INDIAN INSTITUTE OF TECHNOLOGY BOMBAY
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NPTEL ONLINE CERTIFICATION COURSE

Molecular Spectroscopy – A Physical Chemist's perspective

Lecture-62

Coupling in AX Systems: Perturbation Theory

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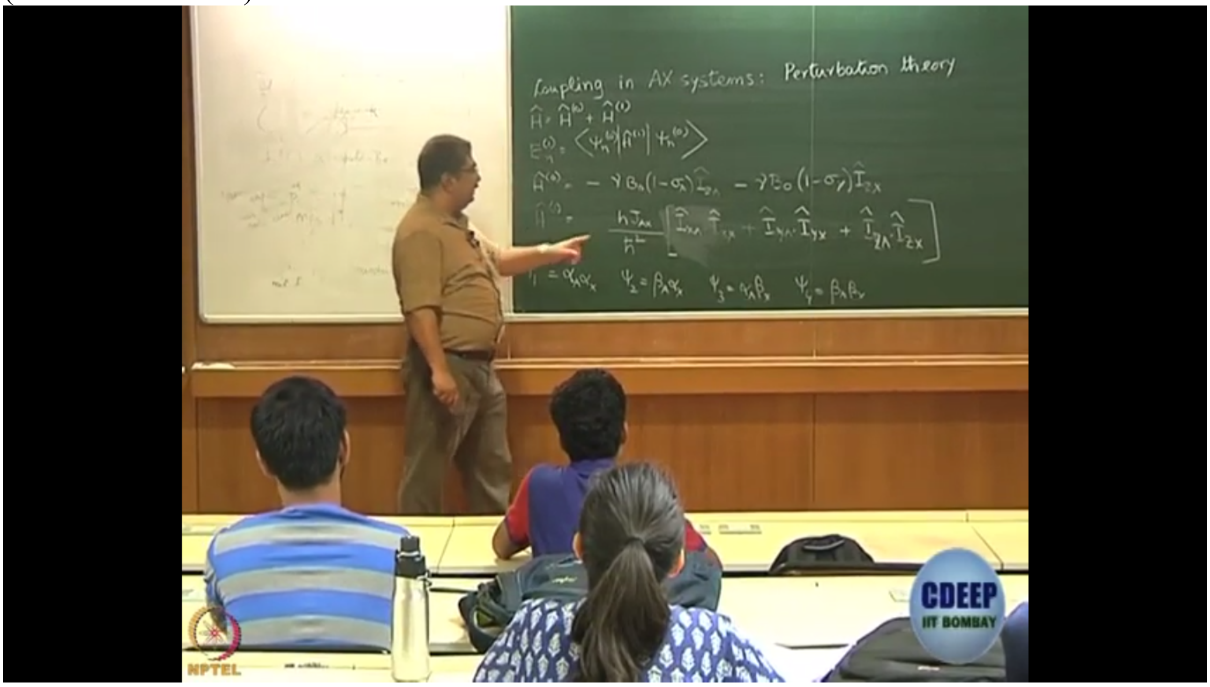


What we want to discuss today is what we started discussing the previous day. It is coupling in AX systems and we are going to handle this using perturbation theory. So we go back to our old friend, the AX system. When I say AX I do not mean halide of element A. I mean two protons with different chemical shifts, σ_A and σ_X. What we'll try to do is we will try to arrive at the answer that we know already. We have already discussed what happens when there is no coupling and when there is coupling between two protons with different chemical Shifts. All we will do today is we'll use perturbation theory and try to understand why is it that we get the picture that we got earlier. It's as simple as that. So today's discussion is really very simple.

Then tomorrow when we come back we ask another question. When we take A and X we said A couples with X, X couples with A. Instead of X if I have another A, A_2, say CH_2 protons of ethanol. We never consider coupling between them, does that mean they don't couple? If so, why is it that they don't couple or is it that they couple but it does not show up in the spectrum? That is something that we will end our discussion in this course with tomorrow. There was another topic that I wanted to discuss and that is the general discussion of everything ranging from AX to AB but there, you cannot use perturbation theory; you have to use variation method.

The good thing about what we discussed today and tomorrow is that you don't have to study. You only have to be attentive in class and then you understand we are not using any new concept whatsoever. So let's begin.

So since we are going to use perturbation theory, we know that we have to write the Hamiltonian as the unperturbed Hamiltonian plus we will restrict ourselves to first order perturbation so the first order correction to the Hamiltonian.

Okay, how do you write the wave function that we will see. In fact, we are going to work only with the unperturbed wave functions; we don't talk about perturbed wave functions at all because all we are trying to do now is we are trying to work out what are the energies corresponding to each of these states before and after coupling that is perturbation. And I think you can tell me what is the expression for the first order correction term to energy. What is the expression for first order correction term to energy? Yes, ψ_n, okay, then I'll write n here. Then $H^{(1)}$ ψ_n. Anything else? Same, not two on one, you are right. You are right if it's two on one then we are talking about a transition, I'm not talking about transition here. I want to determine the energy of the state that is arisen out of coupling that is perturbation. But my expression here is not complete because first of all, let us not forget that we will work with unperturbed wave functions.

