Advanced NMR Techniques in Solution and Solid – State

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Module -2
NMR Concepts and Spin Physics – I

Lecture - 02

Welcome all of you. In the last class, I just started giving a basic introduction to NMR spectroscopy. I introduced some terms of spin physics, like, spin angular momentum, spin quantum number, magnetic moment, magnetic quantum number, gamma and different nuclei how we can find out the spin of the nuclei by using some empirical rule, and what is the difference between 2 nuclei if they have the same spin quantum number I and same magnetic quantum number m, and I showed the gammas are different because the masses are different.

And I said the nuclei with different gamma can be individually studied. So, with that, I also calculated the magnitude of the angular momentum also and we said the spin angular momentum is quantitized along that Z axis; and using that we found out what is the theta, the angle at which these m_I for plus half or minus half are oriented with respect to the magnetic field. Today, let us start the discussion about Zeeman interaction.

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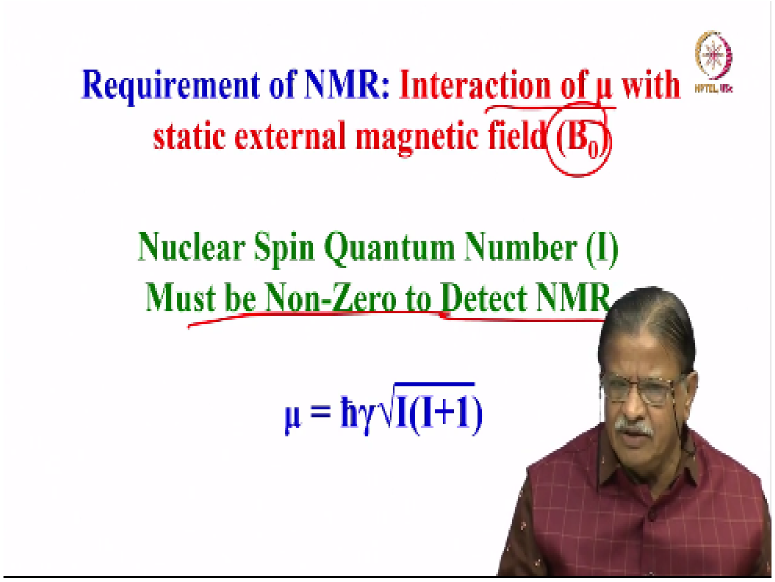

So, Zeeman interaction; the one of the important requirements for NMR is the interaction of the magnetic moment μ with the static magnetic field B_0; this is very important thing. Nuclear spin quantum number I must be nonzero. Remember it must be nonzero to detect NMR. As I told you in the previous class, when I = 0, μ is 0 will μ is 0, there is no question of interaction of the magnetic moment with the external static magnetic field. So, NMR cannot be observed. So, this nuclear spin quantum number I must be nonzero to see NMR. So, this formula we already worked out, I show you μ is equal to gamma into h cross into root of I into I + 1. Of course μ is also a vector, and in principle you can put an arrow at the top of it.

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Interaction of μ with B_0

Nuclear spins starts aligning with the static magnetic field (B_0)

Some align in the direction of the field, some in the opposite direction of the field

Energies of interaction are different

Now, let us see how the μ interacts with the magnetic field B_0. You take nuclear spins, put it in an external magnetic field, static field huge, whose strength is very large. I call it magnetic field B_0. Then what is going to happen? some nuclear spins align in the direction of the field, some align in the direction opposite to that of the magnetic field. There are 2 possible orientations we can think of, because I am dealing with spin half nuclei; remember. Unless otherwise, I mention, most of the time, I will be dealing with spin half nuclei.

And when the 2 orientations are there; 2 possible orientations, then how the nucleus spin behave in the magnetic field. The energies of interactions are also different. The energy of interaction of the spins in this direction and the energy of the spins in the direction opposite to the magnetic field, these 2 are different.

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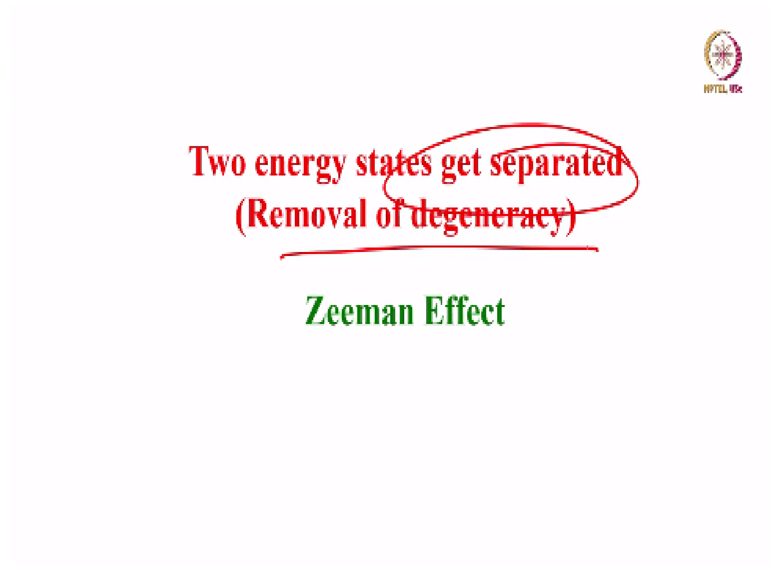

So, when the 2 energies are different, what is going to happen is, when you put it in a magnetic field they get separated out like this. This is called the removal of degeneracy; the degeneracy is going to be removed; and this is called Zeeman effect. This interaction of the magnetic moment with the external magnetic field is called Zeeman interaction.

