INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

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MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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Lecture No. – 63
No Splitting For A2 Systems

Alright, we conclude our course today with the discussion of a question that we had asked earlier that take ethanol, we say that there is a certain kind of splitting of CH3 proton resonances because of the CH2 protons, coupling with CH2 protons. Why is it that there is no splitting of CH2 resonance because of coupling of this CH2 protons, okay.

Is there no coupling? That is what we generally think right when we talk about NMR, I think it is even casually said that protons with same chemical shift do not couple with each other, perhaps that statement has been made in some course or the other, that statement is not quite accurate, there is no reason, why protons with same chemical shift should not couple with each other, after all the basis of coupling is that they are magnets, so why will they not couple with each other.

So today let us see how we can perform a time independent perturbation theoretical treatment of coupling of protons with same chemical shifts and whether that leads to any kind of splitting in the NMR spectrum of the systems.

So what we are discussing today really is no splitting for A2 systems.
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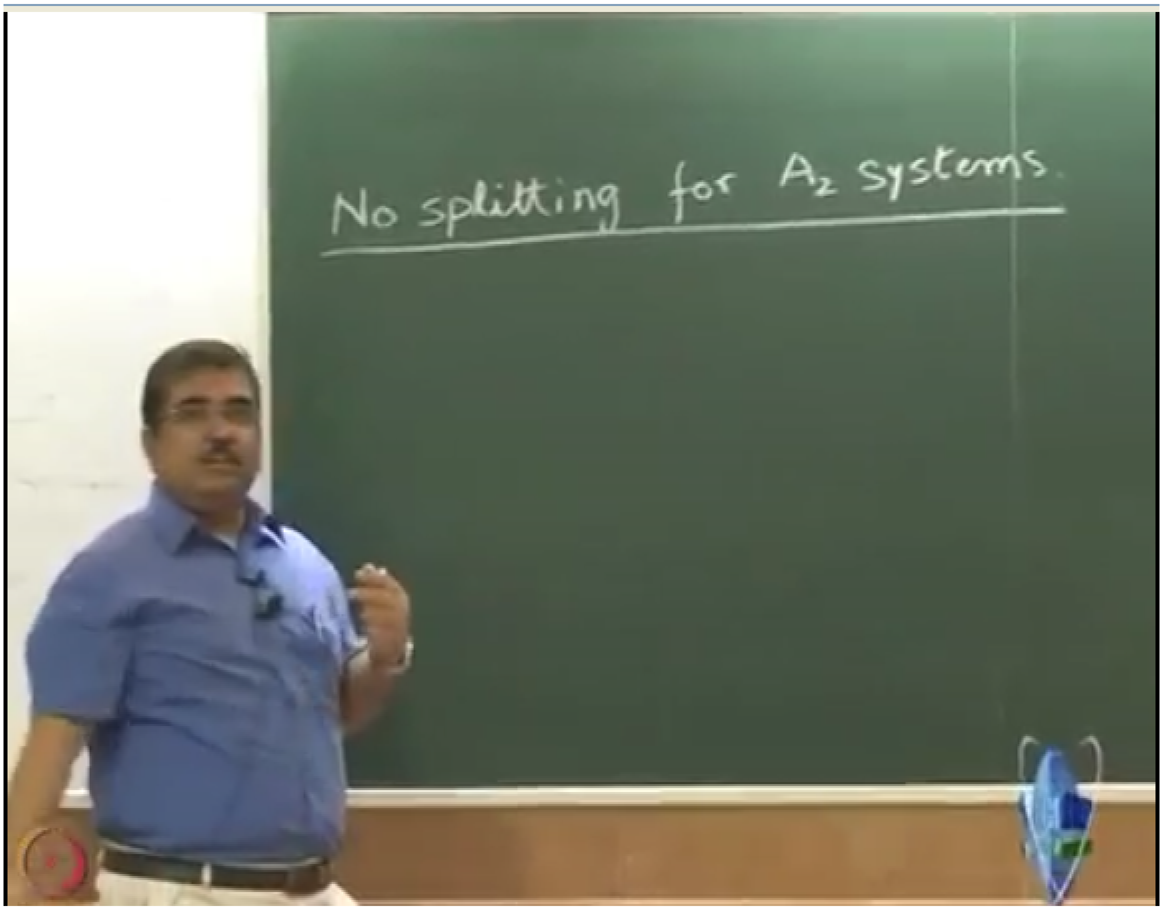

To start our discussion as usual we are going to write the Hamiltonians and we are using perturbation theory, so our job is to first write the unperturbed Hamiltonian and then write the perturbation correction to the Hamiltonian, so can you help me with this? What is the unperturbed Hamiltonian going to be in case of A2 system? Let us remind ourselves what it was for th AX system, yesterday we have discussed the AX system.

What was the Hamiltonian for AX system? –Gamma B0 1- sigma A IZA right, and then what was the next term? –Gamma B0 1-sigma X multiplied by IZX operator, in this case what is the difference from AX system?

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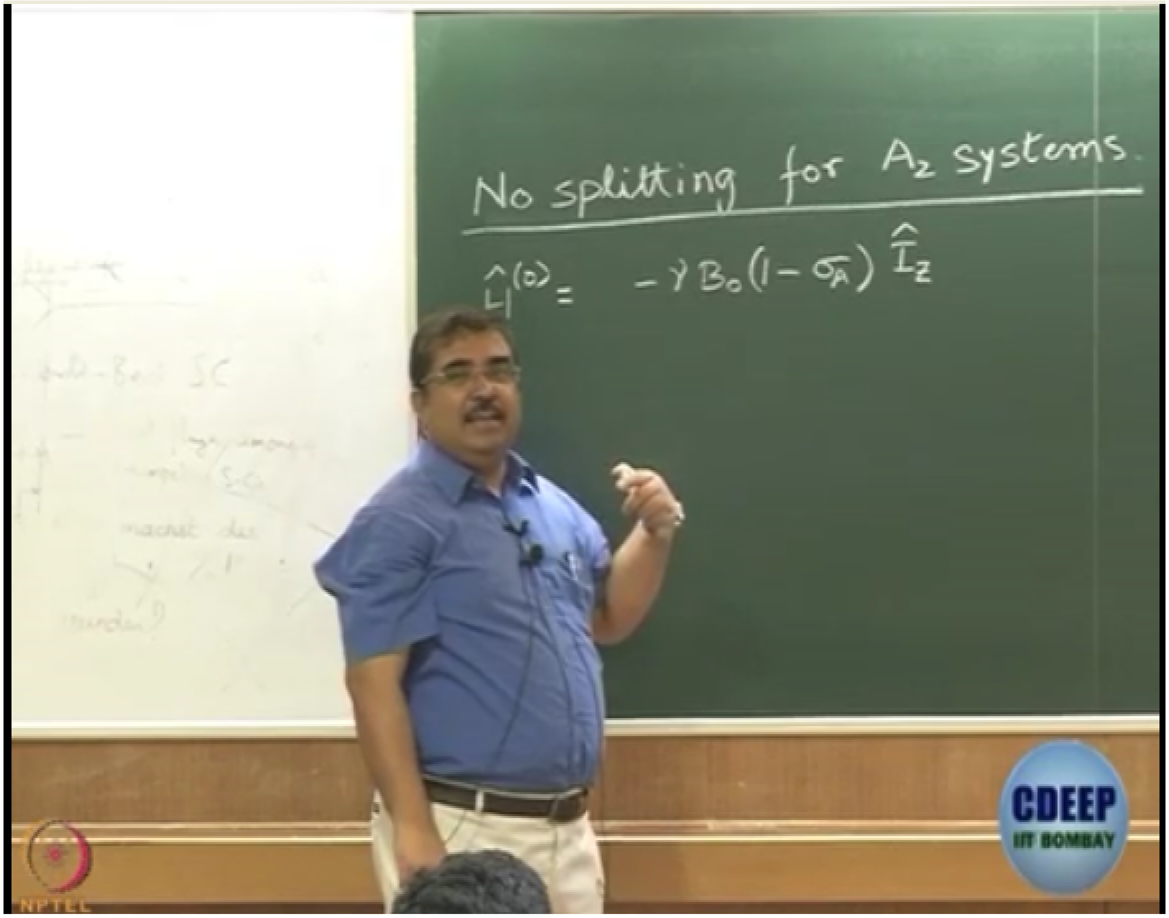

There we had two kinds of shielding constants, right, sigma A and sigma X, here since it’s A2 in both the terms we have to use sigma A, there is no sigma X, right, if that is the case what I’ll do is instead of writing IZA and IZX there are still 2 nuclei right, so I’ll write IZ1 and IZ2 and I hope you don’t have a problem if I write it like this.

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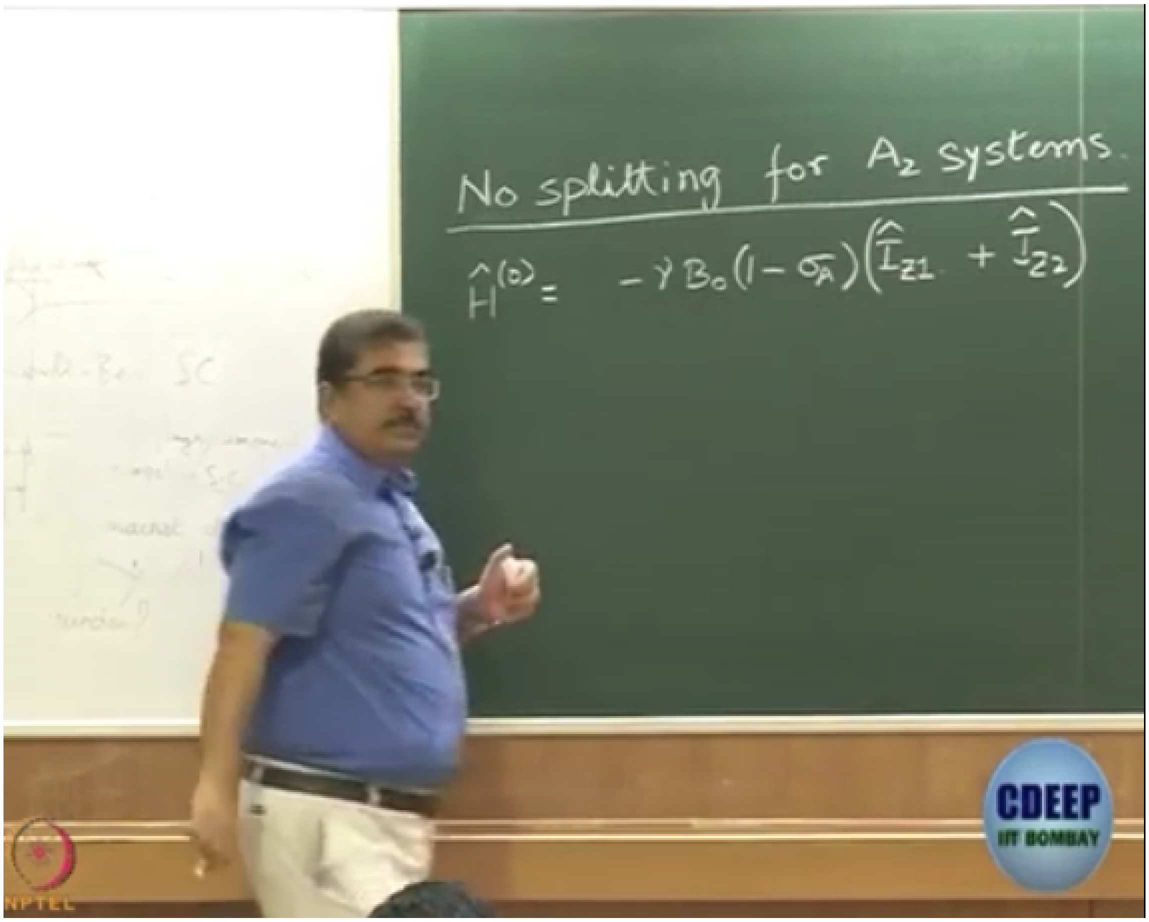

Do we agree that this is the unperturbed Hamiltonian? By the way in case if I have not said it earlier this entire discussion is from McQuarrie and Simon's book, it is also there in Rebel's book but I find McQuarrie and Simon to be very easy to understand in this part so you can follow that book. Are we all okay with the unperturbed Hamiltonian? Right H0 is –gamma B0 x 1 –sigma A multiplied by IZ1 + IZ2, where 1 and 2 denote the two nuclei both of which are of A.

