One and Two Dimensional NMR Spectroscopy for Chemists

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Lecture No -4
Larmor Precession and Energy of interaction

Welcome back. In the last one or two classes we have been trying to understand some of the basic concepts involved in spin physics, which are essential to get into more understanding of one and two dimension NMR spectroscopy. As a consequence, we were trying to understand many things. In the last class we came to the level of understanding the interaction of magnetic moment with external magnetic field μ.

So we found out the energy of interaction E is equal to minus μ dot B, both μ and B are Vectors. This is the total interaction energy.

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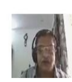
$$E = -\vec{\mu} \cdot \vec{B}_0$$

Both being vectors, we can resolve them into three components

$$E = -(\mu_X B_X + \mu_Y B_Y + \mu_Z B_Z)$$

Magnetic field is assumed to be applied under Z direction

$$E = -(\mu_X B_X + \mu_Y B_Y + \mu_Z B_Z)$$



Also we discussed, remember this interaction energy was negative. Why it is negative? because we said it is to ensure that spins oriented in the direction of the external magnetic field here lower energy then opposite to that, that is only the concept. As a consequence, negative sign was incorporated into this equation. Now this was the general expression for the interaction energy, but I also said the interaction energy of magnetic moment which in the direction of the magnetic field, and the opposite direction of the field are different, that is what we said in the previous class.

This results in difference in the energy states with get separated out in the magnetic field. This is called removal of degeneracy. Remember I discuss in the last class, the energy states are degenerate in the absence of the magnetic field. But in the presence of the magnetic field energy states corresponding to the orientations in the direction of the field and in the direction opposite to the field are getting separated out.

And also I said these two different energies. The interaction energy with magnetic field for the magnetic moment in this direction and for the magnetic moment in the opposite direction with the magnetic field are different. So, now we will work out interaction energy for each direction of orientation, for each component of μ. But before that let us see, as I said μ is a vector and B is a vector, that is B_0 is the static magnetic field, the main magnetic field I said is always referred to as B_0, that is important thing.

And this being a vector we can this into resolve into 3 components, and in the dot product you can write this as μx Bx + μy By + μZ BZ, I am resolving these vectors. And magnetic field is assumed to be along Z axis, we always take the direction of the magnetic field is Z-axis. So when I resolve these things then I consider only the direction of quantization that is μ_Z with the Z direction of the magnetic field. So, I will consider only μZ and Bz, as a consequence these two terms get eliminated. We do not consider that at all. Understand, this is total energy of interaction, resolve them into three components each, took the dot product of that and expanded like this. Now, I am telling magnetic field is assumed to be along Z axis, as a consequence I do not consider X and Y components, they get eliminated.

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Energy of Interaction of magnetic moment with magnetic field B_0

$$E = -\vec{\mu}_Z.\vec{B}_0$$

Substituting for μ_z

$$E = -m\hbar\gamma B_0 = m\hbar\omega_0$$

Where $\omega_0 = -\gamma B_0$

Then we are left with only E equal to minus μZ BZ, ok. Now this interaction, what we do, we know what is μZ and substitute μZ, which we know. What is μZ? μ is equal to gamma into h cross, that is well known in the previous one of the slides, in the previous classes I showed you. Substitute for μZ, this becomes minus mh cross B_0, which I can consider as; of course I am considering this has only $B_{0.}$ Actually this should be $B_{Z,}$ it does not matter, B_0 is assumed to be along Z axis.

Now E is equal to m h cross omega 0, what is h cross omega 0? Now; omega is equal minus gamma into B0. This term I am resolving it, I am separating out these 2 terms, m h cross I am retaining. minus gamma B0, I call it as omega 0. So the energy of interaction of this one; we can bring it to this form, m h cross omega 0, ok.

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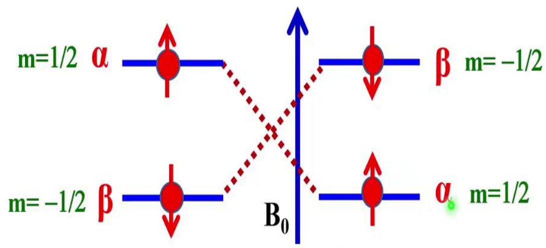
Energy for the states α and β

$$E_\alpha = -\tfrac{1}{2}\gamma h B_0/2\pi$$

$$E_\beta = \tfrac{1}{2}\gamma h B_0/2\pi$$

Notice energy of β state is more than α state



Now we resolve them it into components, energy for the two states alpha and beta. That is plus half state and minus half state, that is alpha beta states. Just find out what is m here, m is equal to plus half and minus half, substitute for that. For half state, minus half, remember there is a minus here, sorry minus component is removed, and E alpha and E beta. There is one mistake I made. This is minus this is plus because E Alpha is equal to this plus half state. E Alpha is equal to half into gamma B 0 over 2 PI. What I did is, it was h cross, remember in the previous equation, it was h cross, h cross is written as h over 2 PI, h is Planck's constant. Same way energy for the beta state is written like this. What is happening here is, this energy of interaction for these two states, energy is always negative here, as a consequence the plus half appears with a minus sign, minus half for the beta appears as a positive sign. As a consequence, notice the energy of beta state is more than alpha state.

