INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

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NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

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MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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Lecture no. – 61
The Fine Structure: Spin-Spin Coupling

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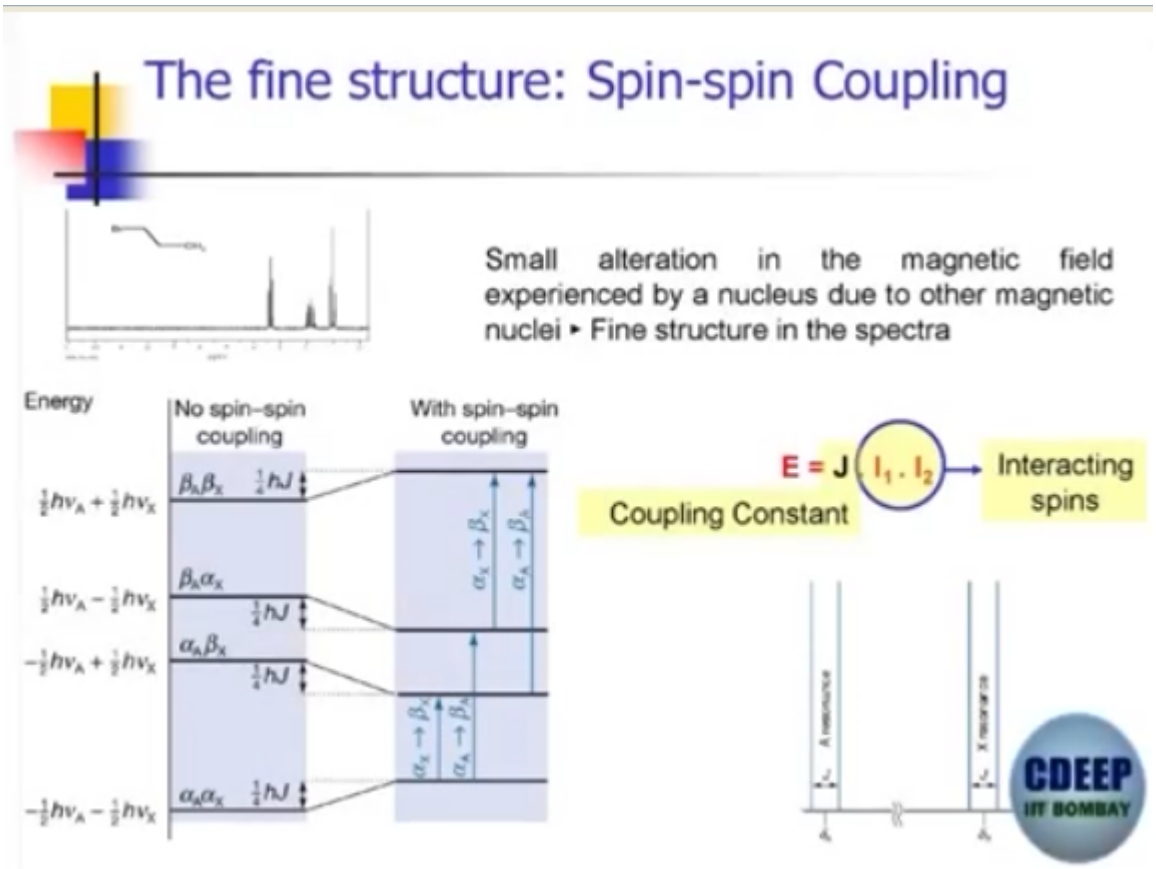

Okay, now we entered the last phase of our discussion of NMR spectroscopy and last or the ultimate discussion of this course, what we would like to do is we'd like to present a little more proper quantum mechanical discussion of something whose results we know already, and that something is spin-spin coupling.

So what we do today is very simple, in fact I'd like you to do it rather than we doing it. We just formulate the problem in terms of the usual quantum mechanics that we know, and we see what kind of eigenvalues and stuff we get, what kind of expectation values we get.