What will be the perturbation term? First order correction to the Hamiltonian, it will be like earlier HJ this time I'll not write JX, I'll write HJ AA divided by H cross square multiplied by what? I1.I2, is that right? So I can might as well expand since we discussed it yesterday, I'll write like this IX1.IX2 + IY1.IY2 + IZ1.IZ2, this here is my first order correction to the Hamiltonian, okay and of course,

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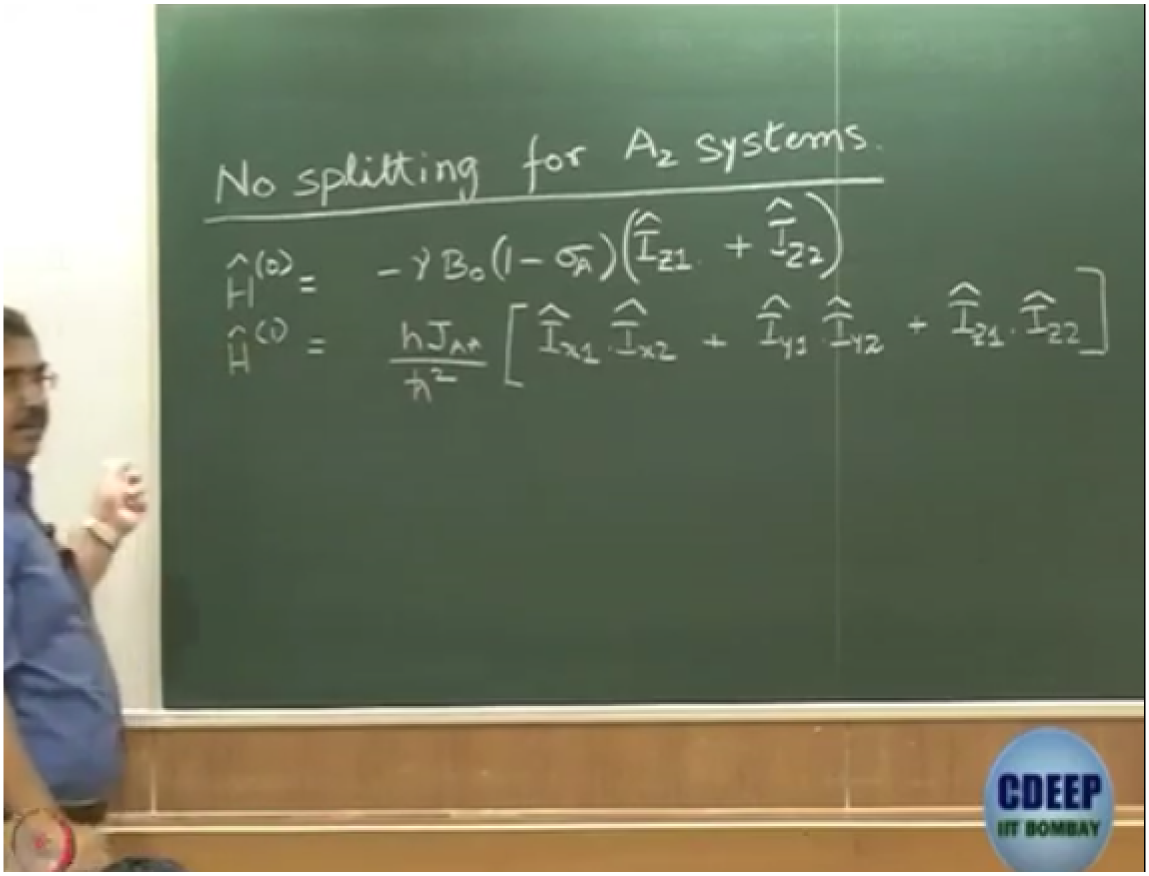

now what is the next step you have to write wave functions right, and as we discussed yesterday it is enough if you work with unperturbed wave functions, we don't really need to bother about what the perturbation functions would look like, because our only job is to find the first order correction to energy and when we want to find first order correction to energy we actually end up using the unperturbed wave function so that is no issue, we don't have to really worry about what changes there in the wave function.

So now tell me what are the unperturbed wave functions? Yesterday I wrote sai, so today let me write phi, just to be inline with McQuarrie and Simon's book this is one of the reason, but phi 1 will be as usual, now I'll write alpha 1 alpha 2, yesterday we had written alpha A alpha A sai, so here I'll write alpha 1, alpha 2 and let me write phi 4 as beta 1 beta 2, what is phi 2 and what is phi 3?

What was phi 2 yesterday? For AX system what was phi 2? Beta 1, beta A alpha X, and phi 3? Alpha A beta X, can I keep the same wave functions? Just substituting A and X by 1 and 2, is that yes, is that a no? Yes, no, why? Why do we take a linear combination? So we come back to something that we learnt earlier remember indistinguishability, yesterday we were talking about AX system, there was a difference between the two nuclei, right, they experienced different kinds of fields, so it was, I could distinguish between A and X, now I cannot, and since I cannot then we have to go back to our old friends, the linear combinations of the wave function, okay.

Same thing that we did in electronic spectroscopy, which does that there we were talking about electronic spins, here we are talking about nucleus spins, that's the only difference, so this is

1/root 2 alpha 1 beta 2 – beta 1 alpha 2, this one is 1/root 2 alpha 1 beta 2 + beta 1 alpha 2, right what is my job now?
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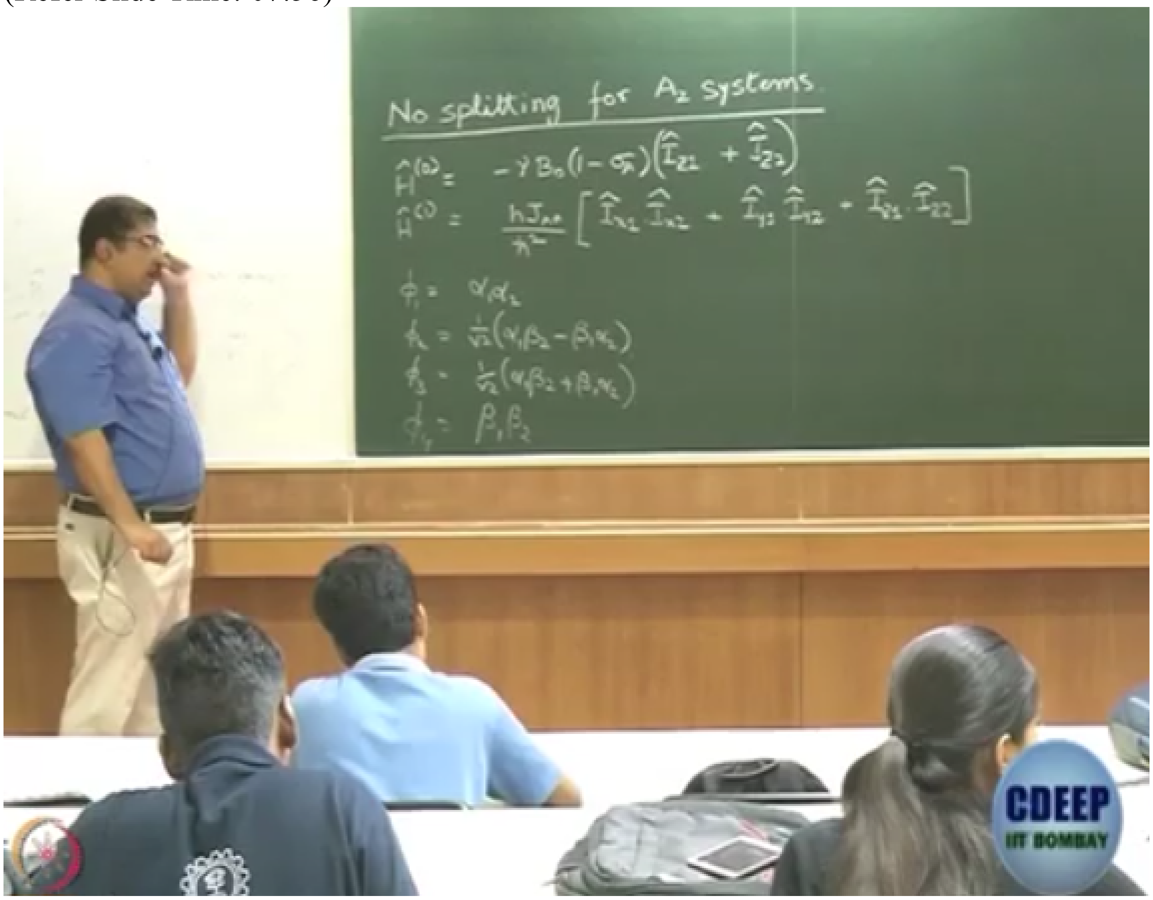

My job is to find the energies of the four levels denoted by the wave functions phi 1, phi 2, phi 3 and phi 4 and work out the transitions, and when we do that as you will see something new will crop up that we did not discussed, that we did not need to discuss yesterday, right, so these two wave functions phi 1 and phi 4 are exactly the same as the wave functions that we handled yesterday, so there is no reason why their energies should be of any different form compare to what we had yesterday, agree? Yesterday also sai 1 was alpha 1 alpha 2, right? Sai 4 was beta 1 beta 2, so whatever expression we got for their energies we should get similar expressions here, you can do the math it will be the same thing, so maybe I'll just write that. Where do I write? Maybe I'll write here, I'll keep that part available.

What will be the energy of phi 1? What was the expression yesterday? Yes -H cross gamma B0 multiplied by, yes 1-, what was that? Alpha A + alpha X divided by 2, isn't it? Sorry, why I'm saying alpha, sorry, sigma, sigma, sorry my mistake, sigma A – sigma X divided by 2, was that right? Today is there any difference between sigma A and sigma X? So what is sigma A + sigma X divided by 2? Sigma A, so now I'll get 1-sigma A that's it, what else did we do? We wrote this as nu 0, actually H nu 0, when nu 0 is a Larmor frequency of a bare proton, so if you want to write it in terms of frequency then this is going to correspond to frequency of A nucleus, alright.