Although we say alpha state is here and beta state is here, for alpha state for m half it is like this. And for Beta state it like this, ok, alpha and beta orientations of the spin in the direction of field in the opposite direction field, for m half, m is equal to half, and m is equal to minus half is given like this. But in the presence of this magnetic field this gets interchanged like this because of the negative. So beta is appearing to be with the higher energy, alpha is the lower energy.

As a consequence, plus half and minus half because already there is a negative sign, E = μ dot B_0, this appears like this. So, in all the books you can find out, beta state is written up, that m = -

half state, and alpha state is written in the lower energy like this. So, this alpha state is with lower energy and the beta state is with higher energy. Although it is written like this, because of the negative sign it happen like this. Notice this change. In most of the books, they write beta as the higher energy state and alpha as the lower energy state like this.

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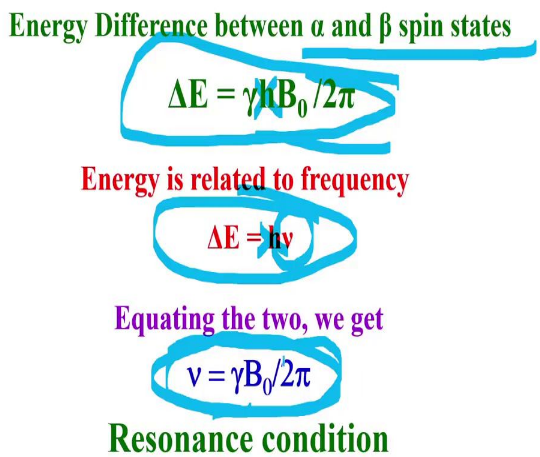

Now what is the energy difference between alpha and beta states. Take the difference between these 2 states. Difference between these two, 1/2 – 1/2 is 1 and – 1/2 +1/2 is 1, you can take either of them depending on alpha beta or beta Alpha, does not matter. If we take delta E one of them, then it turns out be half get cancels out here. You get gamma h B0 over 2 PI, that is the energy difference. This is called delta E. Energy difference between alpha and beta spin states is simply this equation. I am taking the difference, that is all.

E alpha E beta difference is delta E, and that is I am getting it. Now you also know from your basic Atomic Physics you have studied long back; energy can be expressed as frequency. Delta E is equal to hν. Remember long back you would have studied some conversion of energy to frequency et cetera, so delta E is equal to hν. Now equate these two equations, this and this, because both are delta E. Then, what will happen? Bring this to hν is equal gamma h B0 over two pi. What is going to happen now? this and this h will gets canceled out, because you are equating these two, because it is common factor, it gets cancel out. Then what you are left with is ν, which is equal to Gamma B0 over 2 pi. Remember this is the basic equation, very very important. Do not forget this. I am equating energy separation of alpha, and beta states which we calculated based on the interaction, equated this to the frequency to convert into frequency.

Now, I know the energy difference expressed in frequency turns out to be ν is equal to Gamma into B0 over 2 pi. This condition is called resonance condition, this is a resonance condition very important condition. You require this very often in NMR. This is the equation which has given several Nobel Prizes for NMR Spectroscopy for pioneers, ok?

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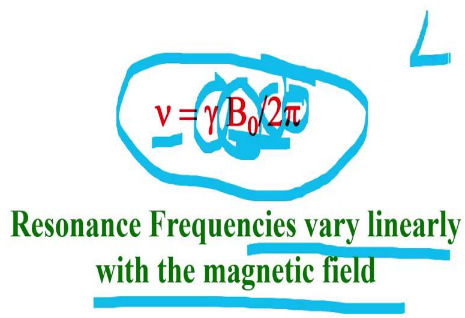

What do you understand further, from this equation? This is a resonance equation, and here gamma is constant for a given nuclei, 2 is a constant, pi is a constant. What is different? Only B naught, B naught is the magnetic field, that is not constant. I can vary, the strength of the magnetic field, it is in my hands, I can vary. I can keep on increasing the magnetic field, increase or decrease, I can change it. As a consequence, ν changes linearly, because all are constants. Resonance frequencies vary linearly with magnetic field. Understand?

