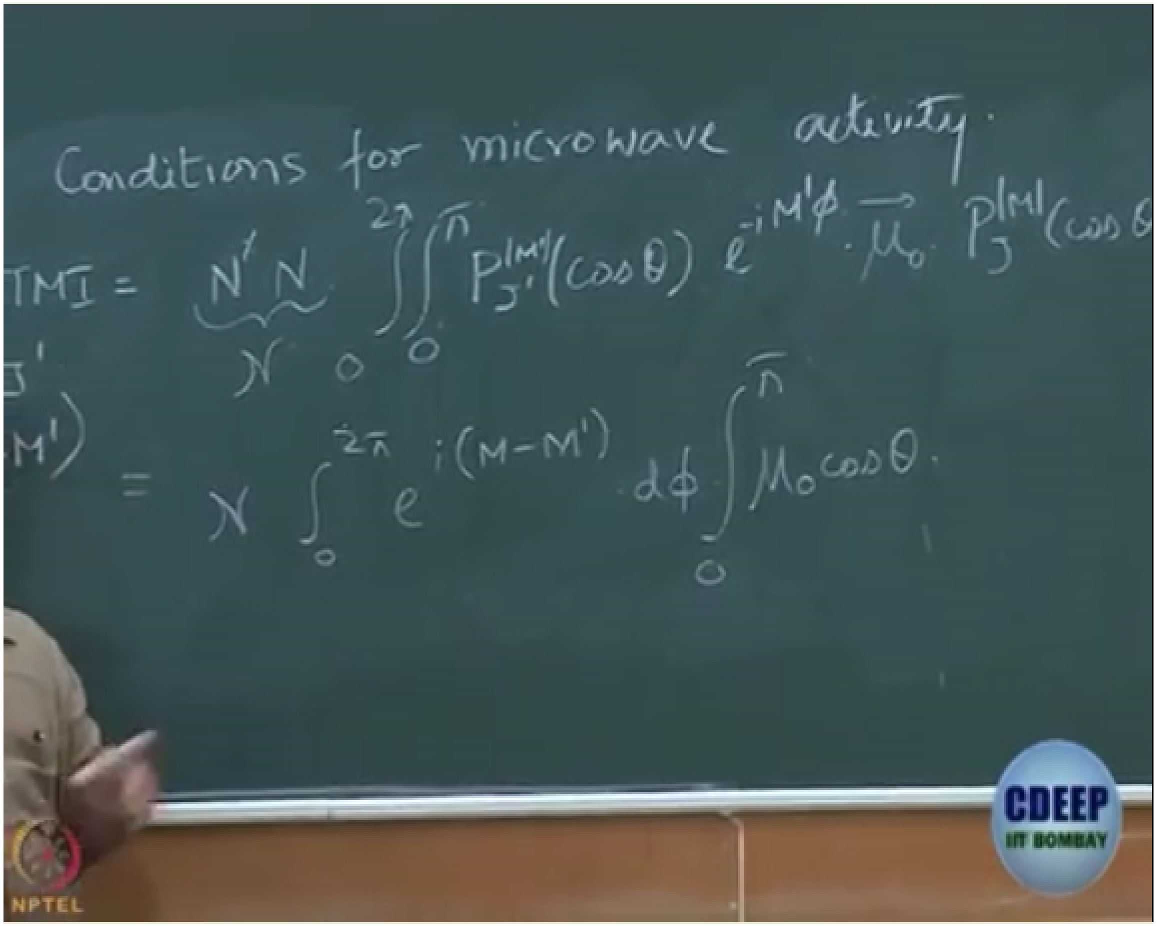

which is in terms of theta, is this clear or did I manage to confused you in the last couple of minutes? I managed to confuse you in the last couple of minutes, yes, sorry, E is to the power, oh, right, right, phi is missing, okay, good, if that is the case then I did not confused you in the last few minutes, good.

Are we clear so far? Can I go ahead? Before I go ahead what is mu 0? That is a constant, isn't it? Doesn't depend on theta, doesn't depend on phi, doesn't depend, well does depend on R, but R is not changing, so I can take mu 0 outside, so I'll write like this, N mu 0 integral 0 to 2 pi E to the power M – M dash phi D phi integral cos theta multiply it by, well I'll write like this P J dash M dash(cos theta) multiply it by cos theta, multiply it by PJ mod M(cos theta) multiply it by sin theta D theta, see if you have understood this? When we work with the Z component of dipole moment this is what my transition moment integral boils down to, are we clear about that or do we have any question? If you have a question please ask now. Are we clear? Sure?

So first thing that we arrive at already before going any further is that, if mu 0 = 0 then what happens? Then transition moment integral become 0 anyway, no matter what the other integrals are, and that means your molecule is not going to absorb any microwave radiation, irrespective of what is J, what is M, okay. So it turns out that a molecule has to be dipolar if it has to absorb any microwave radiation at all, are we clear? So which means that HCL is going to be microwave active, but H2 or CL2 will not be microwave active, you need a permanent dipole moment for microwave activity that is something that we arrive at right away before going any further. You know this already, didn't you? Right, you knew this but then this is how it comes.

Any question? Will come to that, right now we are working only with Z, we are going to talk about X and Z, Y also but then see no matter which component you take, instead of mu 0 cos theta, if I wrote mu 0 sin theta sin phi, mu 0 would still come out, right, so even when we work with X component or Y component or dipole moment, this permanent dipole moment will turn out to be an essential condition, okay, good question. Permanent dipole moment can be anywhere right, permanent dipole moment is along the deduction it is, see if you take HCL you know what the deduction is, I don't know whether HCL is along X or along Y or along Z or along something, okay, for some position you can resolve it into components for any position, okay, which will bring us to an important question in the next class, okay. Any other question? Understood everybody?

What have we obtained so far? Point number one, a molecule must have a permanent dipole moment for it to be microwave active that is something we have established. Now we are going to go to the selection rules, okay, to do that let us handle these two integrals separately, let's call this integral in phi, let's call this I1 and let us call this integral in theta I2, okay, may I raise the first line? Don't forget, as of now we are working only with the Z component of the dipole moment, okay, what is I1? I'm going to write this as delta M, are we okay if I write this as delta M? M-M dash delta M, it doesn't matter if you don't write, E to the power delta M phi D phi, what is that equal to? In fact, in order to work out this integral we need to consider two different conditions, one in which delta M = 0, and one in which delta M is not equal to 0, okay.

