One and Two Dimensional NMR Spectroscopy for Chemists
Prof. N. Suryaprakash
NMR Research centre
Indian Institute Technology – Bengaluru

Lecture - 12
Chemical Shifts

Welcome back, in the last class I introduced to you about interaction parameters of NMR, both external and internal. In the internal interactions that are present within the molecule, I told you about chemical shifts, scalar couplings, dipolar couplings and for spin greater than half nuclei, the quadrupolar couplings. All those things we discussed, and I was telling you more about chemical shifts, why it comes and everything. We start the discussion, more about chemical shifts form today.

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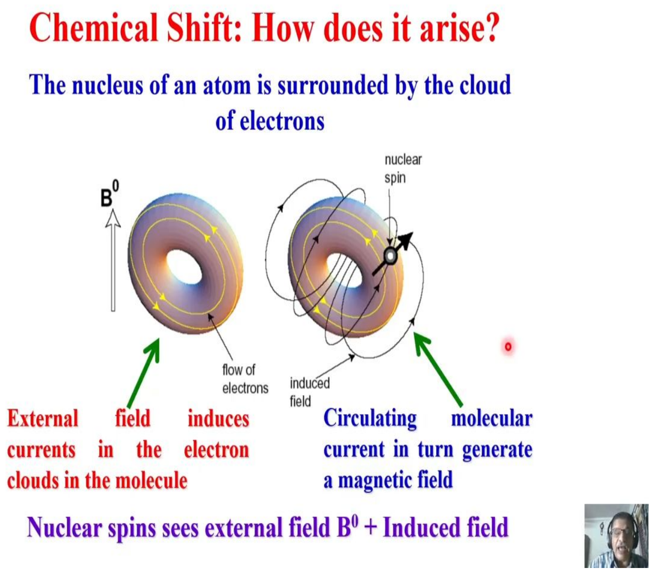

Chemical Shift: How does it arise?

The nucleus of an atom is surrounded by the cloud of electrons

External field induces currents in the electron clouds in the molecule

Circulating molecular current in turn generate a magnetic field

Nuclear spins sees external field B^0 + Induced field

First of all chemical shift, how does it arise? The nucleus of an atom is surrounded by the electron clouds. Please remember that, the nucleus of an atom is surrounded by a electron cloud, it not a bare nucleus. So what is going to happen is, there are 2 interesting phenomena that takes place simultaneously. When you put the molecule of your interest in the external magnetic field, that is a very big magnetic field.

The external field induces currents in the electron clouds of the molecule. It induces current, see the electrons start flowing like this. It induces currents in the electron clouds. Subsequently what happens? The circulating molecular current in turn generates the magnetic field. There are 2 things that are happening, please remember. The external field starts inducing currents in the electron clouds of the molecule. And these circulating currents in turn generates magnetic field. So that means in addition to the external magnetic field, there is some other field which is produced within the molecule. Now what happens to this field? does it add to the external field or subtract from the external field? because of this, now the nucleus which is at the center, what is the field it is going to see? Is it going to see B0 alone are B0 plus the fields generated by these or B0 minus the fields by these electrons, that we will have to understand. So the nuclear spins see the external field, plus field induced because of the electrons. These are the 2 important things, please remember.

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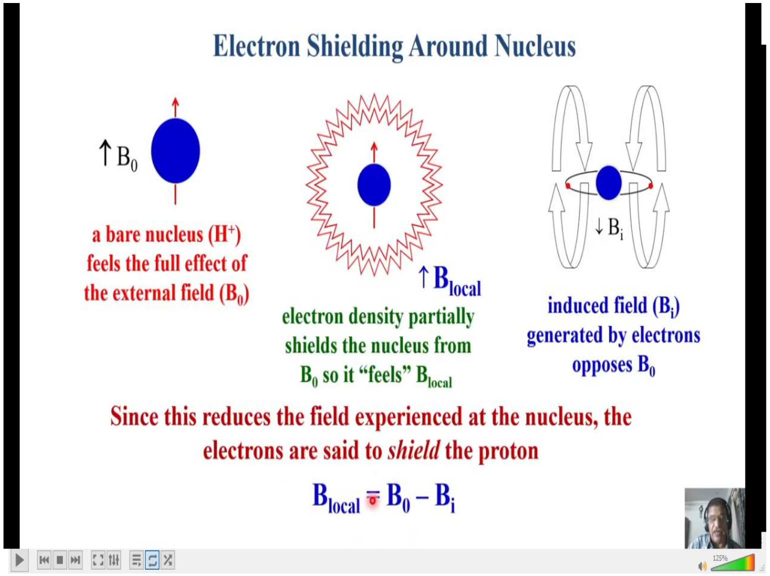

Electron Shielding Around Nucleus

a bare nucleus (H^+) feels the full effect of the external field (B_0)

electron density partially shields the nucleus from B_0 so it "feels" B_{local}

induced field (B_i) generated by electrons opposes B_0

Since this reduces the field experienced at the nucleus, the electrons are said to *shield* the proton

$B_{local} = B_0 - B_i$

So now electron shielding around the nucleus is like this. Look at a bare nucleus. Assume there is no electron at all, a bare nucleus. It feels the full effect of the external magnetic field. The external magnetic field B0 is here, it sees the full effect of it. There is no other thing which is coming into the picture, in between nucleus and the magnetic field. Now consider there are certain electron density, let us say, surrounding this nucleus.

