Principles and Applications of Electron Paramagnetic Resonance Spectroscopy

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Lecture - 03
Electron-Nuclear Hyperfine Interaction - I

Hello. We are going to discuss this Electron Nuclear Hyperfine Interaction. I introduced this last time without explaining what it means.

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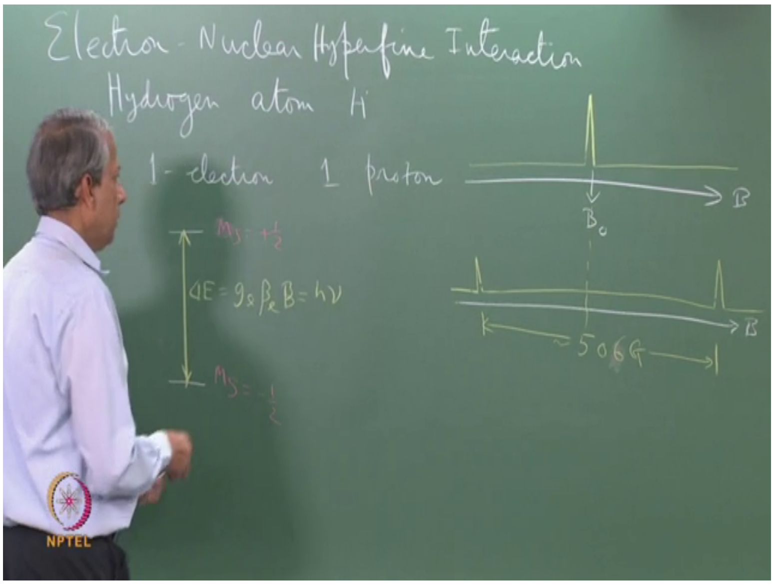

So, today we are going to figure out what it is; electron nuclear hyperfine interaction, I said that this interaction produces lots of hyperfine lines, let us try to understand the origin of that. So, for that let us take a simplest possible system you can think of which is periodical is; hydrogen atom, it has 1 electron of course, and 1 proton. So, what we have discussed so far? If I try to look at the energy level diagram of this in a given magnetic field; for the electron I can splitting of this kind which is the electron demonstrating corresponding to the electron spin, let us call it S of M S is equal to minus half and here M S equal to plus half.

And as we discussed earlier, if this is the case that has to your transition looks like this delta is equal to B and this will be equal to H nu. So, for the feast frequency experiment GPS spectrum will look like; I will draw it here where this is the magnetic field. So, this corresponds to the energy of transition which satisfies this relationship, but what it is found if the experiment is done this spectrum does not look like this what it appears to be this type of function of magnetic field, it gives one line here.

Another line there, we will discuss with respect to spectrum there is no line exactly at the middle of that. So, this line if your line is split into two in case of hydrogen atom, so we call them of course, the hydro hyperfine of hydrogen atom whether this gap is actually almost 506 gauss approximately, quite a large splitting, what is happening there? Why does hydrogen atom give two line and not one as you expected from the certain scenario? So, one simplest way to look at it is that this is probably not the complete energy level diagram of hydrogen atom, something else is happening.

So, if I get two lines then actually there would be two transitions in work there; what is the origin of that? Try to look at it, this electron there and a proton there proton also is a magnetic moment.

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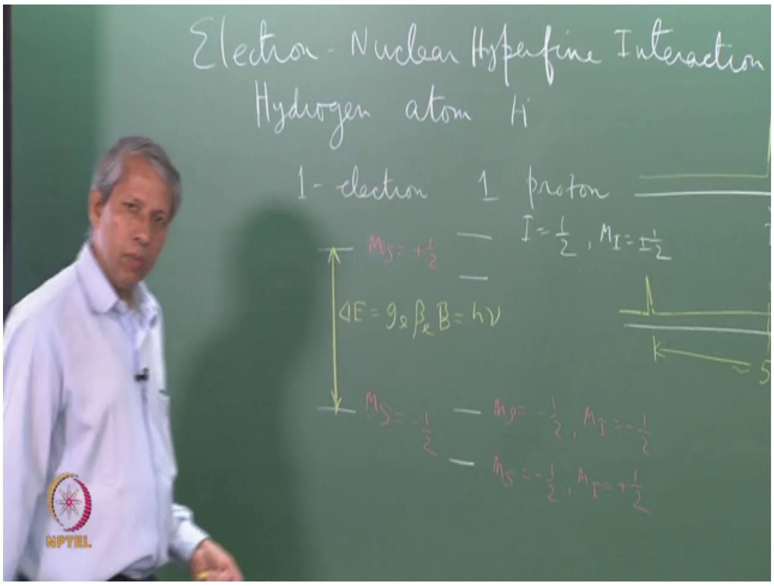

So, in a magnetic field this will also align according to its nuclear phase state which is; I equal to half M I equal to plus minus half. So, it will be either along the magnetic field or opposite direction. Now the electron which is present there in the atom; it finds itself in a presence of two magnetic field, one is external magnetic field that is applied by the spectrometer and the second one is the local magnetic field by proton produces.