What happens when delta M is equal to 0? What does this integral boil down to?
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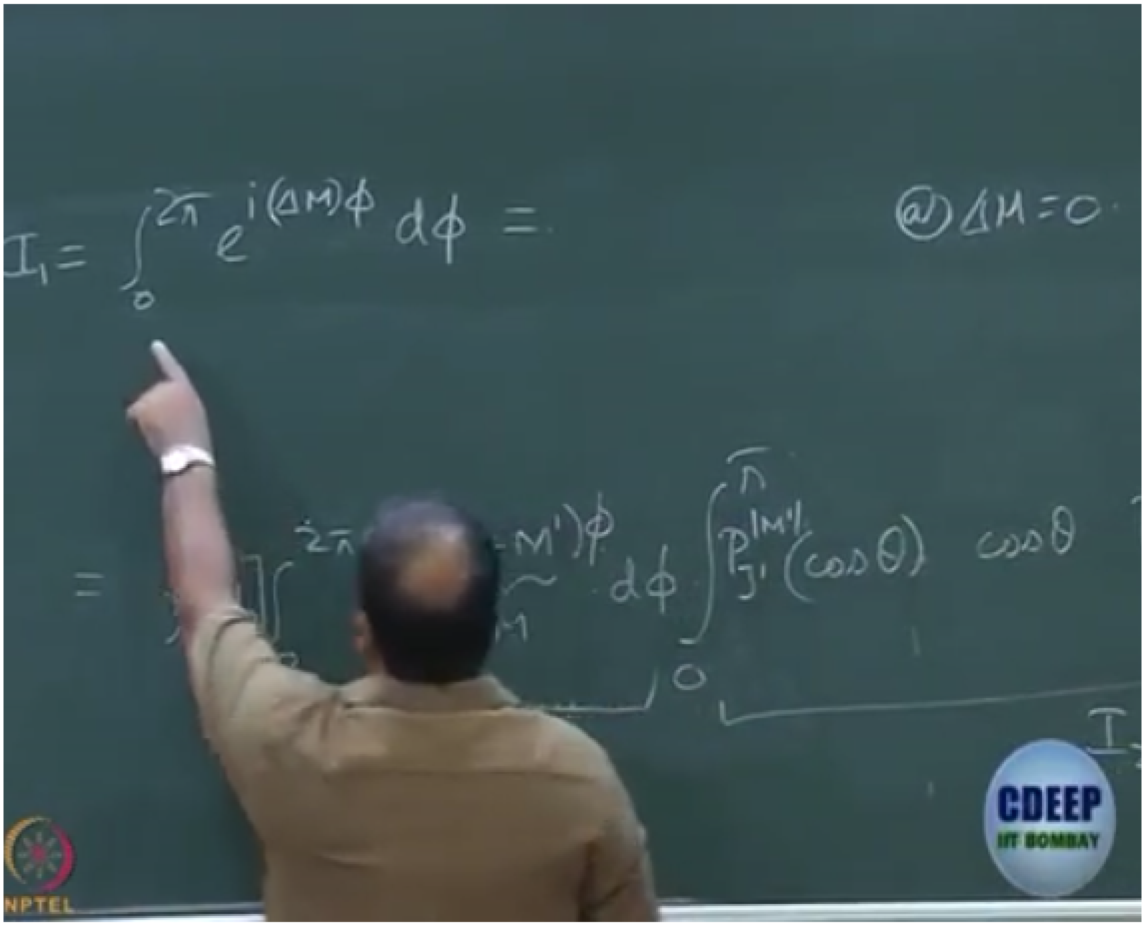

Then it becomes integral 0 to 2 pi D phi which is equal to 2 pi, which is not equal to 0, right,
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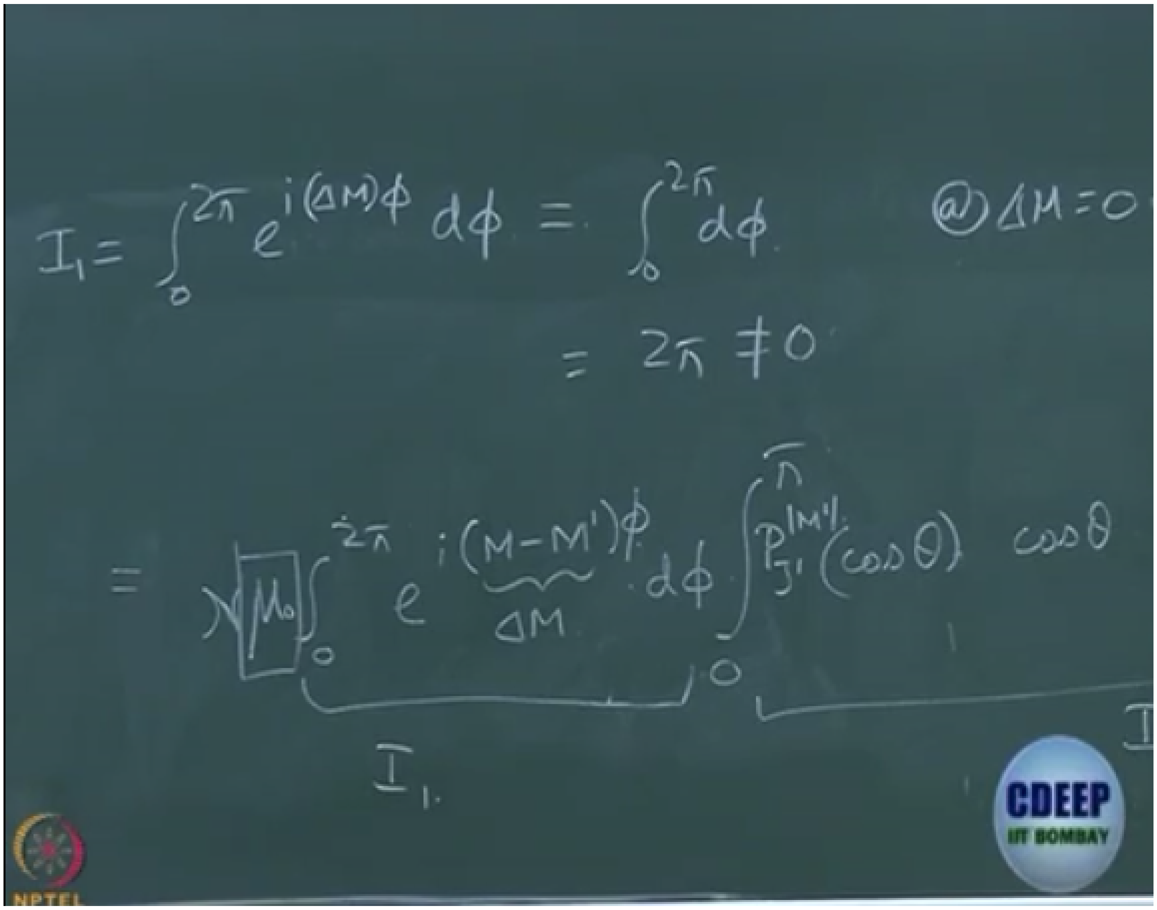

so you see that the integral is nonzero if delta M is not equal to 0, okay, so delta M not equal to 0 trans out to be a selection rule when you work with mu Z, Z component of dipole moment, right, so you've already arrived at once selection rule which we may or may not have known earlier, okay, but as we'll know, as we'll see this is not the only selection rule, delta M can be something other than 0 when we talk about X component or Y component of the dipole moment. Are we all clear? Sure? Okay, so what we see is if delta M = 0, then the integral survives.

What about the situation when delta M is nonzero? Then of course this part is not valid anymore and you have to actually work this out, and to work this out it is waste if we switch over to the trigonometric form, okay, I hope you all know the trigonometric form, what is it? E to the power IK phi or maybe I'll write it directly, E to the power I delta M phi is equal to what? Cos (delta M) phi + I sin (delta M) phi, alright so suppose I put this in here,

