One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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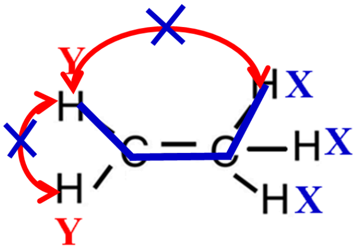
Lecture 10 - Scalar couplings

Welcome all of you. In the last two or three classes, we discussed extensively about chemical shifts, one of the internal interaction parameters within the molecule. And we discussed how the chemical shift arises, what are the parameters or factors which govern the chemical shift. And what happens to chemical shift when there is a symmetry in the molecule, that is the chemical equivalence of different protons in the molecule. And we also understood how do we express chemical shift in ppm, and we measure the frequency of the signal with respect to the reference and divide by the resonating frequency, then we know we can express the chemical shift in ppm that is what we understood. And as I said chemical shift when expressed in ppm removes field dependency, there is no field dependency. And for different nuclei to express chemical shift or to measure the frequency, we have different references. For proton, carbon and silicon, I said tetramethylsilane can be used. For different nuclei, we have different references. I also discussed extensively, how do we convert ppm to frequency and frequency to ppm for different nuclei, in the same spectrometer or in different spectrometer; how do you convert it. And I also showed that there is a field dependency for the chemical shift, especially when expressed in frequency, you can see that there is a better dispersion, better dispersion gives better resolution. You get better resolution as you go to higher and higher frequency. AT higher frequency spectrometer, the peaks start moving far away, the dispersion becomes much much better, very easy to analyze. And we discussed at stretch about factors governing the chemical shifts like effect of electronegative atom, isomeric effect coming because of electron donating group or electronic withdrawing group, both in aliphatic and phenyl groups, the delocalization of aromatics, what is going when there is electron donating group or electron withdrawing group is there, what will happen, how orthon para positions are selectively affected and the meta position is less affected compared to these two. This is the case, for let us say, for electron donating group if it is present. It gets reversed when you have electron withdrawing group. Similarly, what will happen to the magnetic anisotropy, if you have a C triple bond C, C double bond, C single bond, C. triple bond, C in acetylenic group, what happens to the protons if it is situated within the cone of the charge distribution curve, what happens if it is situated outside, whether shielded or deshielded, which depends upon whether it is single bond, double bond or a triple bond. Extensively we discussed all those things. We can keep on discussing about it at for hours and hours. At the moment, I have given you the basic idea about chemical shifts.

With this idea, we will go ahead and try to understand another interesting internal interaction parameter called scalar coupling. If you understand these two, by and large you can interpret any NMR spectrum, especially the chemical shift and also the multiplicity pattern that is important. So, we will understand another important factor which governs the NMR spectrum; that is called the scalar coupling. This is called spin-spin coupling, also called indirect coupling. It, yet again as I told you, is a magnetic interaction.

It is because of an interaction between two nuclear spins, where the magnetization or the polarization is transmitted between one nuclear spin to another nuclear spin mediated through chemical bond, covalent bond. If there is a covalent bond, then what happens, this nuclei can give its polarization to this nuclear spin and there is an interaction between these two. When these two are interacting some effect is seen. What is going to happen for the NMR spectrum? What is that effect? That is what we will discuss today in spin-spin coupling. We can discuss spin-spin coupling, scalar coupling at stretch, a lot of things we can discuss. Before that, I will summarize some salient points of scalar couplings. What are the scalar couplings salient points? First of all, I told you it is a covalent bond mediated interaction. There must be a chemical bond for one nuclear spin to interact with another nuclei spin, for J coupling to occur. For example, in a molecule like this, this interaction is allowed.