What was the correction term? What was the first order correction? HJ, there it was? AX, here it is AA divided by 4, okay, I'm not doing the math, please do it yourself you come to the same result,

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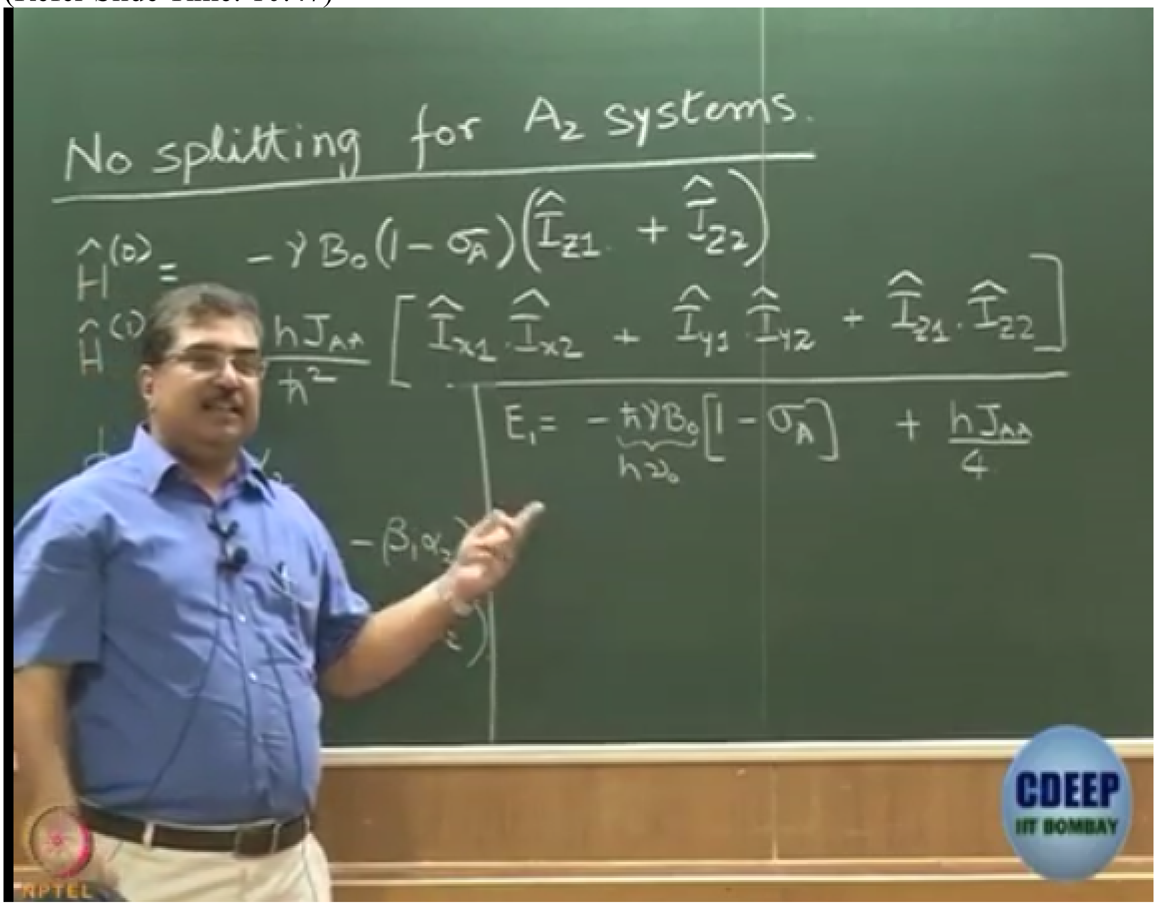

the math is exactly similar to what we did for AX yesterday with one less complicating factor there is no sigma X, there is no JX everything is A, there is no X, okay, so E1 I hope we can agree on that, what is E4? Maybe like yesterday we'll write the same thing, E4 will be just this thing with a plus sign, what about this? Will this become minus? No, so both alpha alpha and beta beta states actually get de-stabilize as a result of coupling, so the second term will still have a plus sign, the only difference that we'll have as you saw yesterday is that in case of level 1 will have a minus sign here, there will be a stabilization, in case of level 34 there will be de-stabilization and we'll have +1.

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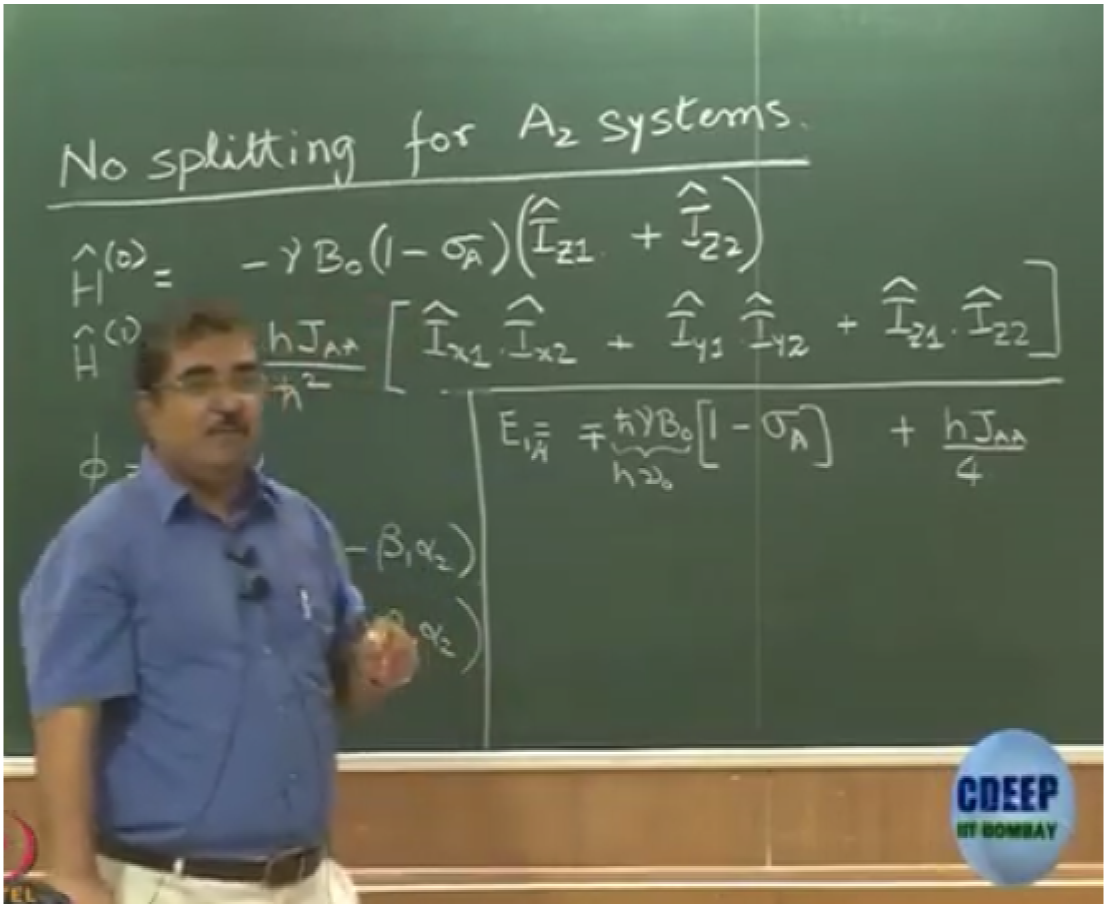

Now let us see what is going to be the scenario for E2 and E3? E2 and E3 of course should be different from what we obtained for the AX case, right, because the wave functions are different, let's see what it is. This is where I'll write the energies, and this is where I'll work it out, so let's work out E2(0), how do I get E2(0)? I make this Hamiltonian operate on phi 2, right, so what do you get then? –Gamma B0 1 – sigma A IZ1 + IZ2 this whole thing operates on 1/root 2 alpha 1 beta 2 – beta 1 alpha 2, what do I get? What do I get? How many terms do I get? IZ1 operates on alpha 1 beta 2, and on beta 1 alpha 2 so two terms there, IZ2 operates on alpha 1 beta 2 and beta 1 alpha 2, two terms there, but one thing I hope we can understand is that, since I'm using IZ it will always be eigenvalues, isn't it? It will always be an eigenvalue equation.

And eigenvalues are going to be either +H cross by 2 or –H cross by 2, so what I'll do is I'll write these eigenvalues here, and I'll write the wave function here, oh 1/root 2 is common let's not bother about that, that will come anyway, okay.

So what happens when IZ1 operates on alpha 1 beta 2, how much do I get? I get back alpha 1 beta 2 first of all, what is the eigenvalue? Yes, little louder IZ1 operating on alpha 1 beta 2, so beta 2 is the constant as far as IZ1 is concerned, and what do you get when you operate IZ1 on alpha 1? H cross/2 alpha 1 right, so that's why I've written alpha 1 beta 2 there and the eigenvalue is H cross/2.

What happens when IZ1 operates on beta 1 alpha 2? –H cross/2, and I write this one here –beta 1 alpha 2, is that okay? Next is IZ2 has to operate on alpha 1 beta 2 and –beta 1 alpha 2, IZ2 operating on alpha 1 beta 2 what do you get, what is the function I get back? Alpha 1 beta 2, and what is the eigenvalue? IZ2 operating on alpha 2 and beta 2 – H cross/2, excellent, now when IZ2 operates on –beta 1 alpha 2 I have –beta 1 alpha 2, this I can close, what is the eigenvalue? IZ2 operating on beta 1 alpha 2, I've taken the minus there already so +H cross/2.

So what do I have here? I have 2 into the wave function isn't it? So it is an eigenvalue equation, but what is the eigenvalue? 0, is that right?

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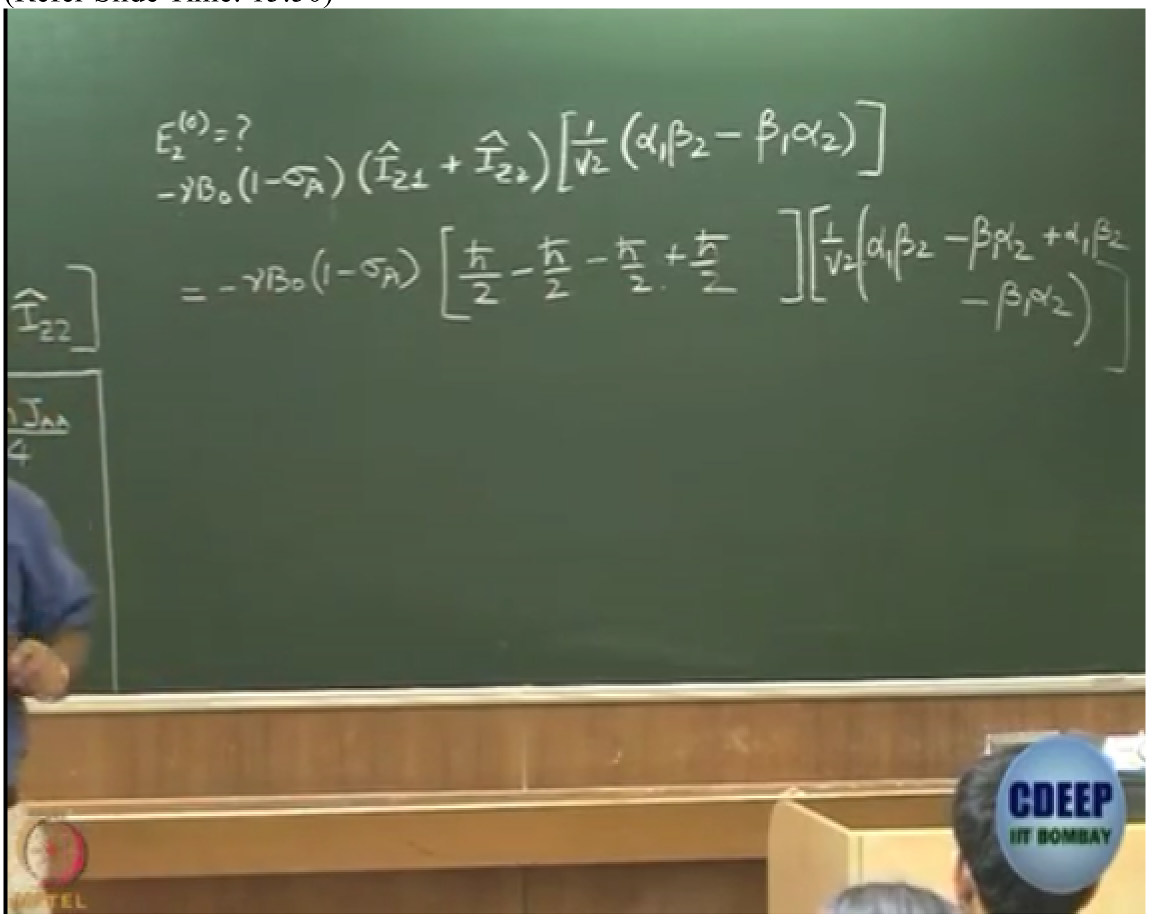

Eigenvalue is 0, is that surprising? First time I was surprise, why is it not surprising? You do so much of math and then get eigenvalue 0, why is it surprising, I should be surprised.