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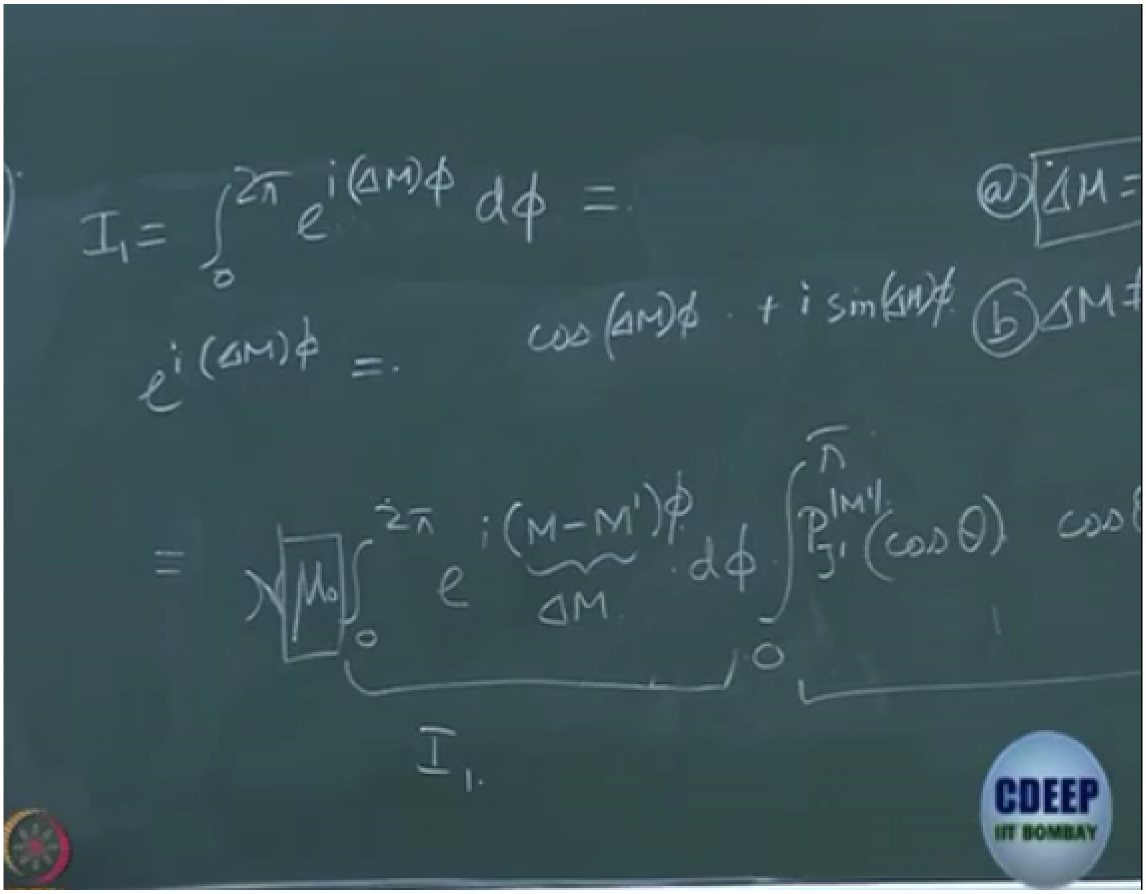

so this would be equal to integral 0 to 2 pi, this D phi will be integral 0 to 2 pi cos delta M phi D phi + I integral 0 to 2 pi sin delta M phi, yuck, D phi.

What is the integral in this case? Integral cos K phi D phi between limits 0 to 2 pi,
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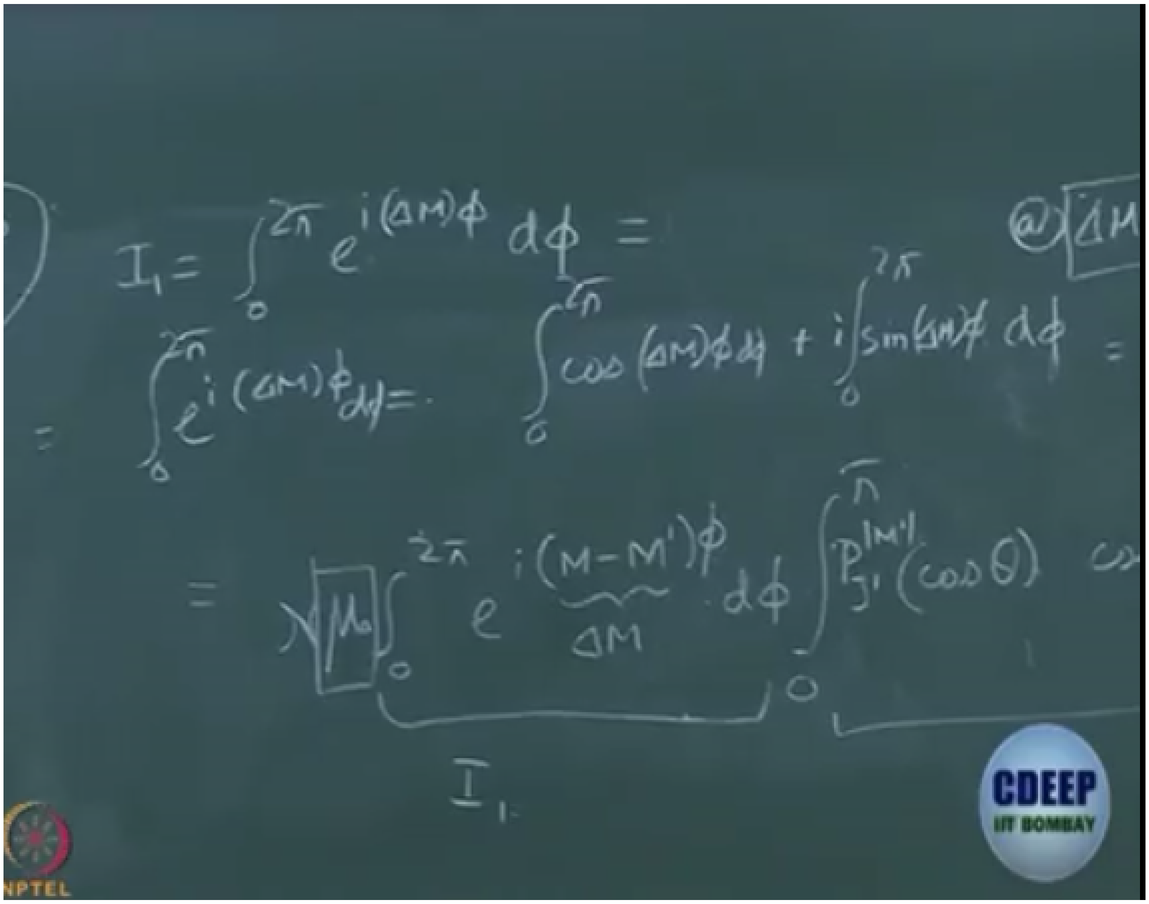

0 and 2 pi are the same points in space isn't it? So whatever is the value of cos phi will be the same, well cos K phi, so the first integral is 0, similarly second integral is also 0, okay, so what we see is very important than that in case of delta M = 0 transition takes place, in case of delta M is not equal to 0 transition cannot take place that is the selection rule already, okay, when you work with the Z component of the dipole moment then it is essential that there should be no change in M, okay, if you want to think physically, what does it mean?

