One and Two Dimensional NMR Spectroscopy for Chemists

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Lecture - 23

Active and Passive Couplings

Welcome back, yesterday we discussed about splitting pattern and we worked out how many peaks we get when one spin is coupled to N chemically equivalent spins. By family tree approach when one is coupled to N other protons, we wanted to find out totally how many peaks we get at the chemical shift of each proton and also total lines you can expect in the spectrum. So, we took the example of weakly coupled spin systems like, 2 spins, 3 spins, 4 spins and showed how many peaks we expect.

But remember those examples, you should never forget, that I took the example of them where all these spins are weakly coupled. This type of intensity pattern, and everything you cannot work out so easily using family tree approach on the spin systems that are strongly coupled, it is not possible, Just for making you understand in the most realistic situation weakly couple spin system were taken, and most often you come across that, first order analysis is possible, easily we can analyze the spectrum, and this is the way you understand the multiplicity pattern. That is what I was telling you. Now, we will go further today. I will introduce one more term called active and passive couplings. The interesting thing, what is an active coupling and what is a passive coupling?

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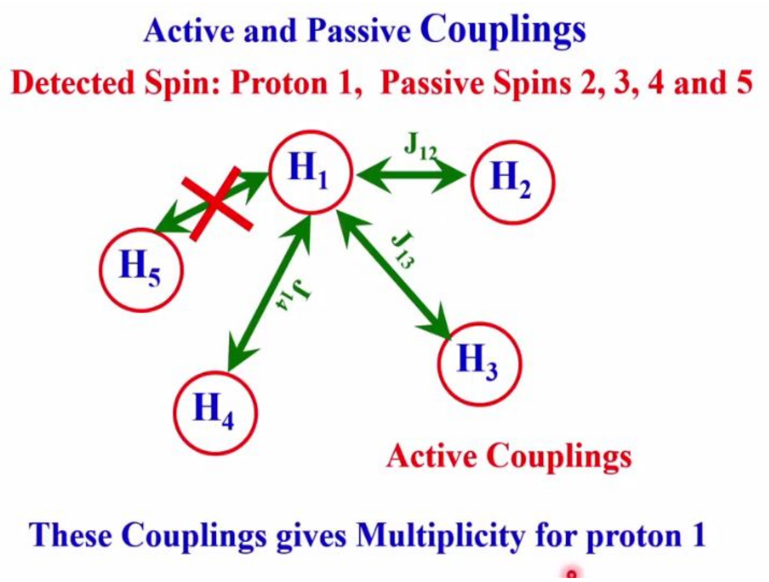
Active and Passive Couplings

Detected Spin: Proton 1, Passive Spins 2, 3, 4 and 5

Active Couplings

These Couplings gives Multiplicity for proton 1

We looked an example like this. Again I take example of 5 protons, which are coupled among themselves. This is the couple spin system. Remember I told you about the coupled spin system in one of the classes. When 1 proton is coupled to remaining other protons of different coupling strengths, it forms a coupled spin system, no matter one of the coupling may be very small, or 0, but it should be a part of the coupled spin system.

Now, in the coupled spin system, we come across situations, I want to tell you what is active coupling and what is passive coupling? Look at this 1. Now, I am going to look at the proton 1, that is there are 5 protons, this is the chemical shifts of 1, 2, 3, 4, 5, 5 different groups of peaks are there, 5 different chemical shifts in the NMR spectrum, proton NMR spectrum, 5 different peaks are there; and each of them are coupled and pattern is different like we saw, you know, A M X, and four spins coupled. We have different patterns depending upon the strengths, although number of peaks are different depending on the coupling strengths, and intensity will be all same. That is what I said. Now, let us extend the logic. I am going to consider proton 1. I will detect this one that means, I am at the chemical shift a proton 1, let us say proton 1 is here. This is coupled to proton 2, what is coupling strength? J12; because I do not know what is the value? but it is coupled with proton 2 it is J12. It is also coupled to proton 3. It is J13. It is also coupled to proton 4, J14. And it need not be coupled to J15, does not matter. But these are all called active couplings. When I look at this spectrum at this chemical shift of this proton 1, I see, all though all these are coupled spin system, only this is coupled with these 3, because of this we see a doublet, doublet of a doublet, 8 lines at the chemical shift of this proton. From the 8 lines you measure this coupling, this coupling and this coupling, you can get. It easy to measure coupling strengths at the chemical shift of proton 1, by seeing the multiplicity of 8 lines. And that is called active coupling. The couplings that you are measuring at the chemical shift of proton, which are observing. They are called active couplings. Remember, active coupling is the one where you are going to see the interaction strengths, you can measure them at that particular chemical shift. Now this coupling is 0, no problem. These couplings give rise to multiplicity for proton 1. So active coupling gives multiplicity at the site of this one.

