Principles and Applications of NMR Spectroscopy
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Module 02
Lecture No 10

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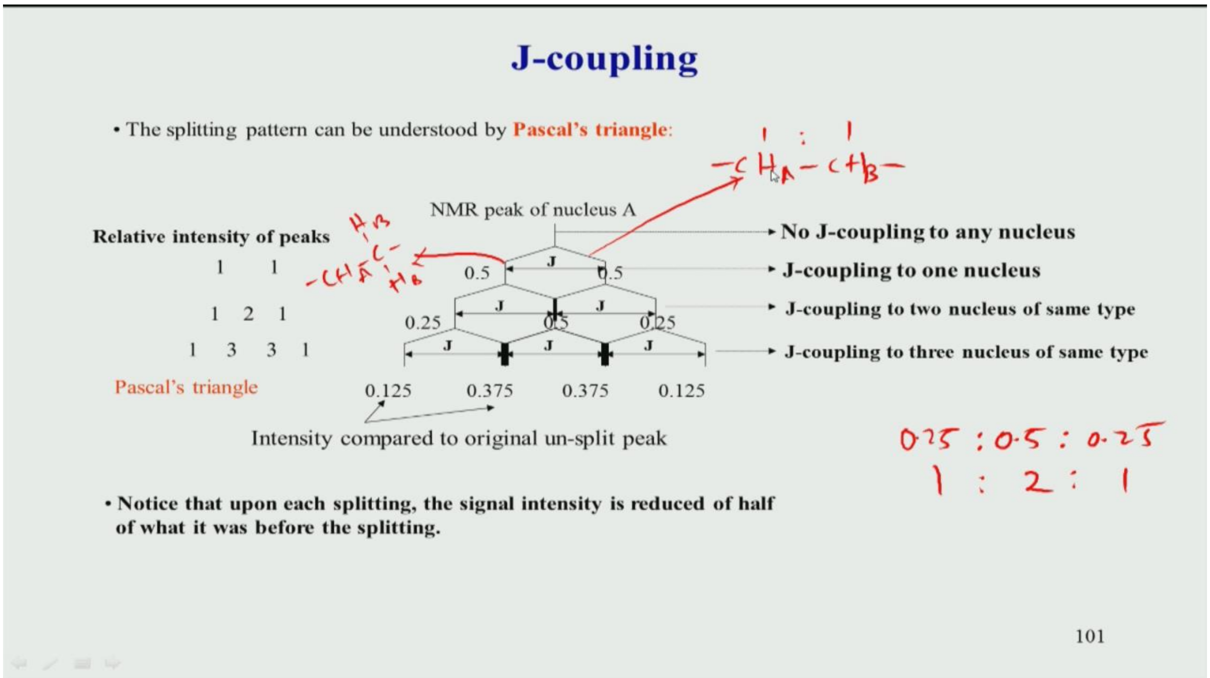

J-coupling

- The splitting pattern can be understood by **Pascal's triangle:**

Relative intensity of peaks

1 1

1 2 1

1 3 3 1

Pascal's triangle

→ **No J-coupling to any nucleus**

→ **J-coupling to one nucleus**

→ **J-coupling to two nucleus of same type**

→ **J-coupling to three nucleus of same type**

Intensity compared to original un-split peak

- **Notice that upon each splitting, the signal intensity is reduced of half of what it was before the splitting.**

1 : 1

$-CH_A-CH_B-$

H_B
$-CH_A-C-$
H_B

0.25 : 0.5 : 0.25
1 : 2 : 1

Welcome back, in the last class we saw how we can calculate the j-coupling pattern based on the number of hydrogens to what the given hydrogen is coupled. so, this was using this Pascal triangle which is shown here. so, we can see that there is 1 hydrogen coupled to 1 hydrogen we got a doublet because of the splitting and that get split because of in the 2 into equally half signals, so you get 0.5, 0.5 which is has a ratio of 1 is to 1 the relative intensity.

So, you can further split the signal into 2 more signals, in case there are 2 protons to which this hydrogen is coupled, so you get further 3 peaks, but remember the center peaks from here and here they combine. Therefore, instead of four different peaks you are getting actually 3 peaks because the central peaks of the 2 splitting we (())(1:08) combine. So, you get 0.25, 0.5, 0.25, so you get 1 is to 2 is to 1.

So in this manner you can continue further and see what happens if there are 3 hydrogens coupled to 1 or 4 or 5 or 6 and in this manner you can continue to calculate the different splitting pattern which will give you the different relative ratio. So, the main point here is that we are looking at relative intensity ratio which is shown here. So, if I have a peak 3 peaks which are 0.25, 0.5 and 0.25 ratio, it becomes 1 is to 2 is to 1, so this is a triplet because there are 3 peaks.

So, you have a quadrate, you have a pentade, you have a sixtate and so on and that is how the splitting pattern goes around goes above. So, we can see continue with this j-coupling today and see what are the different more important points about the j-coupling. How they can give us information about structure and so on. So, one thing is that what we saw in the previous slide is that hydrogen atom A had the same coupling value to the different hydrogens.

