

One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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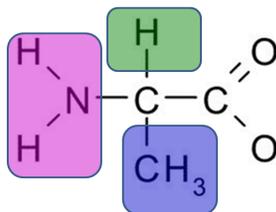
Lecture 06 - Interaction parameters

Welcome all of you. In the last couple of classes, I discussed fundamental concepts of NMR spectroscopy starting from the spin of the nucleus and then how do you arrive at the nucleus spin by an empirical rule and what are the nuclei which gives rise to NMR. We discussed about interaction of nuclear spins with the external magnetic field which we called as Zeeman effect and then degeneracy of the transitions in the presence of the magnetic field will be removed, from energy states we calculated the energy between these two states. And the energy difference between these two we calculated for a particular frequency which we observed to come in the radio frequency region. And we arrived at the resonant condition ν is equal to γ into B naught over 2π . Same thing conceptually we understood by classical phenomena. The nuclear spins or the ensemble of nuclear spins in the absence of the magnetic field are all randomly distributed. Once you put them in a magnetic field there is a preferred alignment of the nuclear spins in the direction of the field and in the direction opposite to the magnetic field. According to Boltzmann rule we also understood that more spins are there in the direction of the magnetic field than opposing it. And then we worked out what is the population different for different magnetic fields and we found out that it is very small.

We said NMR is highly insensitive and also we understood what are the factors which are responsible for this sensitivity of the NMR signal. They are magnetic field γ temperature, etcetera. We found out at low temperature, the sensitivity becomes better and better. When the temperature is infinite, the spins populations in both the energy state spins become equal; that is called a saturation. During saturation we do not get any signal and we also understood about how do we get the signal. It is by applying a radio frequency pulse, that is by perturbing it, we induced transitions. And we understood what is a random phase approximation. We introduced the concept of bulk magnetization. The bulk magnetization is stationary and it is in the direction of the magnetic field. To detect NMR signal we have to perturb it by applying a radio frequency pulse in a direction perpendicular to it. Then we collect the signal as a function of time. This signal is called free induction decay. We do the Fourier transformation of it and we get the NMR spectrum. And we also understood what is the line width of the peak, by uncertainty principle and also what are the selection rules for observing the transitions in different coupled energy spin system. The examples of allowed transitions in a single spin,

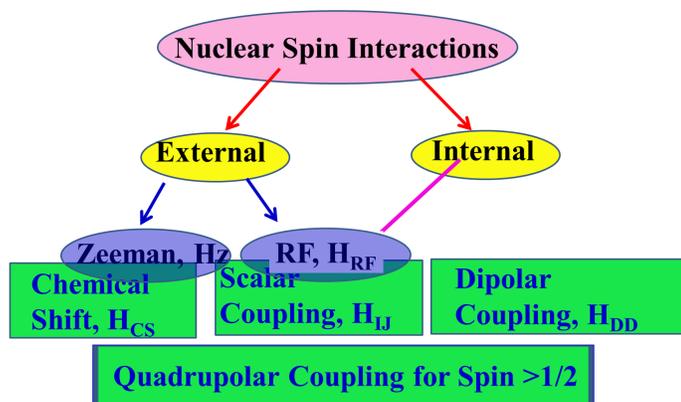
coupled two spins, three spins etcetera we understood. Also we know from all these examples, there should be change in the magnetic quantum number between two energy states, which is either plus 1 or minus 1. These are all allowed transitions. That is the selection rule. Anything other than this are forbidden transitions.

So, everything we discussed and now we will go further. Today we are going to discuss about what is called internal interaction parameters, which are responsible for NMR spectrum. Real application of NMR comes into picture only because of these internal interaction parameters are present. Further today, I am going to discuss more about what is called chemical shifts. For example, consider a hypothetical molecule like this.