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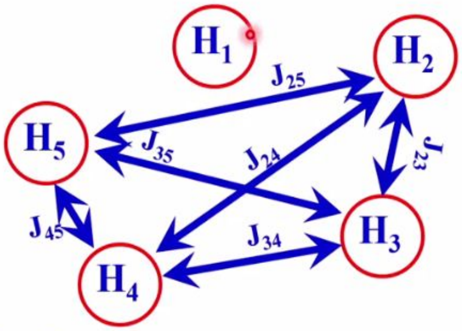
Active and Passive Couplings

Detected Spin: Proton 1, Passive Spins 2, 3, 4 and 5



Passive Couplings

Will not be shown at the chemical shift of proton 1

Now another thing will extend the logic what about this coupling? 2, 5 what about 3, 5? If there is coupling strength of 3, 5, what about, 2, 3? what about 3, 4? what about 4 5? what about 3, 4? I am sorry, 2, 4. These are also there, couplings. They are in a coupled spin system. When you observe this, you do not observe multiplicity because of other proton couplings, but these were not absent they are present, but you do not see it here. You do not see it at the proton chemical shifts or at site of 1. These are called passive couplings.

Passive couplings are not seen when you detect the proton of a particular spin, which is an active spin, in which case we call this at the active spin. And these are called passive couplings and the couplings which I showed in the previous case, these are called active couplings; it is an active spin; these are active couplings, which are seen at the chemical shift of proton 1. And these are all passive couplings, which are not seen at the chemical shift of proton 1, understood the logic?

What is an active spin and what is passive spin. This is an active spin, and all the protons which are coupled to this are active spins, when I am observing this, when I look at the chemical shift of this one, all of the couplings to other protons are active couplings. When I am observing this, it is an active spin and these are all passive spins. So, coupling among the passive spins are called passive couplings. These passive couplings are not seen at the site of the active spin. Very interesting point; one must remember really useful in understanding and analyzing the NMR spectrum later.

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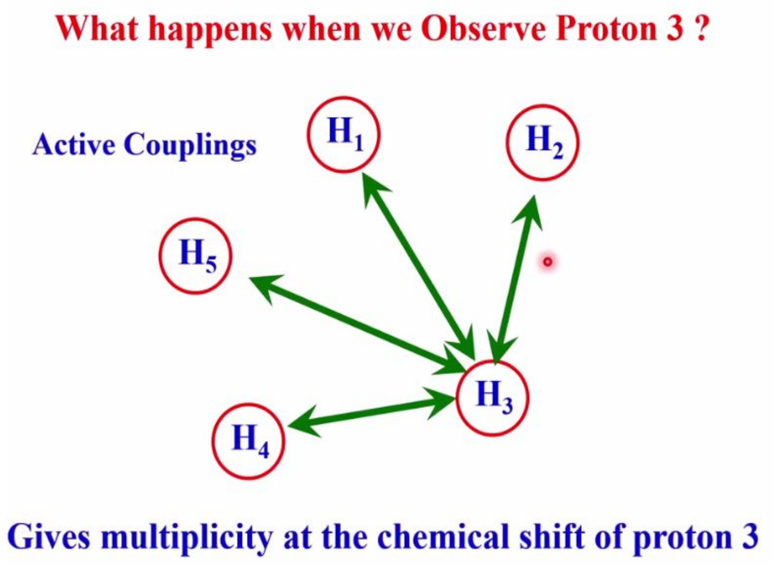

What happens when we Observe Proton 3 ?

Active Couplings

Gives multiplicity at the chemical shift of proton 3

Now I will ask a question. Now I am going to observe proton 3. Now when I am observing proton 3, which is an active spin? Active spin is proton 3, what are the passive spins? 2, 1, 4 and 5, these are all passive spins, and this is my active spin. Now what if I am looking at the chemical shift this proton in the spectrum. What are the couplings you are going to see? Coupling of passive spins with the active spin. That is what you are going to see here.

