Principles and Applications of Electron Paramagnetic Resonance Spectroscopy

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Lecture - 15
Theory of First-order EPR Spectra - II

Hi there. We are discussing the quantum mechanical treatment of the various magnetic interactions of hydrogen atom.

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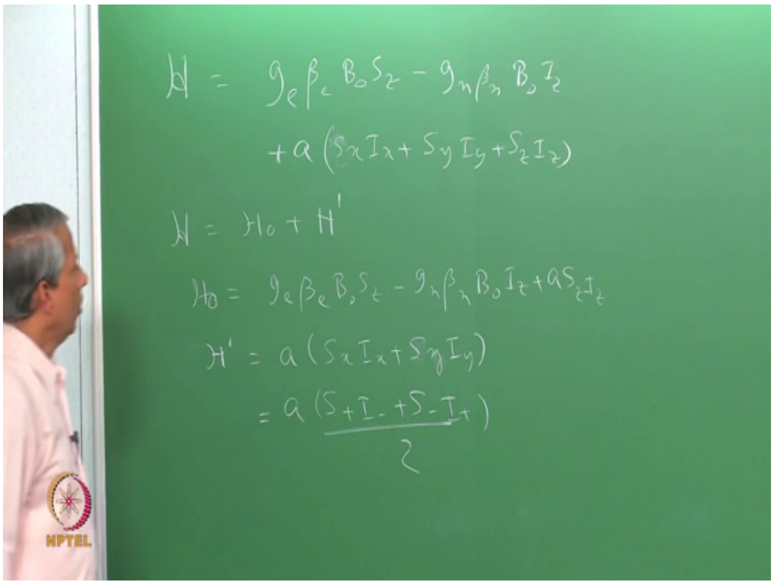

We have seen that the total Hamiltonian of hydrogen atom can be written as this is the electron Zeeman term; this is the nuclear Zeeman term plus a I z. This is the hyperfine interaction term. Now you also saw that we could write as a 2 parts a 0 plus H prime. So, H 0, you call the (Refer Time: 01:22) Hamiltonian or the main Hamiltonian which includes this one that is the most significant interaction is there and the perturbation is this; this can also be written as a S plus I minus plus minus by 2 ok.

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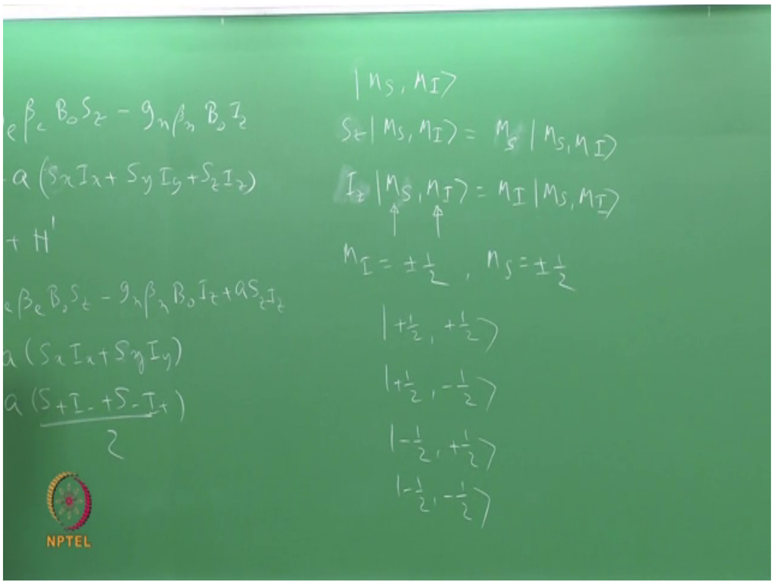

So, this is the main Hamiltonian this is the perturbation Hamiltonian, we can now try to find out the Eigen states of this and corresponding energies. So, for that the Eigen state can be thought of as a product function of the electron spin and the nuclear spin the symbolically we write them as M S comma M I and without knowing the expression form we can use the property that when let us say S z operates on this one it will give me the electron spin angular momentum quantum number which is M I; M S the electron spin component of the quantum number.