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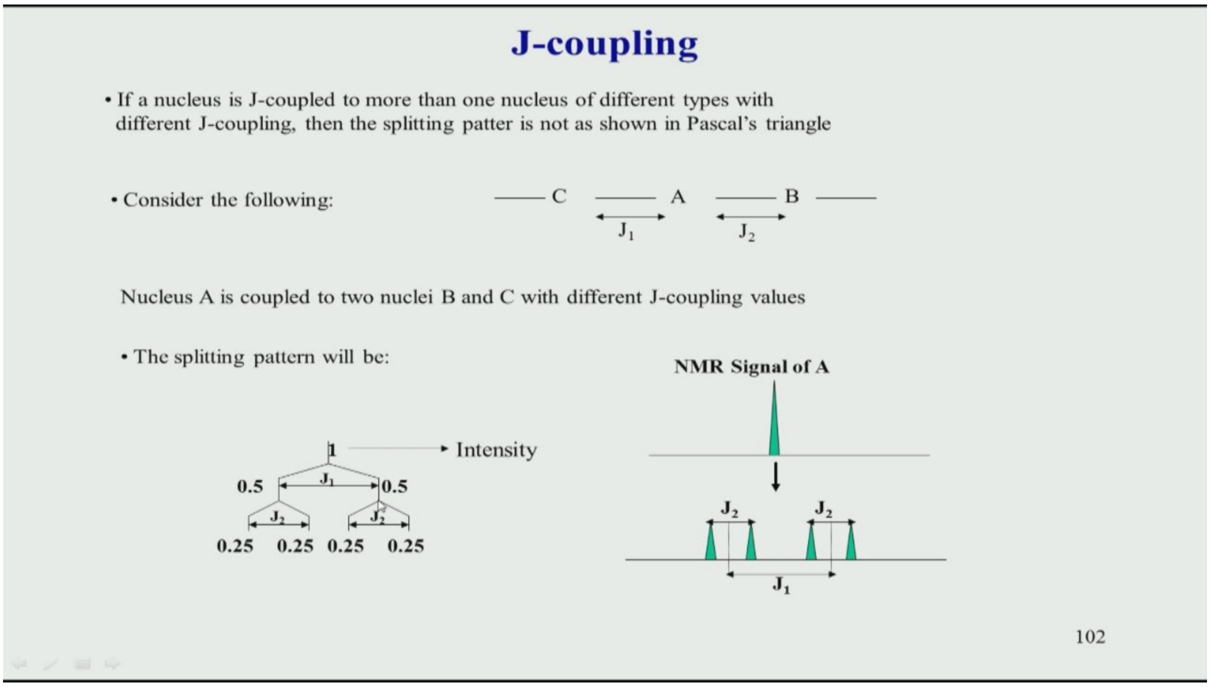

J-coupling

- If a nucleus is J-coupled to more than one nucleus of different types with different J-coupling, then the splitting patter is not as shown in Pascal's triangle
- Consider the following:

Nucleus A is coupled to two nuclei B and C with different J-coupling values

- The splitting pattern will be:

NMR Signal of A

So is that why the n + 1 rule is applicable but that is not always the case. If a nucleus is j-coupled to more than 1 nucleus of different types of different values, then you will have different j values. So example, let us see here, suppose we considered the hydrogen atom A, it has a coupling j1 to a hydrogen atom which is 3 bonds away C and or it has another coupling value j 2 to another hydrogen atom on this side. So, you see these 2 j values are not the same now, so therefore if I consider this hydrogen atom as 1 and this hydrogen atom as 2. So, this hydrogen will not be split into 3 peaks, n + 1 rule is not applicable here the reason being that each j value is not the same. So, in such a situation how do we calculate the coupling pattern?

So, this is shown here, so what basically we have to consider is like this. So, first you start you start with 1A, this is 1 hydrogen atom which is unsplit which is 1 line. Now, when you considered j1 coupling it will get split into 2 so that is why it is 0.5 and 0.5. Now, because of the second j value that is j2 here, each of these peaks will be further split into 2 peaks. So, now it has each peak here, so this 0.5 becomes 0.25 and 0.25 and the separation between these 2 lines is now j2.

Similarly, this peak which was split because of j1 gets further split into 2 and you can see here the splitting distance is now j2. So, therefore these 2 central points, so the main point here is these 2 lines here in the earlier slide we saw that they collapse, they combine and they join and become 0.5, but here they remain separate and the reason they remain separate is because j1 and j2 values are not same.

If j1 and j2 are same then this 2 lines would have become combine into 1 because they would have come close to each other and they would have actually come at the same position, because of these difference in j1 and j2 they no longer come at the same position. So, they are separated and instead of 3 peaks now we end up with a 4 peak pattern. And what is a relative intensity now? The relative intensity is 1 is to 1 is to 1 is to 1, so all of them are equal and that is what we shown here, so this is called a doublet of a doublet.

So, basically the first the original peak get split into doublet because of the bigger coupling and then further it gets split into smaller coupling because of another coupling and that is doublet further, so we will say a doublet of a doublet. So, the main point to remember here is that you have to first consider the bigger coupling value and then go to the smaller coupling value. So, decide first which is the bigger value that mean if you know the value and then based on that you split it first and take the smaller value and split it further. So this can be continued if there was j3 another coupling to A. Let us say 1 more atom here could have been j3 and so on, so you can do this n number of times the simply considering this kind of a diagram which is called Pascal's triangle.

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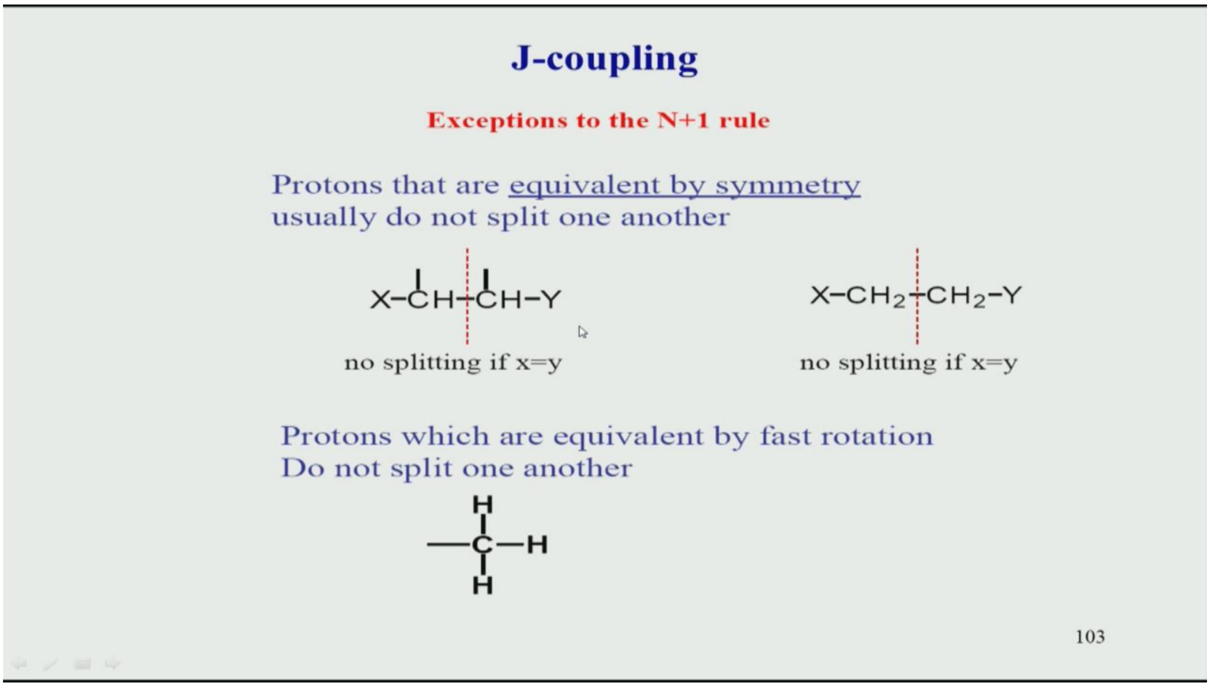