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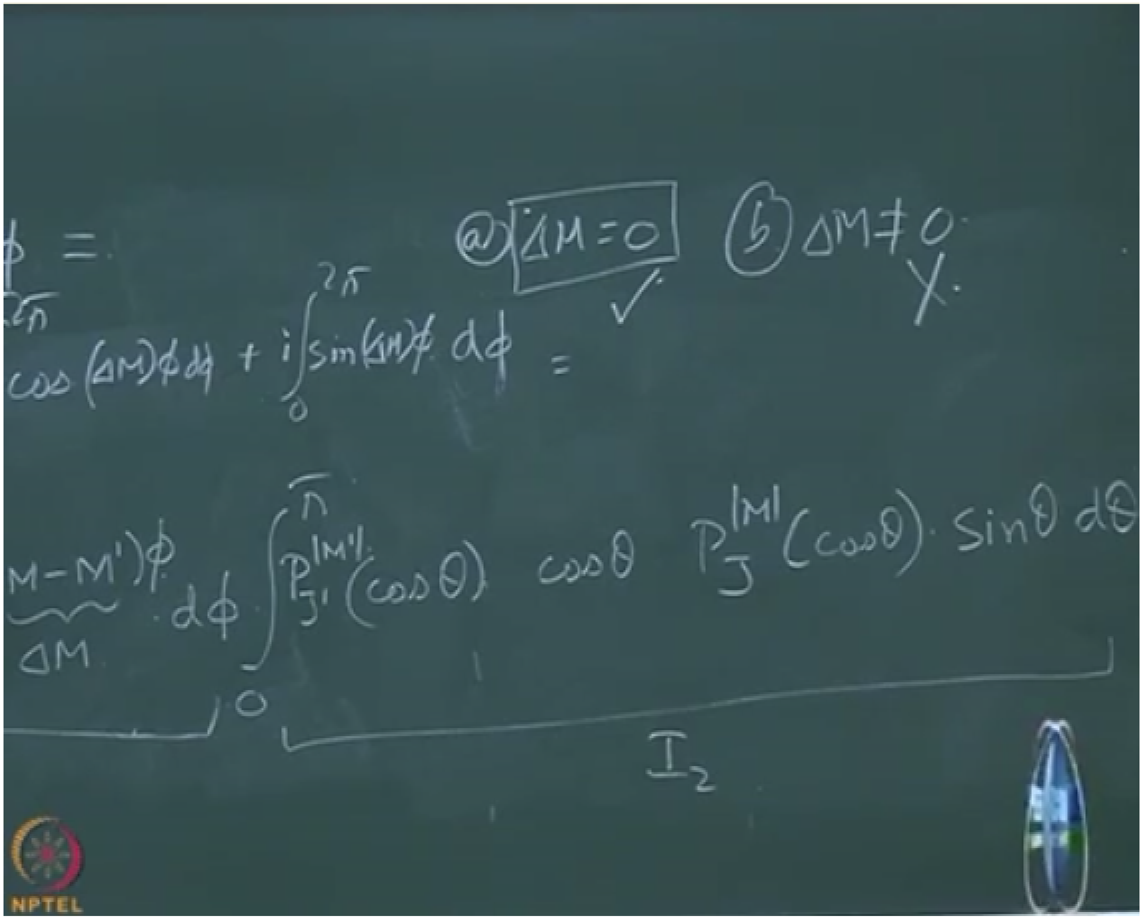
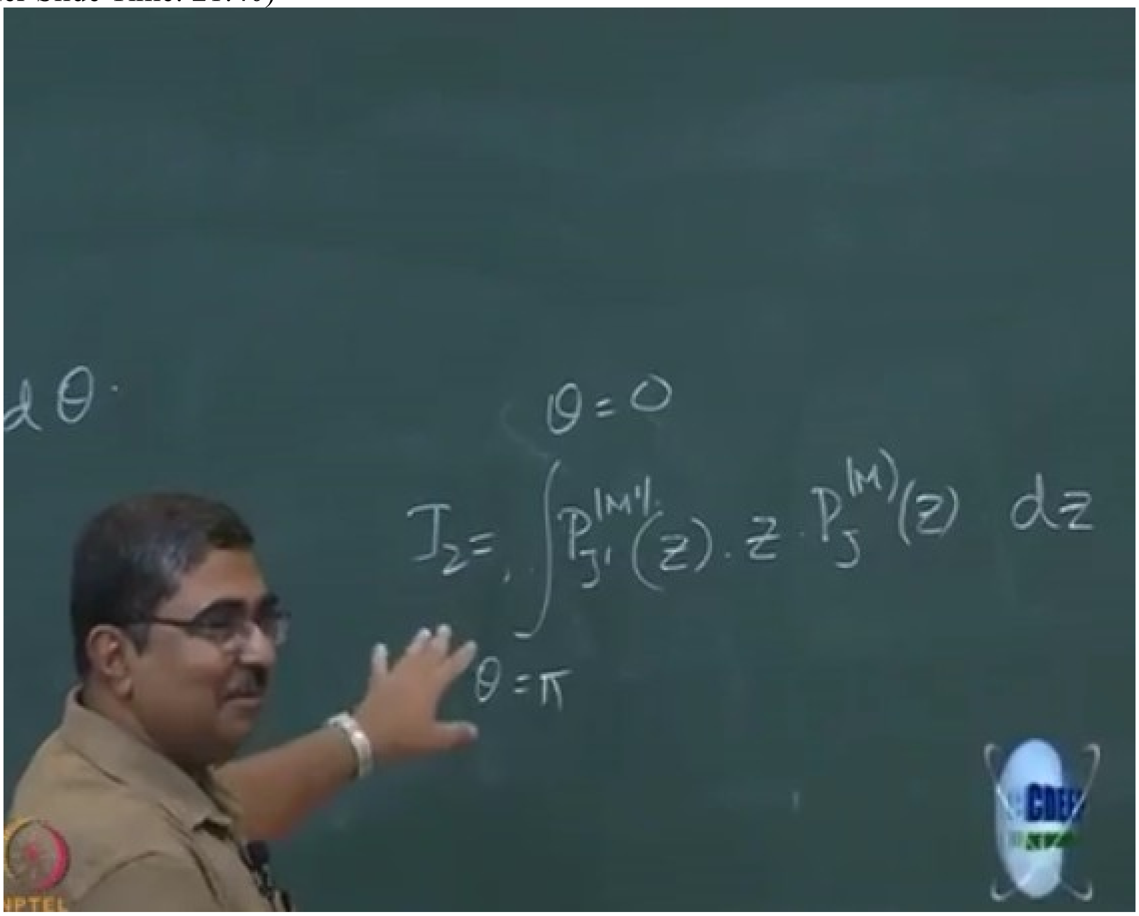


What is M? Z component of angular momentum, okay, if you are working with mu Z, right, that means actually well we'll study this later, it means that you're working with the Z component of the electric field that you are using, okay, field is in this direction, angular momentum is also in this direction, is there any reason why the angular momentum would turn? No right, that is why delta M cannot be equal to 0 when you are working with mu Z.

More about this when we come to it from your time dependent perturbation theory, but let us now move on to I2, are we okay with I1? Do we agree that delta M must be equal to, must not be equal to 0? Yes, sorry must be equal to 0, what am I saying? Delta M must be equal to 0, yeah, yeah, yeah, of course, what is saying is that we agree that using mu Z delta M has to be equal to 0, but can it still be nonzero using mu X and mu Y, the answer is maybe yes, we'll see to it, we'll see, we don't know yet, but when we talk about mu Z definitely delta M has to be equal to 0 for the transition to have any chance, okay.

It is still going to be a disallowed transition if I2 is 0, alright. So let us now see what I2 boils down to? Don't forget we are working with the Z component of the dipole moment, and since we are going to do work with I2 and we are already done with I1 instead of writing it once again, may I just erase everything other than I2? Great, thank you. This here is I2, let me write this in a little simpler form, let us say Z is cos theta, okay, in that case what is DZ? –sin theta D theta, alright, so see in I2 I can write this as PJ dash M dash(Z) instead of this cos theta I can write Z, instead of this one I can write PJ mod M(Z), and what is sine theta, D theta? That is –DZ right, so I can write as, write it as DZ and I can just swap the limits isn't it, instead of 0 2pi, theta = 0 2 pi it becomes theta = pi 2 0, did I go too fast?