Similarly, I z operating on M S M r will give M I M S M r. So, these 2 identifies the possible component of the angular momentum. So, M I takes the value of plus minus half and M S also takes the value of plus minus half. So, you have got 4 possible combination in a correspondingly 4 y functions are there and we should get 4 energy levels alright. So, they are designated by plus half plus half and minus half. So, you can find out the energy of this H 0 Hamiltonian with respect to this 4 wave functions how do they look like using this formula very easily to find out that; let us say g e beta e B 0 S z operating on plus half plus half will give this operating on this will give plus half divided by 2 this.

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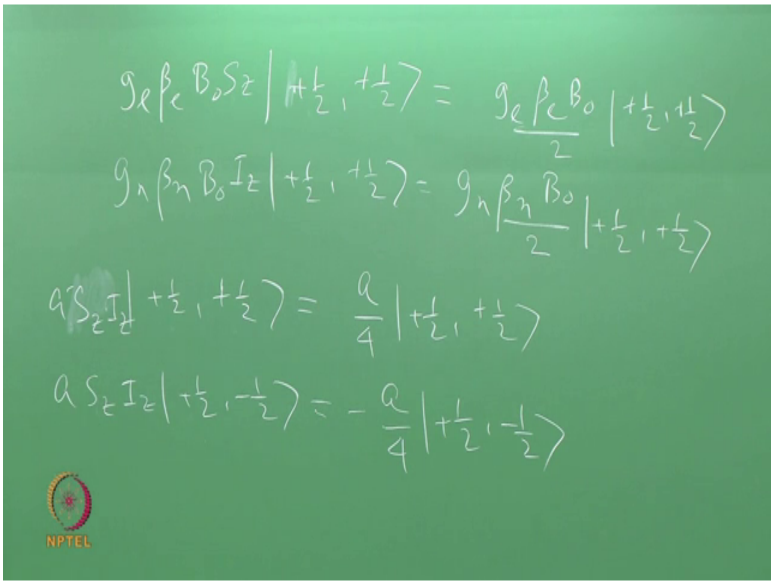

Similarly, I z operating on this will give similarly you can find out all the other terms here, then a operating on let us say plus half plus half will give a I z this operating on this give plus half this operating on this gives another plus half. So, this gives a by 4 plus half plus half. So, suppose we have another one let us say S z I z plus half minus half. So, this operating on this gives plus half this operating on this gives minus half the net resultant will be minus a by 4 plus half. This way we can find out all possible energies of the 4 states.

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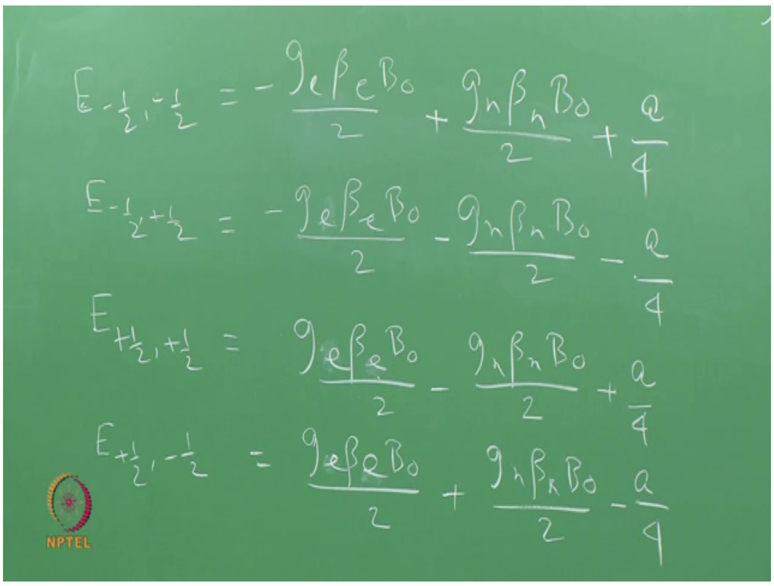

So, these are given here let us call it here energy of this a by 4 a by 4. And other 2 I will write at the top of this. This is e minus half minus half this gives minus g n beta n B 0 by 2 plus a by 4. So, this 4 different wave functions give rise to 4 different energies and then how they are arranged they are arrange in according to of course, the various values of this here the there is a mistake here sorry this is this mistake corrected ok.