See earlier what did we have, we had alpha and beta right, so stabilization of one, de-stabilization of one was not the same, so you had some net energy, in this case one is alpha one is beta both are equivalent, so stabilization of one is exactly offset by the de-stabilization of the other, energy is 0, okay, so what we learn is that your energy of, well at least E0 le tem write of level 2 that is 0, okay, Akansha? I'm sorry, can you say that again? How did I get this? Let's do one term then, open which bracket? No we did everything, so what do we, if you open the bracket you have I, I'll just write I1 and let me call this, I don't know chi 1 and chi 2, so I'm going to have, this is I1, this is I2, so I have I1 chi 1 – I1 chi 2 + I2 chi 1 – I2 chi 2, is that right?

And then let us look at one of this term, so what is I1 chi 1? That is your, you can write like this I'm not writing 1/root 2 here, beta 2 IZ1 alpha 1, isn't it? Because IZ1 will not operate on beta 2, beta 2 will be a constant as far as its concerned, what do I get sum here? IZ1 alpha 1 is H cross/2 alpha 1, so you get back H cross/2 alpha 1 beta 2, see H cross/2 alpha 1 beta 2, that is how you evaluated every term. Yes, each term is H cross/2 but then it's not always H cross/2, if it is beta wave function it will be minus, so that's why in two cases it is +H cross/2, in two cases it is –H cross/2 that is why it cancels off. Are you satisfied? You understood? Very good.

She doesn't look very convinced, which multiplication? So that is what I just explained, this part you are okay right, so I have to do it term by term, isn't it? What is the first term? First term is IZ1 operating on alpha 1 beta 2, so let me explain in a different way now, so what I have is IZ1 operating on alpha 1 beta 2, that is the first term here.

So what will be the second term? IZ1 operating on –beta 1 alpha 2, so –IZ1 operating on beta 1 alpha 2. What is the third term? IZ2 operating on alpha 1 beta 2. What is the last term? -1Z2 operating on beta 1 and Z, alright.

Now what I am saying is IZ1 operates on alpha 1, but not on beta 2, so beta 2 is a constant as far as this operator is concerned, so you can take beta 2 out. Here also you can take alpha 2 out, in this case take alpha 1 out, and with this case take beta 1 out, what is IZ1 alpha 1? Yes, so that way we get, yes, what are you saying? Okay, you're right, you're right, so let me, I think, yeah, I made a mistake, fine, so let me write like this, yeah, okay, you have to take into account, then it falls in place, right, it will work out, fine, so we get 0, work it out for phi 3 you will get 0.1 second, okay.
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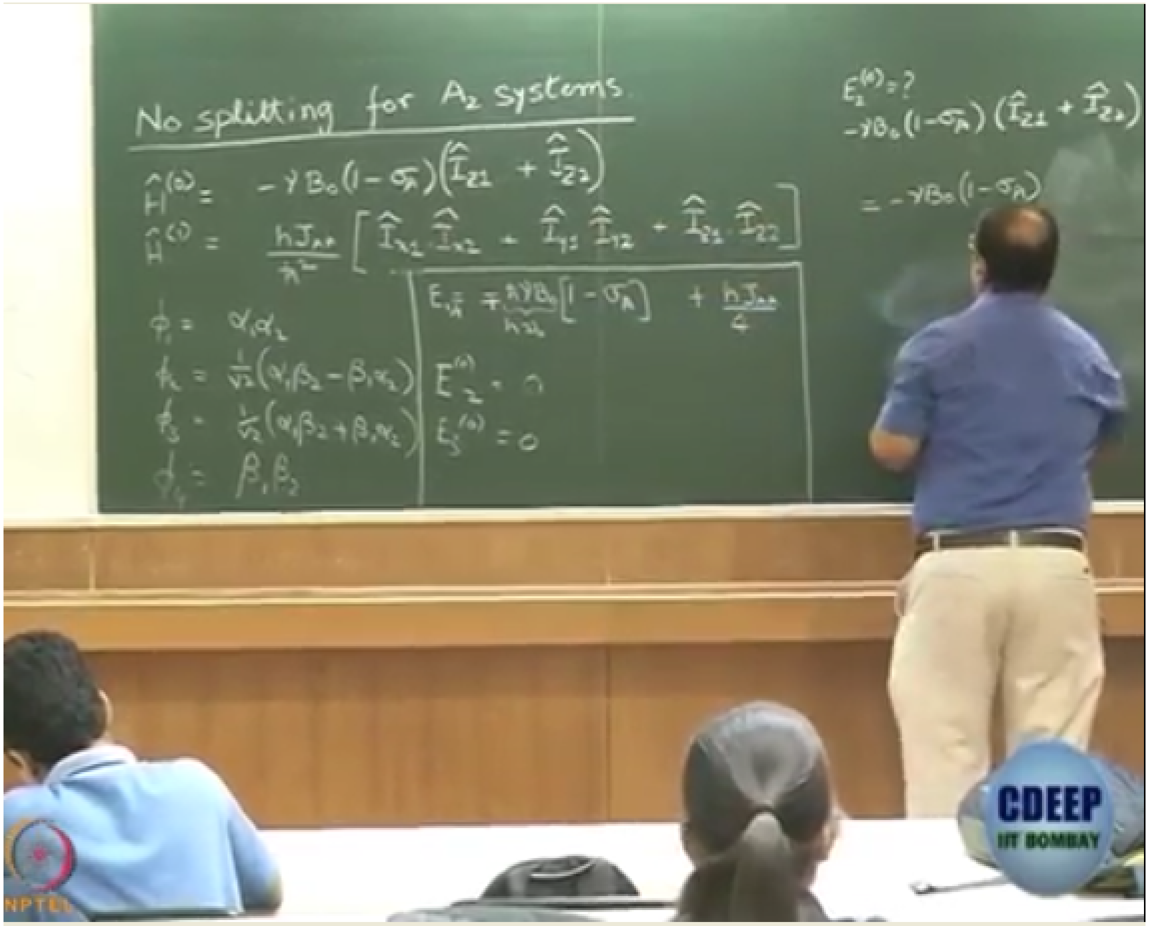

So now what is the picture that we get for the uncoupled scenario? This is your phi 1, this is phi 2 and phi 3, this is phi 4, what is the energy gap here?
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This is 0, this is your –nu 0 multiplied by 1 – sigma A, what is that? Well that H multiplied by that, so essentially this is H nu A isn't it? See if I just write in terms of frequencies this is nu A.

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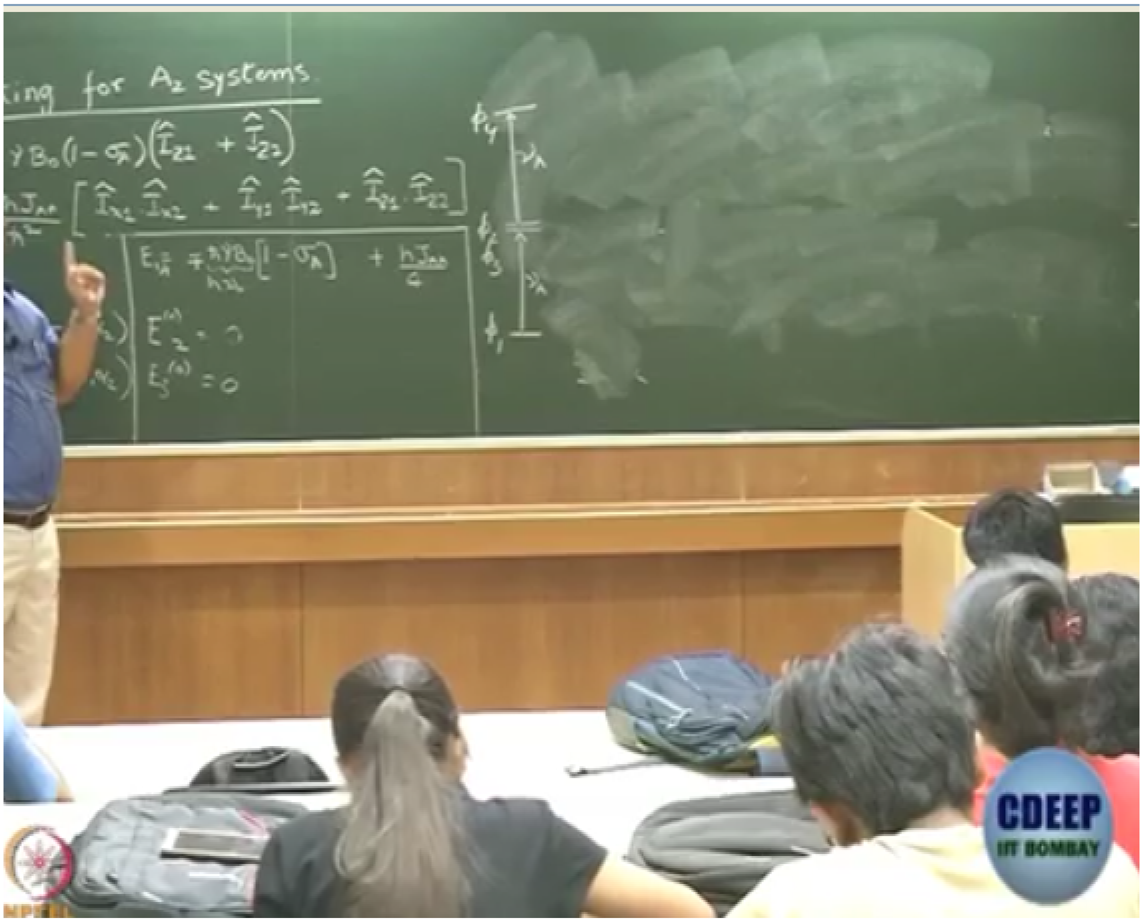

What about this? This is 0, this is + nu 0 multiplied by 1 – sigma A that is once again, if you write in terms of frequency this is nu A, so in the uncoupled scenario you expect to get one line at the resonance of A, okay.

Now what is the correction term? Now to do the correction term again we have to remember what we get, so tell me IX operating on alpha, what do I get? IX operating on alpha, yes, H cross/2 multiplied by beta, it's not an eigenvalue equation. EY operating on alpha what do I get? Yes, IY operating on alpha this is what we discussed yesterday right, IH cross/2 multiplied by beta, and IZ operating on alpha that we know it is H cross/2 alpha that is the only eigenvalue equation, okay.