Like what I said for the earlier proton, now for this one, when this is active spin, you always see the couplings between active and passive spins at the site of active spin. Now, I see this coupling, I see this coupling, I see this coupling and I can see this coupling. So, when I go to the chemical shift of proton 3, I will see coupling because of this, it will be a doublet, doublet a doublet, doublet of doublet of doublet, it is DDD. So, it is further split.

So, when I see these and analyze the multiplicity of this proton or this chemical shift, I get 3 coupling strengths. So, this is an active spin, these are passive spins. So, when you are observing a proton you always measure couplings between active and passive spins, and you do not get the coupling between passive spins.

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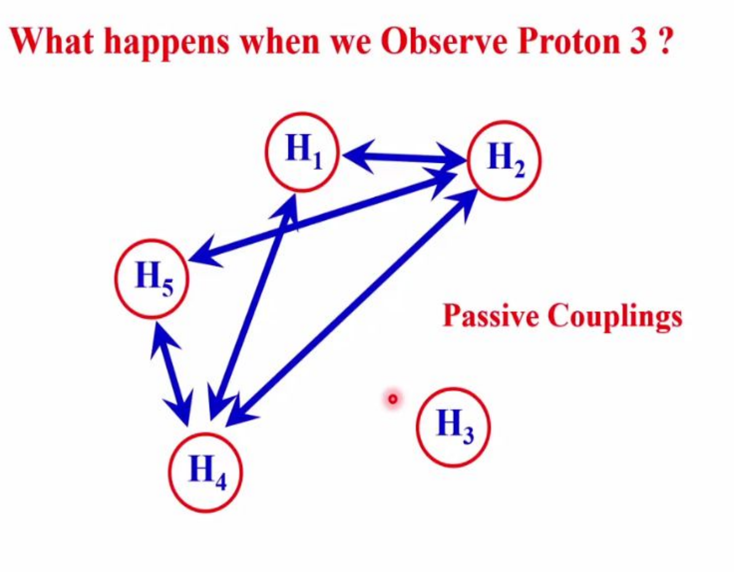

What happens when we Observe Proton 3 ?

Passive Couplings

These things you will not see at this site. Remember this, these couplings are called passive couplings, you will not see at this. You understood? I have given you 2 examples, about active spins and passive spins, I hope you would have understood something now, at some point you would have got Right? and, this will not get reflected at the chemical shift proton 3.

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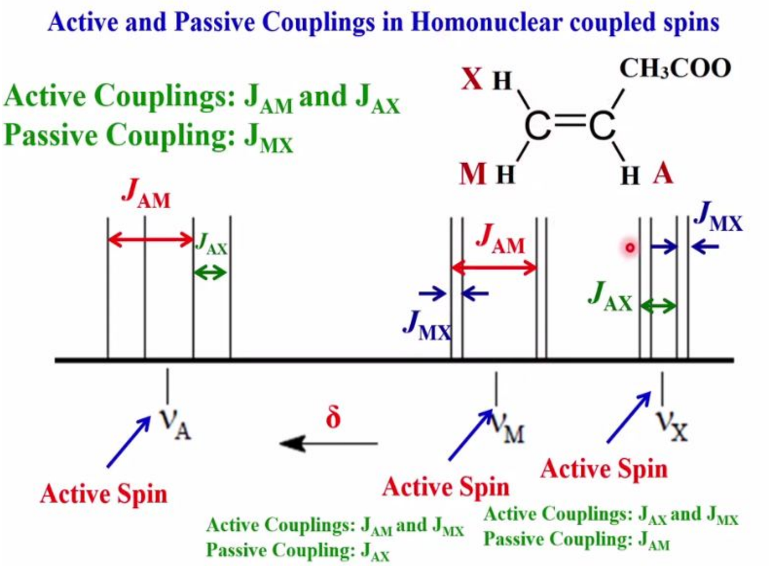

Let us take a realistic example of active and passive couplings in homonuclear coupled spin system. I will take an example of a molecule like this, an hypothetical molecule, 3 spins coupled together. Forget about this CH3COO group, this is not coupled to any of these things; that is distinct. So, we will not worry about this, we worry only the chemical shifts A, X and M, the only 3 protons and only 3 chemicals let us worry. Let us say spectrum is taken, proton spectrum you get, this is the proton spectrum.