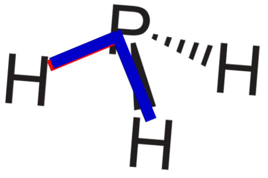


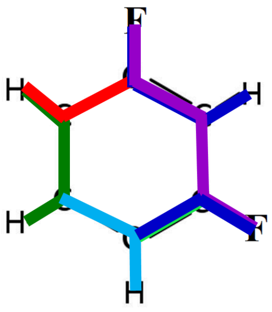
This proton can give its energy to this carbon, this carbon to this carbon and to this proton. The polarization transfer takes place through chemical bonds that is allowed, whereas direct polarization transfer from this proton to this proton through space is not allowed. This is one of the salient features of scalar coupling. It is a covalent bond mediated interaction. Again, this is also not allowed through space. Second, also this coupling is always denoted by $^{n}J_{ij}$ is a term we use, it is like chemical shift is always refers to as delta ppm. I said chemical shift is refers as a ppm scale is also called delta scale. Coupling is referred to as $^{n}j_{ij}$. n is the number of bonds, consecutive bonds separating the two interacting spins. For example, this proton and this proton are interacting. They are separated by one, two and three bonds. So, this is called $^{3}j_{ij}$ between this proton and this proton. So, nij, n is a number of bonds, consecutive bonds, separating the two interacting spins. J coupling also depends on the electron charge density at the side of the nucleus and are not averaged out in the solution state. It depends upon the charge at the side of the nucleus, but they are not averaged out like dipolar coupling, which I said earlier. That means, it does not depend upon the orientation of the internuclear vector. That is why J coupling is called scalar because it does not depend upon the orientation of the internuclear vector.

Third important point is the strength of this interaction. The interaction strength is few hertz to few tens of hertz. For example, the J coupling, could be 10 Hertz, 5 Hertz or it could be 1000 Hertz, depending upon nuclei of interest or depending upon the interacting spins, two spins which are interacting, also whether it is homonuclear or heteronuclear. So, the strength can vary from few hertz to few tens of hertz, sometimes hundreds of hertz.

The coupling interactions between two spins can extend beyond one bond, two bond or three chemical bonds. For example, there can be this proton to this proton interaction, it is two bond coupling, $^{2}J_{HH}$. This to this is possible, three bond coupling, $^{3}J_{HH}$. This is four bond coupling, $^{4}J_{HH}$. This is $^{5}J_{HH}$, 5 bond coupling. This is $^{6}J_{HH,}$ 6 bond coupling. So, it can extend to several bonds, but remember the value of the coupling can be positive, negative or 0. The J coupling can be even 0 or it can be some value plus 5 hertz or it can be minus 5 hertz, possible. It has a value which can be either positive, negative or 0.

Coupling can be between homonuclear and heteronuclear NMR active multiple spins. For example, if I consider a molecule like this, there can be two bond coupling between this proton to this proton. There can be one bond coupling between this phosphorus and fluorine, it is possible. This is possible and this is also possible. Two types of interactions are possible here.





This proton and this proton, the coupling is there through bond, the homonuclear coupling. Proton and phosphorus coupling is the heteronuclear coupling. That is also possible. Consider a molecule like this. Now, we have metadisubstituted benzene, fluorine and fluorine. There is a symmetry here. Do not worry about more about symmetry and everything. Just for the sake of understanding, I am telling you, there can be a coupling between this proton to this proton, three bond coupling, the homonuclear proton-proton coupling. There can be coupling between proton and fluorine, again three bond heteronuclear coupling. There can be coupling between this carbon and this proton, two bond coupling heteronuclear. This one bond coupling C-C, homonuclear, two bond coupling carbon and fluorine, heteronuclear and four bond coupling between fluorine and fluorine, homonuclear. Three bond coupling between fluorine and proton, again heteronuclear. So, many possibilities we can think of in a given molecule. There could be n number of homonuclear couplings, then can be n number of heteronuclear couplings possible. So, any coupling can be between both homonuclear spins and also heteronuclear spins.

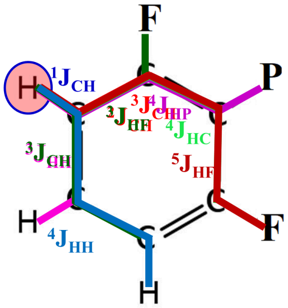
And coupling constant is a scalar quantity. It is always expressed in Hertz. It is just a number. If I say 10 Hertz, just number, so coupling constant 10 means 10 hertz, that is all. It is a scalar quantity. It is always expressed as jij.