Now I double the magnetic field. Let us say at a magnetic field of 4 Tesla, resonance frequency some frequency that is the frequency ν. And now I double the magnetic field to 8 Tesla, the frequency will be 2 ν. So it linearly changes.

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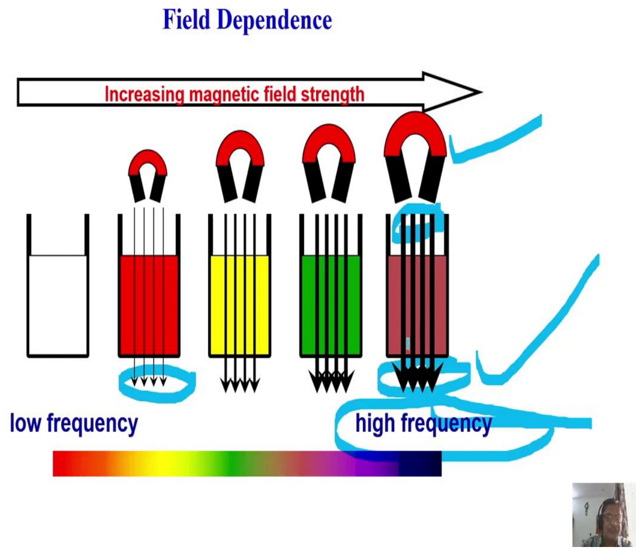

Resonance frequency depends on the magnetic field, which has a linear dependence. So this explains this diagram, this figure, what happens as a function of increasing the magnetic field. Look at this one, the magnetic field keeps on increasing in this direction. And as the magnetic field increases, look at the colour, it is getting changed from low frequency it is going to higher frequency region. That means higher the resonating frequency, in the resonance condition ν is increasing, you are getting higher and higher resonating frequency.

As the magnetic field is increasing, the resonance frequency also keeps on increasing. Another thing if you notice, this size of the arrows, arrows thickness is also increasing when the magnetic field changes. What does it mean? There is some more meaning in that. What it means is the sensitivity of detection also is more. As the magnetic field goes up, signal which is weak gains more sensitivity, you get more signal. Ok. The magnetic field you are increasing, the line of force is increasing, now the resonanating frequency increases and also sensitivity will go up. Ok.

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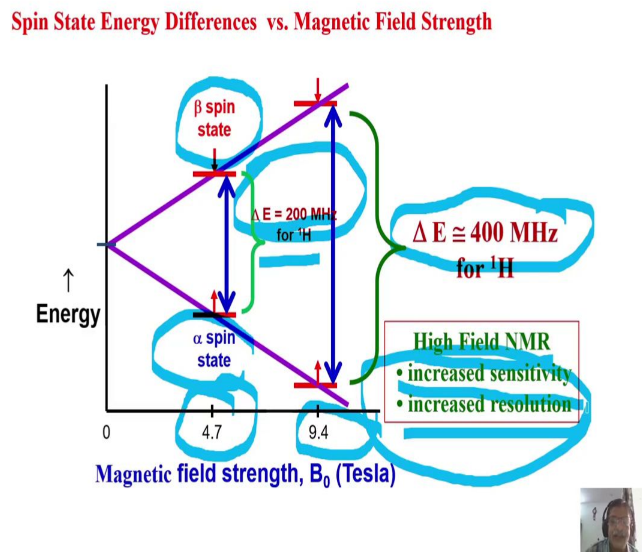

This is a diagram with energy level separation. It tells you what happened to 2 spin states, and I am taking the example of spin of half nuclei, when I double the magnetic field. These are the two energy States. This is a alpha state and this is a beta spin state. This separation we calculated the energy for this magnetic field of 4.7 Tesla, put it into the equation ν equal to Gamma into B naught by 2 phi. B naught is 4.7 tesla. Gamma is known, 2 pi is known, you calculate Delta E. It is equal to 200 megahertz in a magnetic field of 4.7 Tesla.

Now here we have doubled it. What is happening? Energy separation also doubled because it is linearly varying magnetic field. Frequency is linearly varying with the magnetic field. As a consequence energy levels separation has to increase. Otherwise frequency will not increase, right? So this drawing tells you as you increase the magnetic field, the energy between two alpha and beta states have increased linearly. if you change linearly, it increases linearly. At 2 places we saw it doubled and energy levels exactly get doubled, the resonance frequency is 400 mega hertz now, which was 200 MHz here. When you changed the magnetic field from 4.7 to 9.4 Tesla the resonating frequency which was 200 Mega Hertz became 400 Mega Hertz for protons. So, what do you understand from this? Higher the magnetic field we have better resolution and increased sensitivity. We talk more about resolution and sensitivity as we go ahead but this point it has to be clear for you, higher the magnetic field, higher the resolution and higher the sensitivity.