Now, you see that two are element of the proton spin so; that means, the local magnetic field that the proton produces either adds to the external field or it subtracts the external magnetic field. So, depending upon therefore, the proton spin state; this energy level is going to split now. So, here suppose it appears this way this splits into two; similarly this will also split into two depending upon the what nucleus spin is associated with? The electron spin of minus half. So, this could be now M S equal to minus half and M of I is equal to cross of let us say, this could be M S equal to minus of M I will also give a minus half.

Remember that electrons even zee man interaction is much stronger than an nuclear zee man interaction, but here we are now looking at the electrons zee man interaction, but it is a interaction of the electron magnetic moment interacting with the nuclear magnetic moment, so the splitting is given by this.

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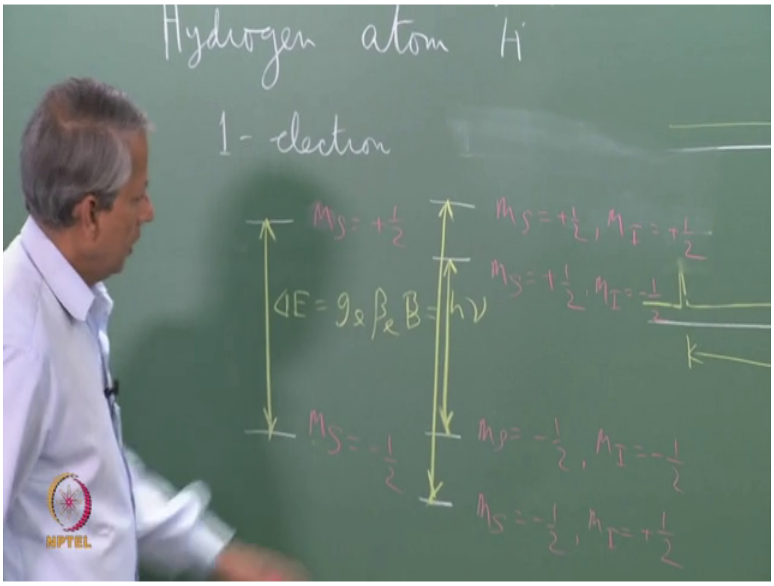

Similarly, here M S equal to minus half and M I equal to; that is in this way sorry M S equal to plus half and M I equal to minus half and this will be M S equal to plus half M I is equal to plus half there.

So, why this arrangement is of this kind? That we will see in the later very soon in fact, but let us take it to be true, now there are 4 errors now; where earlier were 2; EPR spectroscopy it is a electron spin which changes, nuclear spin does not; NMR spectroscopy; nuclear spin that changes, not the electron spin.

So, here if we draw the line correspondingly without flipping the nucleus spin, you see that one transition will go from here to there; M S equal to minus half, plus half M I remains plus half and plus half. Here another one; M S equal to minus half to plus half, M I remains same in minus half and minus half. So, you see that the two transition corresponds to two different energies and that will be reflected here in two different types of magnetic field.

So, this splitting that we see here is therefore, coming from this possible orientation of the nucleus spin in a magnetic field. See in one proton, I get possible orientations of two types, I get two lines of this kind.

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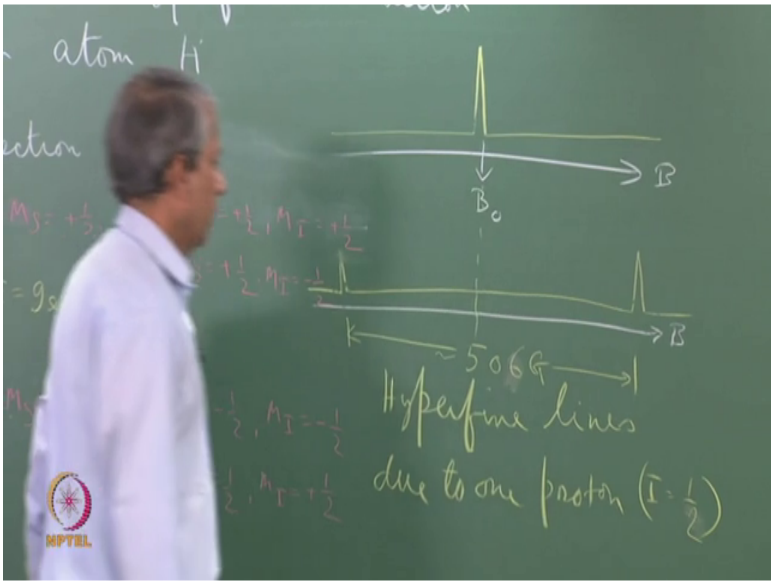

So, I get two lines here and these are called hyperfine lines coming from the one proton; spin I equal to half. Now suppose I have got more than one such nuclei which has got spin halfs in it; what could be the simplest example?