There are electrons moving around the nucleus. This electron density partially shielding this nucleus. So in addition to B0 it also sees some local field. The nuclear spins see this local field, in addition to external B0 field. It shields the local field, and this induced field generated by these electrons are always opposes the magnetic field. That is the main magnetic field B0. Please understand the point, bare nucleus sees the complete effect of the external magnetic field. If you have electrons moving around the nucleus, surrounding this, this shields the nucleus and the nucleus spins also sees the local field. This local field is coming because of the electron which induces this small field, which is called Bi, it opposes the main magnetic field B0. So what is going to happen, since this main magnetic field is opposing that, the electrons are said to shield the protons or electrons are set to shield the nucleus.

So it is shielding, a sort of a shield for the nucleus. It cannot directly see this one, something is coming in between, something is shielding. So the electrons shield the nucleus, so the nuclear spins do not see the external field fully, it also sees the local field produced because of the electrons. So this local field, as I said, opposes the main magnetic field. We can say the strength of the local field is B0 minus the induced field.

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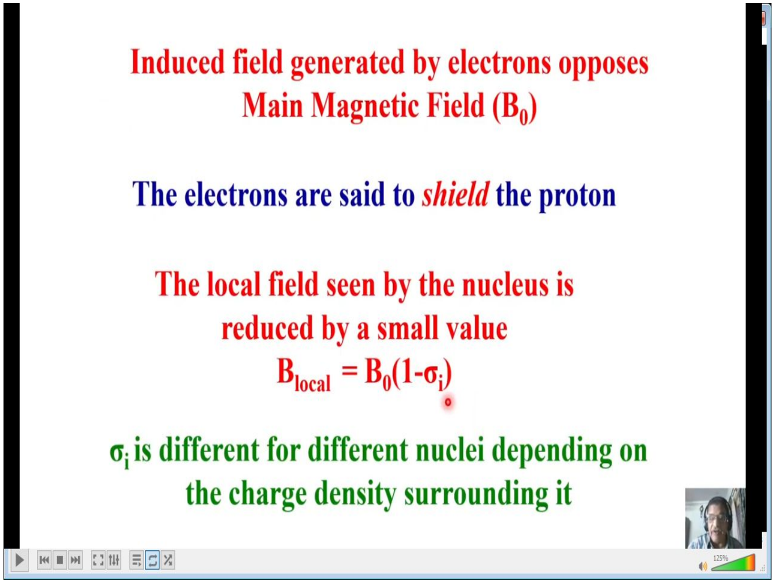

Induced field generated by electrons opposes Main Magnetic Field (B_0)

The electrons are said to *shield* the proton

The local field seen by the nucleus is reduced by a small value

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

σ_i is different for different nuclei depending on the charge density surrounding it

The induced field generator by electrons opposes the main magnetic field, I said, and that is the reason why we say electrons shield the proton, and the local field is reduced by a small amount. What is that small amount? The field seen by the nucleus is reduced by a small value that is B0 into 1-sigma i. that is an equation. The local field you can calculate, which is B0 into 1 – sigma i and sigma depends upon the type of nucleus.

It is different for different nuclei, depending upon the charge density surrounding the nucleus. Please remember, sigma is not same. In the example of the molecule you have, the sigma will be different for CH group, different for NH2 group and different for CH3 group. That as a consequence, the local fields for different groups are different. Though you have one molecule we have different functional groups, as a consequence, each functional group has a separate local field. That is because they have different sigma values. Remember this point

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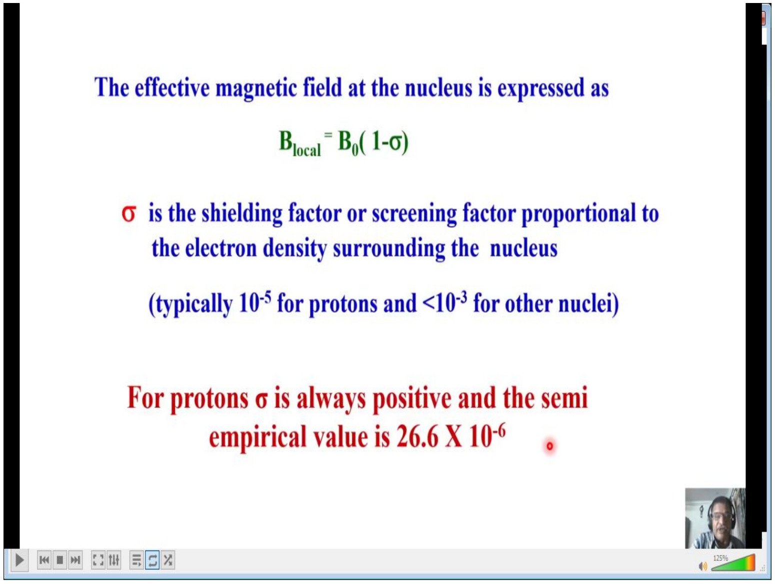

The effective magnetic field at the nucleus is expressed as

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

σ is the shielding factor or screening factor proportional to the electron density surrounding the nucleus