What is the logic when 3 protons are coupled, X, A and M, the first thing, we should have a look at the spectrum, all are equal intensity. When 3 protons are coupled, use my formula. When A is coupled to M and X. There are 2 other protons, which is coupled to, 2 to the power of 3 – 1, that is 2 to the power of 2, 2 square. And at each chemical shift you have, at chemical shift of A, you get 4 peaks because of coupling to this. At the chemical shift of M you get 4 peaks because of couplings to A and X. At the chemical shift of X, you get couplings, AX and MX and you get 4 peaks.

See, always you get 4 peaks of equal intensity. This is a weakly coupled AMX spin system. We worry about weakly coupling later. But this is the spectrum of equal intensity. As I was telling you always, although you get 4, 4 lines, but the pattern is not same, the multiplicity pattern is different. Remember, this is has largest spread here. This dispersion is more than this one. See here this spread is larger and this spread is smaller.

So here this is larger than this, and this is smaller. Why? Because when I am looking at A, A can have coupling to this and this trans coupling and cis coupling of 3 bond. When I am looking at M, M can have a cis coupling to A and germinal coupling to A; and when I am looking at X, X can have a germinal coupling to M and trans coupling to A. So all are of different strengths. As a consequence, these multiplicity patterns are not identical for all the 3 proton. please understand, it is important now, they are not identical, they are different. As a consequence this is the spectrum. Let us analyze it, and get always all the coupling information from the peaks. Now you can understand, what is active and passive coupling by analyzing the spectrum. Let us concentrate on this region, What is the region, this corresponds to proton A, so proton A center of this multiplicity pattern gives you chemical shift of A. That I have been telling you, do not get confused.

Now the 4 peaks are there. When this I am observing, what is my active spin? When I am observing this proton, remember, this is the active spin; proton A is an active spin. So what are the passive spins, X and M are passive spins. It means remember I said at the site of the active spin, you always get coupling between active and passive spins. So at this site of A, I get coupling between active and passive spins. So I get the couplings between this spin and passive spins. This is active spin and this is passive spin. So, at the site of A which is active spin, I get AX coupling and AM coupling, they are active couplings, very interesting Right. So, what about MX coupling? that is a coupling between passive spins. I told you coupling between passive spins is not reflected at the site of the active spin. You always get coupling between active and passive spins, and not coupling between passive spins at the site of an active spin. It is a very important statement. Please remember, you need it to analyze spectrum very often.

You go further now, this is an active spin and active couplings are AM and AX, passive coupling is MX and what is going to happen is this; I will consider this, it is a large coupling AM coupling, no, this should be AX coupling, does not matter, the trans is large and this other coupling is a small coupling, this is AX and this is AM, because this AM vicinal three bond coupling smaller than trans coupling, that is a realistic situation.

But let us assume, whatever may be the case, this is the way you understand, this large coupling is one of them and this separation gives me small coupling. So, at the site of this, I get AX coupling and AM coupling which are active couplings, between active and passive spin. These are called active couplings. Coupling between active and passive spins are called active couplings and passive coupling is coupling between passive spins, I do not see MX here.

Go further, at the chemical shift of M what is active spin? M is active spin. So, what are the couplings you will see at this site? coupling between active and passive spins. So these 2 are passive spins. So I get a JAM coupling and JMX coupling here, what about JAX coupling? it is passive and you do not see that. So in this case, active couplings are AM and MX, you will see and passive coupling is AX and you will not get here.

Now go to a chemical shift of this, this we can interpret now going to chemical shift of X. What are you going to see in the X? X is the active spin. What are the passive spins? M and A. What are the couplings you see here? Couplings MX and AX, they are active couplings. What is coupling AM, it is a passive coupling. So, because you are observing X, so this you will not see. so active couplings AX and MX and AM coupling is passive you don't see it. You understand how the active or passive couplings influence a spectrum. If you have a 3 spin system like this, just by looking at the pattern of the spectrum, you can start analyzing, always keeping in mind when your particular chemical shift of the particular proton you are looking at is an active spin, the remaining are passive. And at this site you always get coupling between active and passive spin. No coupling is in between passive spins. With that point you can analyze any spectrum given like this, get the point. This is what it is. You can analyze everything here, all the couplings can be measured very easily.