Another important factor is the magnitude of the spin-spin coupling, the strength of the coupling, scalar coupling is larger for one bond coupling. If the two spins are separated only one chemical bond, the strength is more. If it is separated by two consecutive bonds, strength is much less. If it is three bonds, consecutive bonds. separated by three bonds, even less. Four bonds, it is less. It is just an order in which the coupling strength decreases. But there can be violations. It is not that this should always be like this formula. It is generally the case, but there is a possibility that three bond coupling can be larger than two bond couping also. It is possible. But this is the general trend. So, as a number of consecutive bonds increases, the strength of the interaction keeps coming down.

The coupling constants are independent of the magnetic field. Remember, I told you, chemical shift has a field dependence. As you keep on increasing the magnetic field, I said there is more and more dispersion is there. Peaks are moving away. There is a field dependency for chemical shift. But for the scalar coupling, there is no field dependency. It is independent of the applied magnetic field. Coupling constants, whatever the value you measure in a particular frequency of the spectrometer, go to any other spectrometer, to any other frequency, the coupling constant remains same. It does not depend upon the magnetic field.

And the splitting patterns is independent of the sign of the coupling constants. We will discuss that later. For example, I have a doublet here. I measure this coupling, some value. Doublet comes because of splitting, because of j coupling. Some value, let us say 10 hertz. I make it minus 10 hertz. This pattern remains same. It would not change. You will not be able to find out by just by looking at the spectrum, whether it is positive or negative. The splitting patterns are independent of the signs of the coupling constant.

And one spin can simultaneously experience coupling with several other chemically inequivalent spins with different strengths. For example, look at this molecule. Then, I will consider this proton. This proton can have a coupling, scalar coupling with lot of other nuclei.



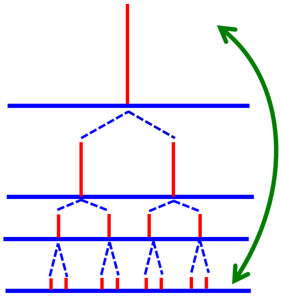
For example, it can have one bond coupling between carbon and proton. This proton can interact with this carbon, one bond, j coupling is possible. Two bond, this proton can couple to this carbon. That is also possible. This proton can couple to this fluorine, well three bond coupling is possible. It can have a four bond coupling with this carbon, heteronuclear coupling. It can have four bond coupling with this phosphorus, heteronuclear coupling. It can have five bond coupling with this carbon, heteronuclear. It can have 5 bond coupling with this fluorine, heteronuclear again, and it can have 3 bond coupling with this proton, homonuclear proton-proton. It can have 3 bond coupling between this proton and this carbon. It is also possible. It can have 4 bond coupling with this proton and this proton. See, 1 proton, 1 hydrogen in this molecule can have 10 different couplings. It can experience different couplings. It can couple to any of these nuclear spins and the strength of the interactions will be different, need not be same. This 1 bond carbon coupling may be 150 hertz or 200 hertz. This can be 10 Hertz. This can be 50 hertz like that. Different interaction strengths are there, but one spin can simultaneously interact with all other spins. This has 10 couplinga. Similarly, if you look at this proton, you can work out. You can find out this kind of 1 bond coupling here, 2 bond, 3 bond coupling with this, 3 bond coupling with this, 3 bond coupling with this proton like that. You can work out. This can also have 10 different couplings. So, each spin in a given molecule can have n possible interactions, n types of interactions with different nuclear spins with the strength being different also, need not be same.

Of course, so far I was telling you, we get the J coupling only mediated through covalent bond, but in some rare examples of molecules like this, you can get coupling between this fluorine and this CH3 proton and this fluorine not mediated through covalent bond directly through space. Similarly, here through space coupling of substantially large value you can see. In these cases, this coupling is not covalent bond mediated.