I am showing you here hypothetical molecule and in this hypothetical molecule I have three functional groups which are put in three different colors; green, purple and blue. These are CH proton, NH₂ and CH₃. What is my resonance condition? let us say, I put this molecule in a magnetic field, in a strong external magnetic field static field B_0 . According to my resonance condition ν is equal to γH into B naught over 2π ; γ is a constant for a given nucleus. Now I am looking at the protons NMR; that is hydrogen. So, γ is of proton, I fix this magnetic field as a constant. So, B_0 is constant, I know 2 is constant, I know π is constant. So, what do you understand from this equation? The resonance frequency for CH group NH₂ group CH₃ groups is same. All the three have the same resonating frequency, the same frequency will be there if you calculate according to this equation. This equation does not distinguish resonating frequency for different functional groups. It only gives for a particular nuclei for a particular γ what is the resonating frequency. As a consequence, not only for this hypothetical case, if I consider for any molecule of your interest, if you take NMR spectrum, it should give only a single peak; nothing else. You cannot get anything more than a single peak. If this was the case then what is the use of NMR? This is a question we have to ask; what is the use of NMR, if you get only one peak for any molecule of your interest. And there is nothing wrong. This is 100 percent true, because of this equation, the resonance condition that we have worked out. But what makes NMR, very powerful is the nuclear spin interactions, the internal interactions within the molecule. That is what is going to make NMR a very very powerful technique. What are these internal interaction parameters? The nuclear spins are undergoing some interactions within the molecule. We will understand that and that is what makes NMR very

interesting.

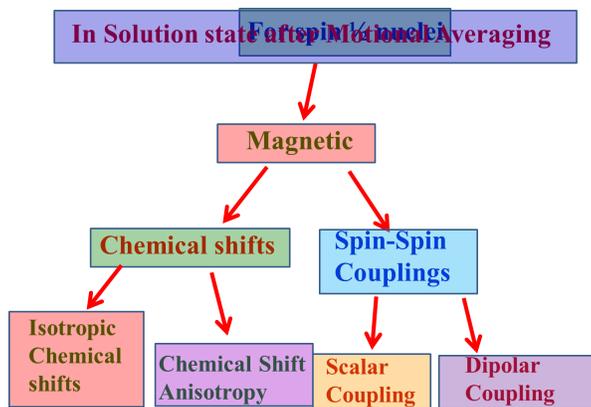


If I consider the nuclear spin interactions, I can classify this into two types. One is external interaction, and the other is internal interaction. The external interaction can be again two interactions; one is a Zeeman interaction and the other is RF interaction. This we discussed extensively in the last couple of classes. What is a Zeeman interaction? you put the sample in an external magnetic field, I told you the nuclear magnetic moments interact with the external magnetic field. Remember I calculated the energy E equal to minus μ into B_0 . I said magnetic moments interact with the external magnetic field that is a condition to see or observe NMR; the interaction of magnetic moments with an external magnetic field. It is a basic requirement. If μ is 0, because I is 0 then there is no NMR. That is what we discussed. So one of the important interactions is the Zeeman interaction. It is an external interaction and nuclear spins are interacting with the external magnetic field; that we discussed. Another is RF, we have to apply a radio frequency pulse in a direction perpendicular to the magnetic field to induce resonance. That is what we discussed, and I said bulk magnetization will be tilted to x-axis or y-axis by applying a RF pulse in a direction perpendicular to the bulk magnetization. It is an external interaction. You are applying RF pulse from outside. So these two are external interactions which we already discussed and from this we observed we are going to get only a single peak for any molecule of your interest, by my previous slide ν equal to γ into B_0 over 2π . So this we discussed at length, and we understood we get only one peak for any molecule. Now what is important is internal interactions. We will look at the internal interactions. The internal interactions is another thing. We have four different categories within the molecule. Internal means within the molecule I am talking. One is chemical shift, other is scalar coupling, third is dipolar coupling and fourth is quadrupolar coupling. Remember this quadrupolar coupling is exhibited only by the nuclear spins whose spin quantum number is greater than half. The nuclear spin quantum

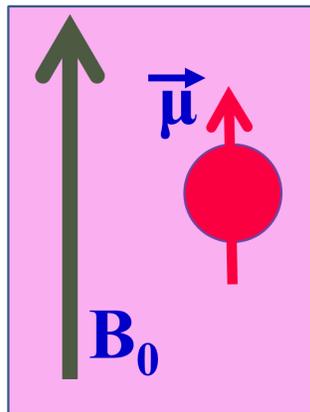
number of this particular nucleus should be greater than half. Only such nuclei give rise to quadrupolar interaction. All other things spin half nuclei will give this, this. Then this quadrupolar coupling is only for spin greater than half. Now the internal nuclear spin interaction can be further classified into two groups one is a magnetic interaction other is electric interaction. The magnetic interactions are two types; chemical shifts and spin spin coupling. The electric interaction is for quadrupolar spins only, for spin greater than half. Remember all interactions in NMR are magnetic, except quadrupolar interaction for spin greater than half. Understand the major differences all interactions for spin half nuclei are magnetic. When you have a spin greater than half, you have quadrupolar interaction, that is electric interaction.