(typically 10^{-5} for protons and $<10^{-3}$ for other nuclei)

For protons σ is always positive and the semi empirical value is 26.6×10^{-6}

So the effective magnetic if you express like this, this is called a screening factor, also called a shielding factor, which is directly proportional to the electron density surrounding it. So higher the charge density higher the sigma, remember this. The shielding factor is larger and larger because it is proportional to the electron density surrounding it. If there is more and more electronegative nucleus more electrons are there, more charges at the site of the nucleus, this is larger and larger. What is the value of the sigma? Typically, it is of the order of 10 to the power of -5 for protons and around 10 to the power of -3 or less for other nuclei. The value of sigma for protons is 10 to the power of -5. The protons sigma is always positive. It is positive, there is a way you can calculate sigma, everything, there is a huge discussion we can do. A lot of discussion can be done on the chemical shift, how to calculate sigma, we can go more and more deeper into the theory. Let us not bother about it. For our course, just for understanding, please remember for protons the screening constant or the shielding factor is always positive. And its semi empirical value is 26.6 into 10 to the power of -6. This is the semi empirical value I am just quoting without going into the details of how we calculate this thing.

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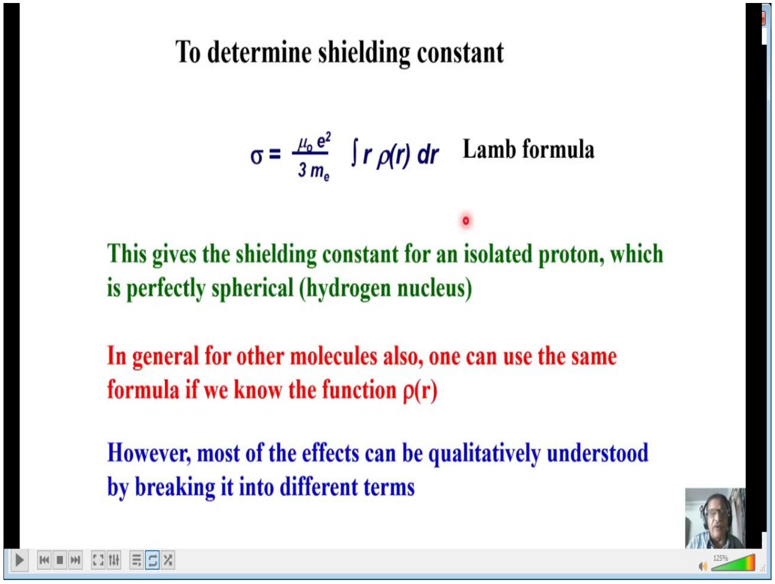

To determine shielding constant

$$\sigma = \frac{\mu_0 e^2}{3 m_e} \int r \rho(r)\, dr$$ Lamb formula

This gives the shielding constant for an isolated proton, which is perfectly spherical (hydrogen nucleus)

In general for other molecules also, one can use the same formula if we know the function ρ(r)

However, most of the effects can be qualitatively understood by breaking it into different terms

So to determine the shielding constant we also use a formula, you may ask me a question, how did I get this 26? I said I dont want to go into the theory, I simply give you one formula, this is called Lamb’s formula. The formula given by Lamb. This a lamb’s formula, this gives shielding constant for an isolated proton, which is perfectly spherical. Take hydrogen nucleus proton, I showed you in the first example, a bare nucleus no electrons at all. An isolated proton is always perfectly spherical. For other molecules also, in principle we can use the same formula to generate this, but we must know a factor called row of r, that is an important factor in this formula. It is not easy to know these for all the nuclei, other than protons. But qualitatively we know these values as we go ahead, I will tell you, it depends upon several factors called diamagnetic contribution coming because of s electrons, paramagnetic contributions coming because of P orbits, p electrons, etc, also it depends upon the neighboring functional groups attached to the proton of our interest. So the various factors add to this. So sigma can be calculated accordingly but this a general formula, you remember. If you want to know how screening constants are determined, what is shielding constant? There is a general formula called Lamb’s formula, which is utilized.

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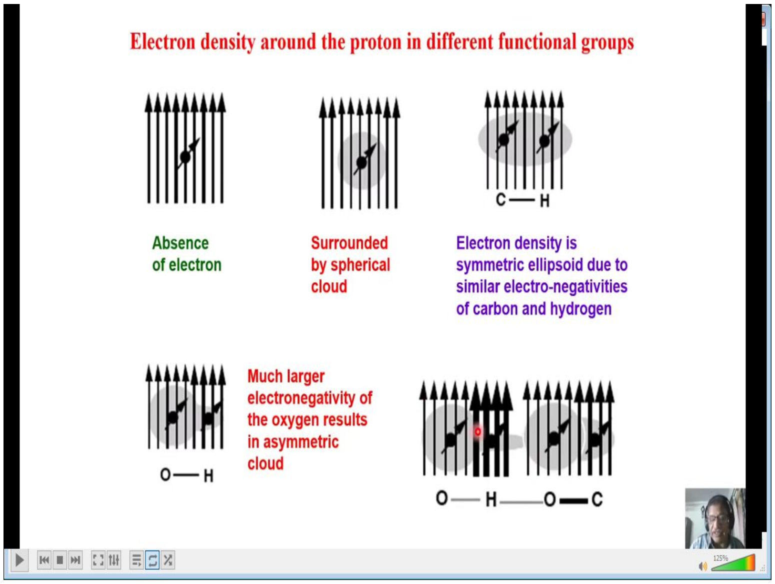