Your question? Sorry, minus sign, okay, minus sign will come if I just write like this theta = pi to theta = 0, just switch the limits, are we okay? Clear because, now there is another Vikas in class, (Refer Slide Time: 21:40)



yes, sorry, yes so that's why I've written theta = pi and theta = 0. No, I'll do that in the next step, but I thought that if I just write it, right away people might get confuse, so I'll do it right now, so when theta = pi, what is the value of Z? Cos theta, okay, let's do the easy one first, when theta = 0, what is Z = cos theta? 1, and when theta = pi, what is Z = cos theta? -1 or +1? Sure? Okay, let me see, all sin 10 cos right, I remember this from my school days, all sin 10 cos so it is -1. -1 to +1, do you agree with me that -1 to +1, for Z -1 to +1 covers all the possible values of Z, right, Z is cos theta right, cannot be more than +1, cannot be less than -1, so -1 to +1 for Z is equivalent to –infinity to +infinity for a variable like say Cartesian X.

Are we clear with that? Maybe I should have written Q so that you don't get confused anyway, now I have to evaluate this integral, to do that I am going to use this recursion formula, see I know already isn't it,
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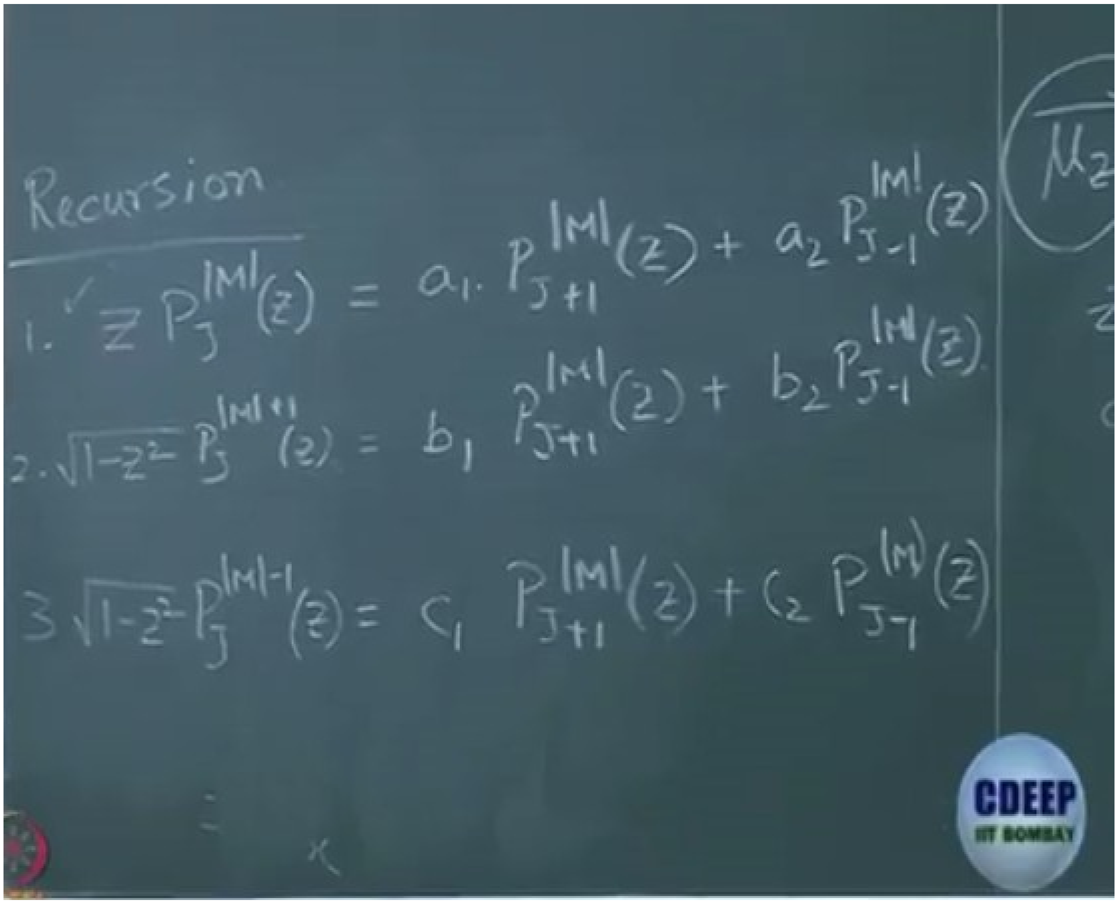

Z multiplied by PJ M(Z) = A1 multiplied by P J+1 M(Z) + A2 multiplied by PJ-1 M(Z) so now into Z(Z), okay, I can substitute it that, so instead of this I can write A1 P J+1 mod M(Z) + A2 into P J-1 mod M into Z, agree or disagree?

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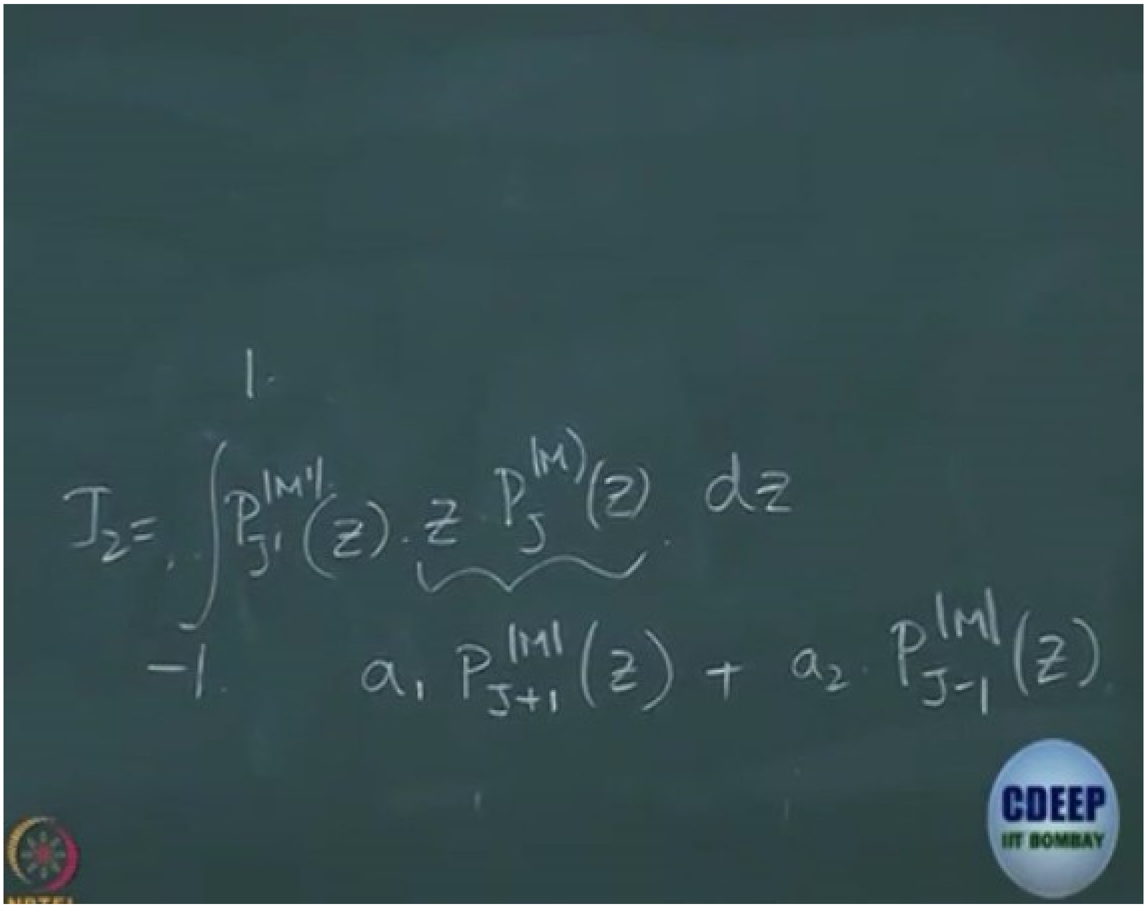