It is because, it so happens the lone pair electrons of these 2 nuclei are in within Van der

Waal contact. There is a direct transfer of polarization between these 2 spins. As a consequence, we can see this interaction, but not through covalent bond, through direct. These are all rare examples, not always, but all the time, the majority of the cases are 99.9999 percent of the cases except one or two rare examples like this, the scalar coupling is an interaction where the polarization is transferred through covalent bonds. That is the important thing.

And one particular peak can split into multiplicity of peaks due to coupling interactions. I told you in one previous molecule which I showed in the benzene ring. One proton can have 10 different couplings. What happens when one proton is coupled to other one proton, or is coupled to several other protons or several others. like carbon, fluorine a phosphorus. When it interacts with other nucleus spin, then this peak will divide into 2. One will become 2, 2 will become 4, 4 will become 8 like that. There is a multiplicity because of interaction. There is splitting of the energy levels. As a consequence, particular proton or particular nuclei which you are observing can give rise to multiplicity pattern.



One peak for example, will be a singlet without any coupling. If it is coupled to another proton, it can become a doublet. If it is coupled to another proton, it will become doublet of doublet; when coupled to another one, it will become doublet of doublet of doublet, eight line pattern. But remember this, let us say, intensity of the peak is 100. When it divides into 2, it will become 50, 50. When it divides further into 4, it will become 25, 25.25,25. When it divides further, it is 12.5, 12.5, 12.5 and 12.5. Like that it goes. We add up all these intensities, 12.5 into 8, it will become 100. So, this is the peak intensity. So the total intensity of a particular peak will remain same if you measure the intensity of the entire multiplicity. That shows the peak integral area gives you the proton count. If this total area corresponds to one proton, then all the multiplicity area if you consider, it corresponds to one proton. let us say one CH proton, which is divided into 8 peaks because of coupling with 3 other protons. But the total integral area is same as this one. So, the multiplicity will be there, but the total integral area of the uncoupled peak, and the multiplicity coming because of coupling with other protons remain same. Remember the total integral intensity of the uncoupled proton and the multiplicity pattern coming because of coupling with several other protons, the total area remains same. That is why we can get the proton count if you get the integral area. Is it clear?

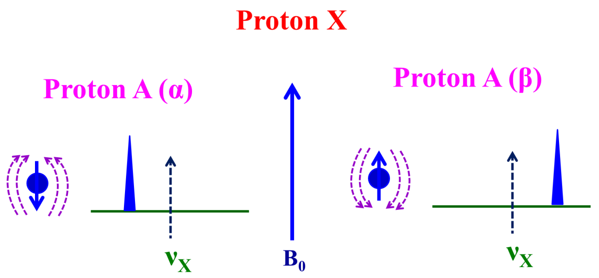
Now, let us go to the next one. The multiplicity of the peaks due to coupling with chemically equivalent spins is always given by a formula called 2NI+1, especially in the weakly coupled case. I will tell you what is weakly coupled and strongly coupled when we go ahead. But remember there is a multiplicity and that multiplicity can be understood by this formula. And for coupling among equivalent spins, we can also get the relative intensity of the multiplicity. Here we said for chemically equivalent spin there is multiplicity because of 2NI+1. And I can measure the intensity of each of these peaks, that is given by what is called a Pascal triangle or the coefficients of binomial expansion. When you go ahead further, we will discuss that. I will show you. I explain everything in detail. So, these are some of the salient points of scalar couplings. Before we go further, we should know what are the factors. The scalar coupling is a very simple, very small interaction especially when we are dealing with protons. But so many information is available. These are all the features, salient points which you should remember when you want to understand scalar coupling.

Now, as I told you when these two nuclei spins are interacting, when there is a scalar coupling, I said there is a multiplicity coming because of splitting I showed you in the previous slide. One will become two, two will become four, four will become eight. How that peaks are coming? How so many peaks came? How one became two, two became four? This is because the energy levels of the particular spin gets split when it interacts with another proton or another spin. This when the energy levels are split, the number of transition become more. As a consequence, we get multiplicity.