Electron density around the proton in different functional groups

Absence of electron

Surrounded by spherical cloud

Electron density is symmetric ellipsoid due to similar electro-negativities of carbon and hydrogen

Much larger electronegativity of the oxygen results in asymmetric cloud

Now let us look at the electron density, how it affects the different nucleus; how different nucleus see the different charges surrounding it based on the functional groups? As I said bare nucleus in the absence of electron, it is perfectly spherical, uniform charge distribution surrounding it, charge distribution is perfectly spherical, and uniform, no problem at all. Look at this one, I have taken nucleus, if you can carefully see there is a gray color circle here, which is depicting the charge distribution. This is also spherical, understand. I am taking the example of the nucleus where the charge distribution of electrons surrounding it is also a spherical, the spherical cloud of electrons. There also you will see it is uniform, no problems at all. But in the molecule, you do not have proton alone, single proton or you do not have a bare nucleus alone. You always have molecules were have different atoms are bonded we have a bond. There are different functional groups attached to it. It is not just one bond, there will be several bonds several groups will be attached. As a consequence, in such groups the charge density is not always spherical. Now look at the CH bond, the charge distribution in this case is spherical, but you see here the gray color drawing, what you are seeing, it is an elliptical in shape. The charge density at the site of carbon, at the site of nucleus you have to see, the total charge distribution if you see at the site of this entire CH bond, it looks like an ellipsoid.

Elliptical in shape, it is there it is symmetric, an ellipsoid, that is one thing. Whereas, when you come back to this one OH, oxygen is attached to hydrogen. Oxygen is more electronegative, you all know that oxygen is electronegative and because of this the charge density, charge distribution is not symmetric, like spherical circle, it will not be a symmetric like ellipse, Look it has a different shape. The more charge density is at the site of oxygen, which is electro negative and it is less here. The oxygen pulls the electron of the hydrogen towards it. This charge density is not like, but it is a different shape. We will go one more step further, for the OH will add another bond O double bond C, it joins the OH. Some hypothetical molecule, do not worry whether it is practically feasible molecule or not.

Let us look at this type of bond, the charge density of OH we knew. Now this O and carbon is different compared to proton and you see the charge density, if you look at it, here, this oxygen withdraws more charges from this proton, it is more electronegative; and compared to this carbon, this carbon also has depleted charge at the site of this carbon nucleus. So, like this the different functional groups if you study at the site of a particular nucleus of your interest, you see the arrows, which depicts here the charge densities will be different.

More electronegative atom attached to it, more electrons are depicted here, at the site of the hydrogen. It withdraws the electrons form it. It is the electron withdrawing group here. So, of course you can also have electron donating group, then it will have more charges at this site, instead of depletion.

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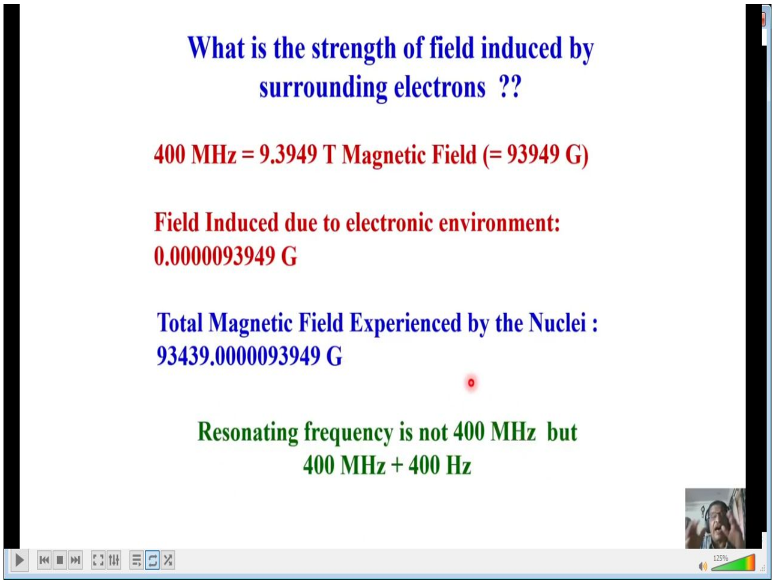

What is the strength of field induced by surrounding electrons ??

400 MHz = 9.3949 T Magnetic Field (= 93949 G)

Field Induced due to electronic environment:
0.0000093949 G

Total Magnetic Field Experienced by the Nuclei :
93439.0000093949 G

Resonating frequency is not 400 MHz but
400 MHz + 400 Hz

So, now all these what I am trying to say is, these electrons will induce a field. Now the question is because of the different charge distribution, how much is the induced field? Remember induced field Blocal we found out, because of the induced field, the B local is different. electrons induces the field and the nuclear spin sees the local field. What is the induce field strength? We have an external magnetic field, I told you whose strength is of the other several Tesla, whereas what is the amount of field produced, induced field here? Let us calculate, we can even calculate. Let us say I have a 400 mega Hertz spectrometer which corresponds to magnetic field of 9.3949 Tesla. I have taken up to fourth decimal place. Let us keep it only this much accuracy, understand for 400 mega Hertz spectrometer the field is 9.3949 Tesla. You know one Tesla is 10 to the power of 4 Gauss.