J-coupling

Exceptions to the N+1 rule

Protons that are equivalent by symmetry
usually do not split one another

$X{-}CH{-}CH{-}Y$

no splitting if x=y

$X{-}CH_2{-}CH_2{-}Y$

no splitting if x=y

Protons which are equivalent by fast rotation
Do not split one another

So, now j value we can look at the exceptions, so this is what we saw in the earlier case that in this case if these 2 hydrogens suppose that, x and y, they are not the same then in that case these 2 hydrogens are not similar and therefore, this value, this will be split by this hydrogen and this hydrogen will be split by this hydrogen. So basically the point here is the protons which are not equivalent, they split each other so that means if they are equivalent by rotation then they do not split. So, what is shown here is the methyl group? So, if you see in a methyl group, they are chemically equivalent because of fast rotation and because they are chemically equivalent because of fast rotation this hydrogen is this hydrogen do not split each other, but remember that it is note that there is no coupling between these 2.

There is a coupling but we cannot see it in NMR spectrum if therefore, that means between any 2 hydrogen atoms, if they are chemically equivalent then they will basically not split each other but it does not mean that there is no j-coupling it is that thus that the NMR is not capable of revealing the coupling between 2 equivalent hydrogen atoms. So the methyl groups always will come as a single entity, but if they are coupled to another hydrogen here then they will be hydrogen will be split because of 3 into the quadrate. So, this is what we saw in the last class but if you look at these 3 together they do not split individually each other within this methyl group. So, methyl group protons are equivalent.

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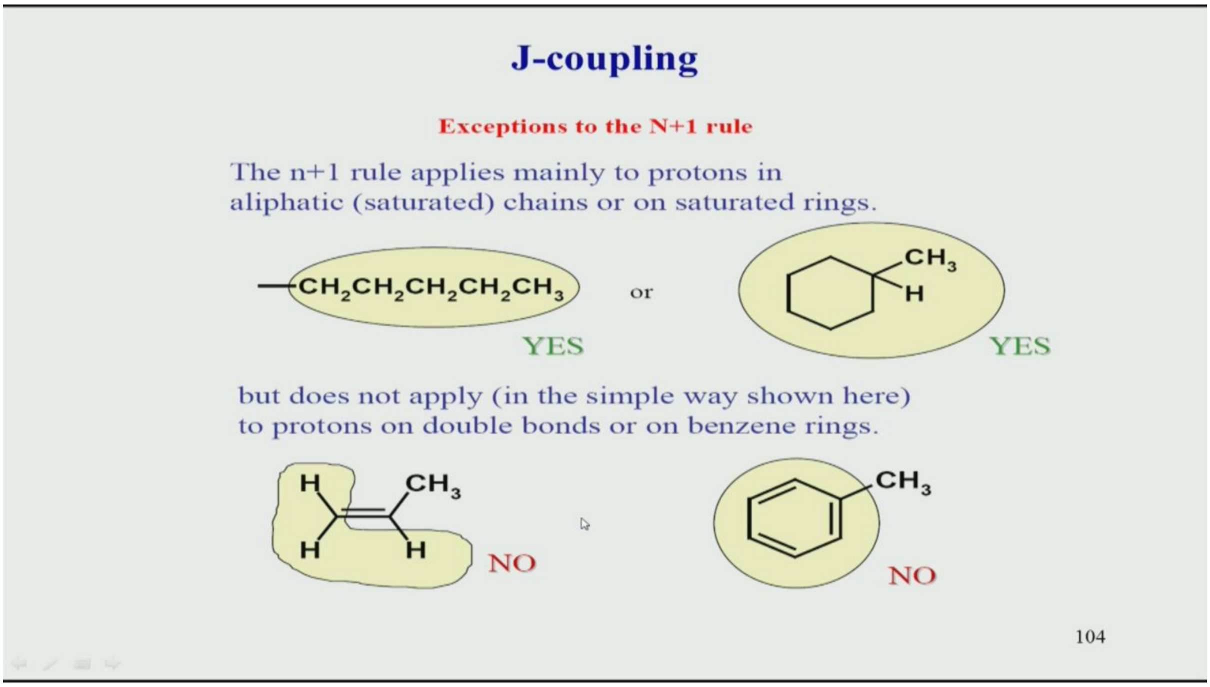

J-coupling

Exceptions to the N+1 rule

The n+1 rule applies mainly to protons in aliphatic (saturated) chains or on saturated rings.

but does not apply (in the simple way shown here) to protons on double bonds or on benzene rings.

So, there are different exceptions to this n + 1 rule we saw already that exceptions basically based on the coupling value. So for example, if you look at this hydrogen here, this particular hydrogen this has 1 hydrogen (())(7:16) coupling here 1 value, but it will have a trans coupling to this hydrogen another value. Similarly, it will have a coupling to this hydrogen some other value. So you see, what happens is there is 1 here 1 here, so if you ignore this hydrogen. So, let us ignore this hydrogen for time being, even if you consider this hydrogen is coupling to this and this you may think that there are 2 hydrogen. So, its coupling to this will be n + 1 that is triplet means this hydrogen you may say that it will may expect as a triplet but that is not correct because the coupling of this hydrogen to this hydrogen is not the same as coupling of this hydrogen to this hydrogen.

So, therefore this hydrogen will show a doublet because of this and another doublet because of doublet of a doublet will come for this particular hydrogen and not a triplet that is 1 is to 2 is to 1 what you expected if you use the n + 1 rule. So, this is basically the different ways of examples how the n + 1 sometimes applies sometimes it does not apply.