What happens when IX operates on beta, what do you get? IY, this is something we discussed yesterday without derivation, this is what comes from the spin matrixes since we don't really talk about, we do not have the scope to get in to the quantum mechanics and all that we have to take this extrametrical. IY operating on beta gives us, yeah what is this one? Minus, so this is the thing to remember, -IH cross/2 alpha, IZ operating on alpha that of course we know is –H cross/2, sorry why am I writing alpha? IZ operating on beta that of course is –H cross/2 beta, alright.
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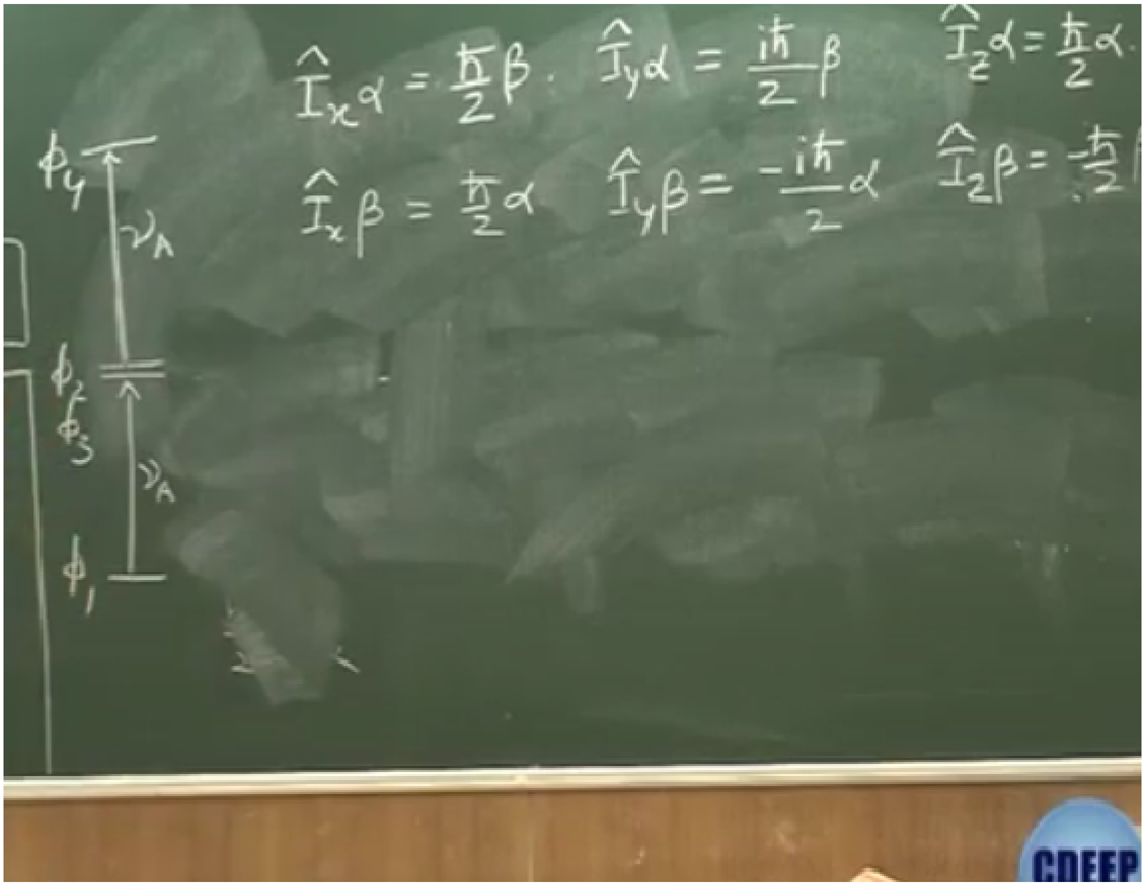

Now so essentially we have to see what happens when this operator operates on things like alpha 1 beta 2 – beta 1 alpha 2 or alpha 1 beta 2 + beta 1 alpha 2, so to make our job easier at the end, let us do something, let us see what is IX1 IX2 operating on alpha 1 beta 2, what is IY1 IY2 operating on alpha 1 beta 2 and so on and so forth, we'll just write down those terms and then we'll take it from there. So IX1 IX2 operating on alpha 1 beta 2, that will be IX1 alpha 1 operating multiplied by IX2 alpha not alpha, beta 2, what do I get? IX1 alpha 1 is what? H cross/2 beta 1 and IX2 beta 2 is H cross/2 alpha, 1 or 2? Alpha 2, so I get H cross square/4 beta 1 alpha 2, is that right? So this is what it's going to happen throughout, okay, as long as you are using X or Y, 1 and 2 will get interchanged,

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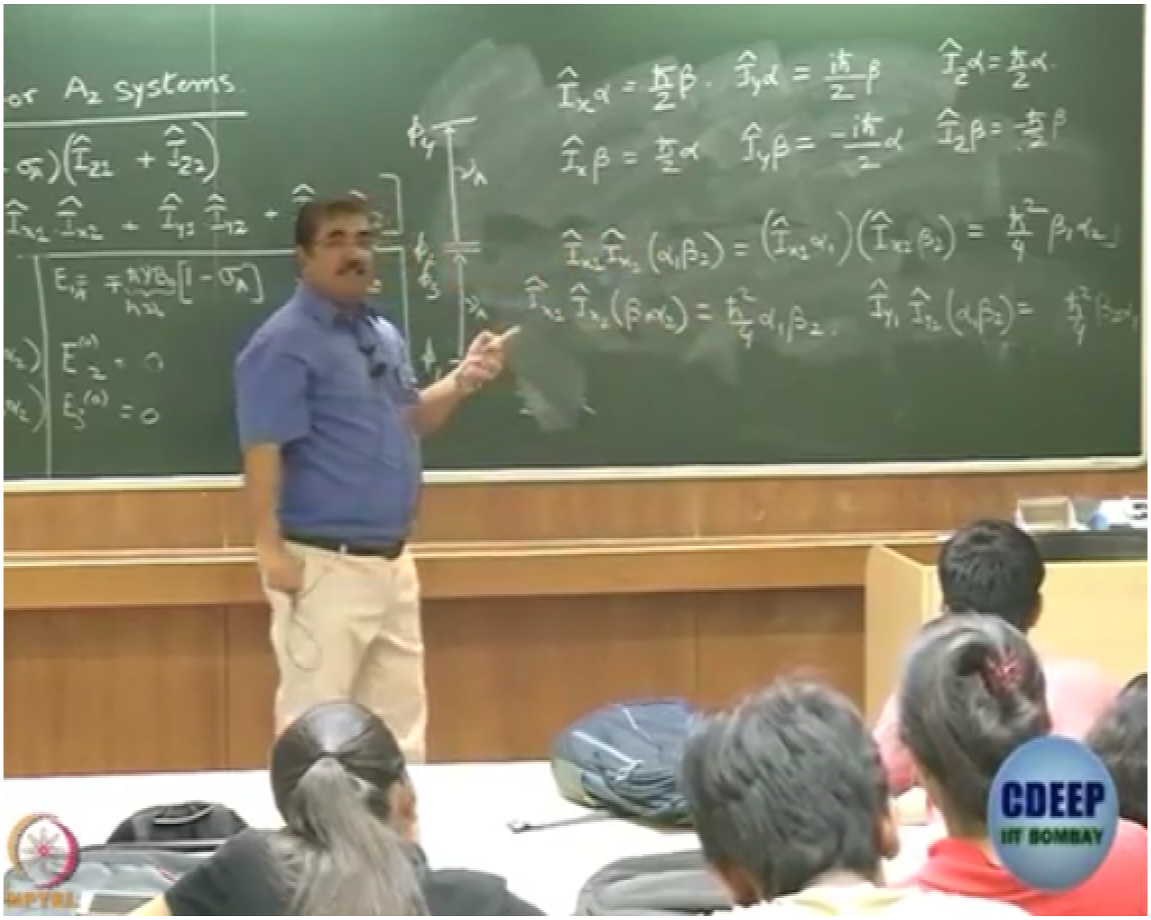
as long as you use Z they will not get interchanged, and it will always be H cross/4, whether there is a plus sign or minus sign that we have to see, okay.

IX1 IX2 alpha 1 beta 2 that is done, what is your IX1 IX2 beta 1 alpha 2, what will it be? Now I think we can work it out mentally. IX1 IX2 beta 1 alpha 2 what will it be? H cross square/4 alpha 1 beta 2, is that right? Then IY1 IY2 alpha 1 beta 2 what will that be? IY1 IY2 alpha 1 beta 2, so first of all it will become beta 2 alpha 1, then you have H cross square/4 also, what is the sign? (Refer Slide Time: 27:50)



Plus right, I x I is -1 and there is a -1 already. Oh sorry, sorry, sorry I change the sequence as well as the indices, beta 1 alpha 2, okay.

What is IY1 IY2 operating on alpha 1, alpha 1 beta 2 we've already done, so beta 1 alpha 2. What will it be? H cross square/4 alpha 1 beta 2, plus or minus? Plus, IZ1 IZ2 alpha 1 beta 2 what is that? –H cross, and this time there is no exchange so alpha 1 beta 2, H cross square/4 alpha 1 beta 2, and what is IZ1 IZ2 operating on beta 1 alpha 2? IZ1 IZ2 operating on beta 1 alpha 2 what do I get here? Did I write the minus sign? Yeah –H cross square/4 beta 1 alpha 2, okay, this is what we'll need in order to work out the correction, okay.

Now what is the expression, what is the expression for the first order correction to energy? First order correction is sai 0, first order correction to Hamiltonian sai 0 integrated with all space, right, this is what we have learnt from perturbation theory, so essentially what we will try to do is, we'll try to evaluate this H1 sai 0 and then lets multiply by sai 0 integrate over all space.

What is H1 sai 0 let us see. We are talking about phi 2, right? What is H first order phi 2? That will be HJ AA, achha, now what we have seen there is that no matter which term we use will always get either + or –H cross square/4 right, so I can take H cross square/4 outside the bracket so that H cross square and this H cross square will cancel, and you are left with HJAA divided by 4, I'm trying to evaluate this, what happens when this first order correction to Hamiltonian operates on phi 2, right, phi 2 is alpha 1 beta 2 – beta 1 alpha 2, now take any of this operators, operate on any of this terms you always get either + or -H cross square/4, right, so I hope it's not very difficult to see that H cross square/4 will be common outside the bracket, and the moment we do that this H cross square that H cross square will cancel, you will be left with HJAA divided by 4, now that will be multiplied by whatever, right.

So once again let us try to do it like this, here I'll write the numbers, here I'll write the wave function, achha, so IX1 IX2 operating on phi 2, 1/root 2 is common anyway so I'll write it here, so IX1 IX2 operating on alpha 1 beta 2 what do I get? Alpha 1 beta 2, why did I erase it? That is the first thing I erased, is that right? Okay, so H cross square/4 I've taken out, so here I get 1, achha so if I write it that way again I'll land in the same problem, isn't it? So let's now try to do that, okay I have understood where the problem was. The problem was in my writing, 1/root 2, okay, I can take H cross square/4 outside the bracket there is no problem with that, isn't it? Sorry, okay let's see, we'll just do it, 1/root 2 you can take that's not a problem,
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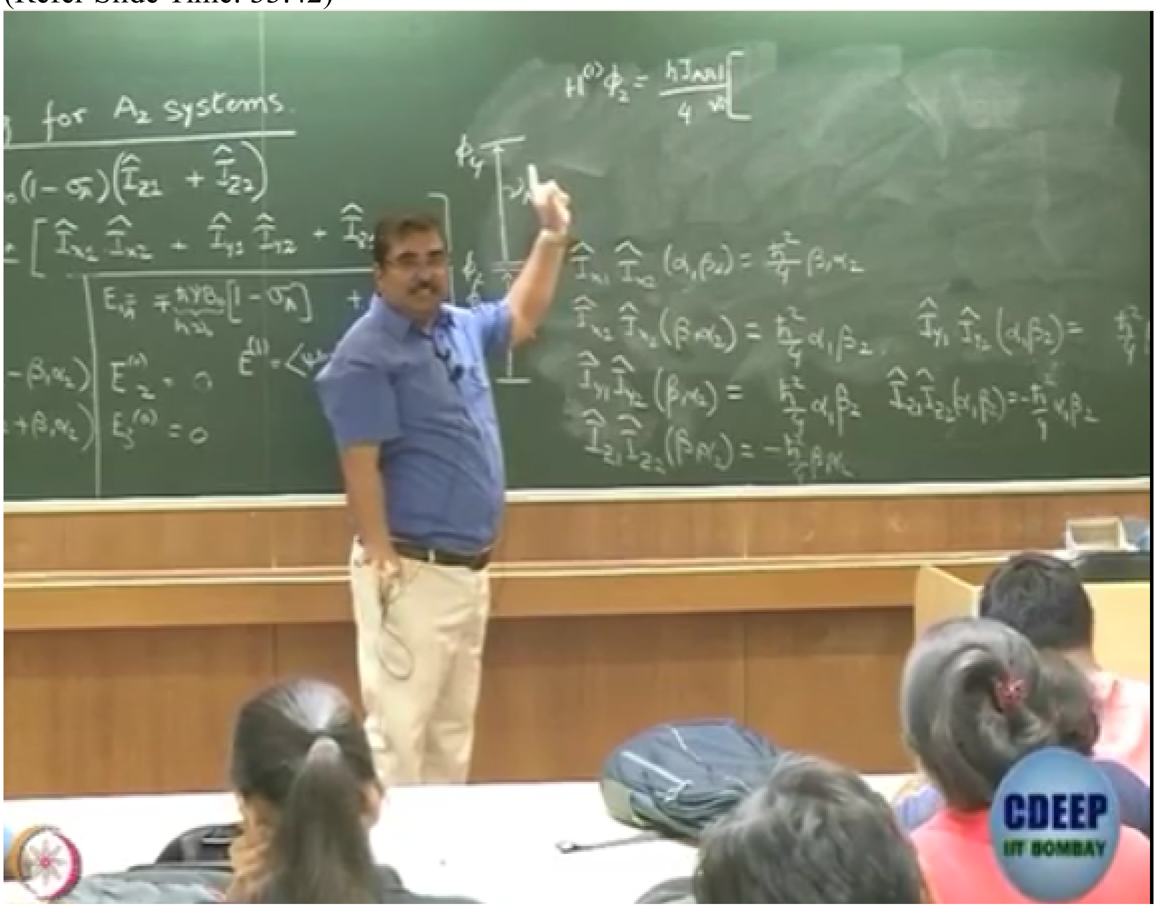