When expressed in Gauss, it is 93949 Gauss. Ninety three thousand nine hundred and forty nine Gauss. You can calculate the field induced, you know how much is the field induced? It is 0.0000093949 Gauss, five zeros after decimal. Very, very small, negligibly small. The total magnetic field experienced by the nuclei is now 93439.0000093949 Gauss, My God, such a small field, then what is going to happen? Your resonating frequency is not just 400 mega Hertz it is 400 megahertz was for this field, small field induced by the surrounding electron adds to this main field. Of course as I said induced fields opposes, I will tell you more about it. I am taking the example here, just addition of this value just for the calculation purpose. The resonating frequency is now just not 400 mega Hertz, it is 400 megahertz + 400 hertz. you see this, you can calculate for this magnetic field. what is the resonating frequency? you can calculate, it 400 hertz. For this magnetic field it is 400 megahertz. For the total magnetic field of 93439 plus this value, totally this value and 93439.0000093439 Gauss, the resonating frequency is not 400 megahertz, but 400 mega Hertz + 400 Hertz, you understand.

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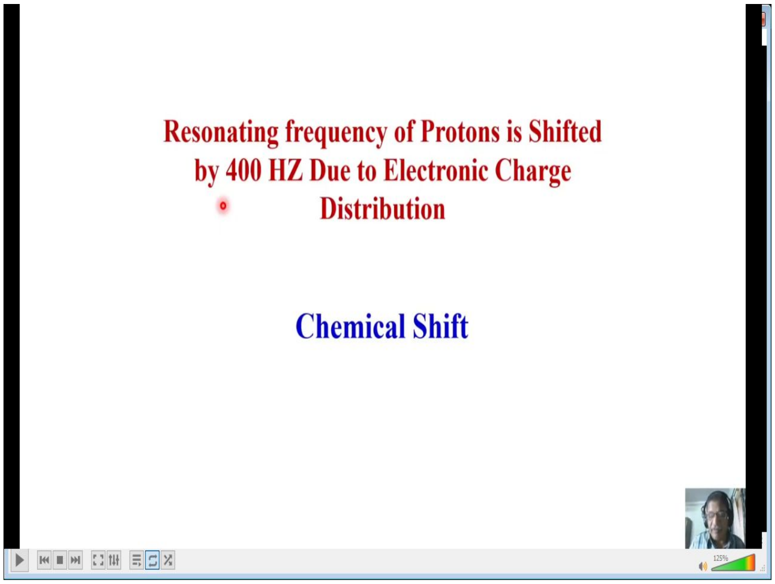

Resonating frequency of Protons is Shifted by 400 HZ Due to Electronic Charge Distribution

Chemical Shift

So resonating frequency of protons instead of exactly at 400 MHz, it is now shifted by 400 Hertz. You understand, due to electronic charge distributions, it is shifted by 400 Hertz. I said here plus 400, even though the induced opposes. You take minus 400 does not matter. Again it is shifted by 400 in the opposite direction, does not matter. That is why I did not bother about the sign, whether, it is an addition or subtraction in the previous slide.

Consequence of that, the resonating frequency of protons is shifted by 400 Hertz and because it is shifted due to the chemical environment of this nucleus is called chemical shift. Please remember, that resonating frequency the protons is shifted by 400 hertz in our calculation because of the electronic charge distribution due to the chemical environment of this nucleus, it is called chemical shift. The chemical environment shifted this peak.

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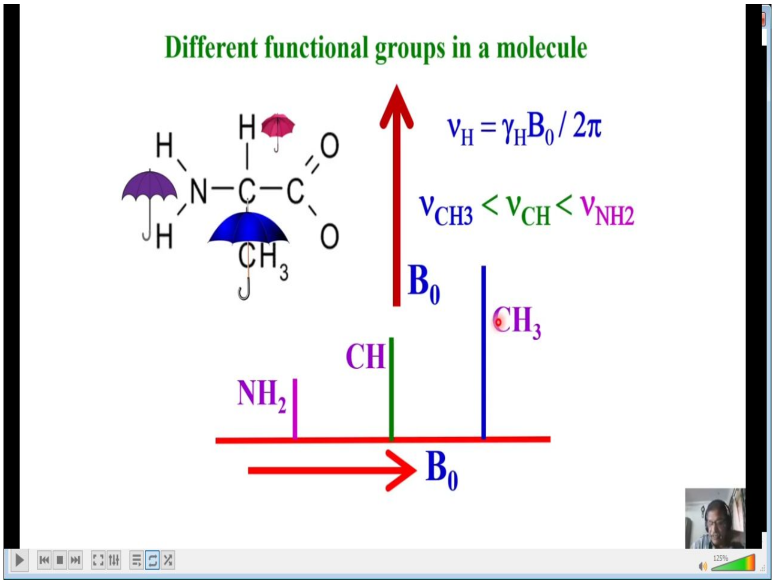

Different functional groups in a molecule

$\nu_H = \gamma_H B_0 / 2\pi$

$\nu_{CH3} < \nu_{CH} < \nu_{NH2}$

Now what happened to the different functional groups in a molecule? There are variety functional groups, how do they shift? Consider now the example of a molecule like. This is the very first example, in the very first slide I showed you in the chemical shift. This one has 3 different functional groups, but when I went into my equation I showed they all give rise to a single peak. But now what is happening is, the shielding is different, electronic environment at the center of CH3 is different, at the state of NH2 is different, at the site of CH is different.