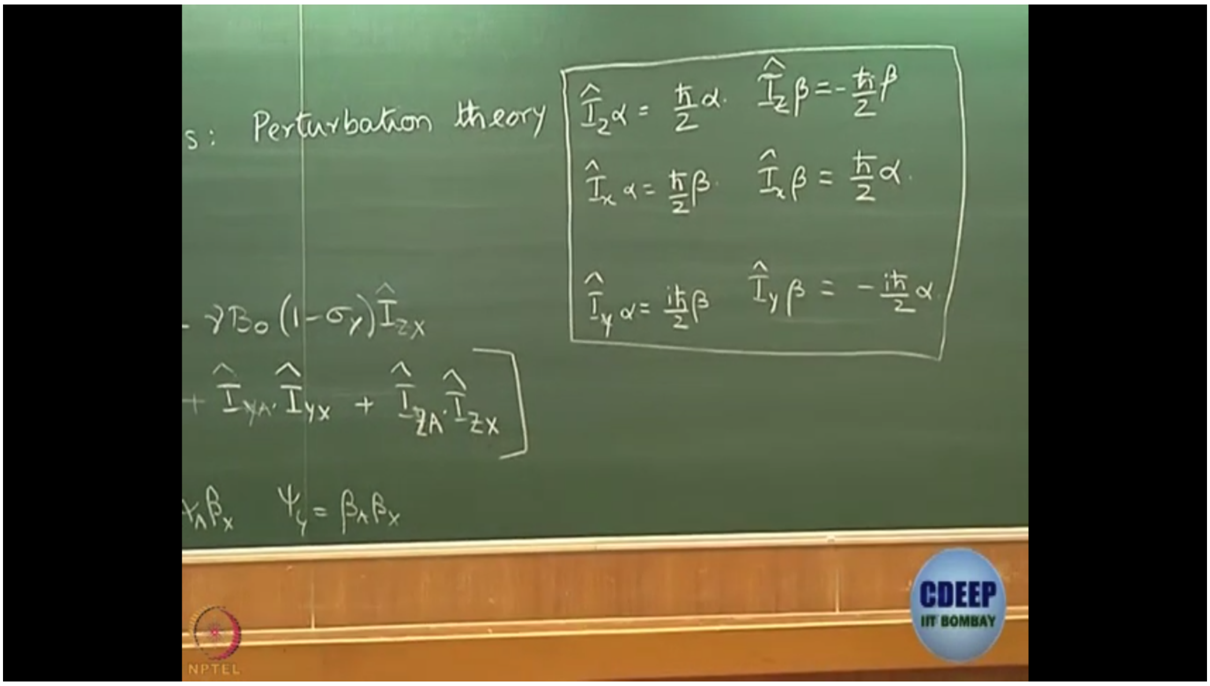
Remember, when we try to -- this is the beauty of perturbation theory. Everything changes; energy changes, Hamiltonian changes, wave function also changes. But then all changes are small. So when we want to work out the first order correction to energy that itself is a small quantity, there is no need for us to worry about what is the perturbed wave function. We can get away working with the unperturbed wavefunction because the terms involving the perturbation terms of wavefunction are really very small and therefore, they're neglected. But I also have to complete this.

This is the expression for first order correction to energy. Does it ring a bell whoever had forgotten? I hope you have you now remember. That being said, let us now write down the

Hamiltonian for this AX system. What is the unperturbed Hamiltonian? $-\gamma B_0(1- \sigma_A)$. Since I am talking about AX, I'll write A and X. It's just that later on when we talk about X, Y, Z components don't t get confused between that X. $(1- \sigma_A)$ $I_{ZA}-\gamma B_0(1- \sigma_X)I_{ZX}$. Here let us remember that I have to write X. I'll write X for the nucleus and I write x for the Coordinate. Okay, so this is my unperturbed Hamiltonian. What is the correction term we said for coupling? hJ, now what I will do is I will write J_{AX} just to remind ourselves that we are dealing with the AX system, we are talking about coupling of A with X, divided by $\hbar^2$. Anything else? $I_A.I_X$, and as we know when we take the dot product of two vectors or two operators we can just write it like this. $I_{XA}.I_{XX}+I_{YA}.I_{YX}+I_{ZA}.I_{ZX}$. So this is what we have to work with essentially, and let us not forget what the wave functions are. What are the Wavefunctions; ψ_1. Ψ_{10} is fine, what is ψ_{10}?

We are talking about nuclear spins and we are talking about proton. So what are the only two wavefunctions that are there for each; $\propto$ and β, and as you know lowest energy one is $\propto\propto$. So I'll write it like this a little different from what we wrote earlier; $\propto_A\propto_X$, then I think it's easier to understand. Okay, what is ψ_2? $\beta_A\propto_X$. What is ψ_3? $\propto_A\beta_X$. What is ψ_4? $\beta_A\beta_X$. Question?

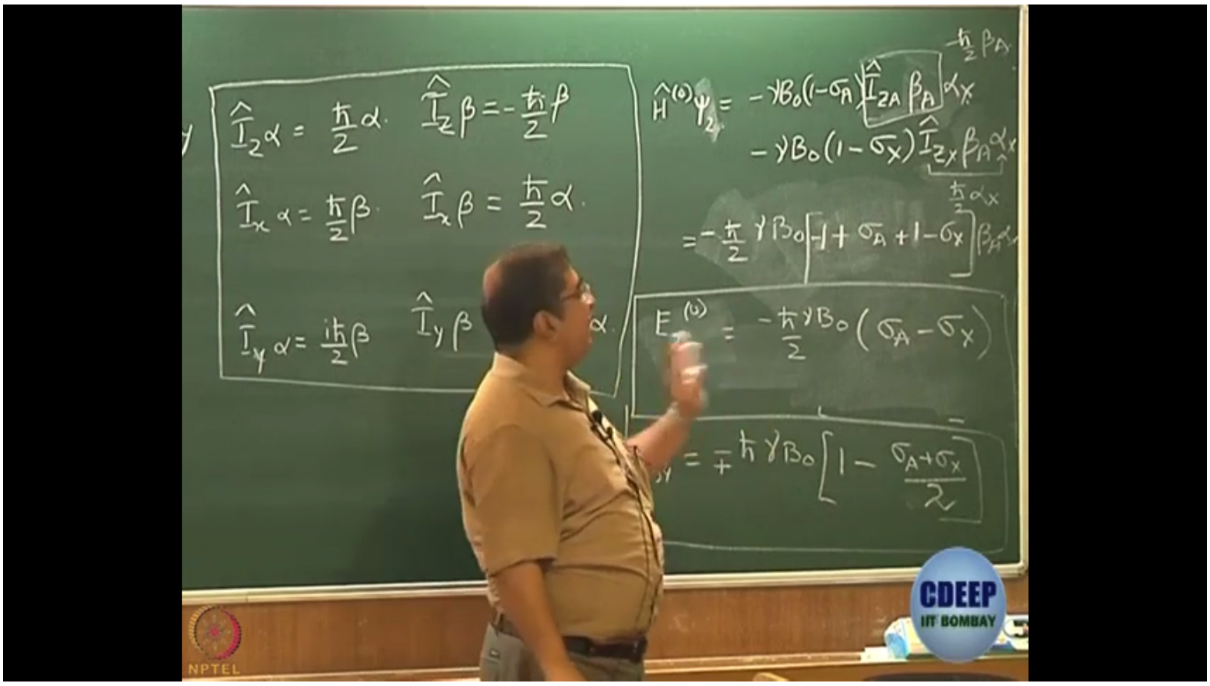
Of course, these are all unperturbed wavefunctions. Are we okay with the wavefunctions? I'll not even write the 0 if you are okay with that. Are we okay so far? Not written anything new.