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Resonance Frequencies at different field strengths

B_0 (In Tesla)	MHz
1.4092	60
2.3487	100
4.6975	200
7.0462	300
9.3949	400
11.7437	500
18.7899	800
23.4874	1000

Ok this table gives you a feel for what is happening when you increase the magnetic field and how the resonant frequencies are changing. Look at it, we will concentrate on this magnetic field, if this is approximately 4.75 Tesla, resonant frequency is 200 Mega Hertz. I go to double, I will go to 9.4 Tesla, the resonating frequency gets doubled. I go double of this, I will make this 18.8. look it goes to 800 megahertz. If you keep increasing the magnetic field, it is linearly changing, that is the resonating frequency is linearly changing.

So, it is the important concept you must remember and B0, magnetic field is always expressed in Tesla in NMR and the resonating frequency is always expressed in megahertz, ok.

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Where does NMR Spectroscopy appear in the EM Spectrum?

With this we have understood all about resonance, in the sense, what is the resonance condition everything, we can even calculate the frequency. We know delta E, we know ν is equal to gamma into B0 over 2 PI. We know what is B0 and what is gamma over 2 PI we get the resonating frequency. Now remember in the very first class when I showed the electromagnetic spectrum, I said NMR appears in the radio frequency region.

I suppose you remember all these points. am I right? now let us understand. We will find out where does NMR spectroscopy; where does the frequency if I calculate, for a different magnetic field appear. We will do that.

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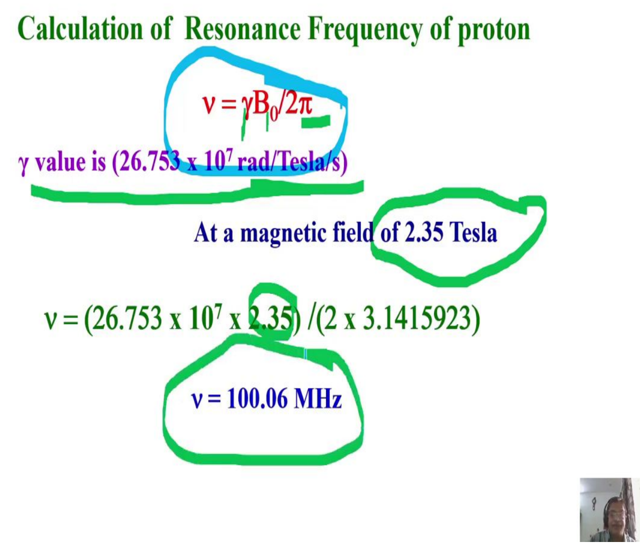

We will calculate resonating frequency of proton using this resonance condition. Of course, I have been telling you that the gamma of proton is 26.75 into 10 to the power of 7 radian per Tesla per second. Now I am taking magnetic field as 2.35 Tesla, this is in Tesla and this gamma is in this unit. I know 2 and I know Pi, and the Pi expressed in radians, 3.1415926, that value you should not forget. That should be in your fingertips always. Substitute all these values. Ok. ν is equal to gamma you know 2.35 Tesla, I know this thing, I know magnetic field. These are all simple numbers, just plug it into calculator and it turns out be ν = 100.06 Megahertz. I calculated ν is 100.06 Megahertz.

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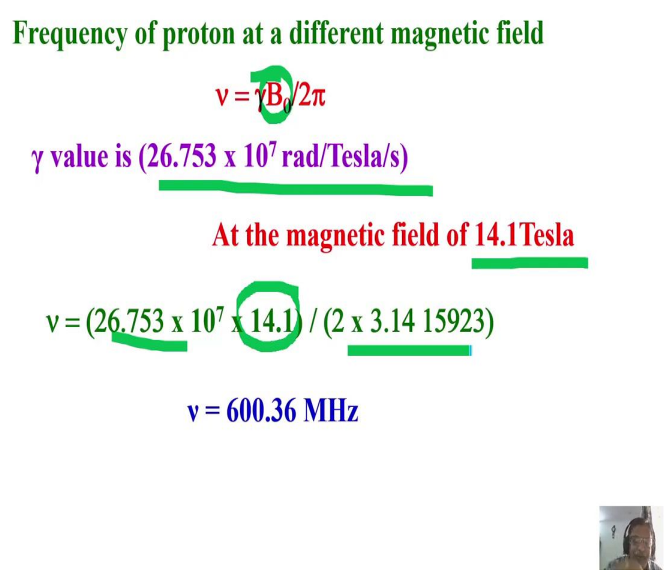

We will do one more experiment, one more calculation. What happens if I change the magnetic field to different value. Now I take magnetic field of 14.1 Tesla, earlier was 2.35 T. I change it to 14.1 Tesla, all other factor remains same, that I am not touching, it has to be same. Plug in the values, only this number is changed now the rest all remained same. And then find out the value it is 600.36 megahertz. what happened? I changed the magnetic field 6 times, the resonating frequency changes to 6 times, that is ok.