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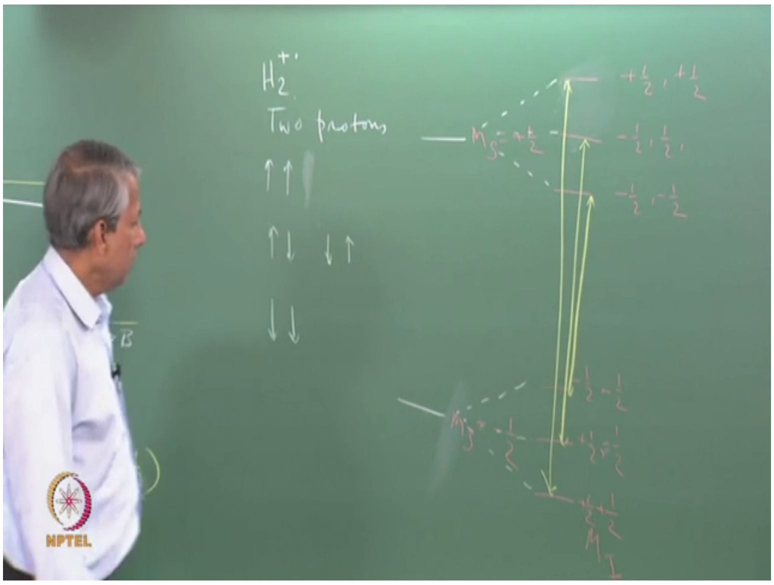

So, hydrogen atom I can go to this hydrogen molecule and is got two protons and there identical in all aspects; we call them two equivalent protons. So, we go through similar argument now that in a magnetic field, these two protons can align; all of them can align this way or this one can be up, other can be down or this could be down this could be up or both could be down. These are the possible nuclear spin orientation in a magnetic field and each of them give us to local magnetic field that the electron will see. So, this energy level that I have drawn here will be modified in this fashion.

I could this two energy level for; now for this electron spin minus half there the possible nucleus spin. So, this will split into this now imagine here the electrons nucleus spin of one is opposite to in second one. So, net local magnetic field due to this combination will be 0, here it will be higher and this will be lower or this will be lower or this could be higher. So, let us write in this fashion that this will be total spin of nuclei could be plus half, plus half, plus half, minus half.

This will be; this are the possible magnetic components there. Similarly here, the electron spin is plus half; this will also have three types of nucleus spin arrangement. So, I write in this way, so I can draw the splitting of the energy levels due to the nuclei could be drawn this fashion that this is a split into three. So, this energy will also split into three; now we follow the same conversion earlier; that when the E P; electron parameter resonance transition takes place; nucleus been do not change, electron spin does.

So, transition from this to this one possibility; another possibilities from this to this and third one is from this to this. We see that since the energy gaps are different, they will appear different magnetic field, but the middle one is exactly the same as here because the nucleus spins are just opposite to each other. So, that does not contribute to any change in the local magnetic field. So, this spectrum therefore, if I have to what predict from here is that; EPR spectrum is this hydrogen molecule ion should look like this function of magnetic field.

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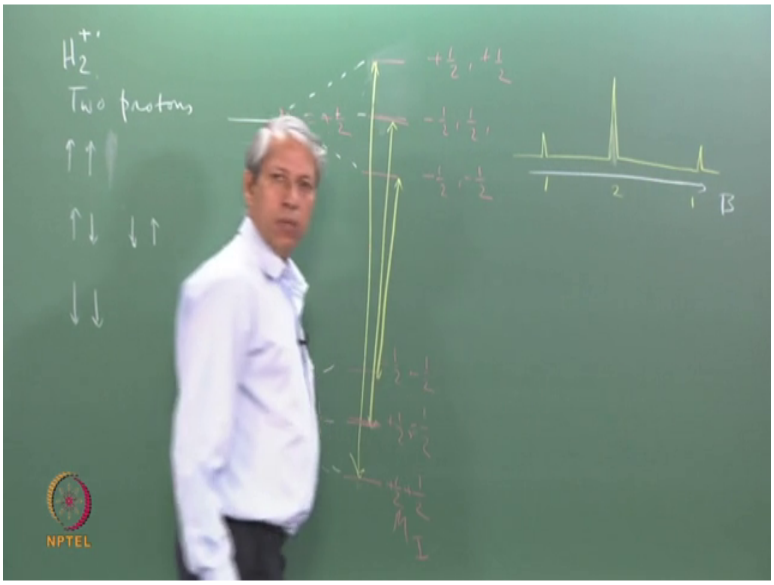

It should look like true; this is the way, but this is not quite true that three lines of equal intensity that comes from this argument, is not quite true; the reason is that see the number of possible allowed nuclear configuration is of this kind. So, even though there are three energy levels; you see that number of molecules that will appear here will be; I say two of them there, similarly two of them there. Because the first proton spin could be up, second could be down or first could be down, second could be up; both are equally likely. So, in a sense there are either call it the true energy levels are there which are degenerate or the number of particles that are distributed here will be such that; will be twice of particles here compared to this and this.