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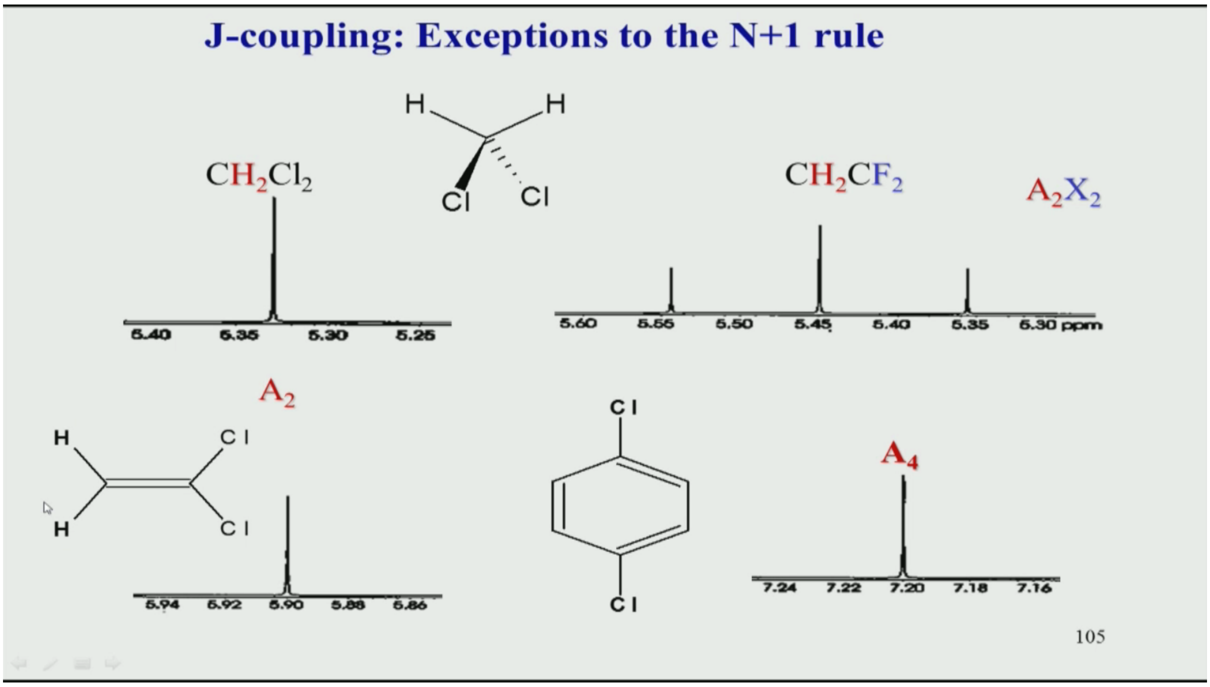

J-coupling: Exceptions to the N+1 rule

CH_2Cl_2

A_2

CH_2CF_2

A_2X_2

A_4

So, we can go this further (())(08:22) the different cases where there is an exception to the n + 1 rule, but these cases they are equivalent hydrogens. So when they are equivalent hydrogen, you do not expect as splitting. So, that is what the point here is that these 2 hydrogens are chemically equivalent, so they will be split because of the flourine. Similarly, here the 2 hydrogens are equivalent so they do not we do not see coupling within these 2. Remember, these 2 hydrogens are germinal coupling. They are coupled to each other but we do not see the splitting because they are chemically equivalent okay. So, this is basically the idea of the j-coupling that whenever we have chemically equivalent hydrogens they do not split each other even if there is a coupling between them because they are equivalent, so we not see that in the spectrum.

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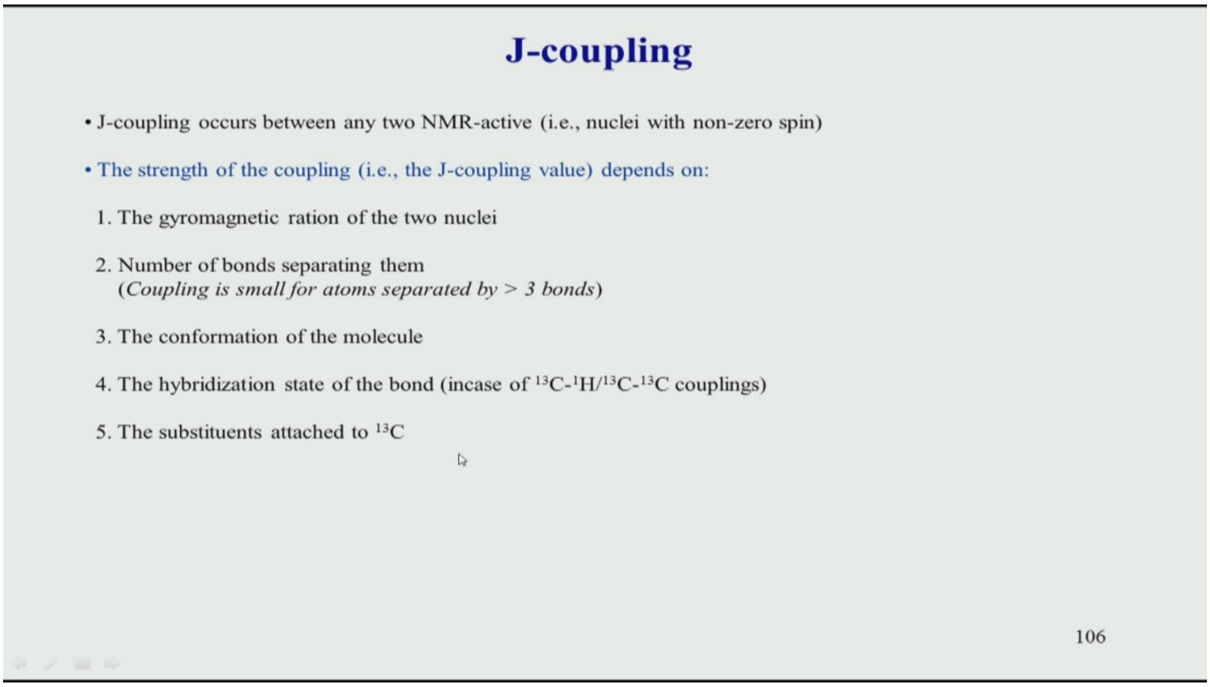

J-coupling

- J-coupling occurs between any two NMR-active (i.e., nuclei with non-zero spin)
- The strength of the coupling (i.e., the J-coupling value) depends on:

1. The gyromagnetic ration of the two nuclei
2. Number of bonds separating them
   (*Coupling is small for atoms separated by > 3 bonds*)
3. The conformation of the molecule
4. The hybridization state of the bond (incase of ^{13}C-^{1}H/^{13}C-^{13}C couplings)
5. The substituents attached to ^{13}C

So, j-coupling actually depend on many things like we saw in the case of chemical shifts. The j-coupling also depends on a variety of factors and this is what a few factors are listed here. of course this is not straight forward to calculate j-coupling in any particular molecule. there are lot of software programs and there are some electronic calculations has to be done but nevertheless some basic rule of thumb or basic rules are there for example, it depends on the gyromagnetic ratio of the 2 nuclei. So, suppose you have 2 hydrogens, the 2 hydrogens coupling will depend on the gyromagnetic, which is same for both, but if you look at hydrogen to carbon it will be less. If you have because carbon is gyromagnetic ratio less, that is number 1. Number 2 factor is also depends on number of bonds which are separating.

So, if you have 2 hydro the hydrogen bond separated by 2 bonds which is called germinal hydrogens, they will have a stronger value of coupling compared to vicinal hydrogens which is 3 bond separations. If we go for longer 4 bonds, 5 bonds and so on the hydrogen coupling becomes weaker and weaker. Of course 1 bond hydrogen is not there we are talk about 1 bond hydrogen to carbon, which is very strong because it is 1 bond. So, the number of bonds which are separating 2 atoms becomes matters fault the coupling. So, this is not generally we are not talking about only hydrogen-hydrogen coupling here. We are talking about hydrogen to x that is hydro nuclear like carbon, nitrogen and any other.

So, this is general concept for any j-coupling in general. It depends on the hybridize conformation of the molecule that is the structure of the molecule because we will see shortly that the 3 bond hydrogen coupling depends on the dihedral angle between the 2 vectors we look at that, it depends on the hybridization state so, sp2, sp, sp3 this different type of hydrogen, this is the in terms of carbon. We are looking at carbon proton coupling there it will matter depending on the hybridization state of the carbon. Similarly, it will also depend on the substituent attached to carbon. So these are some of the few basic points as we go further into hydro nuclear NMR and we will encounter this more right now we will have focusing only on proton-proton coupling.

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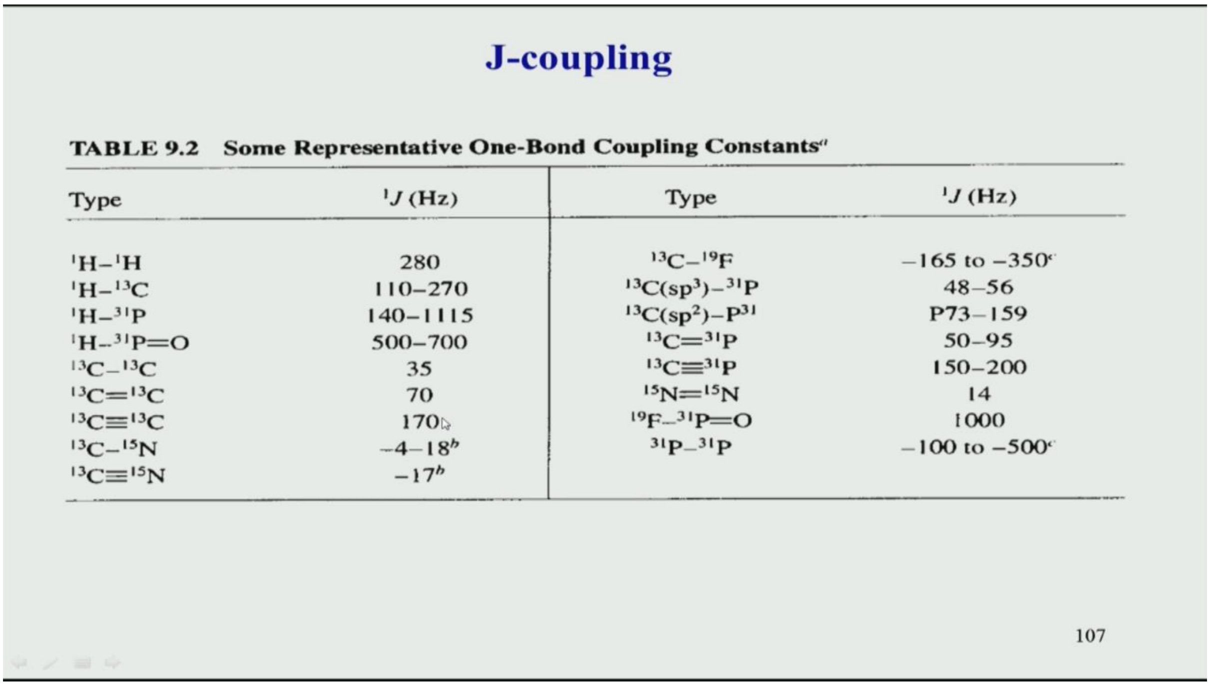

J-coupling

TABLE 9.2 Some Representative One-Bond Coupling Constants[a]

Type	^1J (Hz)	Type	^1J (Hz)
$^1H-^1H$	280	$^{13}C-^{19}F$	−165 to −350[c]
$^1H-^{13}C$	110–270	$^{13}C(sp^3)-^{31}P$	48–56
$^1H-^{31}P$	140–1115	$^{13}C(sp^2)-P^{31}$	P73–159
$^1H-^{31}P{=}O$	500–700	$^{13}C{=}^{31}P$	50–95
$^{13}C-^{13}C$	35	$^{13}C{\equiv}^{31}P$	150–200
$^{13}C{=}^{13}C$	70	$^{15}N{=}^{15}N$	14
$^{13}C{\equiv}^{13}C$	170	$^{19}F-^{31}P{=}O$	1000
$^{13}C-^{15}N$	−4–18[b]	$^{31}P-^{31}P$	−100 to −500[c]
$^{13}C{\equiv}^{15}N$	−17[b]		

So, typically the different coupling values are given here and this is very general typical values. So, you can see that proton to carbon is a both 110 to 270 depending on variety of factors like the hybridization state and substituent and so on and this are (())(11:37) path numbers, We do not have go into detail but this is the idea it will give you the different values. So, the hydrogen-hydrogen couplings and vicinal and general are not listed here that will come up in a next few slides.