This is for proton, both the resonating frequencies of the proton in both the magnetic field ,I took example for calculation, it appeared in Megahertz frequency range, 100 and 600 MHz, does not matter it is some number. It is all in megahertz range that is fine. What about other nuclei.

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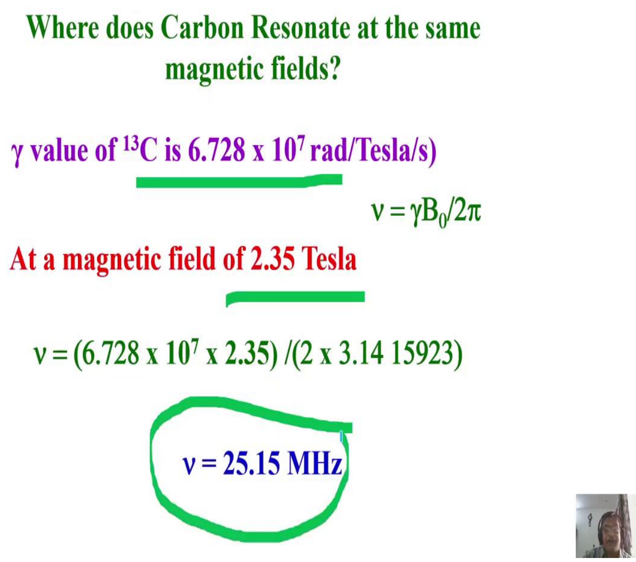

Let us look at the example of carbon 13. Carbon 13 gamma is this. AT the same magnetic field 2.35 Tesla, plug in the value. It turns out to be 25.15 Megahertz. Gamma of carbon is 4 times less than that of proton, as a consequence ν is 4 times less, correct, proton is 100.06 MHz, you worked out and the carbon resonating frequency in the same magnetic field is 25.15 Megahertz.

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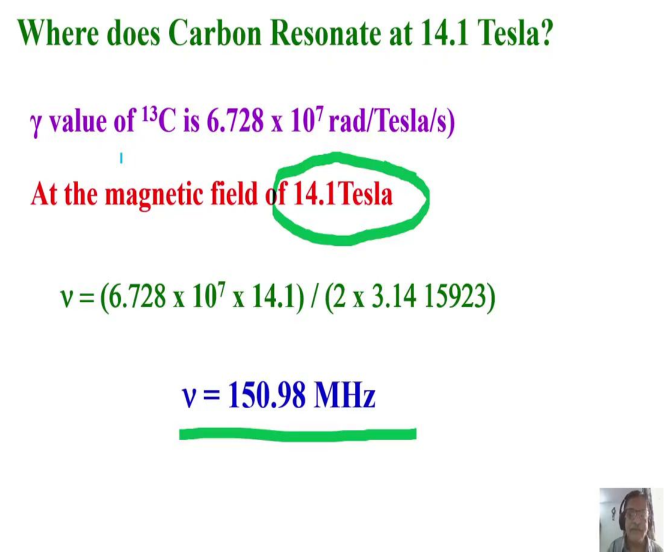

It is good, let us see what happens to the other magnetic field that you calculated for Proton 14.1 Tesla. Plug it in for Carbon 13 gamma, it turns out to be one 150.98, four times less than that of proton. In 14.1 Tesla Proton was resonating at 600 MHz, carbon coming at 150 MHz. In 2.35 proton was 100 MHz, carbon was 25 MHz around that value. Fine, all are in megahertz that is the general conclusion, for all the nuclei we took, the resonating frequencies are all within this megahertz range.

Except one unstable nuclei tritium, no other nuclei in the periodic table can have resonating frequency more than that of proton. Remember, the highest resonating frequency of all the stable isotopes is always a proton. that is the one which has highest gamma. in the magnetic field when all other things are kept constant only gamma is changing, that has the highest gamma. So, no nuclei in the periodic table can have the resonating frequency higher than that of proton. Ok with this we know, it is all in the megahertz range.

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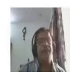
If protons resonate at 300 MHz What is the magnetic field required?

$$\nu = \gamma B_0 / 2\pi$$

$$B_0 = 2\pi\nu/\gamma$$

$$B_0 = (2 \times 3.1415923\ (\text{rad}) \times 300\ \text{X}10^6\ s^{-1})\ /26.753 \times 10^7\ \text{rad/T/s}$$

$$B_0 = 7.04\ \text{T}$$



If the Proton resonate at 300 megahertz, we can one more calculation. Of course this is for you to understand before we go further. Let us say I have given you, somebody told me that he got a spectrum in 300 megahertz for proton, then what was the magnetic field? Of course you can calculate by this equation. You know this equation bring B0 this side, and find what is going to happen. So, it is 2Pi goes here, 2 Pi ν over gamma. plug in the values, simple, you find out B0 turns out to be 7.04 Tesla. So remember these things, you need to calculate the magnetic field or calculate resonating frequency for varieties of nuclei, fine.