Now the chemical shifts is one of the internal interaction, the magnetic interaction. I can classify into two. Again one is isotropic chemical shift, the other is chemical shift anisotropy. This chemical shift anisotropy comes only in a system which is ordered, or partially ordered. The isotropic chemical shift means, in a regular solution state when molecules are undergoing rapid tumbling motion. The thermal agitation is going on then you will not see the anisotropy. Now spin spin coupling again, I can classify into two groups. One is a scalar coupling, other is a dipolar coupling. Further if I take the spin half nuclei, all the types of interactions are present.

Now I consider a general example of any nuclei which spin greater than half we have magnetic interaction, electric interaction, chemical shift chemical anisotropy all those things are present. If I consider only spin half nuclei, that is what we are interested in, and we are going to discuss for the rest of the classes. For the rest of the course we mostly concentrate on spin half nuclei, and we are dealing magnetic interactions so we are dealing with only chemical shifts and spin spin couplings. In the chemical shifts we deal with only isotropic chemical shift and CSA we are dealing only with solids. We are dealing with scalar coupling and if you are dealing with ordered system like partially or fully ordered system we deal with dipolar coupling.

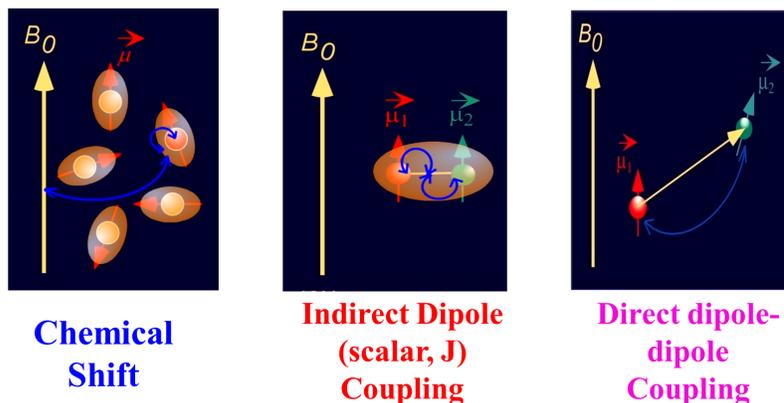


For spin half nuclei all these four interactions are present. But in this course we are not discussing solid-state NMR. Solid-state was discussed in one of my previous courses; in the advanced course. So if you go to the solution state NMR then what is going to happen? there is a motional averaging. Because of the motional averaging this chemical shift anisotropy and the dipolar coupling both will get averaged out. They will not be present. What we are going to see is only isotropic chemical shift and scalar couplings. So remember we are going to deal with only solution state NMR for the entire course. That means we are always dealing with motional averaging; so we do not have to worry about chemical shift anisotropy, we do not have to worry about dipolar couplings. All we have to worry about only two magnetic interactions, that is, isotropic chemical shift and scalar couplings. These are the two parameters which we deal with in the rest of this course. Remember every parameter in NMR is anisotropic. The chemical shift is anisotropic; the anisotropic part gets averaged out, and we get only isotropic chemical shift. The scalar coupling is also anisotropic. The anisotropy gets averaged out. We get only isotropic part. The dipolar coupling is anisotropic, the quadratic coupling is anisotropic. Every interaction parameter in NMR is anisotropic. But when you are dealing with the solution state NMR anisotropic component part will be averaged out and we are left with only isotropic chemical shift and isotropic scalar coupling. Also the anisotropic part of this scalar coupling is averaged out. Okay, now we will discuss all these interaction internal interaction parameters. We will start discussing; of course, this we already discussed.



One of the major external interaction is Zeeman interaction, comes because of the interaction of the magnetic moment with the external magnetic field. It is dominant interaction in NMR. For spin half nuclei the dominant interaction is Zeeman interaction where external interaction the magnetic moment of the nucleus will interact with the external magnetic field B_0 . You may ask me what is the interaction strength? Every interaction can be defined by its strength. What is the energy separation? we calculated

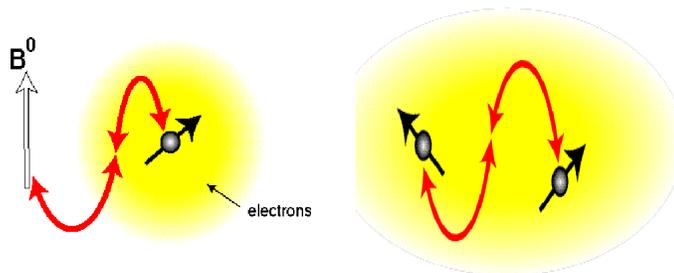
and we observed resonance in NMR appears in megahertz frequency range. That means the Zeeman interaction is of the order of megahertz. The strength of this interaction is of the order of megahertz. Please remember Zeeman interaction strength is of the order of megahertz.