I have written the shielding, the electronic cloud has a bigger umbrella here, it is much more shielded, because of 3 protons, than NH2 which has 2 protons, of course with nitrogen, and CH proton has a smaller shielding. The umbrella size here tells you the extent of shielding. Larger the umbrella, larger the shielding. So now what it means is, the field seen by different types of protons are not same. It is not just only B0. It is in addition to B0 plus the induced field, you understand.

Understand the point, in the previous slide I did not bring in the internal attractions, I said all are same, that is why I said it will give a single line based on this equation. But now we understood the internal interactions as a consequence of different charge distributions. These frequencies are not same and I can tell you the resonating frequency, frequency for CH3 is less than CH and is less than NH2.

That means the fields seen by these different functional groups are B0 plus induced field, which are different. As a consequence you do not get a single peak now for this molecule. You get 3 different peaks, 1 peak for CH3, 1 peak for NH2 and 1 peak for CH, and remember I have written something different here, they are coming at different places because they experienced different magnetic fields that I called as chemical shifts. And in addition to coming at different resonating frequencies, I have written different intensities for these peaks. We will understand that later when we go ahead. That also you should remember. This corresponds to, this intensity of the peak also tells me the number of protons present. This is for 3 times intensity for this. It should have been CH and this should have been NH2 because this is 2H, 2 times intensity. I have made a mistake do not worry. This should be CH2, this should be NH2, and this CH3 in my drawing or if it comes down, I have to make this as double the intensity, does not matter, and this how the spectrum looks.

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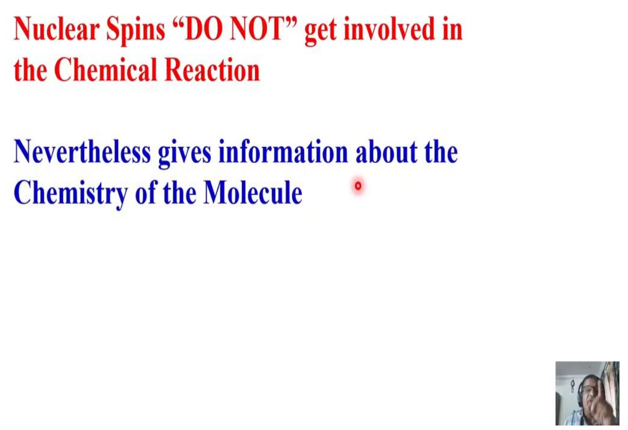

Nuclear Spins "DO NOT" get involved in the Chemical Reaction

Nevertheless gives information about the Chemistry of the Molecule

So what your understanding, nuclear spins do not get involved in the chemical reaction we all know. When you are doing chemical reaction we always start talk about electrons, how the electron is moving or how the reaction is taking place. Nevertheless, the nuclear spins will give information about the chemistry of the molecule. That is what we understood in the previous slide because the charge densities are different, and we get different peaks. So you can understand more about the chemistry of the molecule by seeing the NMR spectrum which is due to nuclear spin, although nuclear spins do not get involved in the chemical reactions.

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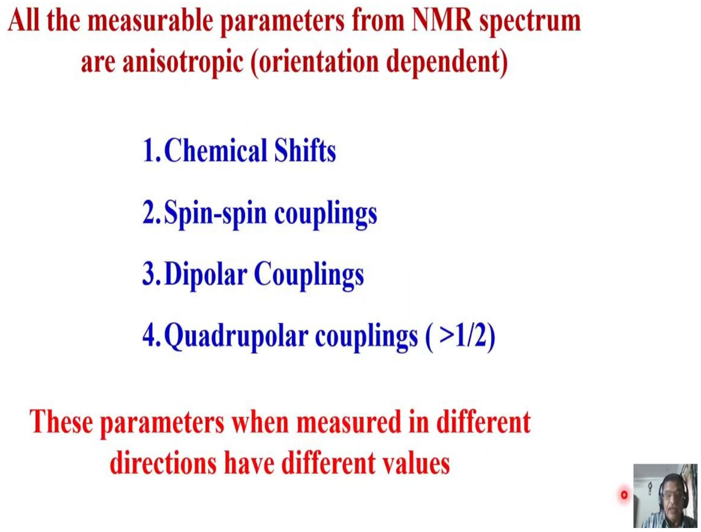

All the measurable parameters from NMR spectrum are anisotropic (orientation dependent)

1. Chemical Shifts
2. Spin-spin couplings
3. Dipolar Couplings
4. Quadrupolar couplings (>1/2)

These parameters when measured in different directions have different values

So this is an important point which I wanted to tell you. Next another thing, the information which I want to tell, you all the measurable NMR parameters from the spectrum are anisotropic. I told you this when I discussed last time also, when I introduced chemical shift, dipolar coupling and J coupling, every parameter is anisotropic orientation dependent and I said some of these motionally get averaged out some are not, but these are the 4 important parameters which we get and these parameters when measured in different directions, have different values.