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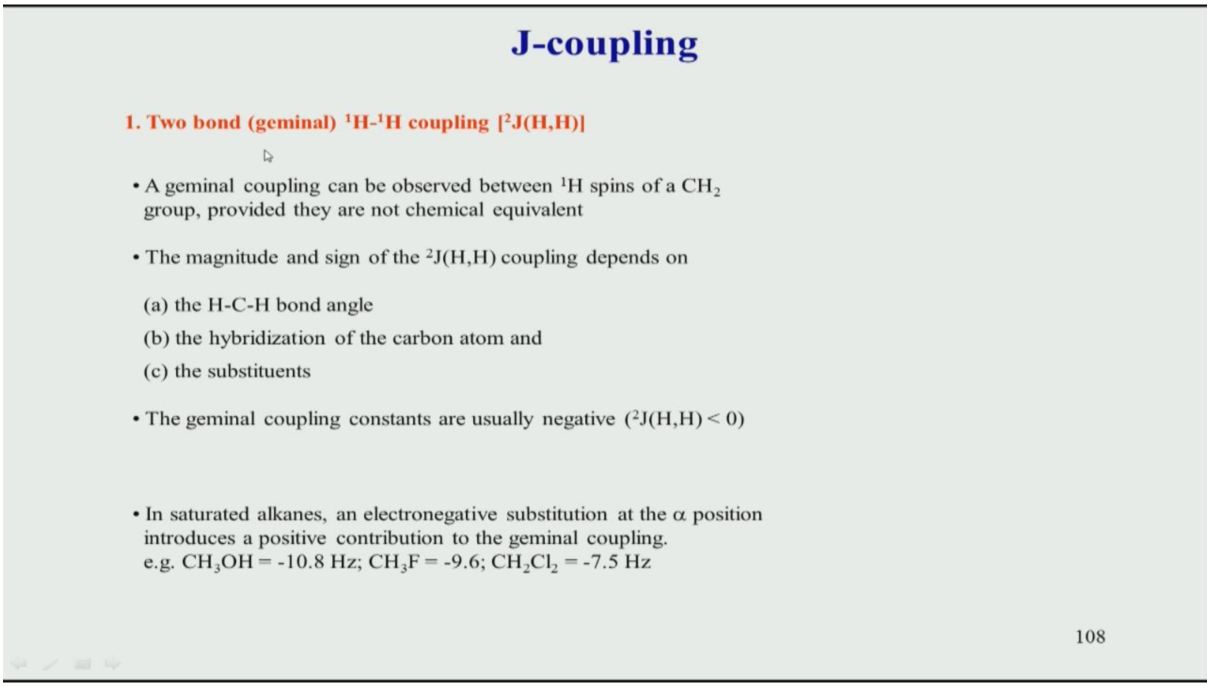

J-coupling

1. Two bond (geminal) ^{1}H-^{1}H coupling [^{2}J(H,H)]

- A geminal coupling can be observed between ^{1}H spins of a CH_2 group, provided they are not chemical equivalent
- The magnitude and sign of the ^{2}J(H,H) coupling depends on

  (a) the H-C-H bond angle
  (b) the hybridization of the carbon atom and
  (c) the substituents

- The geminal coupling constants are usually negative ($^2J(H,H) < 0$)
- In saturated alkanes, an electronegative substitution at the α position introduces a positive contribution to the geminal coupling.
  e.g. CH_3OH = -10.8 Hz; CH_3F = -9.6; CH_2Cl_2 = -7.5 Hz

So, this is what is shown here. So, we have what is called 2 bond germinal coupling that is we saw the typical notation we use in NMR you write like this. So, the 2 superscript j coupling is written like this that means 2-bond hydrogen-hydrogen coupling and it has the germinal coupling can have negative value or it can have positive value. So Couplings can always remember have both positive negative value, although from simple 1D NMR you can never find out the sign of the coupling, so that is why 2D NMR and another other more techniques are available to find out the sign of the coupling, Sign meaning the whether it is negative or positive but a simple 1D NMR will the coupling that do the splitting.

The multiplet peaks which we see because of coupling that from that you cannot figure out whether it is negative or positive coupling, so these are some values given here for different systems. So, the main thing point here is that it depends on the bond angle between the 2 hydrogens. So, this is for the germinal coupling and depends on the hybridization state of the carbon and substituent. So, these are the main 3 factors which influence the j-coupling in case of germinal coupling.

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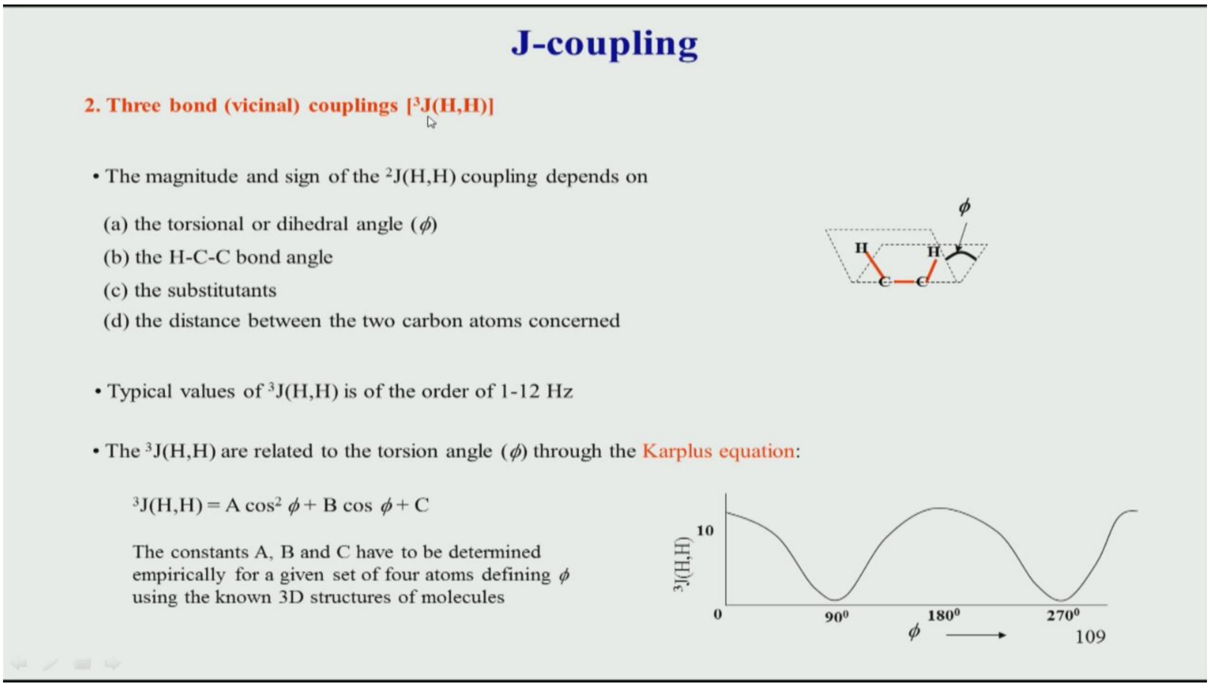