Now one thing that we need to now understand is see, we know very well what happens when I_z operates on ∝ or β, don't we? Say, I_z operating on ∝? What is it? What is I_z operating on ∝? What do you get? What? I thought that there is somewhere we know. What do we get when I_z operates on ∝, ∝ spin? Yeah, 1/2 ħ multiplied by something? Multiplied by ∝ , it's an eigenvalue equation. Is it right or not? It's just MS; it's an eigenvalue equation for the Z component of angular momentum. Okay, what happens when I_X operates on -- I'll write this one as well. I_z operates on β what do you get? B. ħ/2, is it right? That means ∝ and β both have the same eigenvalues for $I_{z.}$ –ħ/2. That is why ∝ is called up-spin and β is called downspin. One of the eigenvalues is ħ/2, the other eigenvalue is -ħ/2.

What happens when I_X operates on ∝? What happens when I_X operates on β? Iy operates on ∝, I_y operates on β, what do we get? Do we know the answers to these? Yes. 0, we don't get 0. Do you know what we get? I just write it for you. I_X operates on ∝ to give you ħ/2. B. So it is not an eigenvalue equation anymore. It's not an eigenvalue equation anymore. I_X operates on β to give you again ħ/2. ∝, not an eigenvalue equation. These comes from what are called spin matrices. We usually in chemistry courses, we do not really study spin matrices and all. So this is one of the few things that we are going to take extrametrical in this course.

Then I_y operates on ∝ to give you I ħ/2. β. I_y operates on β to give you - ħ/2.∝. So as I said for that you need to understand relativistic quantum mechanics. So that is not something that we do in any chemistry course. So we are just going to take this -- I mean you can search Wikipedia, you will get a little more of the answer. Wikipedia has this discussion on spin matrices, but whether you will be satisfied with the answers and you see, again you'll take something extrametrical. So better not lose our sleep, this is what we'll use extrametrical.



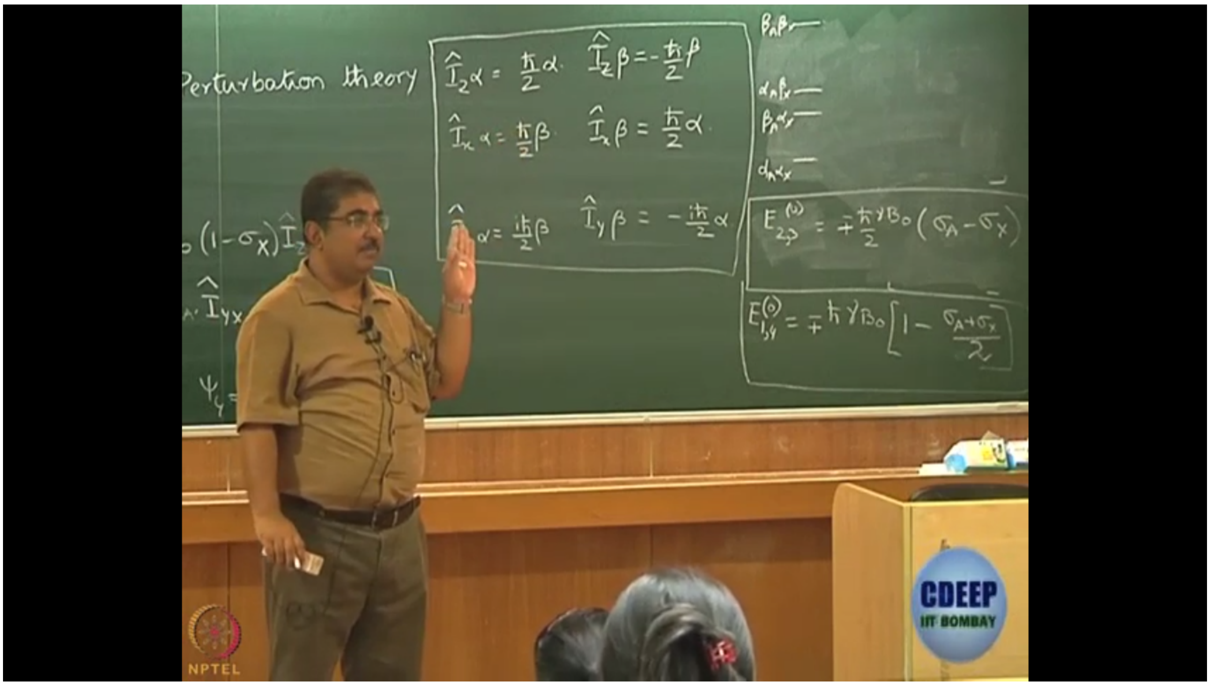
Okay, ok so now we have all the material that we need to start discussing the problem of AX system with coupling and without coupling. What happens when $H^{(0)}$ operates on ψ_1? What do you get? What is ψ_1? $\propto_A\propto_X$. So you get – $\gamma B_0(1- \sigma_A)I_{ZA}$ operating on $\propto_A\propto_X$. Whenever I try to write that X as a small x, please correct me. - $\gamma B_0(1- \sigma_X)I_{ZX}$ $\propto_A\propto_X$.