Do we agree or do we not agree? Strongly agree, strongly agree is an option, you are right, is there anybody who disagrees or is there anybody who has not understood what we are trying to do? No, sure, okay, so I'll just write it like this, alright,

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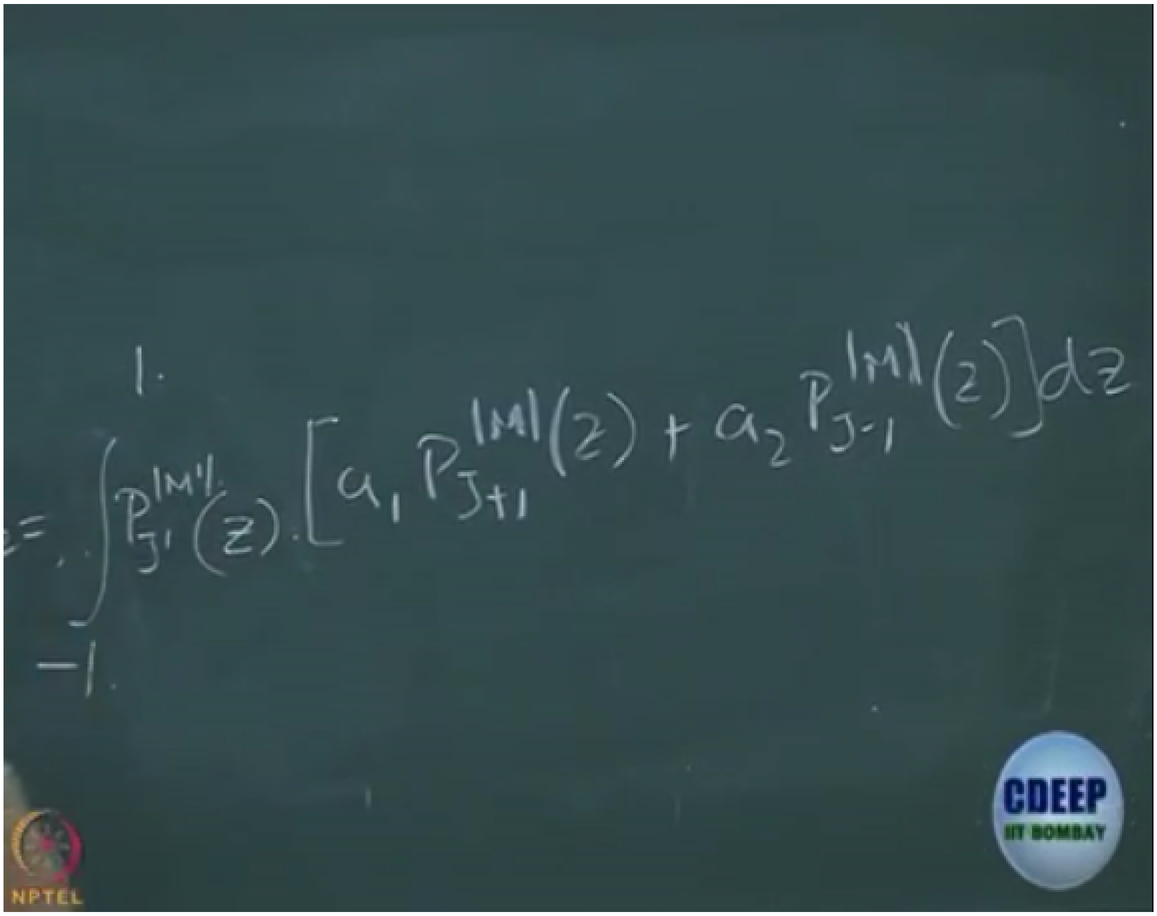

I can write it as a sum of two integrals now, it becomes A1 integral -1 to +1, P J dash, now instead of M dash I might as well write just M isn't it? Because you've already seen from the first, from solution of I1 that M has to be equal to M dash, right delta M must be 0, mod M(Z) P J mod M(Z) DZ + A2 integral -1 to +1 PJ dash mod M(Z) multiplied by, what did I do? This is J+1 isn't it? PJ-1 mod M(Z) DZ,

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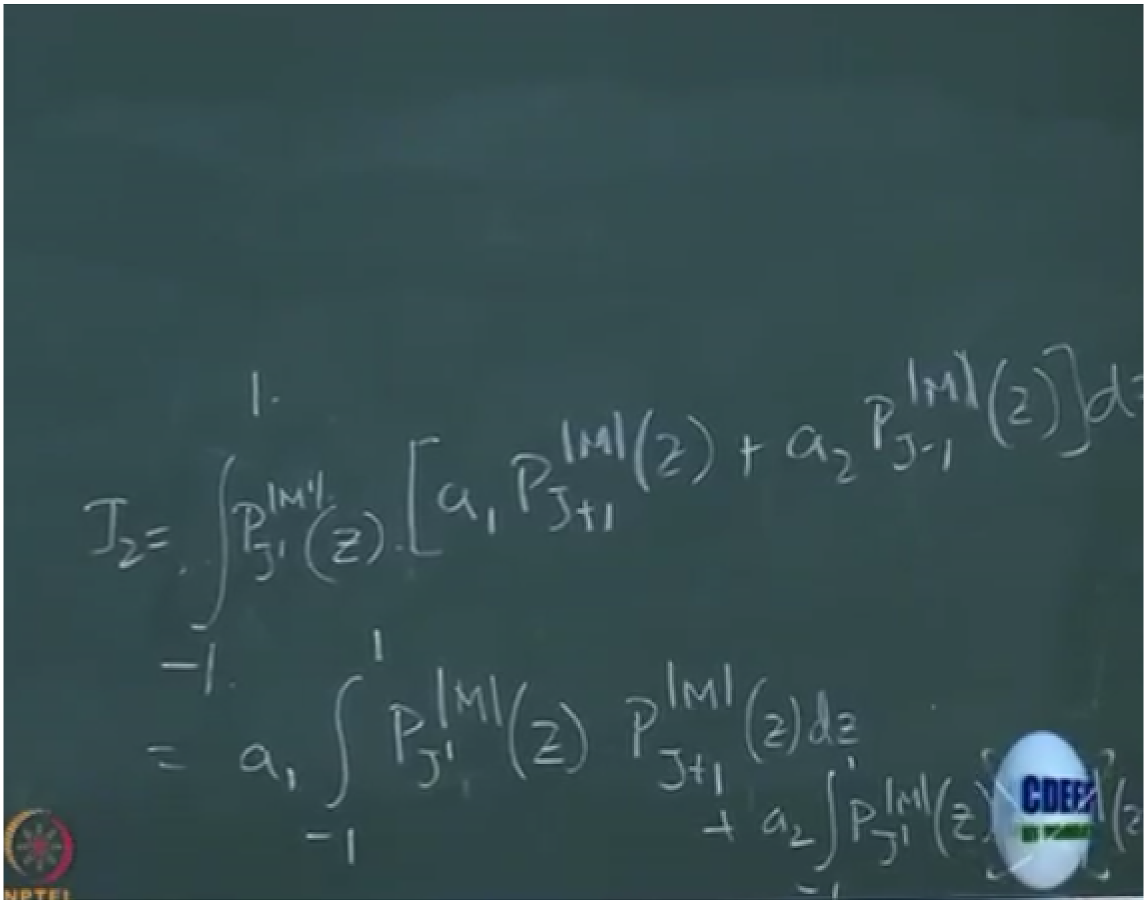

maybe I should write it little more neatly, I2 trans out to be A1 integral P J dash mod M(Z) between -1 to +1 multiplied by PJ mod M(Z) DZ + integral -1 to +1, P J dash mod M(Z) multiplied by P J-1 mod M(Z) DZ, okay.