So, the intensity of the appear line will be twice now; this kind. So, this is if I split 1 is to 2 is to 1 type of intensity for this system there. What we had here? That this four energy levels are there, all levels are almost equally likely. So, intensity of number particles that this molecule transition will be same and number of molecule that this transition will be same will be exactly equal; this will be 1 is to 1. So, you see how therefore, the relative intensity change as the number of nuclei which are produced in the splitting change, here both are spin of systems. So, I get a spinning of 1 is to 2 is to 1.

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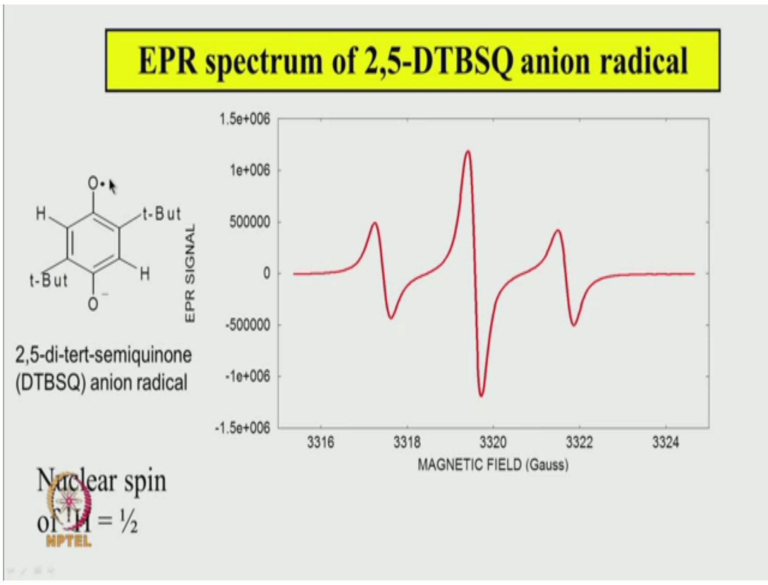

Now, here I could therefore, take the example that I showed last time is that; this 2,5- di-tert-semiquinone anion radical. This is the spectrum which actually intensity is 1 is to 2 is to 1 type of thing.

And the origin of this now could be easy to visualize; there is one proton is here, another proton is here; they are equivalent in all aspects. So, I can have argument of this kind the way this nucleus spins of this two protons are aligned, gives rise to this sort of spectrum with intensity 1 is to 2 is to 1. It also shows lot of other things is that electron though we draw here in the structure; electron is sitting here, but that is only the crudest possible picture. The unpair electron is present throughout the pipe out of the benzene ring and interacting with all the ring protons; the API spectrum shows this. So, in a sense the measure of this splitting here or here is a measure of the; strength of the interaction of the electron and the nucleus.

So, we can continue further with this sort of argument that; if I would more than two spin half nuclei, what will be the corresponding EPR spectrum? Let us do one more and then we will generalize after that. Suppose we have a system of three protons and that is also a radical.

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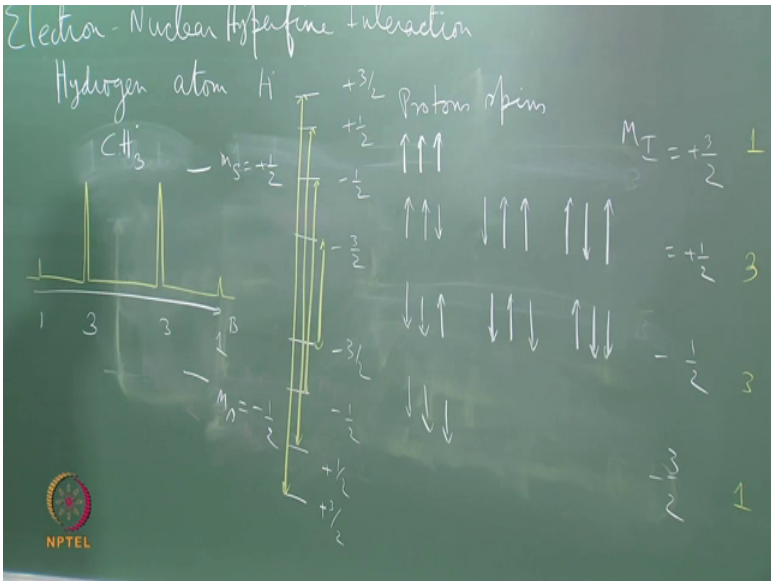

Something I can think of is let us say methyl radical, this three protons are equivalent in all respect. So, I could cross similar energy level diagram with earlier; for electron this is the M S equal to minus half and here M S equal to plus half. Now we have got three protons in all of them we will align in the magnetic field according to plus half or minus half of each of them.