Okay so far so good. Now let us make the operators operate. I_z will only operate on $\propto_A$ l and not on $\propto_X$. When it operates on $\propto_A$ Iz operating on $\propto_A$, do you get? You get ħ$\propto_A$,/2. Here what happens? I_{ZX} does not operate on $\propto_A$ it operates on $\propto_x$. Again, from there you get ħ$\propto_x$,/2. I_{ZX} operates on $\propto_{X,}$ ħ/2. $\propto_X$.

What is the expression then? What can I take out? I can take out ħ/2. I'll take -ħ/2 out. -ħ/2 – okay, I'll take ħ/2 out, no issue. $\gamma B_0(1- \sigma_A)$, what do I get there, $\propto_X B_A$. It's okay. My wavefunction was $\beta_A\propto_X$, I got to be confused. So you don't have worry about that. So I can take ħ/2 common, I can take $\gamma B_0(1- \sigma_A)$ -- this I cannot take common. What do I have left inside, $(1- \sigma_A)$ but that $(1- \sigma_A)$ is multiplied by a minus (-). So (σ_A-1). I can write like this; $(-1+ \sigma_A)$ and then what do we have, $(1- \sigma_X)$, whole thing multiplied by $\beta_A\propto_X$.

So what is the eigenvalue? What is the eigenvalue now? This -1 and 1 they cancel each other. You are left with $\propto_A$-$\propto_X$. So I can jump one step I hope and write E_2 unperturbed is equal to minus -ħ/2$\gamma B_0(\sigma_A- \sigma_X)$. Do we agree with this? $E_2(0)$ is -ħ/2$\gamma B_0(\sigma_A- \sigma_X)$.

Okay with that? Now what will happen if I now go to 3. Ψ_3. What is ψ_3? $\propto_A\beta_X$. So what do you get from here? Here instead of minus you get -ħ/2$\propto_A$ and here, instead of ħ/2, you get -ħ/2 β_X. So what is the expression that I get? Same magnitude reverse sign. So again I can write $E_{2,3}^{(0)}$ is -+(-ħ/2$\gamma B_0(\sigma_A- \sigma_X)$). Do you have to remember all this or can you work it out yourself? You can work it out yourself; it will take no more than five minutes. All right, so please do not remember this expression. Do not remember any of these expressions. The only thing that you need to know is what is the Hamiltonian. Are we okay so far?



What we have been able to do is we have been able to work out the energies of the four unperturbed levels. So I am not drawing to scale, of course. This is your $\propto_A\propto_X$, $\beta_A\beta_X$, $\beta_A\propto_X$, this is $\propto_A\beta_X$.

We have been able to work out the energies of these four levels without coupling. So if you remember the picture that we have shown you earlier, we have shown you the first half. Now when we bring in coupling, we'll get the second half and we'll see how the energy levels go up or go down. Before that are we clear up to this? Is there any question? If there is then this is the time to ask. No question. Very good. I'll keep that one.

So essentially now we need to work out these. So A and X are defined in a particular way. So you can understand that if σ_A is $-\sigma_X$ then only the energy level that we have defined as 2 will have a lower energy than the energy level that we have defined as 3. So that is how it is defined. When you say A and X, it means σ_A is much greater than σ_X. Convention nothing else. Good question. I was hoping somebody would ask that question at some point of time because I never really told you that.

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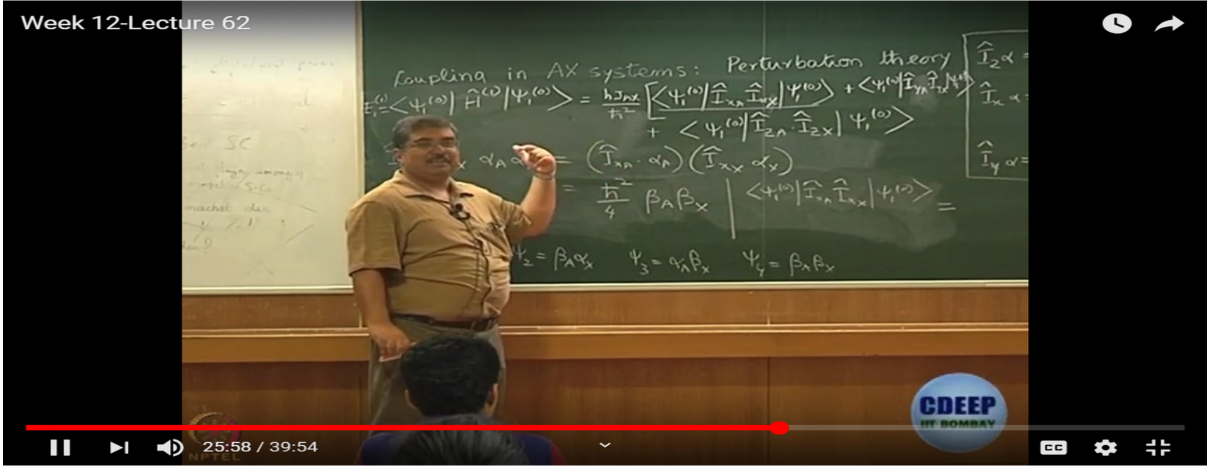

right now now what am I left

Now what am I left with? I have to make these operate right on these wavefunctions and see what I get and to do that what I need to know is these. That's all. Fine, let's begin. So let's work with the first wavefunction. This is what we want to know; $<\psi_1^{(0)}|H^{(1)}|\psi_1^{(0)}>$ that should give me the first order correction to energy of the lowest level. All right, and this I can expand a little bit and write, now I'll bring in this expression. $hJ_{AX}/\hbar^2<\psi_1^{(0)}|I_{XA}I_{AX}|\psi_1^{(0)}>$ I can open a bracket here because everything will be common anyway. $+<\psi_1^{(0)}|I_{yA.}I_{yX}|\psi_1^{(0)}>+<\psi_1^{(0)}|I_{ZA.}I_{ZX}|\psi_1^{(0)}>$. This is what I need to evaluate.