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Radio Frequency Ranges between 20 KHz to Several GHz

NMR is detected in the Radio Frequency Region

All NMR spectrometers operate at MHz frequency !!!

All these things we know, now in the practical applications where we have the magnetic field of the order of few Tesla, such as, 4 Tesla, 14 Tesla, up to 20 Tesla, does not matter we calculated. Even if I have 24 Tesla the resonating frequency turns out to be in gigahertz, that is NMR frequency. But radio frequency range, if you know the radio frequency in the electromagnetic spectrum, it ranges from 20 kilohertz to several gigahertz. 20 kilohertz to several gigahertz, but NMR spectrum, what we saw, its resonance frequency comes in the radio frequency region, the megahertz only.

As a consequence the NMR, because we know the radio frequency range is from 20 kilohertz to several gigahertz, and our calculated frequency are all in megahertz, I said NMR is detected in the radio frequency region. Are you all with me, I just wanted to show you we just calculated the resonating frequency of different set of nuclei for a set of magnetic fields, and we understood that they all come in the megahertz range, megahertz frequency range. But in electromagnetic spectrum, we know radio frequency ranges, are all between 20 kilohertz to several gigahertz. As a consequence, I will say NMR is always detected in the radio frequency region, there is no doubt about it. That means, go to any NMR laboratory, all NMR spectrometer operate at megahertz frequency. You understand? Any NMR laboratory you go, you will see the NMR spectrometer frequency is always mentioned in megahertz.

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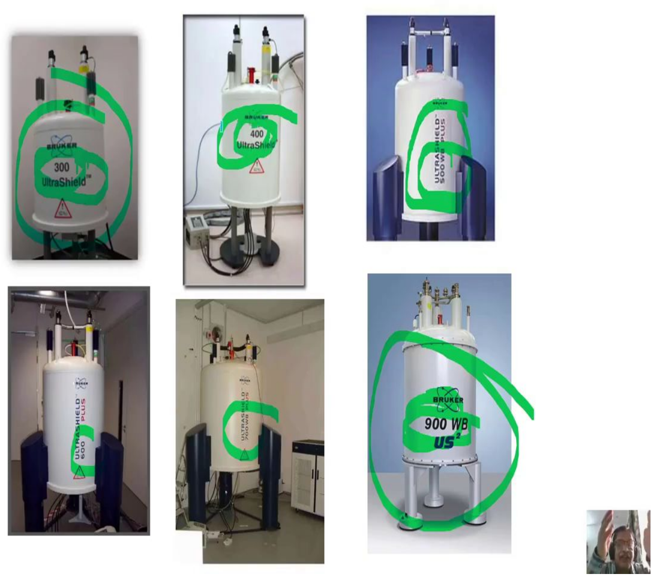

For example go there, go to any NMR lab. In our lab we have many spectrometers, we can see it is written 300, 400, 500, 600, 700, 900, varieties of magnets are there. What do this number refer? These numbers tell you the corresponding resonating frequency of proton in these magnetic fields. In these magnetic fields whose magnetic field can be express in some Tesla, if you take the proton NMR, it comes at 500 Megahertz.

Similarly, in this spectrometer Proton resonates at 900 megahertz, that means magnetic field from here to here is 3 times larger. If this magnetic field is let us say 7 tesla this is 21 Tesla. 3 times larger, that is what I said. But what I am trying to tell you is whatever the number you see on the magnets, when you go to NMR spectrometer, where the commercial spectrometers are there , and the magnets are there, some numbers are written here, that tells you the corresponding resonating frequency of the spectrometer and that pertains to the resonating frequency of protons.

So if I come and tell you I have an 800 megahertz spectrometer, that means I have a magnet written with 800 here, and the console and everything is matched such that that the protons in that field resonate at 800 megahertz. This is the interpretation, you should know.