Other sources of internal interaction for spin half nuclei, we have chemical shift, we have indirect scalar coupling or J coupling; and we have what is called the dipole-dipole coupling. Remember the chemical shift comes because of the charge distribution at the site of the nucleus due to surrounding electrons. We will understand more as you go further.

We also get interaction of one nuclear spin with the other nuclear spin, where the polarization of the one nuclear spin is transmitted to other nuclear spin mediated through covalent bond.

scalar coupling, also dipole coupling. several it but the concept concept is the one nuclear spin nucleus spin

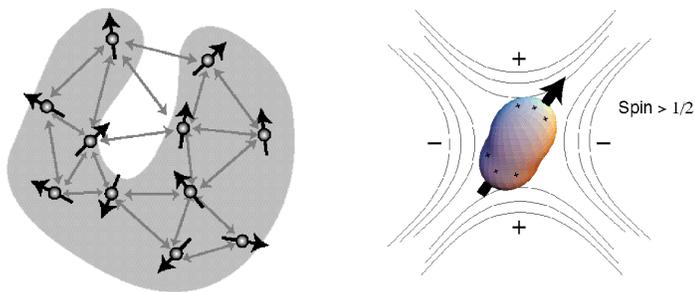


That is called also called J called indirect There are synonyms for is same. The interaction of with the other where the

polarization transfer takes place or the magnetization transfer takes place between two interacting spins through covalent bond. And the third one is a dipole-dipole interaction it is interaction between two nucleus spins but there is no need of a covalent bond it is a spatial interaction The interaction can take between two spins which are coming close in space. It is like each spin is a tiny magnet, you can bring two magnets close to each

other; closer you bring them larger is the interaction. If the spatial distance is very close between them, then the interaction strength is larger. This is a dipole-dipole interaction; and of course, if I say for spin greater than half we have quadrupole interaction. These are the four interaction parameters but for most of the cases since we are dealing with isotropic solutions, we have to deal with only chemical shifts and J coupling, that is all. We don't need to worry about other parameters at all. In the entire course we do not deal with other parameters; we deal with only chemical shift and J couplings. Of course, when I introduce NOE then we discuss about dipolar relaxation, etcetera. But we do not measure the dipolar coupling strengths.

Now, if we come to the chemical shifts; how do they arise? The chemical shift is because of the electronic environment surrounding the nucleus. because of the rotates you know circulating electrons surrounding the nucleus as I said J coupling is interaction of one nuclear spin through other nuclear spin mediated through electrons that is covalent bond mediated through chemical bonds.



Now, other measurable parameters are these it is a pairwise interaction and this is for quadrupolar spins. We will not worry about it now. we will worry start worrying detail more detail about how does chemical shift arise? what is the reason? how we can think of chemical shift. We all know the nucleus of an atom is surrounded by the cloud of electrons and it is like this the external field induces the currents in the electron clouds in the molecule. You put this in the external magnetic field. The external magnetic field induces currents in

$$B_{\text{local}} = B_0(1 - \sigma_s)$$

the electron clouds; and this circulating molecular current in turn generates the magnetic field. The concept is simple, please understand put this molecule or any of molecular of interest in the external magnetic field. The external field induces currents in the electron clouds and the circulating molecular current in turn generates magnetic field. And as a consequence what happens is, the nuclear spins always see not only external magnetic field and also the induced field because of the electrons. The nuclear spin sees the external magnetic field B_0 plus the induced field. That is what we see; the nuclear spins do not see only the external magnetic field but also the induced field generated by the electrons. Always the induced opposes the main magnetic field; it opposes the main magnetic field. And this is local field. The local field seen by the nucleus is not B_0 , but B_0 and some additional factor coming because of the look shielding electrons. This is called shielding constant sigma. So B_0 field gets reduced by this, because of this local field. The local field seen by the nucleus is given by this condition.