So, the major interaction is coming from the electron Zeeman term here. And then this will be very small contribution that will be added to that and this will be also small contribution. So, these are now shown here in this slide.

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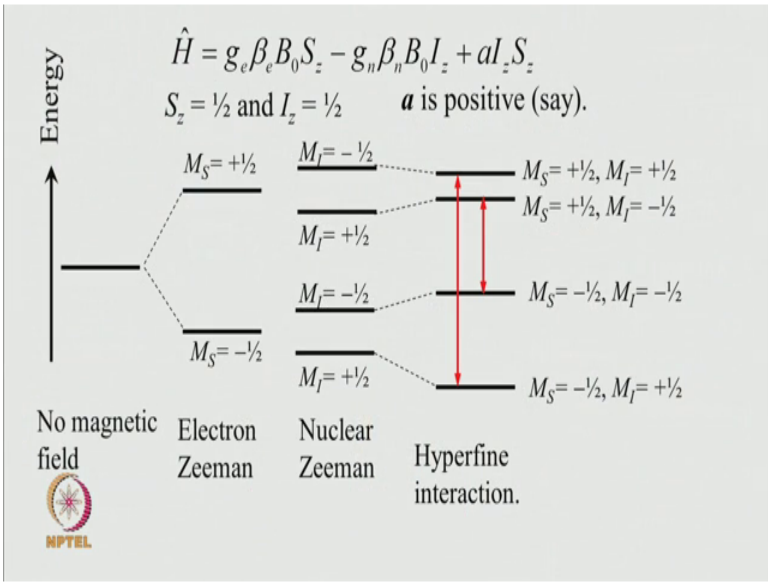

So, when there is no magnetic field, then all the 4 energy levels are same; so first we apply the electrons Zeeman term. So, the maximum splitting is due to that on the electron (Refer Time: 09:17) minus half with the lower energy plus half gives higher energy and then this is the interaction coming from here then we add the nuclear Zeeman term that is here g n beta n B 0 I z.

So, that splits this energy into 2 for mi equal to plus half and minus half plus half here gives negative energy. So, this is lower energy similarly here minus gives higher energy. So, these are nuclear Zeeman term added here then we add this hyperfine interaction here as you mean the a is positive quantity then I z S z when the product is negative that gives lowering of energy and the product is positive it gives higher energy. So, that is the way the further this levels are changed.

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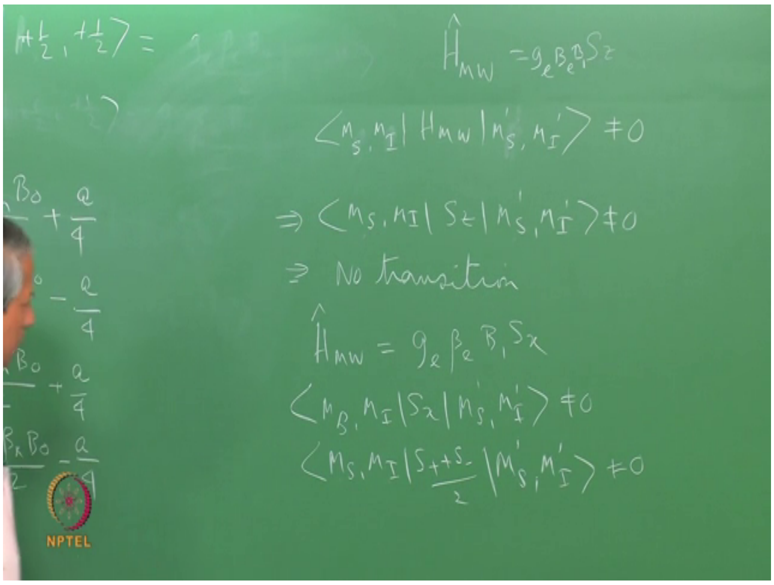

So, having all these 4 energy levels; what are the allowed transitions now? If the micro magnetic field is applied along the z direction, then will say perturbation due to the micro wave, let us say micro wave in the z direction will you have this sort of operator B one is the let us say the magnitude of the micro magnetic field applied under the z direction. So, this 4 energy and the 4 way function that we have there to have transition I must get a matrix end of this kind some M I M S M S M I and M S M I prime this has to be non 0 for transition to take place.