So the way you do it is this, what is the technique that we have used very frequently in this course, when we talk about radiation matter interaction? Yes, radiation matter interaction when we did that discussion of quantum mechanics, which technique did we use? Perturbation theory, right, so that time we had talked about time, in time dependent perturbation theory, for this discussion we need to invoke time independent perturbation theory, so what we do is this,
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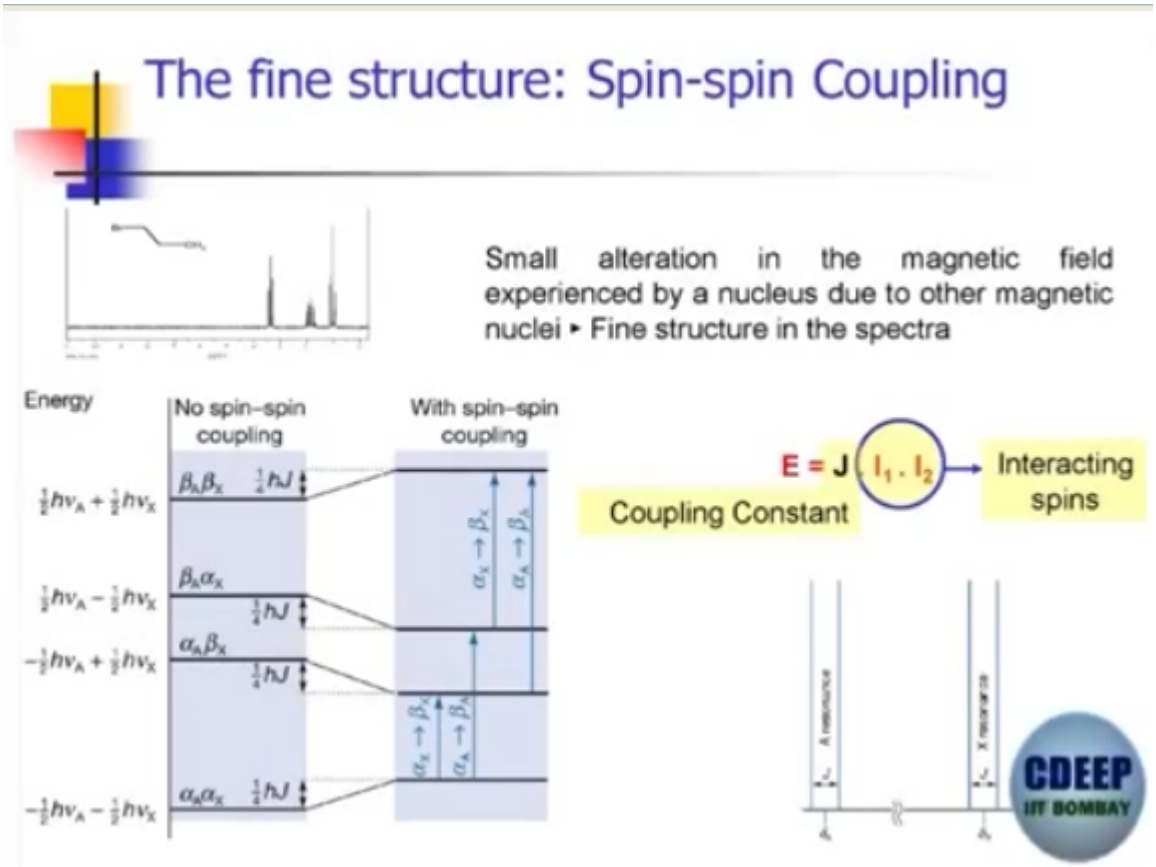

we start with the uncouple scenario, right, we start with the situation where the magnetic field is applied and there are two kinds of spins, two kinds of chemical shifts, sigma A and sigma X, that is the un part of scenario, there is no coupling, then you bring in coupling as a perturbation, when can I do that? When is this treatment going to be actually valid? When the coupling is much smaller than the chemical shifts, isn't it? Or rather when the coupling is much smaller than the difference of chemical shifts that is when this kind of perturbation theoretical treatment is going to be proper, because as you know perturbation theory works only for small perturbations.