This is sigma; called shielding constant. Let us try to understand bit more about what is happening. Consider that I have a nucleus; bare nucleus; no electron is surrounding it. Of course, it is a hypothetical situation. You cannot think of that. Think of a situation I have nucleus, knocked off all the electrons surrounding it. Then this is it.



If you look at the charge distribution at the site of it, there is no charge distribution at all. This how it is; bare nucleus without electrons. Now consider a situation, where I have a bare nucleus put it in an electron cloud which is spherical in shape; the spherical cloud of electrons. And this is the charge distribution. But this is a hypothetical situation. In reality what is happening is, you have chemical bonds. For example, consider the CH bond. Here if I look at the proton or carbon, or either of the nucleus, at the site of this nucleus the charge distribution not spherical. The CH bond has elliptical charge distribution. If you can see here, the charge distribution, unlike here, it is not spherical. It is elliptical; it is a symmetric ellipsoid. We call it as a three-dimensional ellipsoid. It is like ellipse.

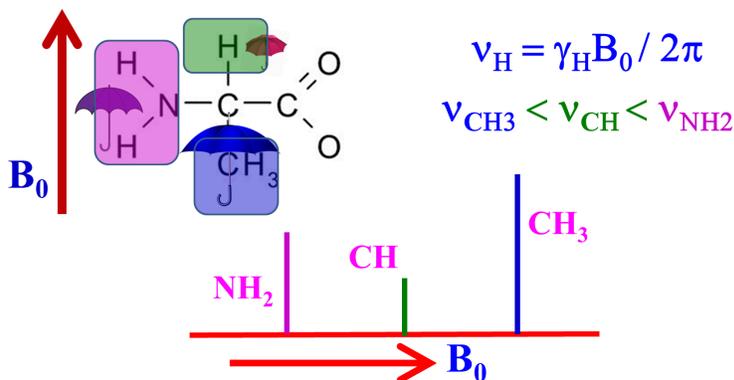


Go to OH bond; here it is not even elliptical it has a different shape, because oxygen is an electronegative atom. It withdraws electrons from the proton. Look at it, the charge distribution is slightly different. It is not same here, it is different. See arrows are different here and here. Look at the arrows, what I have written here, the thickness of the arrows here; they are all same; uniform. Here also same, because it is symmetric. But once you come here, arrow is thick. Here it is better compared to this, more thicker arrow, because the charge distribution is more. This proton more deshielded. Come to another bond like this O-H-O-C bond. Here you see the arrow thickness, even more deshielded here, because of oxygen. You can calculate the charge distribution. What do you understand from this? larger electronegativity results in asymmetric clouds like this. As the electronegativity becomes more and more with the observing nucleus of your interest, surrounded by more number of different electronegative atoms, the charge distribution becomes more and more asymmetric. And it has different funny shapes like this. At the particular site of the nucleus, the shielding or deshielding depends upon the surrounding atom, the neighboring atom, whether it is electronegative or electro positive. Okay, now the question is, these atoms will induce the magnetic field, okay fine, what is the strength of the induced field? The electrons induces the field at the site of the nucleus but what is the strength of this induced field?

Consider as an example, I am looking at a 400 MHz spectrometer. For this 400 MHz for protons, I need a magnetic field of 9.3949 Tesla. One Tesla, I told you is 10,000 Gauss. It is one Tesla. So now what is 9.3949 Tesla. If you express in Gauss it is 93949 Gauss. The field induced now due to the electronic environment is, this one, it is not huge number 0.0000093949; some number I have written. Very small value. The field induced due to the electronic environment is much much smaller. But what is the total field seen by the nucleus? It is this plus this 93949 Gauss plus the induced field, which is very very small. So it will become 93439.000093439 Gauss, very small field induced. But that is affecting. That is seen by the nucleus. So the total magnetic field experienced by the nucleus is, in addition to the static magnetic field, very very minute magnetic field induced at the site of the nucleus, because of the internal interaction. Okay, so what is the resonating frequency now? if I calculate the resonating frequency for this magnetic field, I said 400 megahertz; this is the magnetic field for this. But now I have added some number so resonating frequency is not 400 megahertz and a small value which I have added. Here you can calculate by using ν is equal to γ into B_0 over 2π . I have

deliberately taken these numbers so that this will also become 400. So it will now become, not 400 MHz, but 400 megahertz plus 400 hertz. What does it mean? It means the resonating frequency of protons is shifted by 400 Hz due to charge distribution. It has added another 400 Hz. So instead of coming here, it comes here. The resonating frequency is shifted by some amount due to charge distribution at the site of the nucleus. This is what is called chemical shift. The shift in the resonating frequency due to the chemical environment is called chemical shift. Hope you understood how the resonating frequency is shifted because of the different functional groups in a molecule.