So, I can get this sort of orientation up, up, up; all three should be half, one possibility or this will be up, down, up; only one down; two ups or two down, one up or all three could be down. These are the possible nucleus spin in a magnetic field now; see here that each of them now gives us to local magnetic field that the electron we will see is different for all four of them.

Maximum difference will be here, maximum here and minimum there, but whenever least each of them will be appearing as a splitting of energy levels here now. So, what we expect now? Considering what we have discussed here, this each of the levels will be split into four lines now; so, I will write; so here we.

So, if we write the corresponding total M I; the total nucleus spin, this becomes plus 3 by 2 this becomes plus half, this becomes minus half, this become minus 3 by 2. So, this will split, so it will be; this is the possible values of the proton spin total angular momentum quantum number. Similarly, here this will be minus 3 by 2, minus half, plus half, plus 3 by 2.

Now a same argument as earlier exactly same, the transition will be from the level 1 to the other level which does not involve any change of the nucleus spin. So, that condition is here to here, other is from here to there; then this four transitions are possible there. So, the EPR spectrum will consist of four lines, but will the intensity will be equal? Certainly not; see the way we had this, 1 is to 2 is to 1 intensity ratios, can we now extended to this number of possible arraignment for this, this and this is.

This is 1 type; if you say 1 unit, this will be thrice the number of molecular will be having this sort of nucleus spin configuration; this plus 3, this also becomes 3, this becomes 1. So, the EPR spectrum therefore, look like this function of magnetic field; this will look like this. So, the intensity ratio of 1, 3; 3, 1, so it gives four high profile line, the energy gap of this will be same as this, will be same as this. Because the energy gap between this, this, this is same as this, this and this and that in turn comes from the magnetic field that these sort of arrangement nucleus spin produces at the electron; so, you can see now pattern now.

Let us summarize now, how we can get this various line and then we will generalize it.

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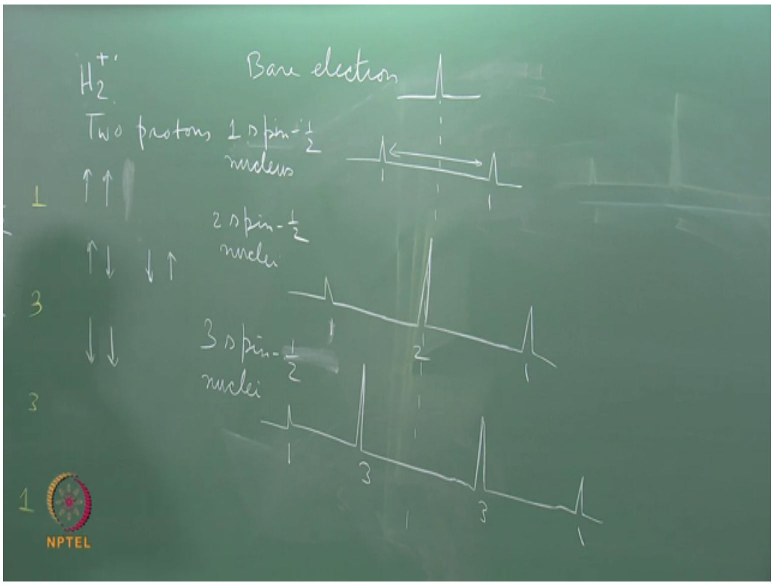

So bare electrons, it gives one line spectrum; 1 spin half nucleus gets splitting of this kind, so this is the center of this one. So, this will by splitting due to the 1 spin half nucleus; in our case it is a proton, the two of them again the splitting looks like this; so, here it was 1 is to 1 and 1, 2, 1. So, I have got 3 spin half nuclei; you can again splitting which looks like this one; 1, 3. So, this sort of splitting that comes from the equivalent nuclei of spin half has certain pattern.

These numbers are supposed to be familiar to some of you; is that they come from binomial expansion of; this is a plus b to the n if you do it.

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Binomial coefficients have exactly same number, so these numbers can be generated in the form triangle, we call Pascal triangle. Let us have our 1 here then 1 is to 1, then 1, 2, 1; then I have got 1, 3, 3, 1. The triangle you generated in this fashion that if we starting from 1; this one step below, I add the number which directly top left and top right; let us take sum of these two; assume there is 0 kept there.

So, here this plus this gives this number, 0 and 1 gives 1. So, in here 1 and 0 gives 1; go down here again I add the numbers which is directly to the left and to the right. Imagine that this is 0 here, so this 1 comes from the sum of this and this is 1, now this 2 comes from sum of this 1 and 1; 2, this comes 1, 1, 0 and 1; this 1 here.

So, every step we just add the two numbers which is the left side and right hand side and add the two and get a number below that; so this triangle is called Pascal triangle. Next one same way; it goes here and here this is 0 there, gives 1 and this and this gives 3 and this and this gives 1 and this and this which is 0; gives 1, 3, 3, 1; we can therefore generalize that.