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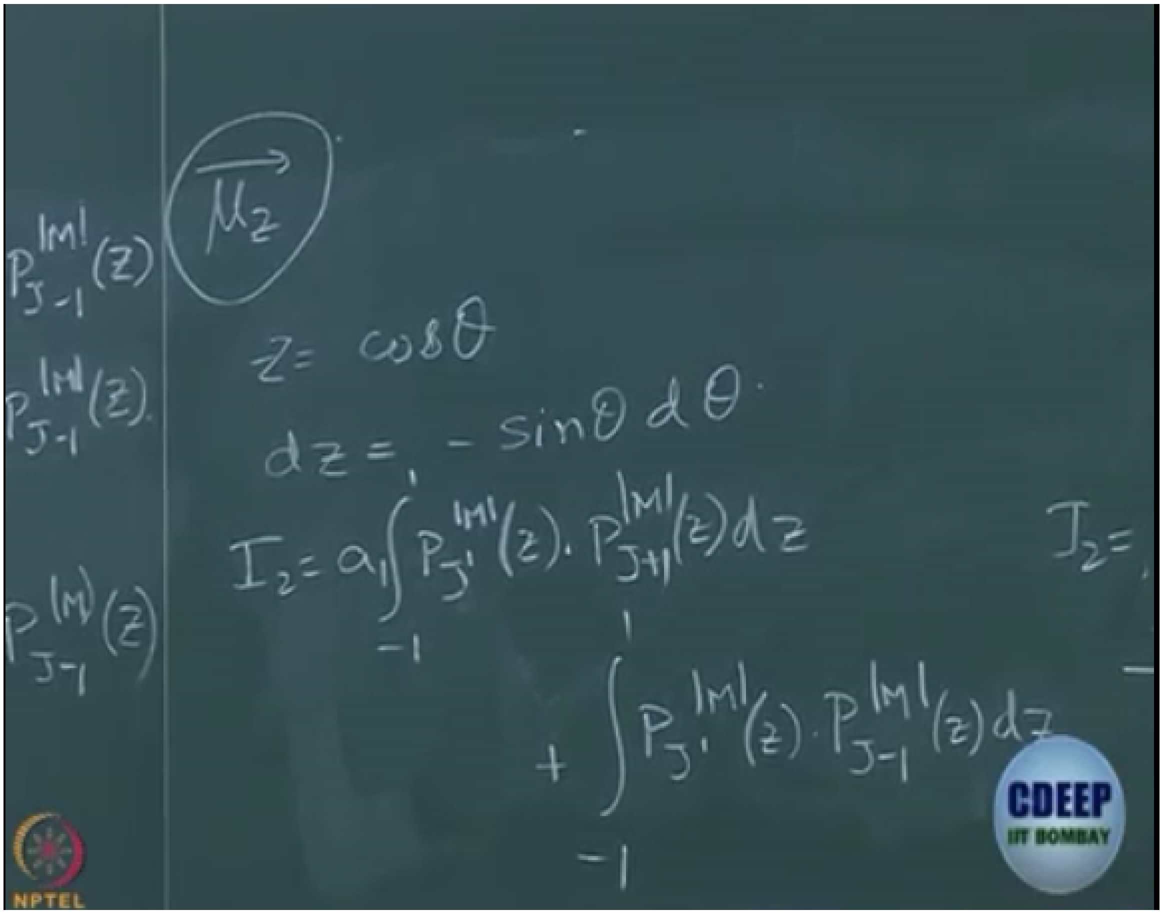

Do we agree that this is I2? Okay, now I ask you the question. These legendry polynomials are wave functions, right, see if I think of different legendry polynomials of the same set, will you agree with me that the form and orthonormal set, right, so a wave function multiplied by another wave function of the same set integrated over all space has to be equal to 0 if they are different, right, and has to be equal to well nonzero, ideally one if they're normalized if they are same. Do you agree?

Now in that case if you agree tell me, when will this first integral survive?
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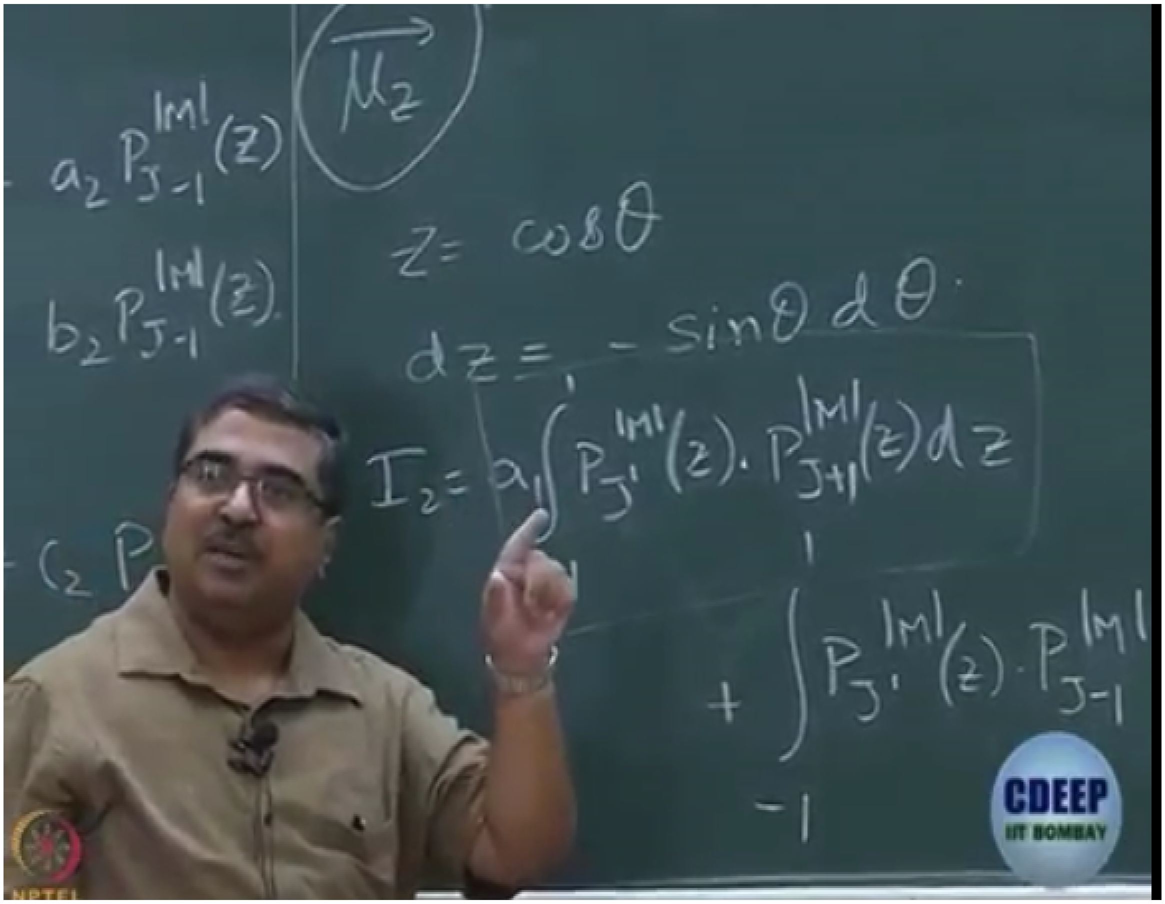

We've already discussed that this -1 to +1 limit is actually all space, right, when is this going to survive there? When will this survive? This will survive only when J dash = J +1, is that right? And in that case the second integral becomes 0.