it will be 1/2 fine, what are you saying?

Right now I've only operated, I'm not integrating yet, it is 1/root 2, it will become 1/2 when you multiply also, okay, so first I get beta 1 alpha 2, then what do I get after that, here? Beta 1 alpha 2 I've written, next is IX1 IX2 operates on –beta 1 alpha 2, then wait, say which one you are operating? IY1 IY2 operates on alpha 1 beta 2, what do I get? Yeah, plus or minus? We need agreement on that, plus or minus? Don't forget we have taken H cross square/4 outside the bracket, okay, IX1 IX2 operating on alpha 1 beta 2 has given us beta 1 alpha 2 multiplied by H cross square/4, then IX1 IX2 operating on beta 1 alpha 2 also gives us H cross square/4 beta 1 alpha 2, but there is a minus sign here already, right, so that's why we have written –alpha 1 beta 2.

Next is IY1 IY2 operating on alpha 1 beta 2, what do I get? H cross square/4 beta 1 alpha 2, plus or minus? Plus, H cross square/4 has gone out, so beta 1 alpha 2. Next one, IY1 IY2 operates on beta 1 alpha 2, what do I get? Alpha 1 beta 2, plus sign or minus sign? Minus, what is it beta 1 alpha 2? Alpha 1 beta 2, then what is the next one?
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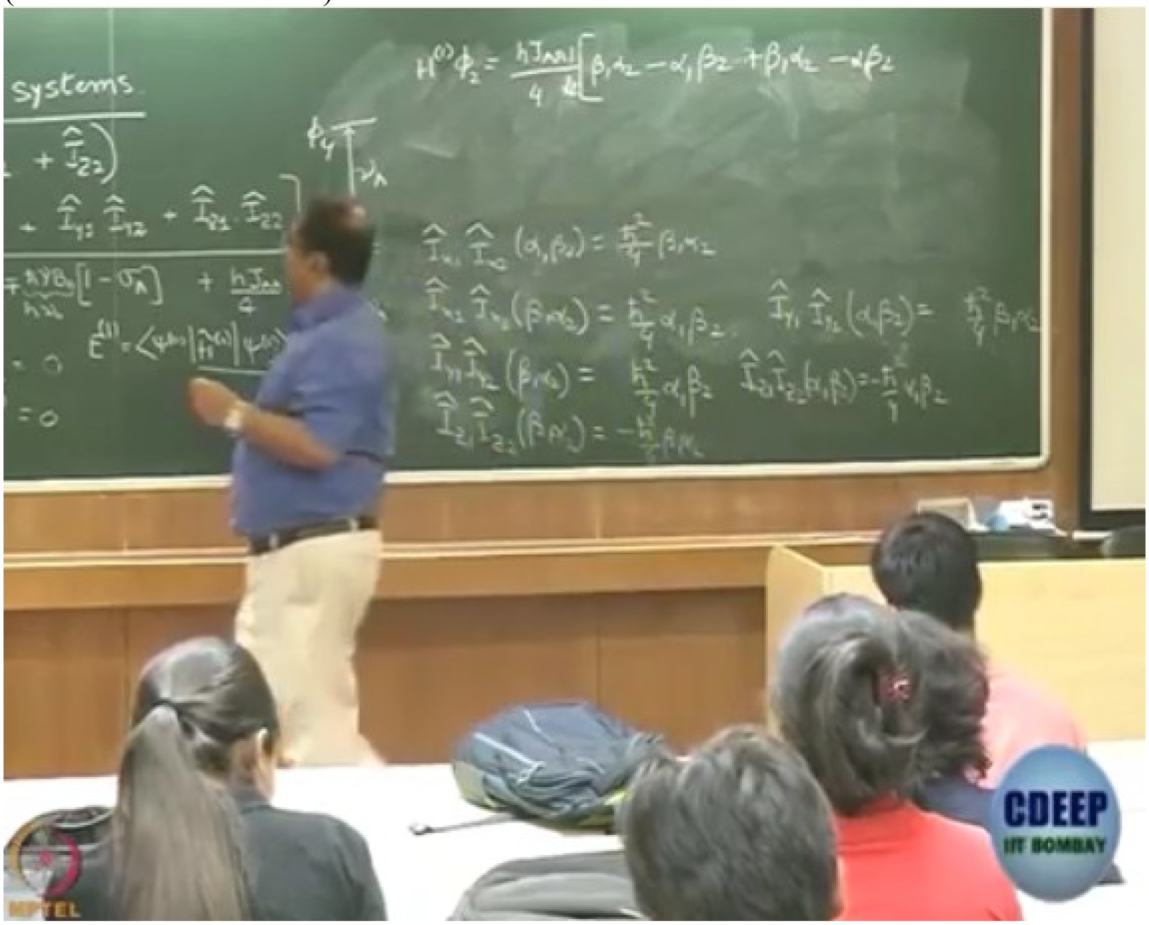

IZ1 IZ2 right, operates on alpha 1 beta 2 what do I get? IZ1 IZ2 operates on alpha 1 beta 2, -alpha 1 beta 2.

Last IZ1 IZ2 operates on beta 1 alpha 2, minus but then there is another minus already, right, plus beta 1 alpha 2 right, what do I have then? What do I have? Beta 1 alpha 2 + beta 1 alpha 2 + beta 1 alpha 2 – alpha 1 beta 2 - alpha 1 beta 2 - alpha 1 beta 2, right, what was the wave function? Alpha 1 beta 2 – beta 1 alpha 2 right, so this is how I'll write it, -3HJAA divided by 4 into 1/root 2 alpha 1 beta 2 – beta 1 alpha 2, is that right?

And what is that wave function? 1/root 2 alpha 1 beta 2 – beta 1 alpha 2,
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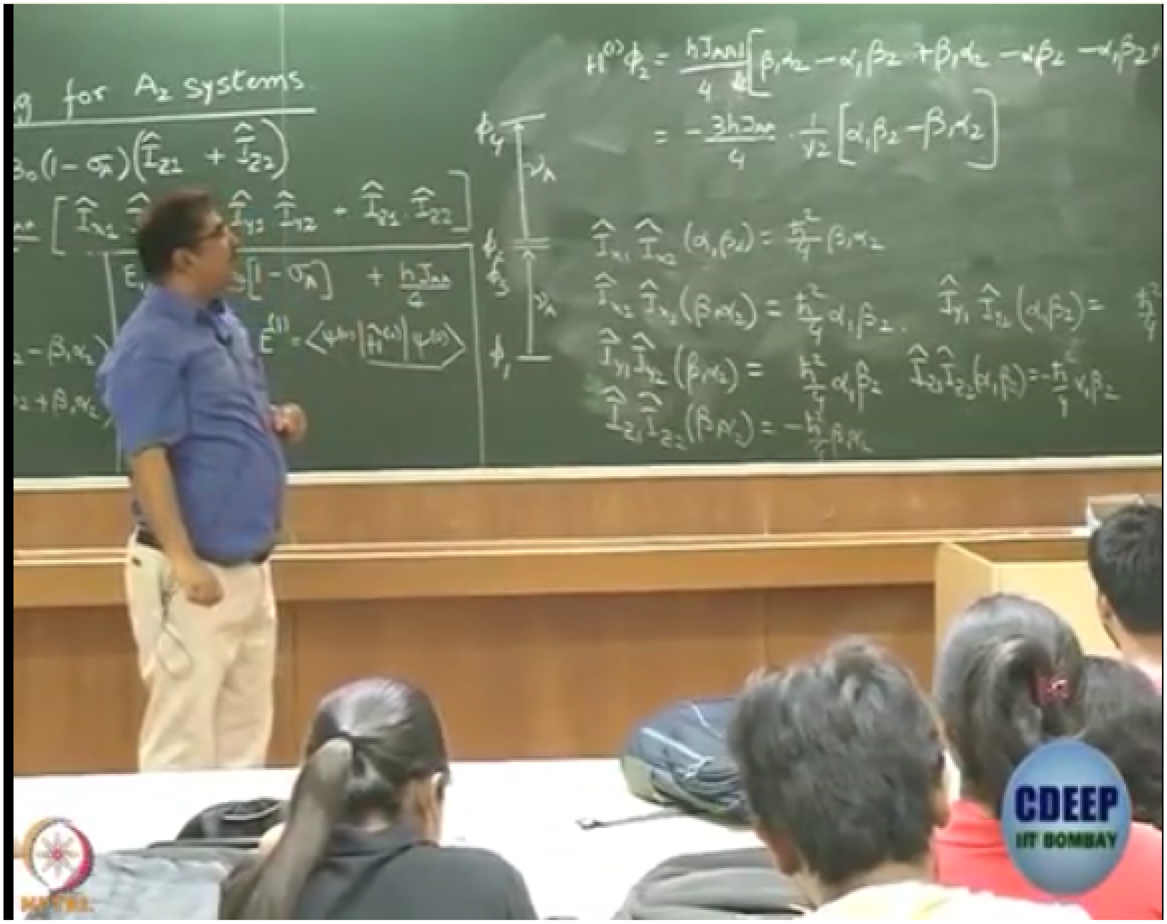

it is phi 2, so I can write phi 2, so then what is the first order correction to E2? You have to left multiply by phi 2 integrate over all space, what do you get? Integral 5 to star, what is it? That is 1, so -3HJAA/4, so what we get is, E2 is then 0 – 3HJAA divided by 4,