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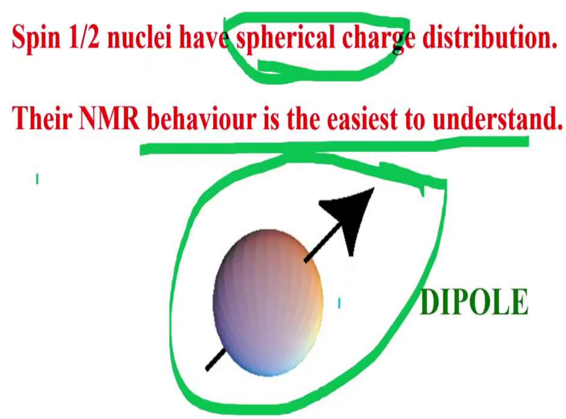

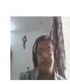

Now we will go little bit more and to understand, we have spin half nuclei, where charge distributions is always spherical, Spin half nuclei it is a dipole, ok, charge nuclei is always spherical and their behaviour is easy to understand. Always in NMR if I take spin half nuclei I can understand their behaviour, their interaction with magnetic field, among themselves everything, etc. is very easy to understand compared to spin greater than half nuclei. Not that we cannot understand, but easiness of understanding is better for spin half nuclei.

Because the spin half nuclei are called dipoles, why it is a dipole? It is magnet with two poles like north and south. So, spin half nuclei is always called a dipole.

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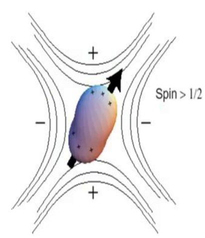
Nuclei with spin > ½ have non-spherical charge distribution.
They are called quadrupolar nuclei

The quadrupolar nuclei have electric quadrupole moment (eQ). The quadrupolar interaction is electric in nature



Spin greater than half, do not have spherical charge distribution. The charge distribution as a different shape like an ellipsoid. The charges are distributed differently, see here it is plus plus, minus minus. Whereas in the previous example you see only two charges, if you say this is plus and this is minus, this is plus this is minus. So only 2 poles are there. But here there are 4 poles 2 positive charged poles for two positive charges, two poles for negative charges, that is why it is called a quadrupole.

Any nuclei with spin greater than half have non spherical charge distribution and such nuclei are called quadrupolar nuclei. and such nuclei have what is called, the electric quadrupole moment. Remember in NMR as you go ahead, in the subsequent classes you understand lot more interactions, so far we are discussing only the external interactions, the Interaction of the nuclei with the external magnetic field. We have many more internal interactions. One such is the quadrupole interaction. All interactions in NMR, except quadrupolar interaction, are magnetic interactions. Only the quadrupolar interaction is electric in nature. Please remember quadrupolar interaction in NMR is electric nature and all other interaction are magnetic in nature.

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Now I will try to give you some classical analogy. So far we were discussing some energy level, spin etc and some quantum mechanics concepts with some physics termm without using rigorous mathematics or anything. This was the thing that was taught for us when we were students, that is with some classical analogy. It holds good. Broadly to a large extent this classical analogy also holds good. We will try to understand this.

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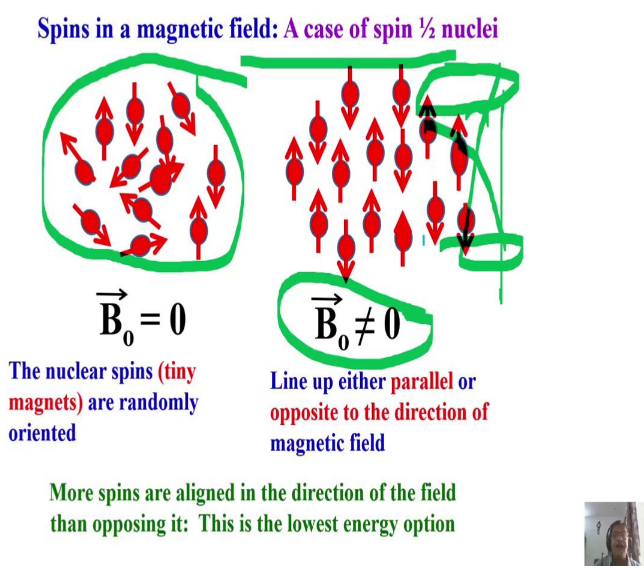

What will happen, now consider the spins in a magnetic field. I can say spin half nuclei. Now in the absence of the magnetic field spins are randomly oriented. Random distribution is there. There is no preferred orientation. Now as soon as we put the sample in a magnetic field which is non-zero, some magnetic field of some Tesla. Look at this, what is happening? Random distribution of this spins changed to preferred orientation like this.

Either they orient up or down, Orient in the direction of the field direction or the direction opposite to that of the field. There are only 2 possibilities. But remember we can have various possibilities of orientation, but preferably we have many nuclei spins, they orient like this and like this and both of them have different orientations making a preferred angle and we also calculated everything.

So some of them lineup in the direction parallel to the field and some of them lineup in a direction opposite to the direction of the magnetic field. Interestingly, most spins aligned in the direction of field than opposing it, because that is the lowest energy option. The energy option is more spins are aligned in the direction of field than opposing it. Please remember my question E =- μ dot B, I put a negative sign to ensure that more spins are aligned in the direction of the field, which has the lower energy, the preferred orientation.