Okay, if your base value is 100 and you do something to the system by which the value becomes 195 then perturbation theory is not going to work, then you need to do something else. Well, we'll do that something else as well eventually maybe on Tuesday, but first let us keep things a little simple.

Now, so we'll use time independent perturbation theory. How do we go about formulating the problem? How do we go about formulating any quantum mechanical problem? What is the first thing to do? Write the Hamiltonian, then think what the wave function can be, then you can arrive at the Schrodinger equation, so what we'll do is you know very well that in perturbation theory the Hamiltonian is given by the unperturbed Hamiltonian + first order correction term, for now we'll leave it ourselves to first order perturbation theory.
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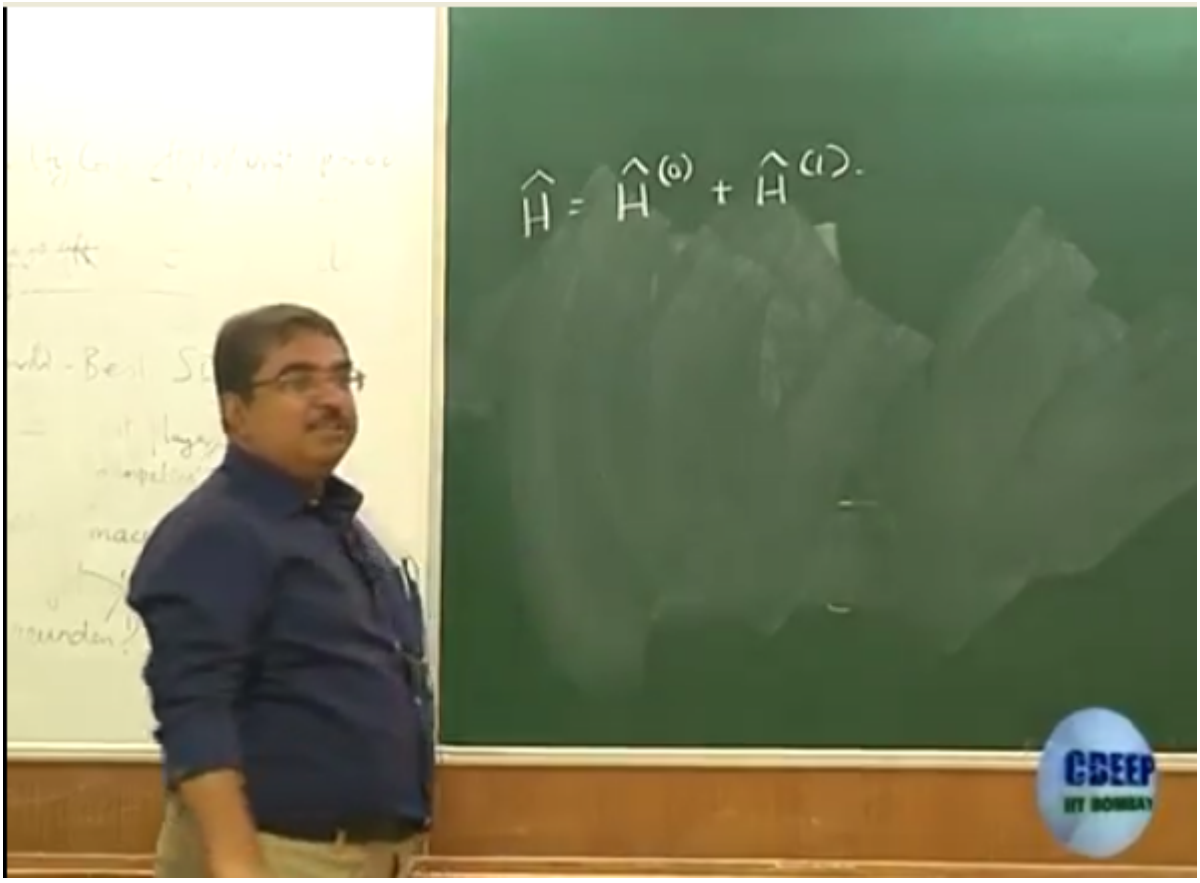