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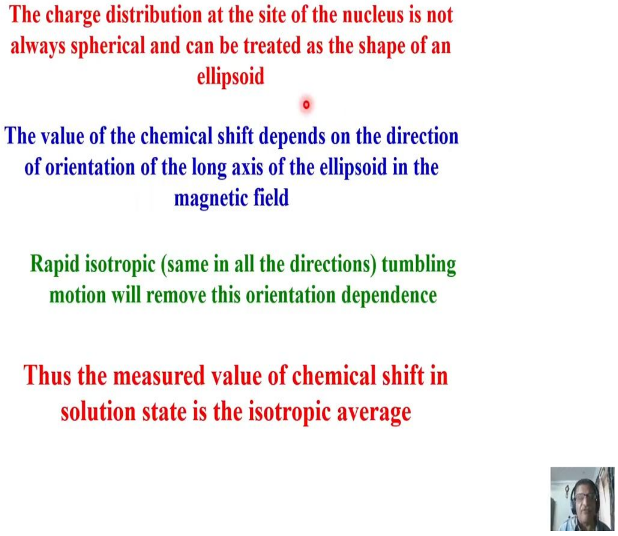

The charge distribution at the site of the nucleus is not always spherical and can be treated as the shape of an ellipsoid

The value of the chemical shift depends on the direction of orientation of the long axis of the ellipsoid in the magnetic field

Rapid isotropic (same in all the directions) tumbling motion will remove this orientation dependence

Thus the measured value of chemical shift in solution state is the isotropic average

So now the charge density distribution at the site of the nucleus is not always spherical, and can be seen as an ellipsoid. So that is why the value depends upon the direction of orientation of the long axis of this ellipsoid. In the case of isotropic motion, that is in isotropic solution, there is motional averaging, as I said these 2 things get completely averaged out. So what does it mean? The rapid isotropic motion in solution averages out all these orientational dependence.

The measured chemical shift value in the solution state is the isotropic average. You get only single value, you do not get chemical shift. In principle you would have got, the different values when you measure in different directions, if you retain the anisotropy. But in the solution state anisotropies averaged out, so the chemical should what the measure is the isotropic average.

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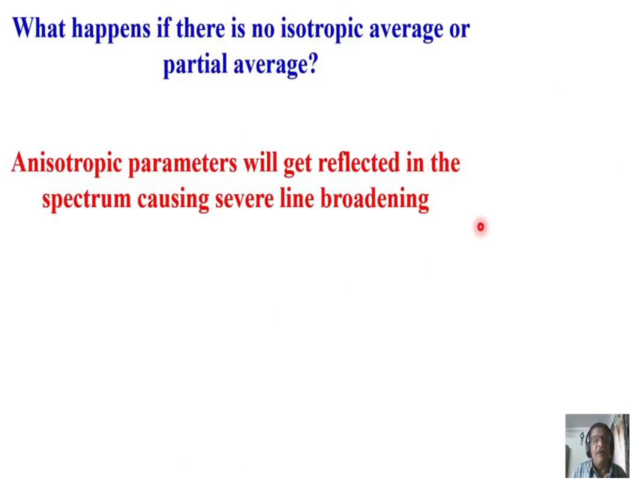

What happens if there is no isotropic average or partial average?

Anisotropic parameters will get reflected in the spectrum causing severe line broadening

What happens? If there is no isotropic average, and it is only partial average, not complete removal. In which case all these anisotropic parameters gets into the spectrum, please remember. Only in the solution when there is perfect motional averaging, totally all these anisotropic parameters will go to 0; that is the isotropic spectrum. If it is not averaged completely, there is a partial averaging, it is possible. There are some anisotropic media, I said in one of my classes, liquid crystal, these anisotropic parameters will get reflected in the spectrum and causes severe line broadening.

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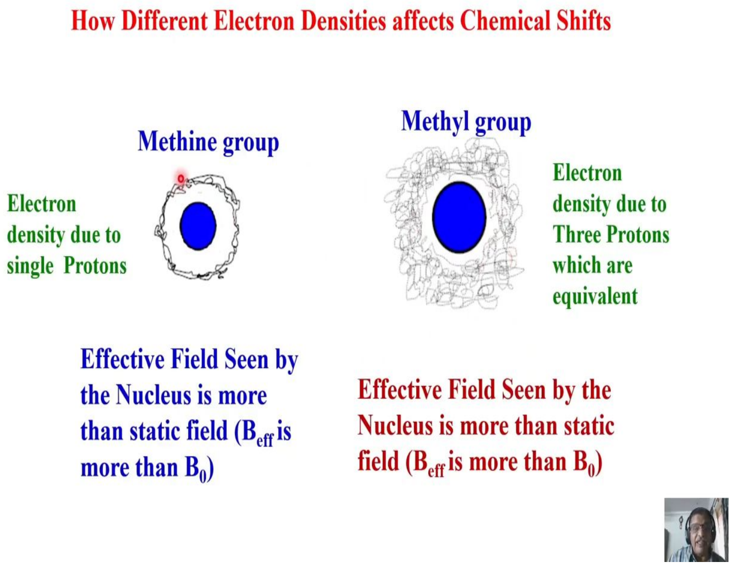