J-coupling

2. Three bond (vicinal) couplings [$^3J(H,H)$]

- The magnitude and sign of the $^2J(H,H)$ coupling depends on
  - (a) the torsional or dihedral angle (ϕ)
  - (b) the H-C-C bond angle
  - (c) the substitutants
  - (d) the distance between the two carbon atoms concerned
- Typical values of $^3J(H,H)$ is of the order of 1-12 Hz
- The $^3J(H,H)$ are related to the torsion angle (ϕ) through the Karplus equation:

$$^3J(H,H) = A\cos^2\phi + B\cos\phi + C$$

The constants A, B and C have to be determined empirically for a given set of four atoms defining ϕ using the known 3D structures of molecules

When it comes to vicinal coupling, when we talking say vicinal the 3 coupling means 2 hydrogens which are separated by 3 bonds 3 covalent bonds. So, this is shown here, so we can see this hydrogen and this hydrogen are separated by 3 bonds which is shown in red color. So, here we do not talk about bond angles we talk about torsional angles or dihedral angles. So this dihedral angle is shown pictorially here you can think of it as an open notebook, a plane which defines these 3 hydrogen, sorry these 2 carbon and hydrogen become 1 plane and this particular proton and these 2 carbons becomes another plane. So you can see that these 2 planes are now at an angle with respect to each other and that angle we call it as torsional angle.

So there is a very famous equation known as a karplus equation which shows how j value, the 3 bond j value is related to the torsional angle. So this is typically the equation is A cos square theta + B cos theta + C and here the values A and B depend on the type of j value you are looking at. So, in in a particular molecule you will have different types of 3 bond j-couplings vicinal couplings and for A that kind of typical type of those couplings will have to empirically experimentally determine or based on the different values measure experimentally.

We can figure out the x by fitting the value of A and B and C if you know the structure, so this is what is shown here. So, we can see from this equation 1 thing is if I know the torsional angle it does not give me the j value uniquely because there is quadratic equations. So quadratic equation will always have 2 solutions for phi, if I know the j value from experiment it does not mean that I can calculate immediately phi value because this is a quadratic in phi the angle phi therefore, it will have 2 solutions.

So, there is always it degeneracy, so which is shown here for example, this particular j value if you take this particular say 6-7 Hertz see, it has 2 or 4 possible solutions, of course they are related by 180 degree rotation because there are 2 possible values which we satisfy this j-coupling. So, this is one of the very famous equations which is used for given phi value to calculate j or vice versa given j value at least estimate what could be the bounds what could be the possible values phi.

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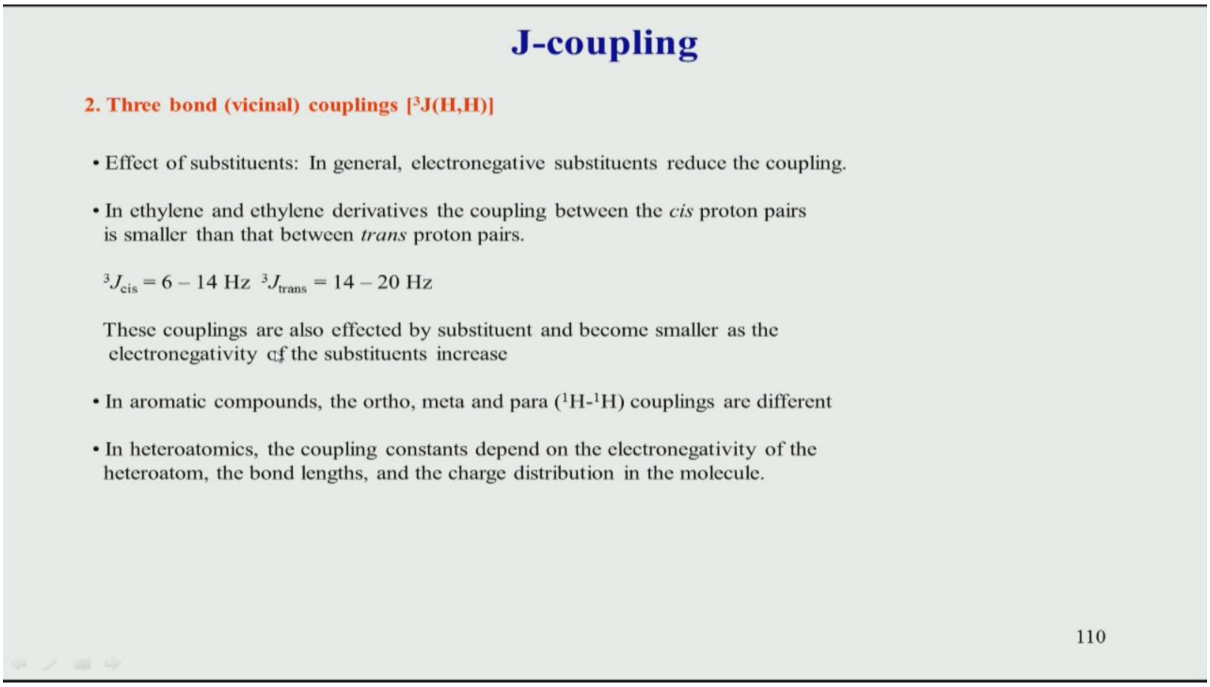

J-coupling

2. Three bond (vicinal) couplings [$^3J(H,H)$]

- Effect of substituents: In general, electronegative substituents reduce the coupling.
- In ethylene and ethylene derivatives the coupling between the *cis* proton pairs is smaller than that between *trans* proton pairs.