All right now I can erase this expression. Let's take these terms one by one. $I_{XA}.I_{XX}$ operating on what is the wavefunction? $\propto_A\propto_X$. Please respond when I ask something, otherwise I am not sure whether you are following anything at all or not. $I_{XA}.I_{XX}$ operates on $\propto_A\propto_X$. What do I get? What do I get? Of course, I can write it like this, $(I_{XA}.\propto_A)$ that multiplied by $(I_{XX}.\propto X)$. Now you should be able to answer looking at this table. So $(I_{XA}.\propto_A)$, what do I get? Yes, $\hbar/2.\beta_A$ and from here how what will I get? $\hbar/2.\beta_X$. So what do I get? $Ħ^2/4.\beta_A\beta_X$.

Now I think you understood where we are going. Okay, don't be a spoilsport. This is what we get. So now we are working with this term, don't forget. If I now try to work that one out, what will I get? Maybe I will do it here $<\psi_1^{(0)}|I_{XA}I_{XX|}\psi_1^{(0)}>$ that turns out to be -- this $\hbar^2/4$ that is common, I will take it outside and now you understand why we had written $hJ_{AX}/\hbar^2$ because we knew and somebody else has done it. We are not doing it for the first time. So it is known that this $\hbar^2$ will keep coming in the numerator. If you have $\hbar^2$ in the denominator already then it will conveniently cancelled and give you a nice expression. That's all. Okay, so I get $\hbar^2/4$ multiplied by integral, now I write this explicitly, $\propto_A\propto_X$. What is this term?

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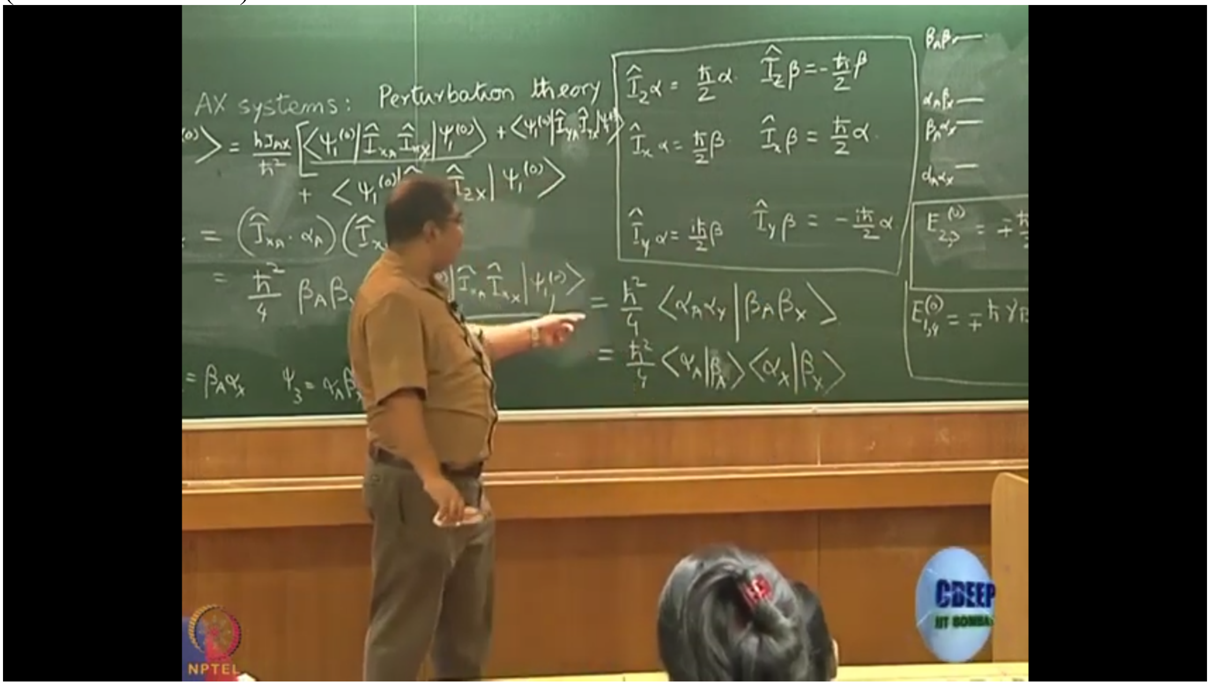

This operating on this, we have worked out to be $\hbar^2/4.\beta_A\beta_X$. So here I will write $\beta_A\beta_X$. This comes out to be $\hbar^2/4.<\propto_A|\beta_A><\propto_X|\beta_X>$. I hope you understand that when I write it like this it is really a double integral, one over the coordinates of A, one over the coordinates of X. So I can always write a double integral as a product of two integrals. That is why I have done what I have done here and now finally we are in a position to allow Manthan to speak. 0 ho jayega. $<\propto\beta>$ that is 0 they are orthogonal. It doesn't matter whether $\propto$, β are of A or whether ∝, β are of X. As if this is not bad enough that the first one is 0, the second one is also 0. So 0 multiplied by 0 is definitely 0.

Okay, so as we had discussed sometimes ago, who physical chemistry mein sab kuch zero ho jata hai. Sab kuch nahin hota hai. Fortunately, a lot of things become zero. So what we see is that this first term conveniently becomes zero.