This was an example I took for homonuclear three spin coupled spins, homonuclear three coupled spin system is different. Now, what happens if I take heteronuclear coupled spin system, which are active and which are passive. You can see in your realistic molecule, you can have different nuclei, NMR active spins can be present and there may be coupling among all the spins. Remember I said the NMR spectrum does not distinguish between active and passive spins, Coupling will be there. It does not distinguish between homonuclear or heteronuclear spins, all coupling can represent in the spectrum, but you have to analyze.

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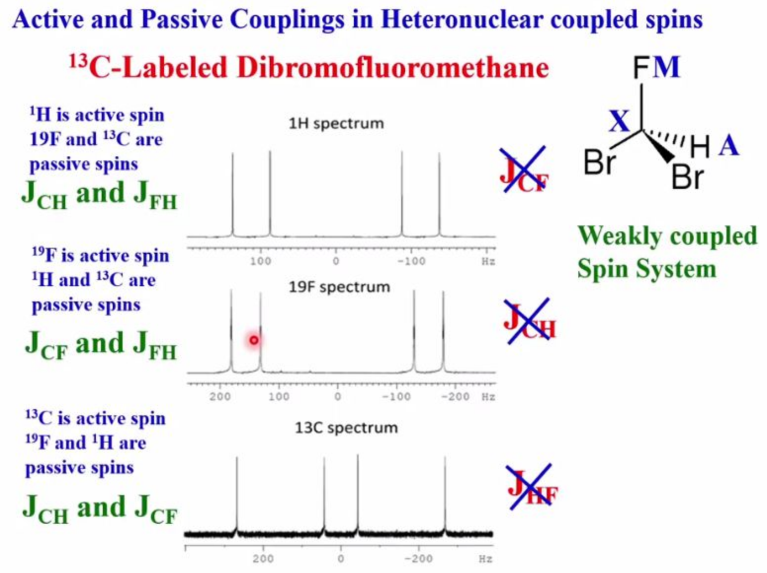

Active and Passive Couplings in Heteronuclear coupled spins

^{13}C-Labeled Dibromofluoromethane

^{1}H is active spin
19F and ^{13}C are passive spins
J_{CH} and J_{FH}

^{19}F is active spin
^{1}H and ^{13}C are passive spins
J_{CF} and J_{FH}

^{13}C is active spin
^{19}F and ^{1}H are passive spins
J_{CH} and J_{CF}

Weakly coupled Spin System

Let us see what happens in the heteronuclear coupled spin system. I take example of 13C labeled dibromofluoromethane. This is the molecular structure. 13C labeled. Label means you should understand in chemistry, I will be enriching that carbon 13 instead of 1% abundance, I will make it 100% by doing some chemistry. Then what happens? It is also like an abundant spin. So I can see the coupling of this to others easily. If it is natural abundant, 1% of abundance, normally we do not see the coupling. We see, but we do not worry about because they are satellites, we worry only about C12 labelled isotopomer, because as I said satellite analysis we do, unless it is important, we do not bother about it. So, now, in this system, 3 coupled, this carbon 13 is labeled. As a consequence, we get the 3 different heteronuclei here, proton fluorine and carbon which is also labeled. So, 3 active spins are there, all are 100% abundance. You know I showed in one of my earlier classes, proton and fluorine are highly abundant spins and with large gyromagnetic ratios and are more or less comparable. And this also is now made abundant. But the gyromagnetic ratio is not in my hand. I cannot change, I can only make that abundant larger, but I cannot control the gyromagnetic ratio. So it does not matter.

As far as I am concerned all the three are 100% abundant now, after 13C labeling. We will look at the NMR spectrum. Now, without showing the spectrum, I will ask a question. If I look at the proton spectrum, what do I get? In one spectrum, you cannot see this nuclei and this nuclei, Right? Because they are different nuclei. if I have to see a fluorine I have to go to fluorine resonance, if I have to see the carbon spectrum I have to go to carbon 13 resonance.

If I see the proton spectrum, I go to proton resonance. Now, we will see, before that remember the heteronuclear coupled spin system are weakly coupled, because the chemical shift separation is quite large. This is in megahertz, this is let us say 500 megahertz, this is 470 megahertz, this is 125 megahertz. See zeeman splitting, if you consider zeeman interaction, they are separated by several megahertz away.