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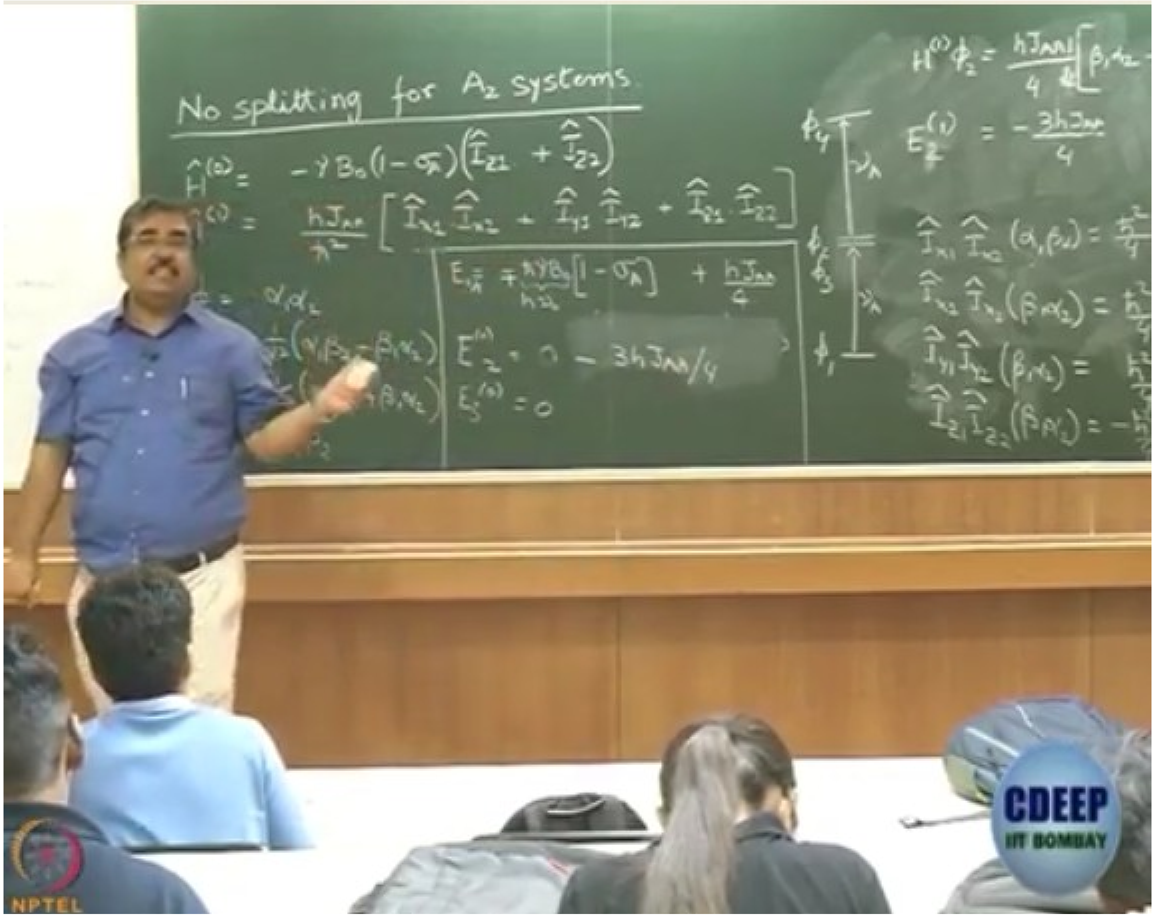

and that is the different result from what we got yesterday for the second energy level, isn't it? Yesterday what we saw is alpha-alpha and beta-beta where destabilized by HJX divided by 4 and alpha beta and beta alpha were stabilized by the same amount, that is not the case here, alpha-alpha and beta-beta are still destabilized by HJAA/4 this time, but what we see is alpha beta – beta alpha is stabilized by 3HJAA/4, alright, so in fact from there itself perhaps we can figure out what will be the first order correction to energy of phi 3, that's total change in energy should be 0, isn't it? Stabilization has to equal to destabilization, so when do you get 0? Yeah, what will be the amount of stabilization of E30? It will be HJAA/4 isn't it? Because 2 into HJAA/4 + HJAA/4 that is equal to 3HJAA/4 that added to -3HJAA/4 = 0, but let us see if you get that.

So let's do the same exercise, but this time I want to use phi 3 instead of phi 2, can you tell me what is H first order operating on phi 3? Phi 3 is, well 1/root 2 is there of course, alpha 1 beta 2 + beta 1 alpha 2 this time, what will it be? Achha I have written, no, it will be H, suddenly I got distracted H, its okay.

What will the first term be? IX1 IX1 it's same thing actually I should not have erased,I should have just change the signs, but anyway I have erased now, cannot un-erase so just bear with me and tell me what the answers will be, IX1 IX1 operating on alpha 1 beta 2, yeah, alpha 1 beta 2 it will get beta 1 alpha 2 right? Plus or minus? Beta 1 alpha 2.

Then IX1 IX2 operating on beta 1 alpha 2, what will you get? +Alpha 1 beta 2, right, yeah, we made a mistake, no right? Next one what is it? Plus, alpha 1 beta 2 or beta 1 or alpha 2? Beta 1 alpha 2, then IY1 IY2 operating on beta 1 alpha 2 what is it? Alpha 1 beta 2. Then last two, IZ1 IZ2 operating on alpha 1 beta 2 – alpha 1 beta 2, and IZ1 IZ2 operating on beta 1 alpha 2 – beta 1 alpha 2, what do you have now? What do you have now? So first of all this is plus, this is HJAA divided by 4, right, that is phi 3, right? So first order correction to the third level is HJAA divided by 4, so this is the energy HJAA divided by 4, simple math but we just said you have to do it.

Now let me erase everything and draw the picture, what happened to this one? This got destabilized by an amount HJAA divided by 4, right, what happened to this? It was destabilized by the same amount HJAA divided by 4, what happened here? Phi 2 and phi 3 will degenerate, right if we did not consider coupling, the energies were 0.

Now phi 2 is stabilized and phi 3 is destabilized, destabilization is by same amount, HJAA divided by 4, stabilization is by Ohman, now I have, I have parallax. Stabilization here is by HJAA, sorry 3HJAA divided by 4, okay, so these are the 4 levels.

So looking at this we might think that we should still have splitting,
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but let us not forget something, alpha-alpha, beta-beta, alpha beta + beta alpha right, and this one is alpha beta – beta alpha, have we encountered this wave functions earlier in electronic spectroscopy, yeah, so alpha beta – beta alpha is unique right, and the other three form a group, what is that group of alpha-alpha, beta-beta and alpha beta + beta alpha what is that called? Triplet, and what about alpha beta – beta alpha? Singlet and we have studied spin selection rule, in fact we derived part of it, what is spin selection rule? You cannot have a singlet to triplet, triplet to singlet transition, so this transition is forbidden, okay.

Phi 1 to phi 2 or phi 2 to phi 3 or phi 3, not phi 3, phi 2 to phi 4 these are all spin forbidden transitions, okay, and what about phi 1 to phi 4? Is phi 1 to phi 4 allowed? Phi 1 is alpha-alpha, phi 4 is beta-beta,
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both are triplet, are they allowed? Is that allowed? Why not? One photon rule, one photon rule right, both have to be flipped that is not allowed, this is also forbidden by one photon rule.

What are we left with? Which are the transitions that are allowed? 1 to 2 is not allowed, 1 to 3 is allowed, achha I have drawn this wrongly right, this is also destabilized sorry, so 1 to 3 is allowed, 2 to 3 allowed? No, 3 to 4 is allowed, what is the energy of this transition?
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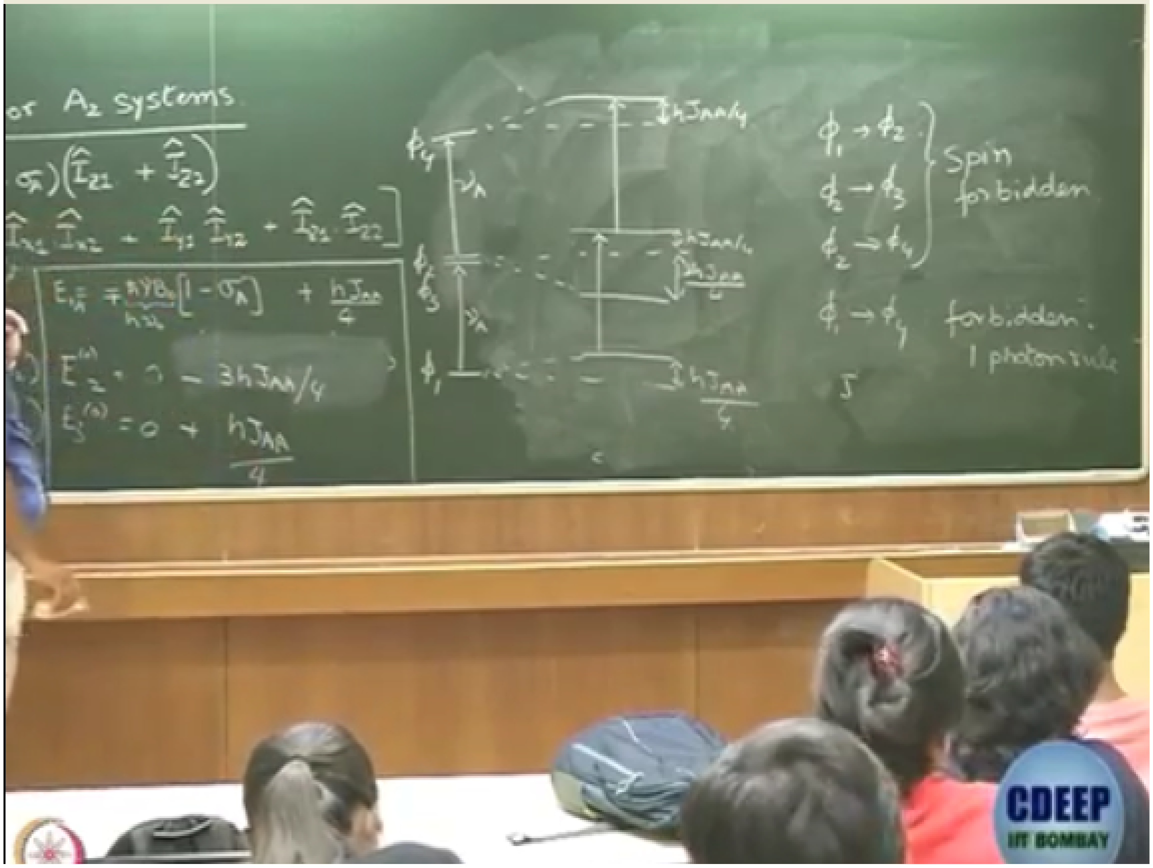

You have this right, this is E1 where this is minus, I'm saying E1 to E2 is allowed, sorry E1 to E3 is allowed right, what is the energy difference between E1 and E3? Yeah sorry, what is the energy difference between E1 and E3? Sorry H nu dot, H nu 0 multiplied by 1 – sigma A and that's it, there is no signature of coupling right, so H nu 0 into 1 – sigma A is the energy gap that we expect in the unperturbed system, right, so what will be the frequency of transition here? Nu A, and what about 3 to 4? What about 3 to 4? What is E4 – E3? Same thing HJAA/4, HJAA/4 will cancel and you left with H nu 0 multiplied by 1 – sigma A,