See if I have got; now four spin of nuclei I can easily predict that spectrum which will look like from this paschal triangle, 1; add that two; 4 this will be 6, add the two; this will become 4, this becomes 1.

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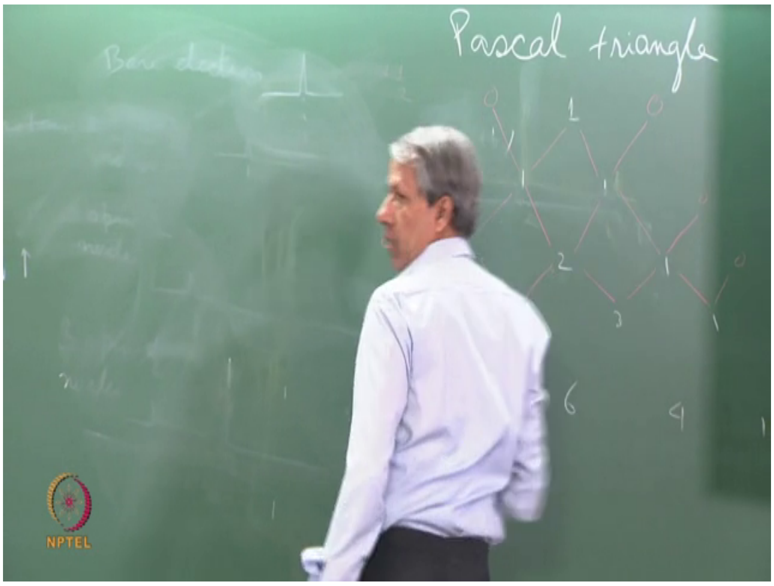

So this is the Pascal triangle, you can keep on generalizing this. So, this example is given here we saw earlier; this one.

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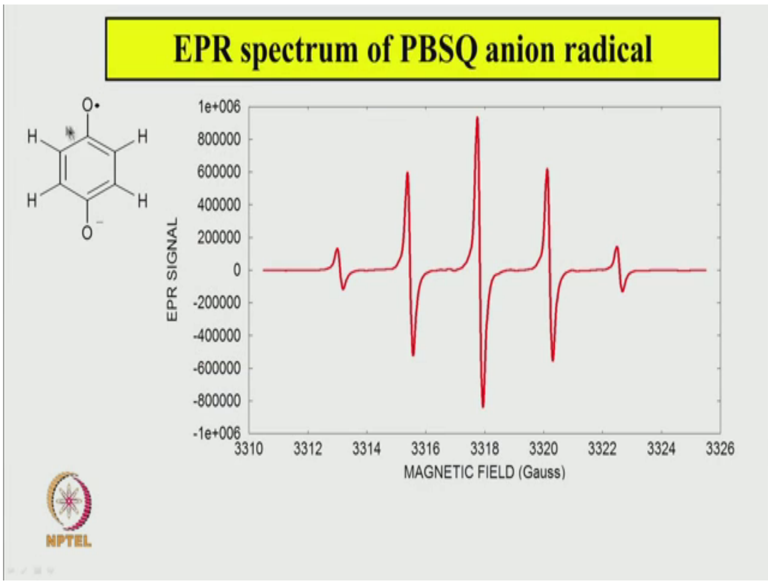

This radical has four equivalent protons, they are equivalent in all aspects. So, four equivalent proton gives rise to five lines as predicted by this generalization, by intensity ratio is 1, 4, 6, 4, 1. So, here if you measure carefully this is almost equal to 1; is to 4; is to 6; is to 4 is to 1. See how beautiful this agrees with our prediction, so this way we can predict the spectrum of more complicated radicals and that sort of example and their interspersion, we will take up later.

And right now, we just summarize that form the EPR spectrum; when you get lots of such hyperfine line, we can very easily get rise or even guess very intelligently the nastier of the radical. What sort of nuclei which are present there, which can give rise to such high profile lines. And from there you can characterize it, almost unambiguously what the radical that could be.

So, before we close; we just take one more example which is somewhat different from spin half. This generalise only for spin half nucleus, suppose the nucleus spin is not half; it could be 1 or one third in spin half, but nitrogen 14 is spin 1. So, what happens if the nucleus spin is 1?