Now, here you see that this is as good as saying that M S M I S z M S prime M S one has to be 0, but then all these 4 energy levels are Eigen state of S z. So, unless these are this is same as this this will not be 0; that means, M S should be equal to M S prime; that means, plus half remains plus half minus half remain minus half so; that means, no transition; that means, no transition. So, micro magnetic field applied around the z direction does not cause any transition that is not surprising we have already seen earlier that the micro magnetic field has to be applied along the perpendicular direction same thing is coming quantum mechanically also.

So, in states therefore, suppose you apply the H microwave along the x direction then this will look like g e beta I B 1 S x. So, in the same argument now what I need here is M S M I S x M S I M M this has to nonzero. Now I can write S x as the resignal lowering operator S plus plus S minus by 2 this one now these can be non-zero if this operating on this gives a function which is same as this one this operating and this gives function which is same as this one and what is more that this nuclear spin part is not involved in this integral.

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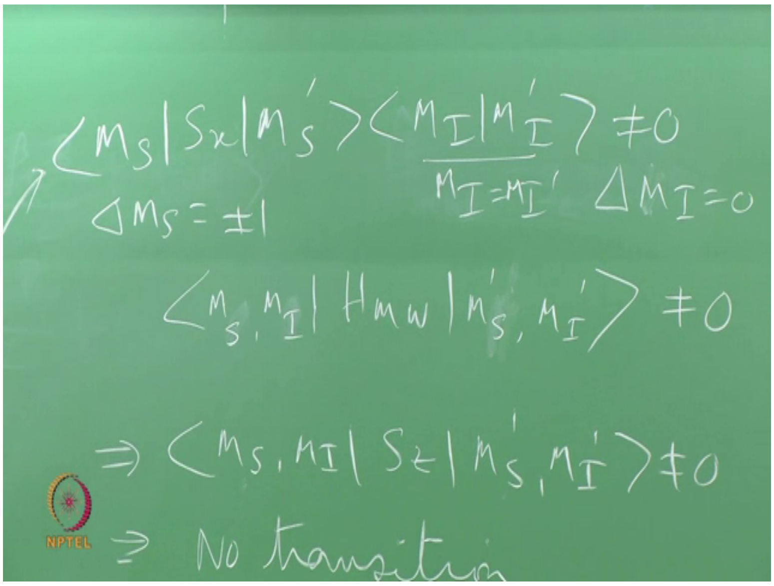

So, this can be written as non-zero; so; that means, this must be I must be equal to I prime or delta I M I must be equal to M I prime or delta M I 0 and here because this can either increase it by 1 unit or decrease it by 1 unit. So, that gives this selection node delta M S equal to plus minus 1.

So, these are selection which is for that and. So, those are the 2 transition allowed which is shown in this slide. So, here this transition takes minus half to plus half for the electron spin without changing the nuclear spin. Similarly, for the other one here electron spin changes a minus to the plus half again without changing the nuclear spin. So, what is energy graph for this you can calculate from this pair and that pair?

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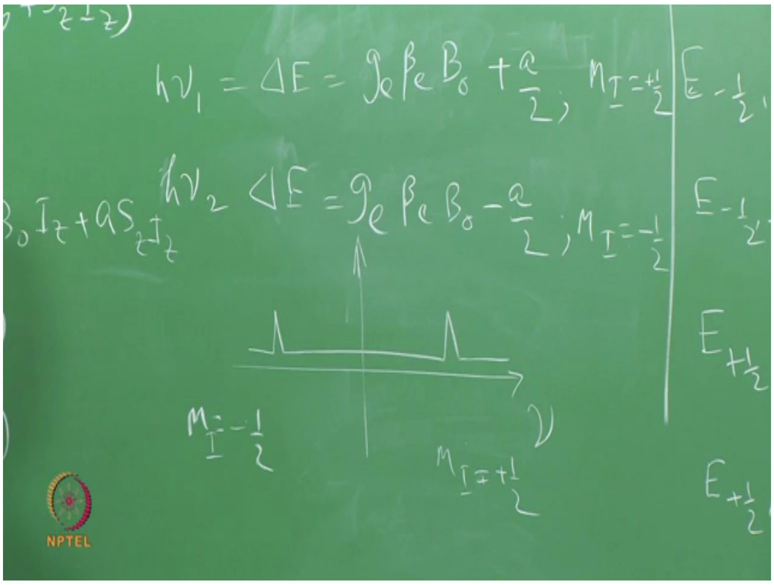

So, one delta e turns out to be g e beta I B 0 plus a by 2 this is for M I equal to plus half and other delta is equal to minus a by 2 this is for M I equal to minus half.