Okay, I will leave it to you to prove to yourselves that the second term also conveniently becomes zero. Why, because look at this; second term is in I_y. See, I_y also operates on ∝ to give you β, operates on β to give you ∝. It's a different matter that you have a minus sign in one case and I there but I x I is just -1. So you just proceed in the same manner you will be able to satisfy yourself that the second term is also happily zero.

So when we did a little bit of introduction in the last class, we had said that when we talk about
coupling, we cannot, when we begin at least, we cannot say that we will only talk about coupling between the Z components. That is not the right way to formulate it. You have to think of X component, Y component everything. But in case of the AX system what we see is that interestingly, the X and the Y components turn out to be 0 anyway. You are only left with the Z component.

So if there is coupling that coupling is through Z component only for AX system. Tomorrow we will see what is it that happens for A2 kind of system.

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All right, what is this? What is this third one? Third one is very easy. Third one is $I_{ZA}.I_{ZX}$ operates on $\propto_A \propto_X$ which I can write as $(I_{ZA}.\propto_A)(I_{ZX}.\propto_X)$. What is $(I_{ZA}.\propto_A)$? $\hbar^2/2 \propto_A$. What is $(I_{ZX}.\propto_X)$? $\hbar^2/2 \propto_X$. So I get now $\hbar^2/4 \propto_A.\propto_X$. Unlike the other two, here we are dealing with an eigenvalue equation.

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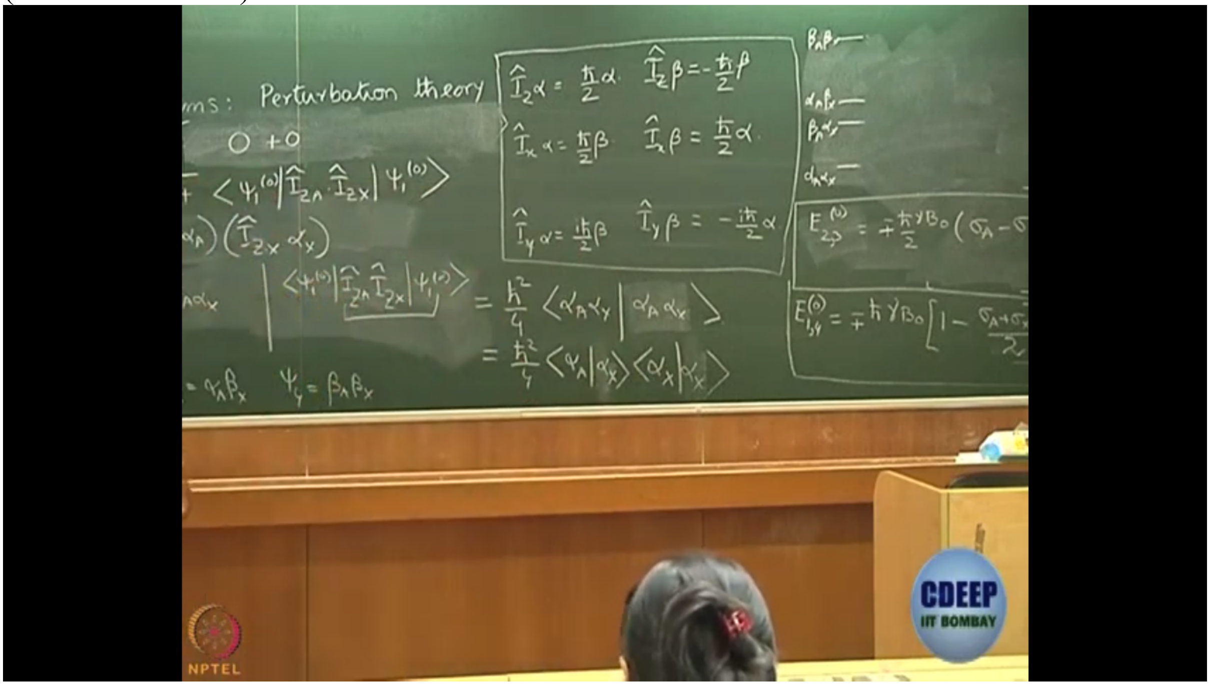

So now when you write this term, what do you get? When you just write Z instead of X or Y, what you get is $\propto_A \propto_X$, and here you have $\propto_A \propto_X$. Toh physical chemistry mein sab kuch sirf 0 hi nahin ho jata hai, kabhi kabhar 1 bhi hota hai.

This is a case when each of these integrals is actually 1. Okay, so what are you left with? You are then left with $\hbar^2/4$.