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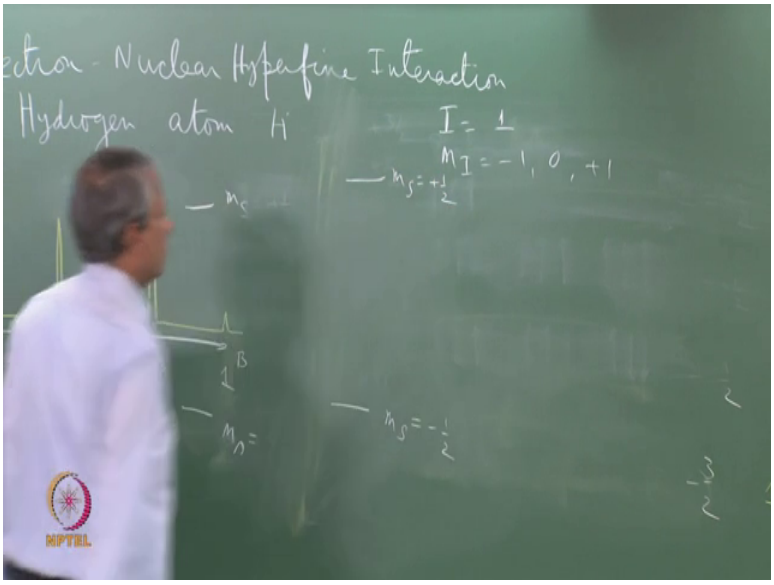

Then I equal to 1 and its component M I will be minus 1, 0, plus 1. So, in a magnetic field this nuclei will also variant in three possible directions and it will produce local radical, which will be having three different values; this will not have no magnetic field. So, if I draw the hypothetically energy level diagram for one electron; interactive with the nucleus of this kind; what do I see? First the electron zee 1 splitting will look like this, this is the M S equal to minus half, M S equal to plus half.

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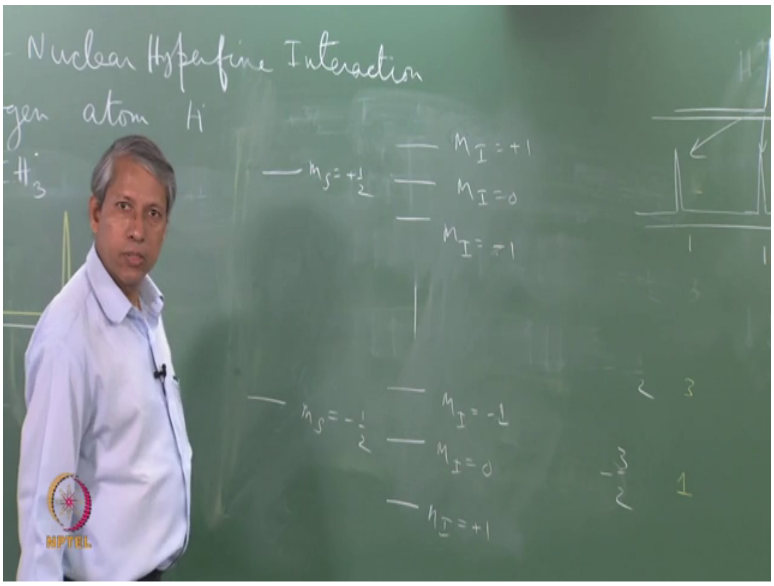

So, when these electronics see the presence of the nuclear spin, it will split into three energy level; M I equal to plus 1, 0, 1; this will split into 3.

M I equal to minus 1, 0; M I equal to 1 and then based on this condition that when the EPR transition takes place, electron spin changes from minus half to plus half, but the nucleus spin do not change. So, that allows me to have this three transition; from one here to here, second here to here and third one is from here to here.

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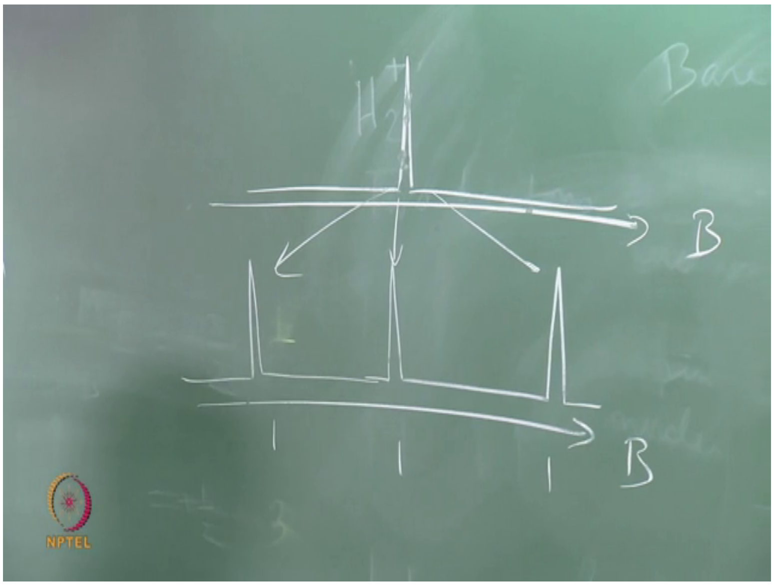

So, these three transitions will be reflected here in a spectrum; that earlier this spectrum was here, when there was no electron nuclear interaction. Now this is split into three because of this three energy levels here, so I get transition which looks like this; one is exactly below the other because this energy level is same as that is here. What about the intensity ratio? You see that each of this three levels have exactly equal population; 1 is to, 1 is to, 1; here also 1 is to, 1 is to, 1.