$^3J_{cis} = 6 - 14$ Hz $^3J_{trans} = 14 - 20$ Hz

These couplings are also effected by substituent and become smaller as the electronegativity of the substituents increase

- In aromatic compounds, the ortho, meta and para (^1H-^1H) couplings are different
- In heteroatomics, the coupling constants depend on the electronegativity of the heteroatom, the bond lengths, and the charge distribution in the molecule.

So, this is a further continuing on the effects that depends on the effects of the substitution. The substituent effects depends on the structure of the molecule and you can see here that in aromatic compounds there are long range couplings and the orthometapara couplings between the hydrogens are different, so now that we have come to the end of the first part of this course. In the first part of this course, we also seen different concepts what is spinning what is rotating flame, what is chemical shifts and so on. So, what you would like to do in the next 15 minutes or so let us recap recapitulate what we have learnt in a first part because in the next class onwards we will be moving on to more advance topics that is actually how to analyze, interpret NMR spectrum, how to record a spectrum.

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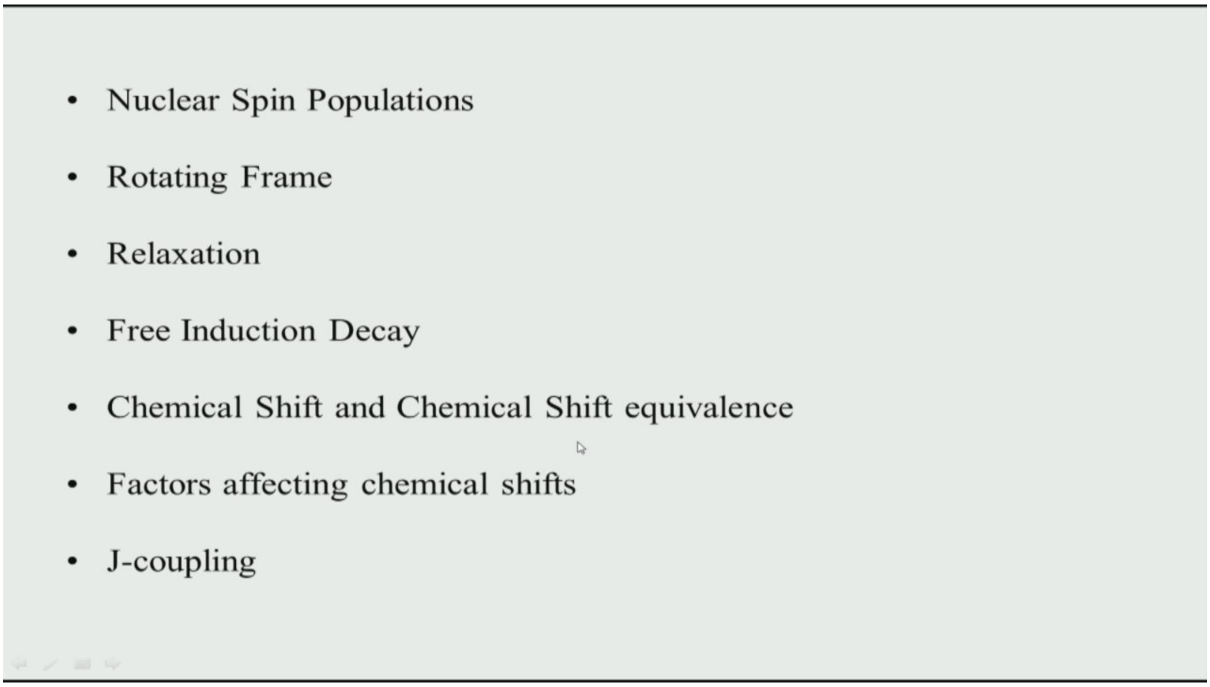

- Nuclear Spin Populations
- Rotating Frame
- Relaxation
- Free Induction Decay
- Chemical Shift and Chemical Shift equivalence
- Factors affecting chemical shifts
- J-coupling

So, let us recapitulate the basics what we have learned in the last few classes. So this is what is shown here, so we have basically seen these are the following different aspects we have looked, at we have looked at nuclear spin, population we looked at rotating frame, relaxation free induction decay, we looked at what is chemical shifts and how what is chemical shift equivalence and then what are the different factors which effect chemical shifts and j-coupling. So, what we will do now, we just go through each of this and quickly you see what are these concepts, so that this will be the not relooking it again as we move on further.

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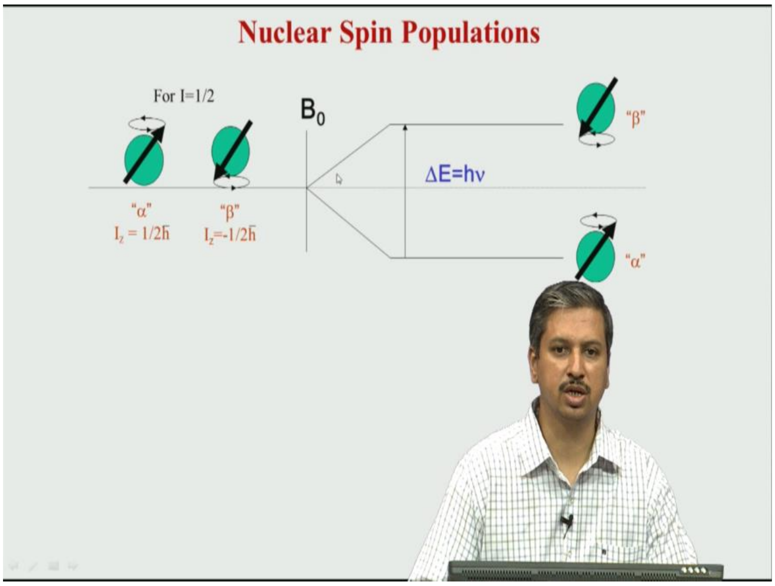

Nuclear Spin Populations

So, nuclear spin population starts from basically looking at how the spins are oriented in the magnetic field. So, when you do not have a magnetic field, this spins are degenerate, the two spins which are oriented alpha half + half and - half, they have no particular orientation but when we apply.