We will understand taking example of two protons which are coupled between themselves. The J interaction always results in splitting of the energy levels, J interaction results in splitting. And how this splitting takes place, how many splittings are there, how one energy state will become two, four or eight depends upon number of spin states of the coupled spins. If one proton is coupled to other proton, other proton may have two spin states, alpha and beta. If it is coupled to two protons, then there are four possible spin states alpha alpha, alpha, beta, beta alpha and beta beta. If it is coupled to three, then you have eight possible spin states. Remember I explained to you earlier, the number of possible spin states goes by 2 to the power of n. We will understand that now more in detail. Then each spin will give rise to multiplicity pattern at the respective chemical shift position based on how many number of spins to which it is coupled to. How it is interacting will decide about the multiplicity pattern.

Now, we will consider for a single spin, what are the possible orientations we discussed. I told you if I have only one proton for example $CHCl_3$, I took the example in earlier case, one proton, isolated proton, we do not worry about the coupling with other things. It has only two spin states because this proton can have alpha state, spin up state, beta state, spin down state. So, there is no other interaction. There are only two energy states. The transition between these two is allowed according to selection rule, which I discussed.

So, you will get one peak. So, single isolate spin without coupling to any other apin, always gives a single peak. That is why I said CHCl3 gives a single peak. Fine. What happens if there are two spins? How many possible energy states are there when there are two spins? especially when they are coupled, when there is an interaction between them?



The spin 1 can have alpha and beta orientations. The spin 2 can have alpha and beta orientations. Now, we can think of the possible orientations, combinations of that. Before that, let us see how it is splitting. Now, we will consider proton 1 and 2.

I call them as A and X, spin A and spin X. Let us consider proton X. There are only two protons we are considering. Each of them alpha beta, alpha beta, two orientations. Let us say this is for A, this is for X. Now, I am considering proton X. This proton X can see proton A either in this state or in this state. They are two different energy states. So, proton X can see proton in the spin up state or in the other state which is spin down state. That is alpha state and beta state. There are two possible orientations. Let us say this is a spin down state, this is a spin up state. Now, what will happen with respect to this original position before interacting with the proton A, this will be the position of, let us say, proton X. Because it sees this in the alpha state, this is moved by certain value because it is seeing the proton A which is in alpha state, there is energy difference, there is small change in the energy. Similarly, this proton X can also see proton A in beta state. It moves towards the right side. The alpha and beta states, one is higher energy state, other is lower energy state. As a consequence, this proton X can see this proton A with some value which is more and with some value which is less. As a consequence, it moves the peaks in two different positions, one to the low field, one to the high field region. You understand, the proton X sees proton A in two possible orientations alpha and beta and it splits this into two and because of splitting of the energy level, one peak moves to the down field, one peak moves to the high field. So, proton X will become two lines, it splits into a doublet because of interaction with proton A. Fine.

Now, what about proton A? We looked at proton X, look at proton A, proton A again sees proton X in the alpha state, proton X in the beta state. Again, it will split into two, one moves to the low frequency, one move to the high frequency region. Essentially, what is happening is when two protons are interacting, each proton will see other proton in alpha and beta spin states. As a consequence, it will become a doublet. So, basically, when you have two protons which are coupled, I call it as a weakly coupled, we will see what is weak and strongly coupled later. Then, at the chemical sheet of position of υA without any splitting, it will be a single peak, at the υX, there is no coupling, it is a single peak. But because of the coupling, each will become a doublet. From the center, it moves by certain amount here, from the center, it moves by certain amount to the left. So, this moves to the high field and this moves to the low field by equal amount. And if I measure the separation between this and this, that is called interaction strength, J coupling, it is a scalar coupling. The proton A is becoming a doublet, and if I measure the doublet separation, that gives me J coupling to A and X, this is called J_{AX}. Similarly, if I take proton X, proton X will become a doublet because of proton A. Measure the separation, this is J_{AX}, exactly same, identical. So, when two protons are coupled, each proton will be a doublet. Remember, each proton will be a doublet and the separation of this doublet gives you J coupling value, that is what you are going to measure and the center of this doublet always correspond to its chemical shift. Center of this doublet correspond to chemical shift of X, center of this doublet correspond to chemical shift of A. The separation between these two doublets correspond to J coupling, you understand. ‘