Of course you know that first order perturbation theory works only to small extent, if you go beyond that you need more terms or you need another technique. What is H0? For a two spin system AX, both are protons but they have different values of chemical shift, okay, the shielding constants I'll write sigma A and sigma X we can write. What will the Hamiltonian be? This we have discussed, is it there? No, okay what is Hamiltonian for a spin in magnetic field? Yes, gamma B naught (1 –sigma), very good, and since I know I have two kinds of sigma I'll write A as well as X, is there a minus before or not? There is a minus sign right, so –gamma, what is gamma? Gyromagnetic ratio or magnetogyric ratio, but plus where it comes, there is something else, but minus is there, -gamma B0 multiplied by 1-sigma A, I'm writing the first term of course there will be a term in sigma X as well, but there is something else there.

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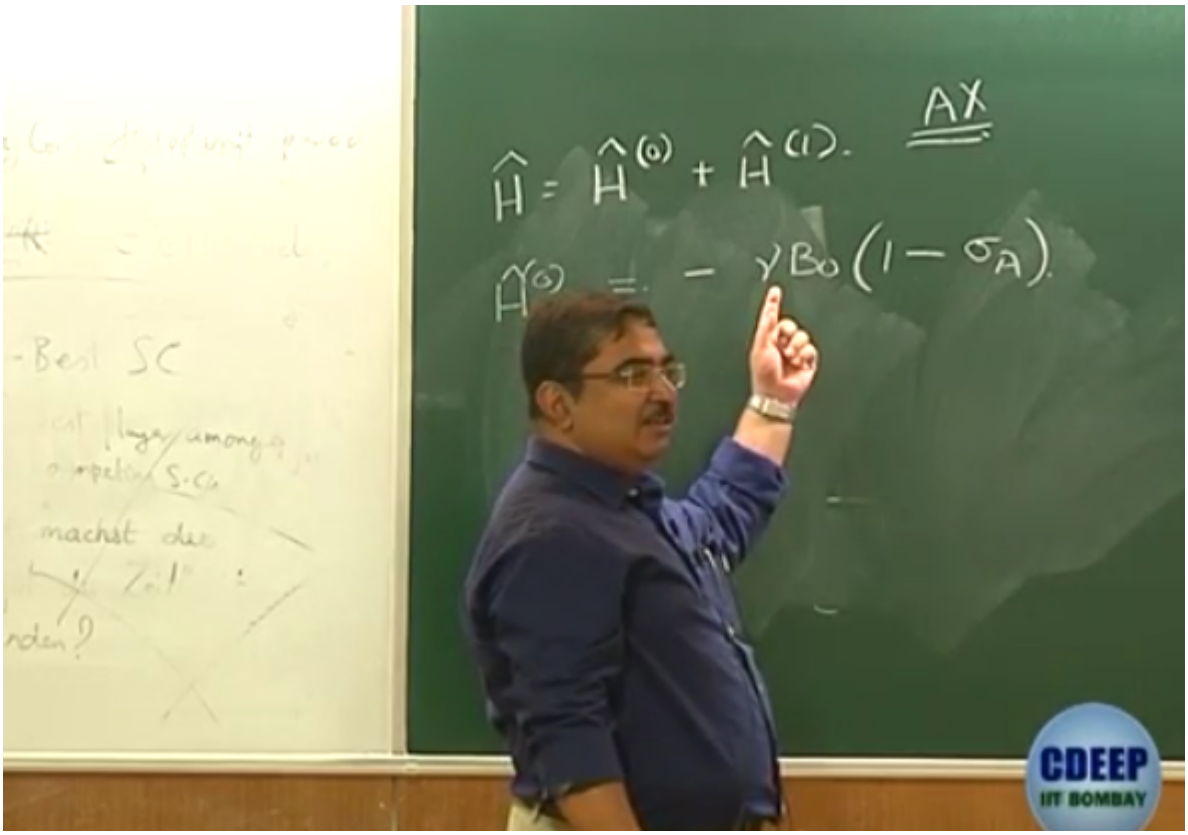