So, the 2 transitions are separated by a by 2 from the position which is g e beta I B 0. So, if there were no hyperfine interaction then the energy would have been this one energy of transition. So, I see the 2 lines which is split which are split from the original line position and what is more here we see that these term the nuclear Zeeman term has disappeared completely from this. So, in this arrangement the way it appears that we do not see any interaction of the nuclear Zeeman term.

Now, if we do the experiment let us say at a fixed magnetic field, then what we see. In fact, the derivation here is based on a fixed magnetic field B 0 is kept fixed here. So, that does not change. So, we vary the frequency then B 0 is fixed. So, this will be equal to H nu; let us call it for first transition this is H nu for second transition. So, is a function of frequency we plot it this will give a peak where V 0 is fixed. So, this will give a frequency of one peak here other peak there the low frequency peak will correspond to M I equal to minus half other one correspond to M I equal to plus half higher energy.

So, this center of this is exactly given by this one. So, this gap is now exactly equal to a.

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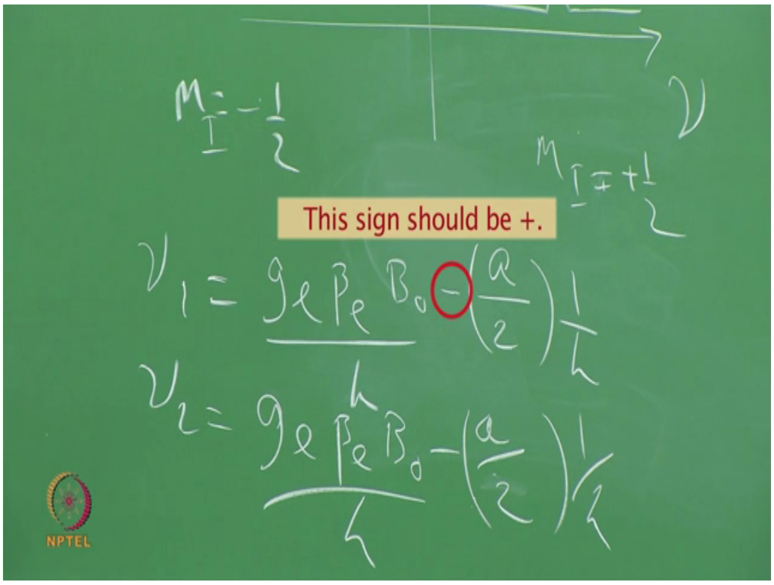

So, we say that in frequency unit this is exactly equal to the hyperfine coupling constant because nu 1 will be and nu 2 will be g e beta e nu 0 by this is the frequency unit. Now if we do a experiment a by keeping the frequency fixed while vary the magnetic field, then h nu is kept fixed.

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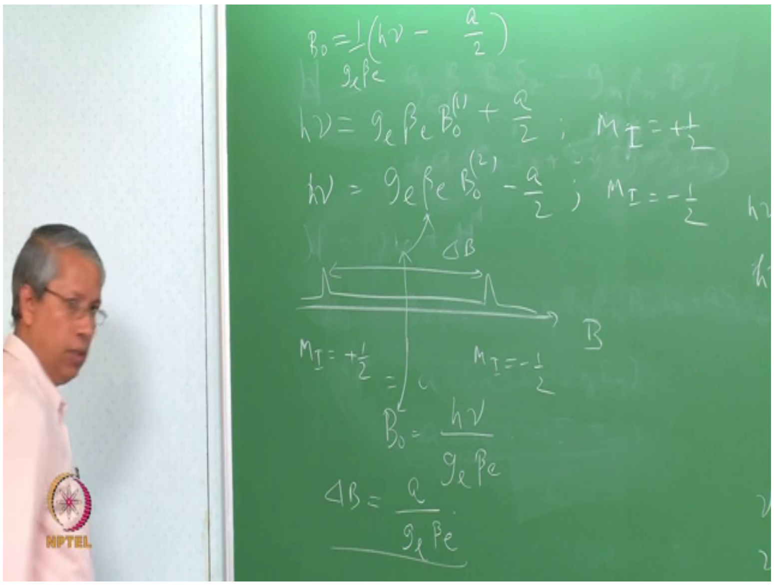