How Different Electron Densities affects Chemical Shifts

Methine group

Electron density due to single Protons

Methyl group

Electron density due to Three Protons which are equivalent

Effective Field Seen by the Nucleus is more than static field (B_{eff} is more than B_0)

Effective Field Seen by the Nucleus is more than static field (B_{eff} is more than B_0)

So now we will understand how different electron densities affect chemical shifts. Consider methine group we have only single proton, the charge distribution corresponds to only one proton. Now effective field seen by the nucleus is more than the static field. B effect is more than B0. Understand, now go to methyl group, there are 3 protons the charges density is different from CH proton. It is 3 protons now, the effective field seen by the nucleus is more than that the B0 here also. Remember the effective is field seen by this nucleus is different from B0, effective field seen by this nucleus is also different from B0. Then what is the difference between these two?

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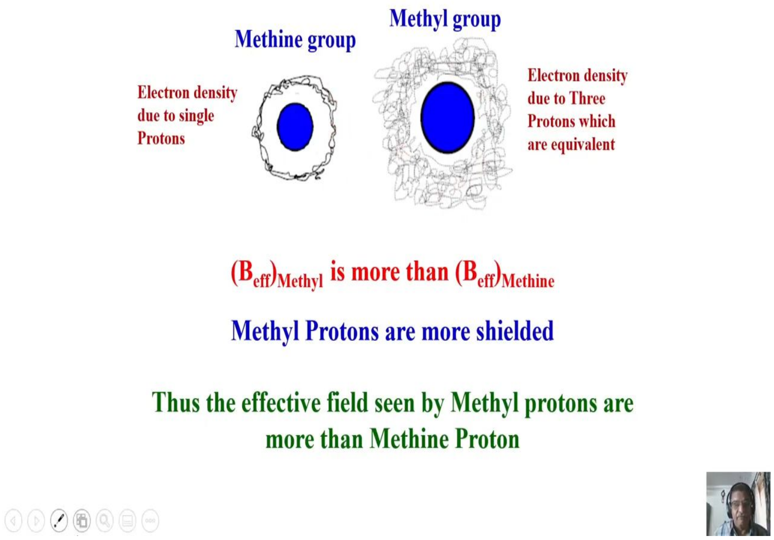

Methine group

Electron density due to single Protons

Methyl group

Electron density due to Three Protons which are equivalent

$(B_{eff})_{Methyl}$ is more than $(B_{eff})_{Methine}$

Methyl Protons are more shielded

Thus the effective field seen by Methyl protons are more than Methine Proton

The difference is B effective of methyl is more than B effective of methine, because this has more charge distribution so, methyl protons I would say are more shielded, the shielding is much more here for methyl nucleus, as it has 3 surrounding electrons. If it has to see the main magnetic field it has to cross this barrier, you remember. So it is more shielded than CH? what does it mean? The effective shield field by methyl protons is more than that of methine protons.

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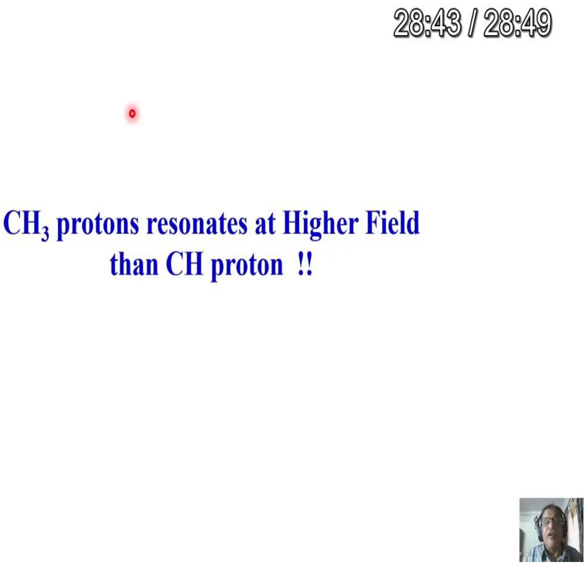

CH_3 protons resonates at Higher Field
than CH proton !!

Essentially in means CH3 protons is resonates at high field, because the field is more, field seen is much more. So resonates at high field than CH group, you understand. Based on the charge density distribution you can even say which proton has higher resonating frequency and which proton has a lower resonating frequency. In this simple example we new methyl protons has more shielded more shielded than CH protons, as a consequence, effective field seen by these methyl protons are more than that of the methine proton. So, CH3 protons resonate at higher field than CH proton, get the point.

So today I am going to stop here and have given you a brief idea about the reasons for seeing the chemical shift. The conceptual understanding of why chemical shift arises, it is because of the motion of electrons, and I said the field induces the motion, the induced motion and the electronic clouds, which in turn can generate the magnetic field which as opposes the main magnetic field.

And then we saw varieties of charge distributions for different functional groups and how different charge density distribution causes the effective field seen by different nuclei and we took the example of the CH3 and CH protons and we said CH3 protons are more shielded than CH protons. As a consequence, we said CH3 proton resonates at higher field than CH proton. So we will stop here, in the next class we will talk more about chemical shifts and their interpretation and everything.