So far this is not an operator right, I'm trying to write Hamiltonian which is an operator, all I have written is I've written something that is a constant, I've written something else that is a constant for instrument and another constant which is your property of the nucleus. What is the operator? What is the operator? You're trying to work with angular momentum right, so Z component of angular momentum and since I'm going to work with A and X both, I'll write A and X in the operator for the angular momentum as well.

Why is it that I write IZ and not I in this case? Why do I write only Z component of angular momentum and not I operator?

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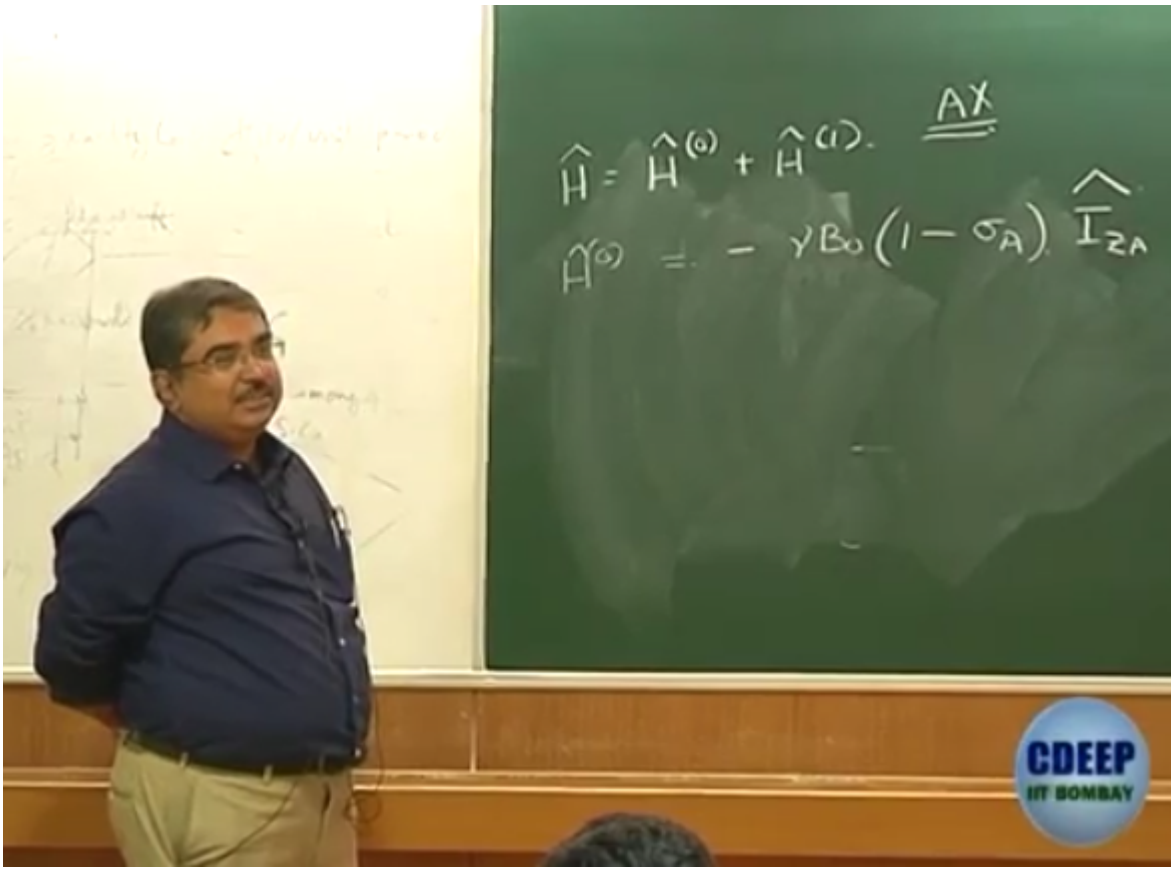