One important point which you should know here is, proton A sees proton X in two spin states, alpha and beta and its energy is split into two. Proton X sees proton A in two spin states and its energy is split into two. The alpha state has lower energy and beta state has higher energy. So, as a consequence, each peak is split into two lines. Please remember the statement, when two protons are interacting, each proton is split into doublet because of its interaction with the other proton. And interesting thing what I wanted to tell you here is, please note, when A is coupled to X becomes a doublet, X is coupled to A becomes a doublet. It means, the interactions in NMR are always mutual. If A is a doublet because of X, X is also a doublet because of A. So, the interactions are mutual. As a consequence, you got doublets in both of them. So, if you measure the doublet separation for each of them, that gives you coupling interaction between A and X. Center of each doublet gives you respective chemical shifts. This is what is important to understand about the interaction, how the multiplicity comes when two are interacting.

What happens if three protons are coupled? You can work out the same way. It is not difficult at all. But remember, when one proton is there, if this is seeing other two protons, each proton will have alpha and beta states. Now, various combinations we can think of. This can see this in both up up, both down down, one up, one down and this down, this up. So, each proton will see other two protons in four possible spin states. Then what will happen? One will become two, here one became two because of two states. Now, there are four possible orientations, it will become four line pattern. If it is coupled to three protons, then you have eight possible spin states, then it will become eight line pattern. That is how the splitting keeps going. Remember, the splitting of the energy levels, a particular proton splits into n number of energy states depending upon spin states of the protons which it is coupled to. One is coupled to other proton, there are only two possible spin states, alpha and beta. If one proton is coupled to two other protons, there are four possible spin states, you will get four lines. If one proton is coupled to three other protons, there are eight possible spin states, you will get to eight lines. Like that, multiplicity comes. So, more about the multiplicity of the coupled spins, we will discuss later. I am going to stop here because time is getting over. Please remember, what we discussed today.

We discussed another interaction parameter, scalar coupling. I discussed varieties of features of scalar coupling. First of all, it is a scalar coupling, is a covalent bond mediated coupling. It is the polarization transfer between two spins takes place through covalent bond. How it occurs, we can explain through Dirac model, but I am not going into the details because in one of the earlier courses, we have discussed this at stretch. But, salient feature you should know, it is scalar coupled, covalent bond mediated scalar coupling, it is just a number, it is called a scalar quantity, it does not get average out, one proton can couple to any other spins, any number of homo and heteronuclear couplings of different strengths. It could be homonuclear and heteronuclear. When one proton is coupled to other proton, it give rise to multiplicity, become doublet, doublet of a doublet, doublet of a double of a doublet, like that. One becomes two, two becomes four, four becomes eight lines. Like a family tree approach, it keeps undergoing splitting. So, all these things we discussed at stretch and I took the simple example of two protons coupled, A and X. A will see X in two orientations, alpha and beta because of two energy states, it will become a doublet. This X will see A in two orientations, alpha and beta, this will become a doublet. And two peaks move equally away from the center, that is what I showed. This is the chemical shift, one peak moves equidistance on left, one peak, move equidistance on other side, right side from the center. And the separation becomes J. That means from the center, it moves by J/2 to the left and J/2 to the right, and the total coupling is J. Similarly, for other spin, one peak moves J by 2 to the right, and the other one peak moves J by 2 to the left, the coupling separation between these two is J_{AX}. This is simply for two spins. We can understand this for more spins later. So, I am going to stop here. We introduced quite a bit about the coupling, lot more to understand about the multiplicity, how it comes etc, which we will discuss in the next class. Thank you.