In other words, you say the chemical shift separation is megahertz away. It is larger chemical shift separation. They are all resonating at frequencies, separated by megahertz. So it is a weakly coupled spin system. You understand, all heteronuclear spin systems are weakly coupled spin systems, because of large chemical shift separation. Now look at the proton spectrum. Very interesting.

Now I am looking at the proton spectrum which is the active spin. All of you must understand, in the case of this one, I am looking at the proton spectrum, this is the active spin, then what are my passive spins? both fluorine and carbon are my passive spins. So, what couplings I see at the proton? Coupling between proton and fluorine, JHF, coupling between proton and carbon JHC. Only these 2 couplings are seen in the proton spectrum. See proton is the active spin, 19F and been 13C are passive spins. I get JCH and JFH in the proton spectrum. JCF I do not see at all. I cannot extract from the proton spectrum, because this is the coupling between passive spins. I do not see at all.

Now go to the fluorine spectrum, in the fluorine spectrum, which is the active spin? Fluorine, which are the passive spins? proton and carbon. Now, when F is active spin, proton and carbon are passive spins. What I am seeing here, the fluorine spectrum, I see JHF and JCF. These are the active couplings, what about JCH. I am observing this, these are passive spins, this coupling between passive spins are not seen.

Now, go to the next example. 13C is active spin. Which are the passive spins, fluorine and proton are passive spins. So what are you going to get in the 13C spectrum? Fluorine carbon coupling and proton carbon coupling. What about FH coupling? No, these two are passive spins and coupling between these passive spins is not seen. So you get only JCH and JCF. JHF is absent, Did you understand. A simple example I took, 3 spin system, to show you what are active and passive couplings. What can we detect when we detect different active spins? And you always remember very, important points. Whenever I am seeing this type of a coupled spin system, all may be coupled, with some coupling maybe 0, no problem. Go to the chemical shift of a particular spin, or a particular nucleus in a molecule, whether it is homonuclear heteronuclear does not matter. When you are observing that spin, that is an active spin, when you are at that chemical shift and then measuring the chemical shift and coupling at that place, analyzing that multiplicity, it is an active spin and you get at that place the coupling between active and passive spin. Go to other proton, that is the active spin, the remaining are passive. There you get the coupling between active and passive spin, and the chemical shift of the active spin. No passive couplings will be seen. Like that, this point if you remember ,very easily you can analyze a lot of spectra. I hope you are catching my point of active and passive couplings. I introduced to you the active and passive coupling and took the example of 3 protons and 3 heteronuclei and I showed you what is an active spin, what is the passive spin? what is the active coupling between active and passive spin, that is what you see. And what are the coupling between passive spins, which you do not seen in the active spin. These basic points you remember. And do not forget because these are all very, very important as you go ahead further.

Now I want to tell you something about what is called sign of the couplings. Remember when I was discussing to you about the signs of scalar couplings, I am sorry about the salient features of the couplings, I did mentioned to you this scalar coupling can be positive, it can be negative or the value can be 0. Let me measure this for example, go back here you measure the separation, they say coupling I say it is 20 hertz. What is 20, 20 is a number. Is it + 20 or - 20? That question can be asked. So, scalar coupling can be positive or negative. It is possible. Then how do you know this separation is 10 hertz, is positive or negative, or the separation 100 hetz is positive or negative? We do not know. So, let us understand what are the signs of the scalar couplings. It is a point you must understand, especially in lot of examples I have seen, when people report the coupling between fluorine and carbon 1 bond coupling JCF, which is usually larger of the add of 300 Hz. They write JCF 300 hertz, it is wrong, because JC,F 1 bond is always negative, we should report as – 300 Hz. Not, just 300 because this coupling is negative, it is known. So, that is why sign of the coupling sometimes is very important to mention. In fact without knowing the sign of the coupling ,sometimes the application of biological studies is very difficult when you want to get some residual coupling. I will explain to you later, when we go further. First understand this one, what is sign a coupling now, and how it is used later.