Abhishek? Hemanth? Okay, even before I go there do you all recognize this? Right, do you all agree, in fact we had said that this is the Hamiltonian when we had started our discussion, now my question is why is it that I'm writing this Z component and nothing else? Hemanth? Yes, how is what? Action should be in the direction of the field, okay, so this is also lifeline but this is not phone a friend, this is friend responds before calling that kind of a lifeline, you are right, so what he is saying is we apply the magnetic field in a particular direction right, of course we are at liberty to take it in any arbitrary reduction, but then it makes so much more sense to define the direction of the magnetic field as the Z direction, that is what we have done throughout, and if the magnetic field is along Z direction then of course X and Y components they don't matter anymore, isn't it? That is why we just write the Z component, you could formulate this problem in such a way that you write I and not IZ, but that would make the problem unnecessarily complicated, makes no sense, so that is why we do it, Z is the direction of the applied field, so this is the first term, what will be the second term?

What will the second term be? Hi Deepthi, second term? -Gamma, gamma B, not gamma B right? Did you say gamma B? Oh gamma that B, I thought it is gamma subscript B, fine, gamma B naught 1 – sigma X, then, yes, very good, so this is my unperturbed Hamiltonian when there is no coupling, right.

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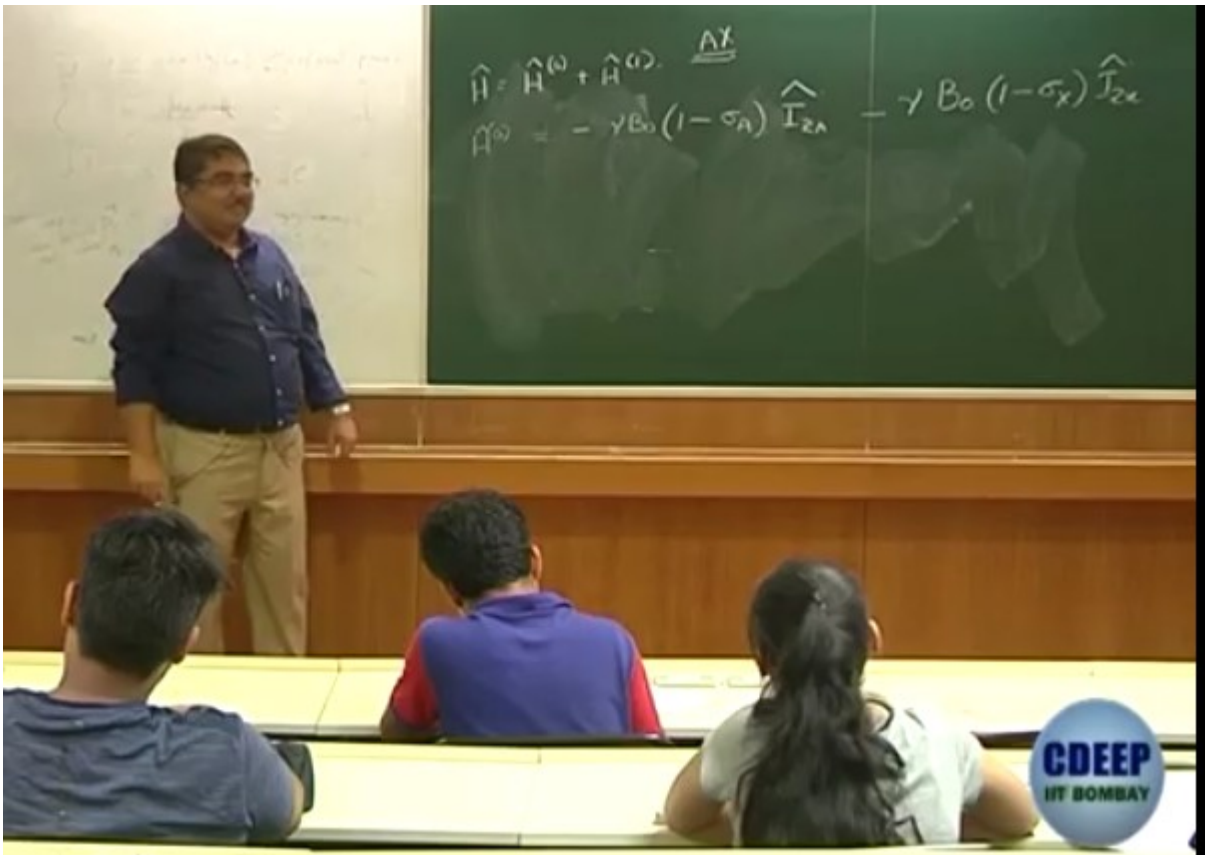