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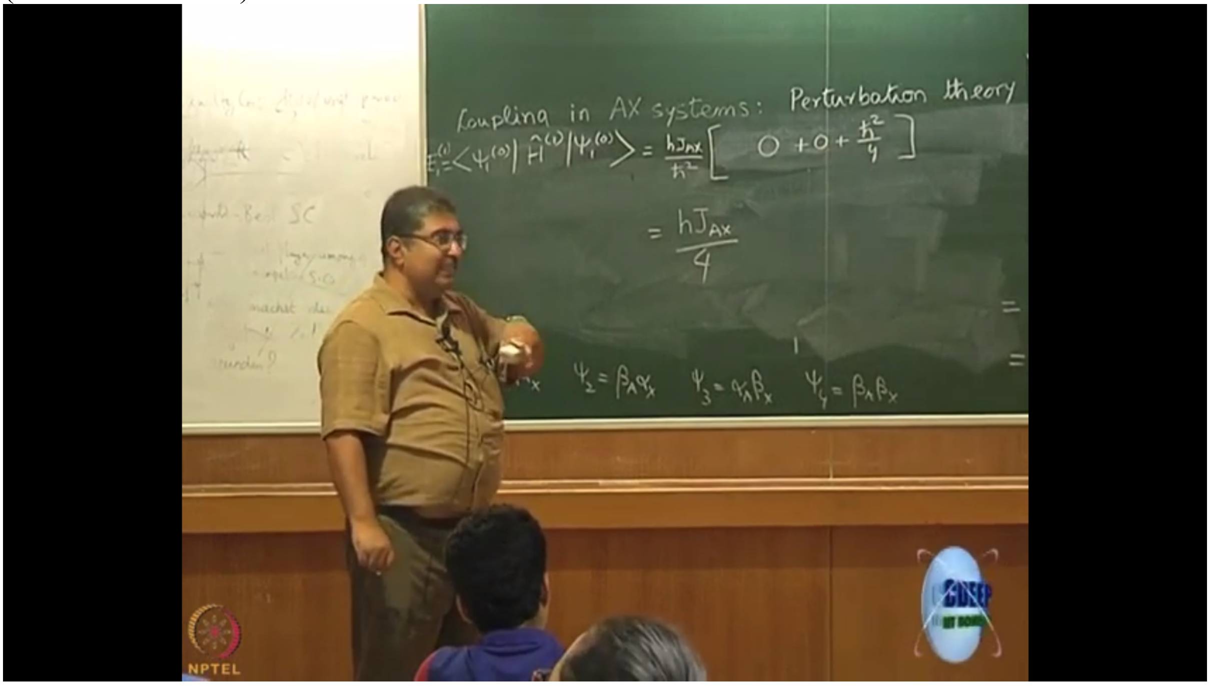

Okay, now what we have not done yet? We have only evaluated the integral. So this is what I get. + $\hbar^2/4$. Can I now erase the rest? What am I left with? This $\hbar^2$ that $\hbar^2$ cancel off, you are left with $hJ_{AX}/4$, the expression that we had written without derivation last week.

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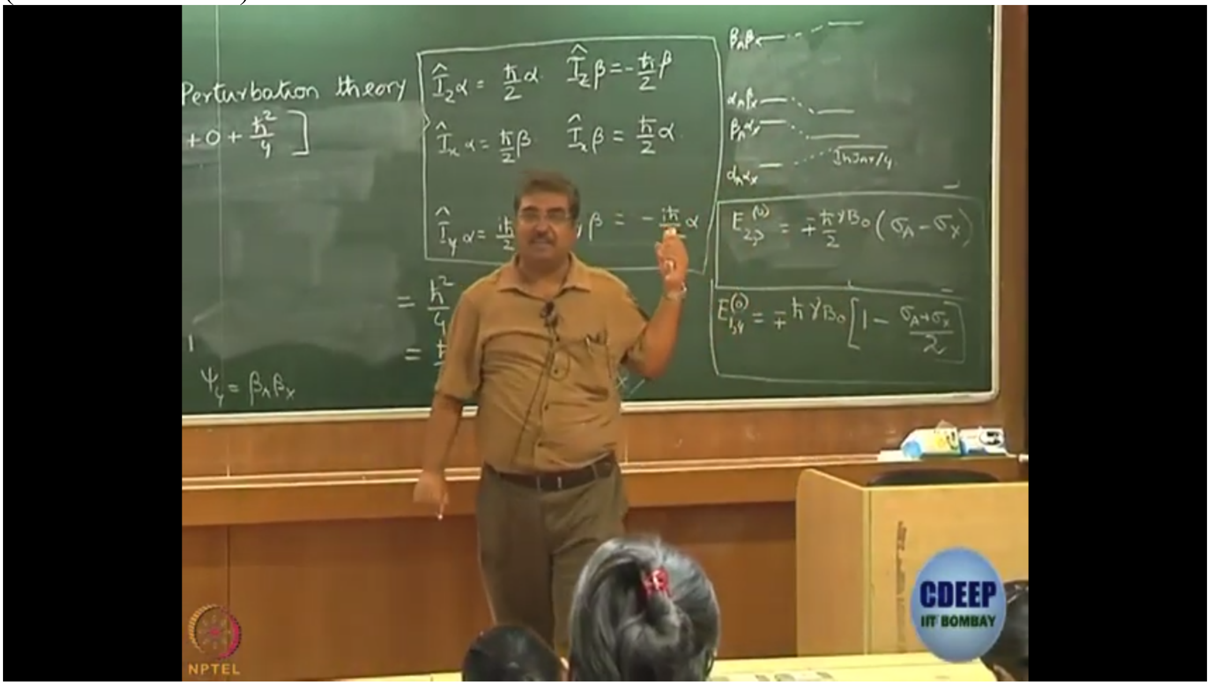

Okay, so what is the energy? What is the first order correction to energy of $\propto_A\propto_X$? It is $hJ_{AX}/4$. Plus or minus? Plus, right? So it will go up like this and this will be $hJ_{AX}/4$. Now if you proceed in the same fashion it is not very difficult for you to prove that this also for $\beta_A\beta_X$, there is an increase by the same amount for $\propto_A\beta_X$ and for $\beta_A\propto_X$ there is a decrease by the same amount. I have drawn a horrible diagram there. Sorry about that. Please look up the book, they are more beautiful diagrams. But I hope it is not very difficult for you to believe at this point after working this out that this is how the energies will change. And now we have arrived at the expressions that we had used without derivation when we introduced the topic.

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So what are the expressions then? Now we cannot write it like this or can we? Yes, we can. We can. If I now remove this, if I write actually the energies of the perturbed system after coupling then in case of levels 2 and 3, I have to add the term $-hj_{AX}/4$ and in this case for 1 and 4, I have to write $hj_{AX}/4$. So far so good? Is there any question?

If I have a transition from say, can I have a transition from 1 to 2, $\propto_A\propto_X$ to $\beta_A\propto_X$? Can I have that transition? $\propto_A\propto_X$ to $\beta_A\propto_X$? Is a transition allowed by our one photon rule? $\propto_A\propto_X$ to $\beta_A\propto_X$ allowed or not allowed? Allowed. What is happening here, which spin flip? Yes, A.