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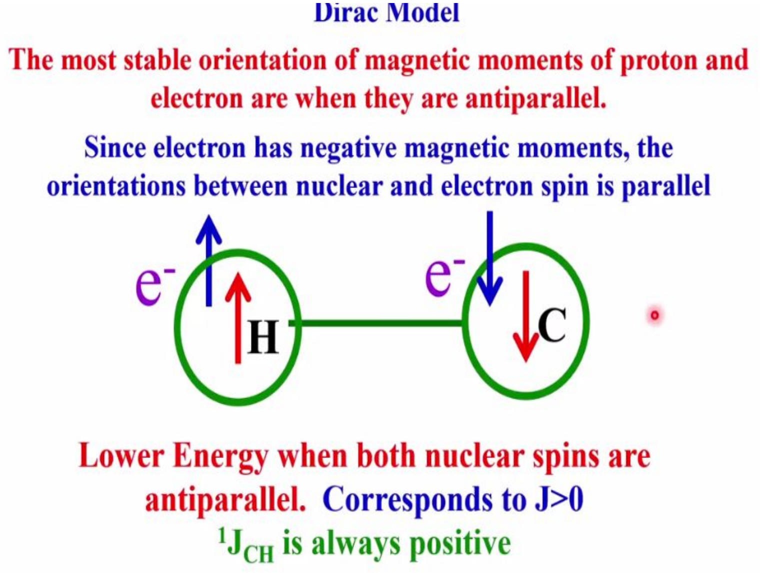

Dirac Model

The most stable orientation of magnetic moments of proton and electron are when they are antiparallel.

Since electron has negative magnetic moments, the orientations between nuclear and electron spin is parallel

Lower Energy when both nuclear spins are antiparallel. Corresponds to J>0

$^1J_{CH}$ is always positive

I consider this, we know this Dirac model, we discussed this when I introduced the salient features of the coupling constant, I said that, the most stable orientation of magnetic moments of proton and electron are the ones when they are anti-parallel to each other. Very first slide when I introduced scalar coupling, I said, the mechanism of coupling I was telling you, when one of the magnetic moment of proton I took, which is parallel to the field and when this is like this, the electron orientation has to be opposite for the stable configuration.

But because electron has a negative magnetic moment, I wrote both are parallel. Then I said according to the Pauli principle, this electron and this electron are paired, and as a consequence of this electron is down, this proton has to be up, or this is as good as telling because the magnetic moment of electron is negative. Again, you do not have to write it up it like this. Now, look at this.

Since electrons are negative, I wrote like this, finally the magnetic moment of protons when it goes through covalent bond, it ensures, by this fermi a contact fermi interaction, I said this is because of the Pauli principle, this model again is called a direct model, totally the classical way in a simple way of explaining this coupling interaction, when this is parallel, it forces the one bond carbon, which is coupled to it with a sigma bond, single bond opposite to this orientation. You understand, because of this fermi contact and pauli principle where these 2 get paired, and because these two again fermi interaction, this proton orientation, this magnetic moment, which is parallel to the magnetic field, forces this carbon to be orienting opposite to that, and this is called lower energy configuration. It is when the both the spins are antiparallel to each other, the nuclear spins, it is lower energy, low energy is a stable configuration, corresponds to J is positive. 1JCH is always positive, the lower energy configuration, now is stable configuration. And when these two are anti-parallel, the convention is the two coupled spins have opposite orientations like this, the coupling is positive. Very easily you can work out, but now 1 bond JCF if you take, I said 1 bond 1JCF is negative, you can work out. Go back and if there is a difference you will see why it is. The lower energy when both nuclear spins are anti-parallel, corresponds to J is equal to greater than 0. That is why if you go back and see in literature 1JCH is always positive. 1JCH is always positive because orientation of this protons spin and carbon spins in one bond, they are always opposite. You can work out by this way, by a simple Dirac model.

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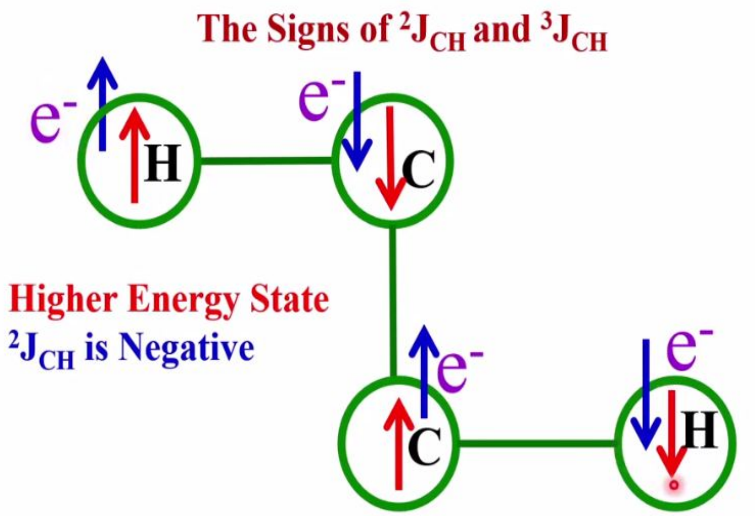