What is the first order correction term? H1, where will I write? I'll write there, H1, H1 you might remember what I had written, it is some constant multiplied by the dot product of the spin angular momenta, right, so it's something like this IA into IX of course these are operators multiplied by I'll write HJ divided by H cross square,

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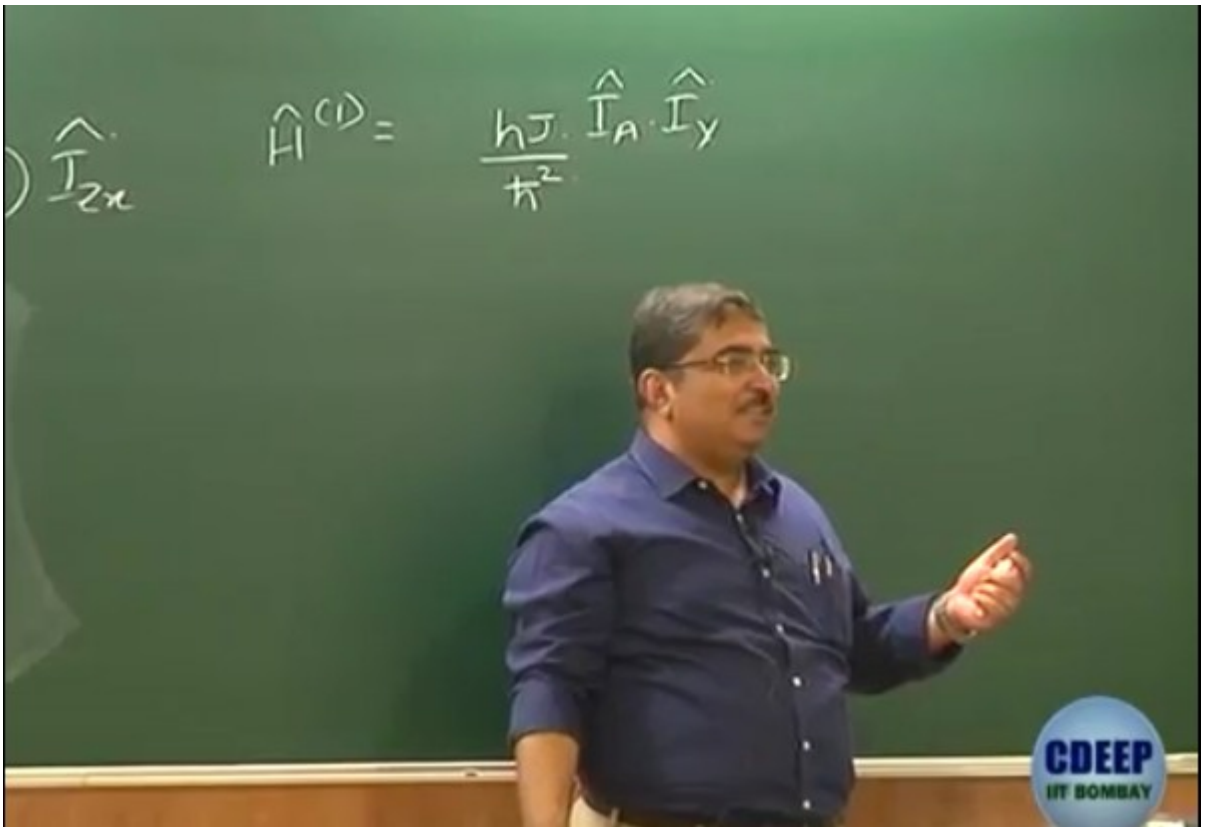