So, for first transition this will be g e beta I let us say B 0 1 a by 2 for M I equal to plus half and this is kept fixed. So, second line will be at B 0 nine 2 minus a by 2 this is for M I equal to minus half.

So, here frequency kept fixed. So, if I plot this as function of magnetic field v 0 and as this is fixed my B 0 comes out to be H nu minus a by 2 divided by g e beta i. So, this will appear at a lower magnetic field this is M I corresponds to plus half. And here M I correspond to minus half see how it changes now then again the exact earlier the center the magnetic field correspond to this one which is given by this is the B 0 then it will be and the gap here delta B will correspond to. So, we call this the hyper fine splitting constants.

Now, we have seen this energy levels and the correspondingly we have found out the 2 transitions and got this relationship that for variable frequency experiment and variable field experiment we have neglected.

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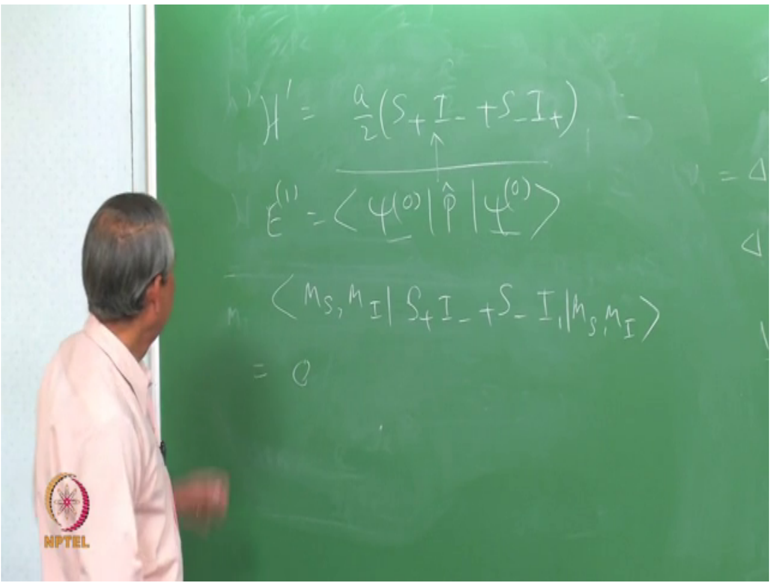

So, far the cross term or the perturbation term which I was saying earlier which is H prime is a by 2 S plus I minus plus S minus I plus. Now effect of this can be seen by considering the first order calculation and a first order calculation the let us say E 1 calculate given as psi 0 perturbation psi 0 first to the calculation here.

Now, here this is the perturbation here and this 0th order of functions are the; of functions that we have here this. So, if I write any of this one M S M I and put this here S plus I minus plus S minus I plus M S prime M I prime. So, here this supposed to be same as here. So, I cannot have prime here this will be same as that. Now, because this is increases the value of M S by 1 unit this decreases by 1 unit per nuclear spin see this will be 0 for all possible this 4 states that we have here.

So, even if we do the calculation of the first order this term does not contribute to the energy level in any way nor does it change the allowed transitions there. So, what we conclude from here is that all possible energies that you have discussed here and the allowed transitions they are correct up to first order of calculation. And here the characteristic feature is that the center of the spectrum corresponds to the exact g value that we can measure from here, and it is symmetric with respect to the center and we can ignore the nuclear Zeeman altogether.

With this, I have shown the final slide here. This is the Hamiltonian which is good enough for our first order calculation nuclear Zeeman splitting gives this and then hyperfine interaction gives splitting here and we can get the allowed transition from this. With this we stop now.