The Signs of $^2J_{CH}$ and $^3J_{CH}$

Higher Energy State

$^2J_{CH}$ is Negative

Now let us go for 2 bonds sign of JCH and 3 bond sign of JCH. I am considering only the proton carbon. Now, up to this we understood. This proton forces this to orient opposite to this. Now continue further because of this, it is orienting like this, as a consequence, this forces it to orient like this. You understand the problem, what is happening, 1 bond, this force this to be orienting anti-parallel to this, continue the same logic here.

Again bringing the Pauli pairing, afterwards you see that this carbon is forced to orient in the same direction as this one, when you go to through chemical bonds, the proton orientation and the carbon which are 2 bonds away, both orient in the same direction of the magnetic field. What did I say in the previous case, when they orient anti-parallel to each other, it is lower energy state. You see, low energy state with anti-parallel correspond to the positive J coupling. Please understand that the convention.

Now, in this case what is happening? They are parallel to each other, it is higher energy state with the unstable configuration, this has a higher energy. As a consequence, we say 2 bond JCH is negative. You understand how we get the sign of the coupling, just by using, here we use the Fermi contract interaction, here to here Pauli pairing, again fermi contact interaction, here to here Pauli pairing, here Fermi contact. We went by the simple Dirac model and we found out 2 bond J CH here is negative, you are all with me I hope.

Now, let us continue further. What happens if I get 3 bond coupling? up to this you have understood? Simply add one more bond. Now how does it work it? Remember, the same way now, there is a parallel orientation with respect to this one. Electron orients in such a way it gets a stable configuration. Again, we say a Pauli pairing and this forces this to be opposite with respect to this. So that means when you consider 3 bonds CH coupling, the orientation of the magnetic moment of this proton and the proton which is 3 bonds away, are anti-parallel to each other. They are opposite to each other. They are not orienting in the same direction. What does it mean? This means it is a lower energy state. But when lower energy state means, this is JCH I wanted to change that. And this is a low energy state and JCH is correct. There was a mistake in it, now I have corrected it. The 3JCH, it is with this proton and this carbon orients anti-parallel to each other that this is stable energy state or energy, and the stable configuration 3JCH is always positive. I hope you understood about the sign of the coupling, how to get the sign of the coupling.

But the next question is how does the sign of the coupling influences the spectrum? What happens when the J is positive? How does the spectrum look when J is negative? How does this spectrum look? Can I get the sign of the coupling just by looking at spectrum? these are the questions which we have to answer.

You understand in this class, I was briefing you about active and passive couplings. I took the example of 3 spins, I explained to you what is the active coupling, what is the active spin? What are active couplings? Active couplings are always coupling between active and passive spins. What are passive couplings? coupling between the passive spins or among the passives.

When you are looking at the chemical shift of a particular proton, that is an active spin, and you will always get to multiplicity at that site, because of the active spin coupling to remaining passive spins. And no passive couplings are seen here. This is logic, I showed the example of a homonuclear case and three heteronuclei case also. I introduce about the sign of the coupling, how the sign of the coupling can be observed depending upon the orientations of the magnetic moments have between 2 different spins which are chemically bonded, especially CH, 2 bond, 3 bond.

And we observed 1 bond CH which is positive 2JCH is negative and 3JCH is positive, based on the alignment of the magnetic moment of 2 coupled spins. If they are anti-parallel it has different state, if they are parallel different state. So, depending upon the lower energy state are higher state, for example, when these 2 are anti-parallel, it is lower energy state. And for example, this and this are anti-parallel, lower energy state; this and this are parallel, it is higher energy state. Like this, you can start understanding about sign of the couplings, I stop here. Next, class I will discuss about how sign of the couplings affect the spectrum and then we start getting more information about other multiplicity pattern and analysis.