In the equation for energy, I put a negative sign and then I ask you why negative sign, that is explained there. This is the reason, more spins are aligned in the direction of the field, than opposing it because it is the lowest energy option.

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Now what happened, let us understand Larmor precession. Spin half nuclei are constrained to adopt 2 possible orientation in the external field given by 2I + 1. But we know what is a magnetic moment direction, although we say in the direction of the field or in the direction opposite to the field, we also know what is the angle of orientation, the quantization direction calculated also right, for spin half and minus half, which is 54.7 you remember. we calculated in one of the previous classes. 2 orientations, one 54.7 in this direction of the field, -54.7 in the - Z direction, the magnetic moment and we calculated quantization direction. There are 2 forces acting on it. One is the large force, the magnetic field, because of external interaction. It wants to keep it aligned along it. The other force spins angular m momentum which wants to keep it spinning at a restricted orientation, which is known, we can calculate that.

There are 2 forces acting on, it is like tug-off war, one is this side and other one this side. In the loose way, I will tell you one is pulling this way and other is pulling other way. It is like tug-off war.

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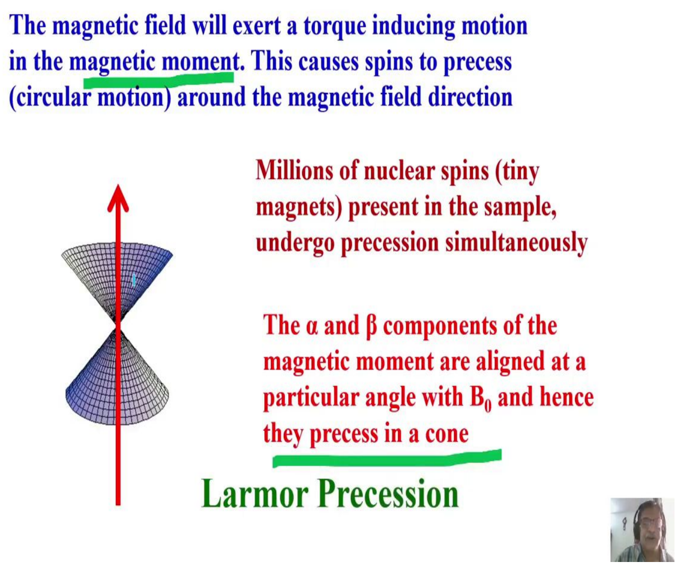

As a consequence what happened, the magnetic field exert a torque, and the torque induced motion into the magnetic moment. That is for spins, it introduces a sort of a torque, torque induced motion. What will happen this torque will make the nuclear spins start processing along the direction of the magnetic field. This is the magnetic field it was like this, some more like this, 2 orientation, but the main magnetic field starts pulling this side but the preferred orientation according to quantum mechanics is like this restricted orientation.

As a consequence what happened, the spin exerted torque, and the spins start rotating in a cone, in the direction of the magnetic field. If one spin is rotating like this, in the opposite direction the field. There are millions of nuclear spin tiny magnet or magnetic moment. They are present in the sample and undergo precession, simultaneously with the same frequency. Frequency will not change. The precessional frequency, that is the speed at which they rotate is same.

Simultaneously undergo precession in the direction of the field in this direction, and opposite to the field. It appears as if they are forming 2 cones like this, alpha and beta components of the magnetic moment aligns in a direction with particular angle in the magnetic field. Because of this torque, this precision is a cone like this. This is important thing, remember the classical analogy, they align, spins or magnetic moments start processing in this direction, you have 2 cones due to 2 preferred orientations, and the torque the magnetic field induces on this spins. This is called Larmor Precession.

Now you may ask one question, spins are precessing, at some speed. What is Precessional frequency? How fast it is precessing? I must calculate right. I should know, if say torque is exerted by the field and the spins, and they start precessing like this, what is the speed? How fast it is rotating? What is the frequency of precision? I must calculate, that is called Larmor frequency.

I will calculate that in the next class and show you what is the Larmor Precession. So I stop for the day. Today we have discussed lot of things, continuing from the spin Physics. Now we have got a classical example, you understood about the degeneracy removal of the states, and we calculated the energy difference between these two states, obtained their resonance condition and calculated the frequencies. And then showed it is in the radio frequency region, for different magnetic fields the difference resonating frequency for different nuclei all come in the radio frequency region. In the classical analogy I said the spins starts precessing like a cone like this and it is called Larmor Precession frequency. In the next class this Larmor frequency and everything we will discuss and continue further, ok we will continue further in the next class.