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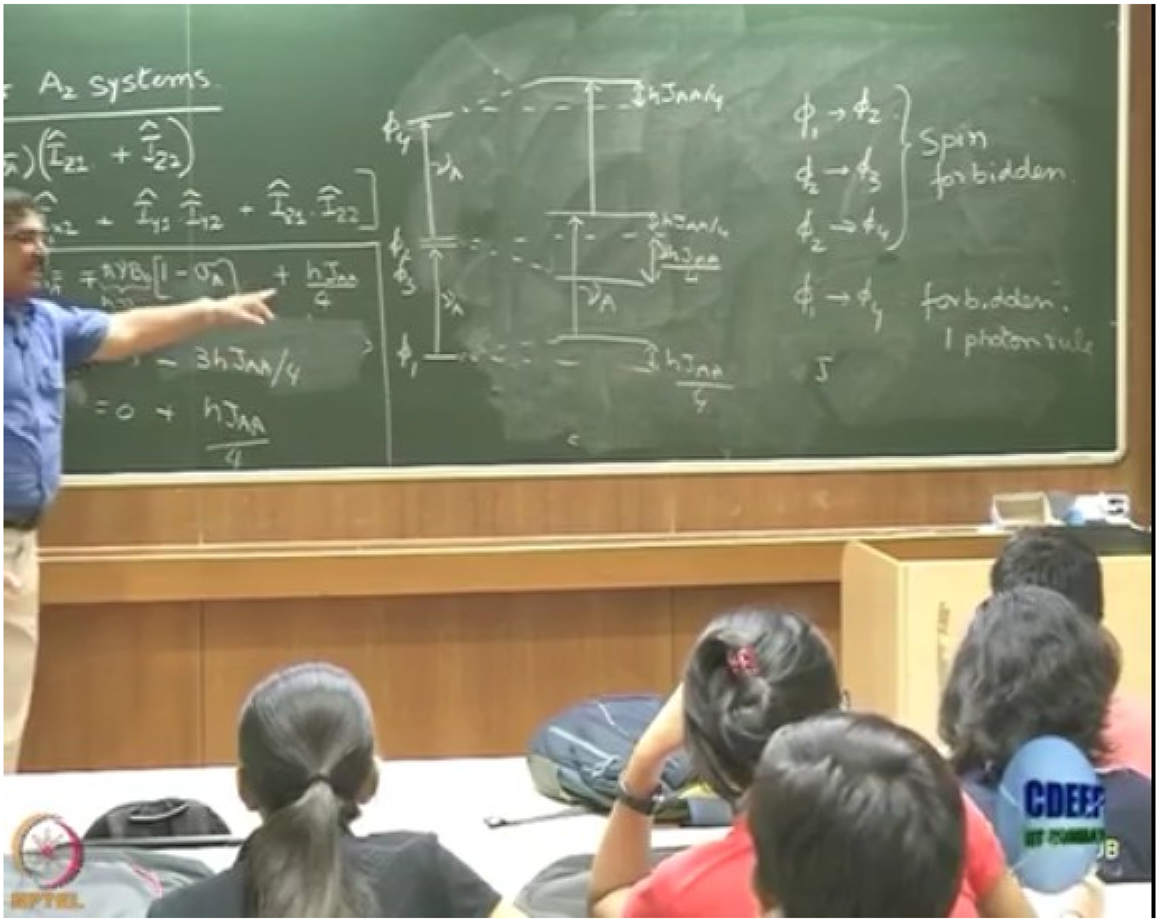

if I write it in terms of frequency of transition again it will be nu A which is nu 0 into I – sigma A.

So what we learn is that it's not as if there is no coupling, coupling is very much there, it is just that this additional spin-forbiddenness comes in for A2 systems, because of the indistinguishability of the protons and that is why the number of allowed transitions goes down, the only transitions that are allowed are between two levels both of which have been destabilized to an equal extent, right, from here destabilization is by HJAA/4 from here also destabilization is by HJAA/4, so it is as if the two levels have just moved together, okay.

Same is true for this and this, phi 3 and phi 4, the two levels have been destabilized by an equal amount that is why you do not see the signature of coupling in the spectrum, it does not mean that coupling is there. Of course you might say that you are making it up, you have just done some mathematical wizardry and you are saying coupling is there, the situation is equally explainable in terms of this diagram, even if I don't invoke coupling, I get the right picture, right, so how do I know? How do I know that coupling is even required in this scenario? Well, we know it because we have only discussed the two extinct right, yesterday we discussed AX, AX means sigma A and sigma X are very far apart from each other, today we have discussed A2, that means the sigma's are exactly the same, what perturbation theory cannot do is discuss situations of AB where sigma A and sigma B are not very far apart from each other, for that you have to use the variation method which we're not going to do in this courses time, but when you do a

variation treatment you see that when you go to AB, the situation is somewhat like this, so we are saying that for AX this is the situation, right, two lines for A, two lines for X.
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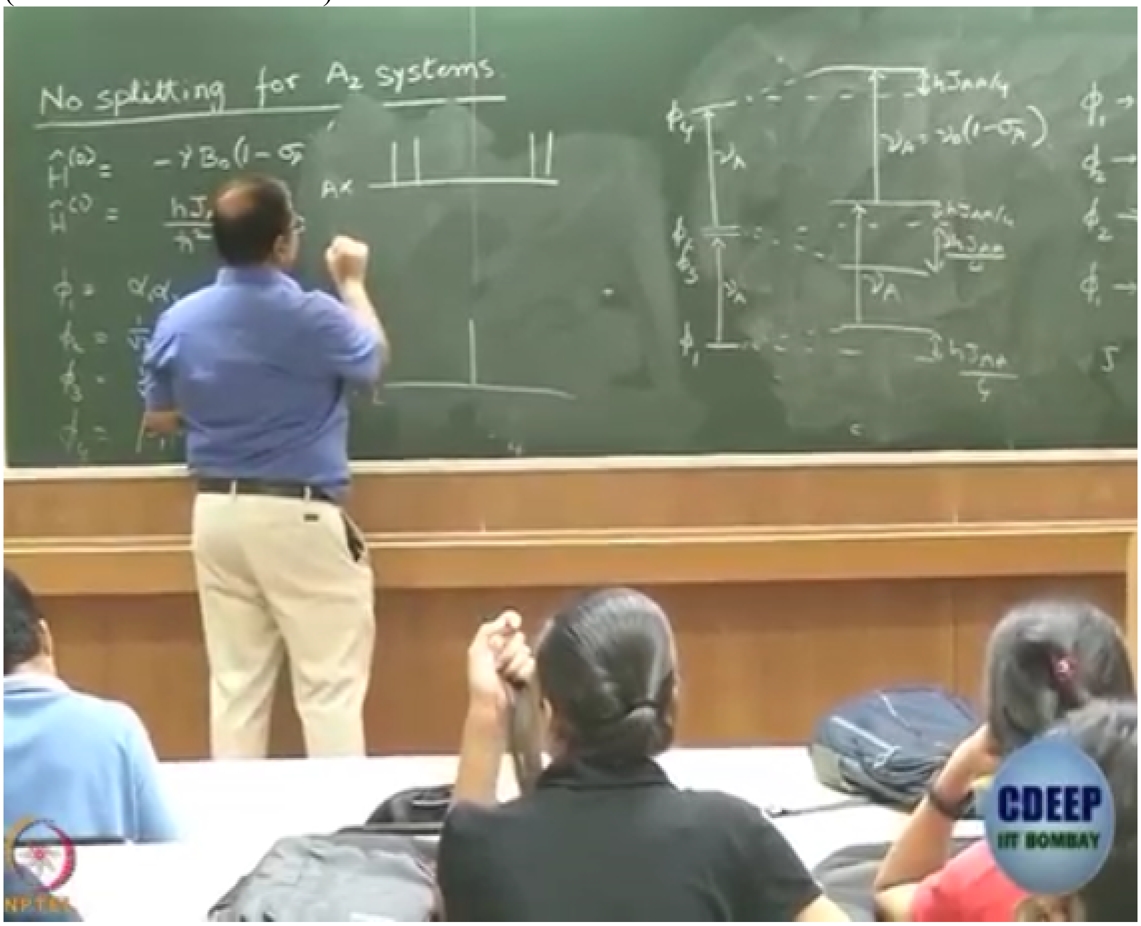

For A2 situation is this, you have one resonance, for AB the spectrum that you get is somewhat like this, this two doublets move closer together and the ones inside gain intensity, the ones outside lose intensity, this are called second order spectra, when sigma A – sigma X is sufficiently large,
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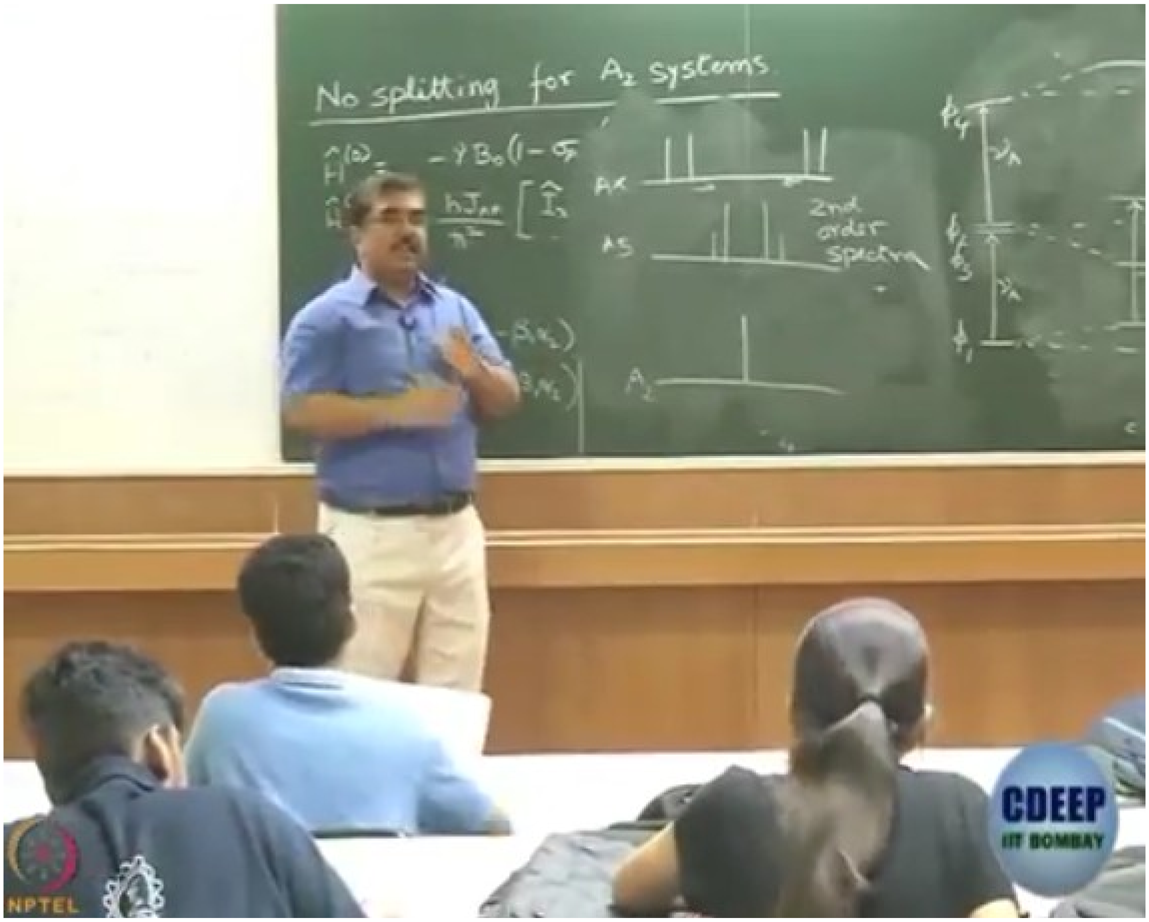

much larger than the coupling constant J, then you get what you call first order spectra, we have discussed first order spectra so far, we call it first order spectra because you can explain those spectra using first order perturbation theory, you call this second order spectra because you have to go to higher order perturbation theory, if not different level of theory altogether if you want to explain this kind of spectra, okay, so you can imagine like this in the hypothetical situation where let us say you have a control over the sigmas, you start with the situation where sigma A, the two sigmas are very different you get double X, then by some magic if you keep on decreasing the difference between the sigmas the spectra start moving closer together, the inner ones become stronger, outer ones becomes weaker, and finally the muds the outer ones are vanished, the inner ones merge together to give you one line, right, of course this is only a very qualitative hand waving way of explaining the scenario, the correct way of understanding it is by using variation method which can take you all the way from A2 to AX, variation method is also discussed in McQuarrie and Simon, it is not in the syllabus this year but you are welcome to read, it’s not very difficult, you can understand if you read it yourself.

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