Now let us go back to the same original molecule we have NH₂ CH and CH₃ groups. What did we say earlier when we did not consider the internal interactions? According to my equation all were resonating at the same frequency, and give us to a single peak. It is because you got a $\gamma B_0 / 2\pi$, were same for all the groups. Now we have understood internal interactions, the charge distribution is coming because of the surrounding electrons. If you use that knowledge, now you see CH₃ has three protons, there are three protons surroundings this and the charge distribution at the site is much larger. The shielding is bigger. I have deliberately put a bigger umbrella. Look at this one. For NH₂ protons, I have put different umbrella. Here the size of the size of the umbrella is different. Look at this, the size of the umbrella is even smaller, so that means the shielding is different. The field induced at the three different sites are different. very very small difference, but there is some significant difference. This may be 400 Hertz, this may be 300; this may be 200 Hz; does not matter. So the resonating frequency is not just 400 Hz, for this is 400 MHz plus 400Hz. So these are different, so as a consequence the resonating frequencies are different. This is more shielded and compared to this and compared to this. We have different resonating frequencies. As a consequence we do not get single frequency. Now we are going to get three peaks one for CH₃ one for NH₂ one for CH and this is the beauty of NMR. Look at it earlier I said we get only one peak now we are getting three peaks.



This is the important concept of chemical shift. please remember the statement, nuclear spins do not get involved in the chemical reaction. But it gives information about the

chemistry of the molecule, because we can understand what is happening at the site of the nucleus because of the chemical environment. Now the time is getting over, so what I am going to do is I will stop here. But remember what we tried to understand today. To summarize today we understood there are different types of interactions. We classified into two types one is external interaction and the other is internal interaction. The external interactions are nothing but Zeeman interaction and RF interactions which we have been discussing since last three four classes. Today we understood what is an internal interaction. The internal interaction is within the molecule. And there are four different types of interactions. We understood chemical shift, scalar coupling, dipolar coupling and the quadrupolar coupling. If we are dealing with the spins greater than spin half then quadrupolar coupling also will be there. But when you are dealing with spin half nuclei, we do not need to consider quadrupolar interaction. That will not come into picture. But remember these all these interactions are magnetic, except quadrupolar interaction for spin greater than half. That is electric interaction. When we are dealing with spin half nuclei, only these three interactions are considered, especially if you are dealing with the solids, the dipolar coupling will be coming into picture, also the partially ordered systems, if you consider dipolar couplings comes into the picture. But when you are dealing with spin half nucleus especially in the solution state the motion averaging removes dipolar coupling also and all other in the anisotropic interactions; like chemical shift anisotropy, and J anisotropy. Everything will go. The dipolar coupling will average out. We are dealing with only isotropic chemical shift and scalar couplings. These are the two parameters that are left with for us to understand. As I told you chemical shift comes because of the surrounding electrons. When you put it the molecule in a external magnetic field, the external magnetic field induce currents in the molecule. The circulating currents in turn generate magnetic field. This induced magnetic field opposes the main magnetic field. We have got a screening constant σ . That we understood and because of the internal interactions which are not identical for different types of bonds. The CH bond has elliptical charge distribution; OH bond is different and different complicated bonds have different types of charge distribution. As a consequence in a given molecule, because of the neighboring atoms, whether it is a electron withdrawing or not, accordingly there is an effect on the particular nucleus, because of the charge distribution. Overall if you calculate the how the charge is distributed they may be different at different chemical sites because of this. When you reverted back to the original hypothetical molecule we understood the charge distribution is different for different sites of the same molecule. As a consequence we have different resonating frequencies. So the internal interactions gives us a different frequencies for different functional groups because of different induced fields. And this is what makes NMR very interesting. As I said the nucleus do not get involved in the chemical reactions, but they give information about the chemistry of the molecules, because the charge distribution is getting reflected at the side of the nucleus by giving different resonating frequencies. We

can understand what is happening at the site of the nucleus. This what we understood. We will stop here. We will continue in the next class; more about chemical shifts and try to understand what is happening for chemical shift in different molecules. I'll stop here thank you very much