When will the second integral survive?
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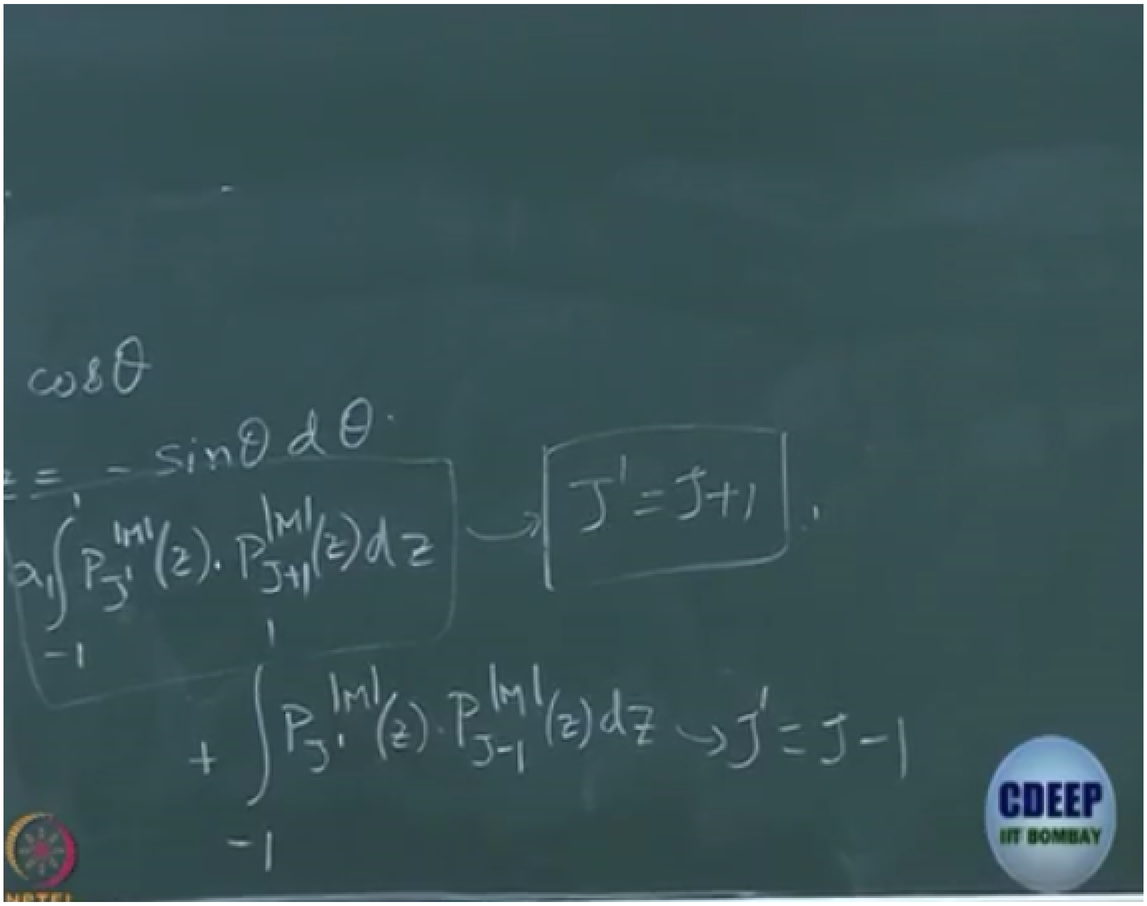

Only when J dash = J-1, is that right? This leads us to the condition that J dash must be equal to J + - 1 or delta J = + - 1, is that right?

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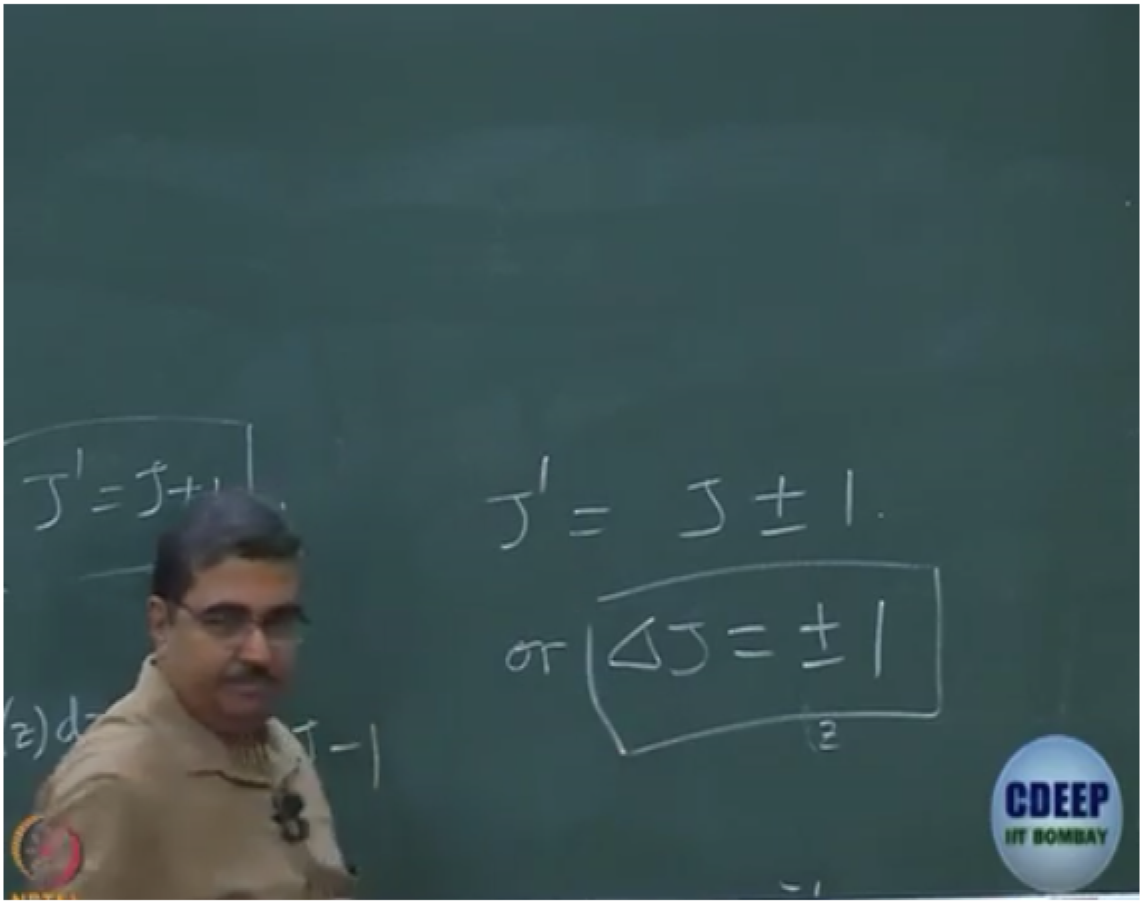

Or is that right? It is right, and that is the selection rule that you're already familiar with, this is how it comes.

Question? Doubts? Comment? Nothing else? Sure? Yes, so see what I'm trying to say is if you are talking about mu Z then delta J = + - 1 is not the only selection rule, the other selection rule is delta M has to be equal to 0, so it's actually a pair of selection rules, delta J = + - 1 and delta M = 0, and of course mu 0 must be nonzero, these three together give you the condition for microwave activity, if you are talking about the Z component of the dipole moment.