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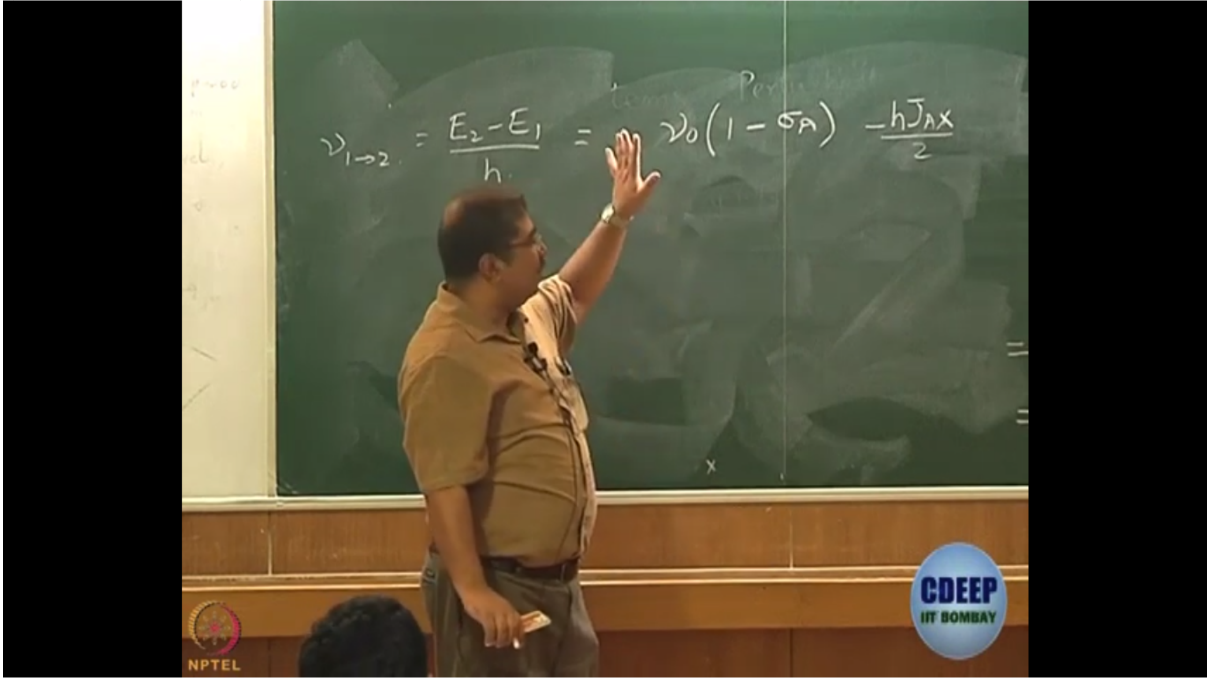

So let us see what is the frequency of this 1 to 2 transition that, of course, will be $(E_2-E_1)/h$. You can see how nicely this problem has formulated itself. There is an h in both the terms. So you just divide, you get it. What do you get $(E_2-E_1)/h$? Can you tell me? Of course, what you do then, you write it like $h/2\pi$ in case you are confused. This will become $h/4\pi$, this becomes $h/4\pi$. What do you get? Can you do this and tell me what you get.

Simple subtraction. In fact, you should be able to guess the answer. I will do the easy part fist. Let's look at the coupling term. I am subtracting E_1 from E_2, am I not? So I have to subtract $hJ_{AX}/4$ from $-hJ_{AX}/4$. What do I get? $-hJ_{AX}/2$. So the second term is worked out. What is the first term? That h is gone, h is gone anyway. Did I make a mistake here? Isn't it 2π? There was no 2 here. Actually, it's something like that. What do you get? You get $(1- \sigma_A)(\gamma B_0/2\pi)$. This $\gamma B_0/2\pi$,have we encountered this somewhere? Isn't that the Larmor frequency for a free proton or bare proton? So I can just write it as μ_0. μ_0 is the Larmor frequency of a bare proton.

So you see now these two terms make perfect sense. The first term is Larmor frequency of bare proton multiplied by $(1- \sigma_A)$ that is the effective magnetic field that is felt by proton A. $-hj_{AX}/2$, the coupling term. This way I leave it to you to work out all the four. What kind of a transition is this? New one, 1 to 2? Is it a transition for A or X? What did you tell me a little while ago? A. So what we see is that instead of getting the resonance here, I get resonance at a frequency that is lesser by an amount of $hJ_{AX}/2$. If you do 2 to 3, can you do 2 to 3 or 1 to 3, can you do 1 to 3? $\propto_A\propto_X$ to $\propto_A \beta_X$? Which spin gets flip, A or X? X. So that should give you the transition energy for one of the transition energies for X.,

You will see again you'll get something like this. Exactly the same thing. Instead of σ_A, it will be σ_X. This term will remain $-hJ_{AX}/2$.

Can I have 2 to 3 transition; $\beta_A\propto_X$ to $\propto_A\beta_X$? No. Why not? So one photon rule; one photon cannot cause a flip of two spins. So this is forbidden. Can I have 2 to 4 transition; $\beta_A\propto_X$ to $\beta_A\beta_X$? Yes. Which transition is that? For X. You work out the energies. Please work it out yourself. Work out the energy, you will see, you will get something like $\mu_0(1-\sigma_X)$ and this time it will be $hJ_{AX}/2$. Similarly, the last one will be for A. So what we have been able to do is we have been able to get expressions for the frequencies of resonance for AX system in presence of coupling and we have been able to prove that that's why we get the separation bites.

Tomorrow, in the last class, we address the question, what happens when $\sigma_A=\sigma_X$. Is there coupling? Is there no coupling? In the spectrum, of course, we do not see any evidence of coupling. Does that mean coupling is not there? That's s what we will see tomorrow.