So, that will be reflected in the intensity of this; it will also be 1 is to, 1 is to, 1. So, the total nucleus here is 1 here, I get three levels compare that with sorry H 2 type of system.

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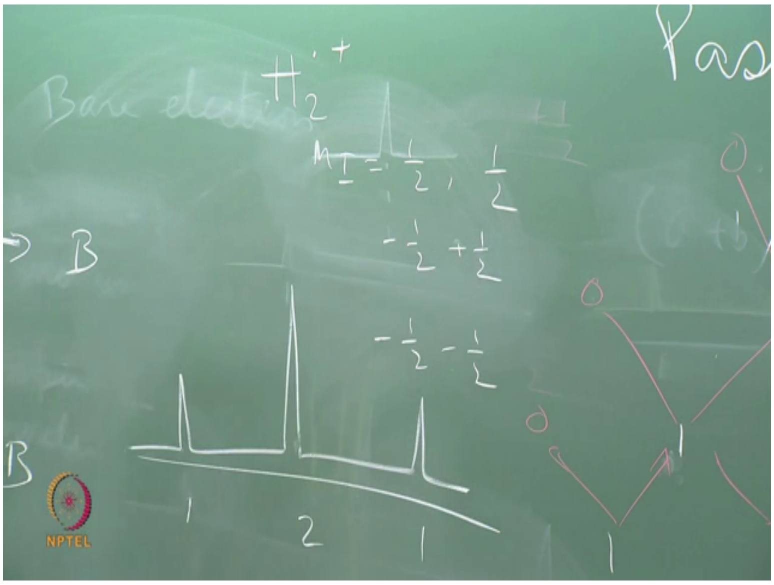

Where was the total nucleus spin was? 1, but they were coming from two protons of M I equal to half and half or minus half or plus half or minus half. So, this give rise to 1, 0, minus 1 which is very similar to this, but here the EPR spectrum look like this diagonal 1 is to, 2, is to 1, but here we have got 1 is to, 1 is to, 1; reason is again obvious that here, this transition involved energy levels were twice the number of particles that could stay here, but here all the levels have just same number of particle.

So, I get 1 is to, 1 is to, 1 here; 1 is to, 2 is to, 1; this also shows the power of EPR spectroscopy that by knowing the; not only the number of lines and its pattern of relative intensity is, I can guess very accurately the type of nuclei which are causing the splitting. If I see 1 is to, 2 is to, 1; I will most certainly be have able to say that 2 spin half nuclei are causing the splitting.

I may not be able to say that it is coming from the two protons, if I do not know the chemical nature of that. But the facts that I see this intensity ratio; that they must come from the two spin half nuclei. Similarly, if I see a pattern of this kind 1 is to, 1 is to, 1 here most certainly say that this comes from the nucleus, whose spin is 1; it maybe nitrogen 14, but unless I know the chemical nature; I will not be able to say that.

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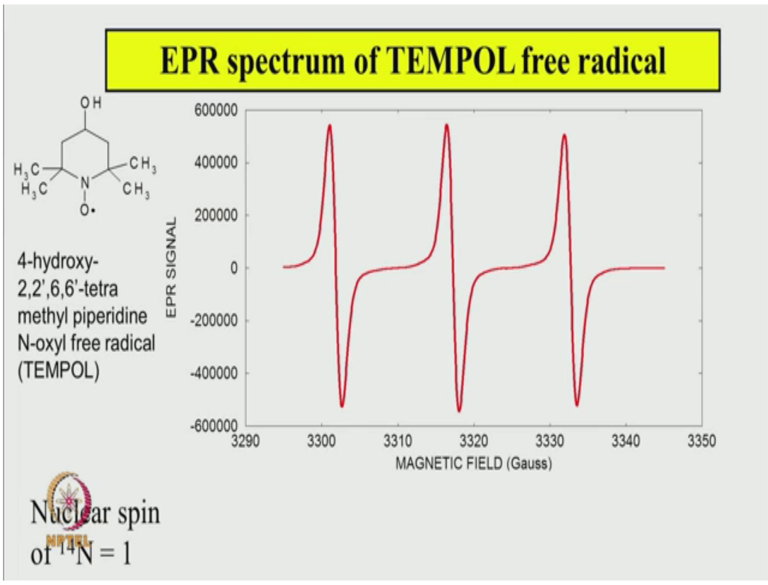

So the example of that is given here; this one, here if you see that this periodical center O dot is near in nitrogen, this nitrogen nucleus spin is 14. So, that is exactly what we have discussed here and we predict that the intensities will be 1 is to, 1 is to, 1 and that is what is seen here.

So, with this we stop our discussion of the hyperfine interaction and later we will continue to find the origin of this interaction.