I see a smile of Neetha's face, she is thinking where did this come from now? See I can read your mind sometimes, yes, will there be H cross in the expression for unperturbed Hamiltonian? There will be. Will there by or will there not be?

Will there be H cross in that expression? We'll come later, it is not there to start with, first you just say gamma B0, 1-sigma A but we'll see where that H cross comes from. This expression we don't write, but what Neetha is asking is this, whether IA into IX, and we all know about J by now, what is the point of multiplying by H and dividing by H cross square? The point is see we are not doing it for the first time, we are just learning something that has been worked out several decades ago, so we know the answer, we know that if we write it in this form, our final answer is going to be in a very convenient form, otherwise you're absolutely correct if you just write some constant capital K here, in fact the first time it was done, I'm sure it was done that way, but as you'll see, as you proceed further we'll get something in H cross squared in the numerator, that is going to cancel with this H cross square in the denominator that will save some chalk later on, and these H, why H because we'll get something in energy, if you write energy in terms of H then of course whatever is multiplied with H that is frequency, that is why.

Now one more thing that I want to ask here is this, here I have written IZX, IZA, here I have written IA.IX, why? Could I have just written, I've written it here, could I have just written, acchha this X should be written properly, this capital X, that's why something was not right, this capital X, if I write it as small x we'll confuse it with the Cartesian axis, so could I just have written IZA.IZX in coupling? Why not? Why do I not write just IZA.IZX? Why do I write IA.IX? We've understood why we work with only the Z components, in the unperturbed

Hamiltonian, in the perturbation term why am I not writing the Z components only, why do I write both? Why do I write the whole thing?

In which direction are we all looing? Hopefully in my direction, you had your chance to speak, you did not take it, now let me speak. Hopefully all of you are looking at me right now right? This is the direction is Z, okay, this is B0, okay, but it's not necessarily you can talk among each other, if you can talk among each other than in which direction do you have to look? Swathi would be a good example for this right now, if Swathi could talk to Shoaib, she could turn around and talk to Deepthi or Abhishek or Viva or she could talk to Vanshika right, so and all this can be resolved in X and Y and Z, right, so when coupling takes place and also it does not matter where I am standing, or if I'm standing here at all, isn't it? When coupling takes place that is independent of the direction of the applied magnetic field, so when you at least write the term for the perturbation, when you write the perturbation term of the Hamiltonian you should write IA, IX both, you cannot just write the Z components, there is no guarantee at least when you start with that interaction will be only along Z direction. Have you understood? Right, okay.

As we will see later on after saying all this, only the Z components eventually matter, so we'll stop here today.

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