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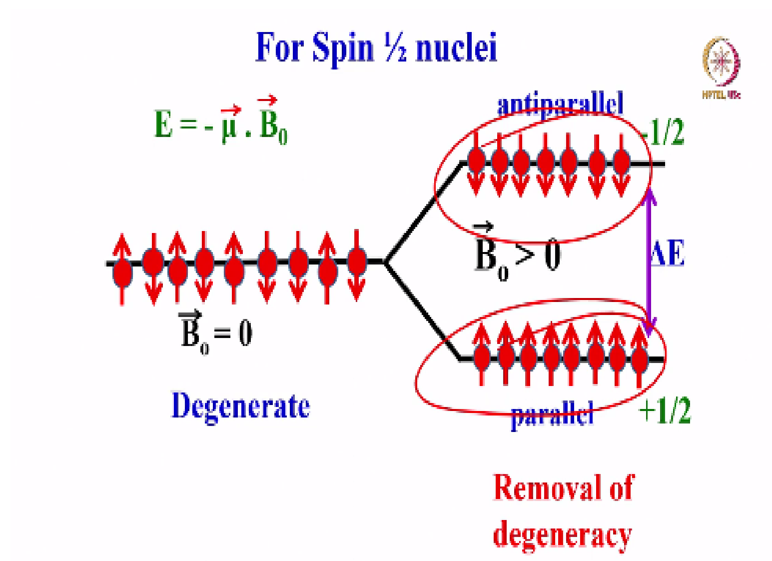

Now for spin half nuclei, the interaction energy is given by $E = - \mu \, xB_0$; both are vectors. it is the dot product. And there is a negative sign for that. We will come to that later. Now we can see for spin half nuclei in the absence of the magnetic field; all the spins are randomly oriented. There is no preferred alignment; you can see spins aligned both in the direction of the field, and in the direction opposite to the field, etcetera. There is no separation of the energy levels. These are called degenerate states.

Moment you put it in a magnetic field,the static magnetic field which is nonzero. As I told you, there is a separation of energy levels; because the spins orienting along the direction of the magnetic field and opposite to the direction of the magnetic field, get separated out. The energy levels get separated out. This is called removal of degeneracy and this energy state corresponds to anti parallel orientation of magnetic spins with respective magnetic field, and the other is parallel orientation; and the separation between these 2 energies called Delta E; energy.

And you can see some spins, which are oriented opposite to the direction of magnetic field, which I have written here, you can see they are all inverted, they are in the opposite direction opposite the magnetic field; and these are all in the direction of the magnetic field. And now, what we did by putting the sample in a magnetic field; we removed the degeneracy. This is the important concept. This is because the nuclear magnetic moments interacts with the external magnetic field. The energy of interaction of the magnetic moment with the magnetic field, we will calculate now.

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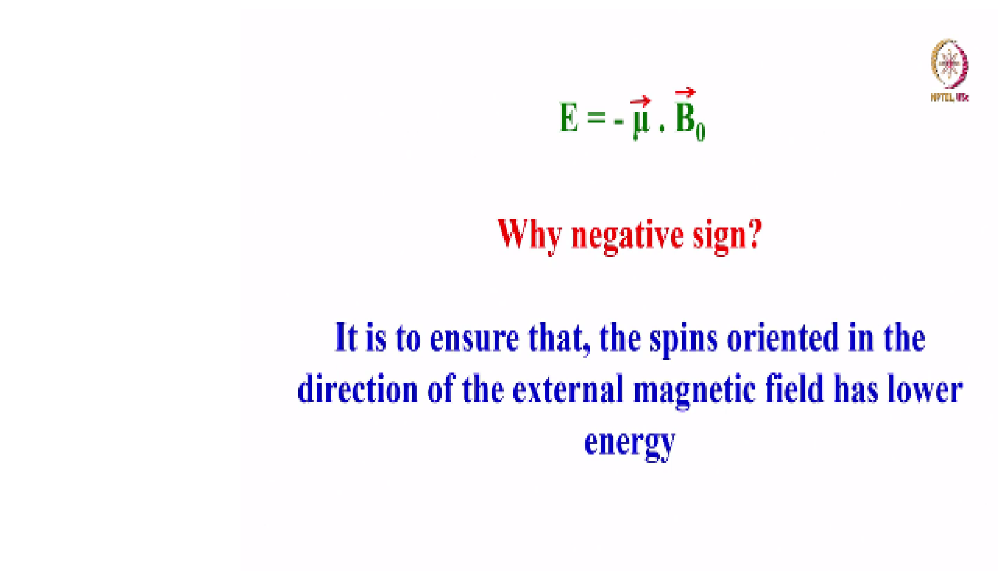

As I said E = - μ x B_0. You may ask me a question what is this negative sign, what is the meaning of telling energy be negative. It is to ensure that spins oriented in the direction of magnetic field has lower energy compared to the one which are oriented in the direction opposite to the magnetic field. It is a convention. To bring in this concept, negative sign is put.

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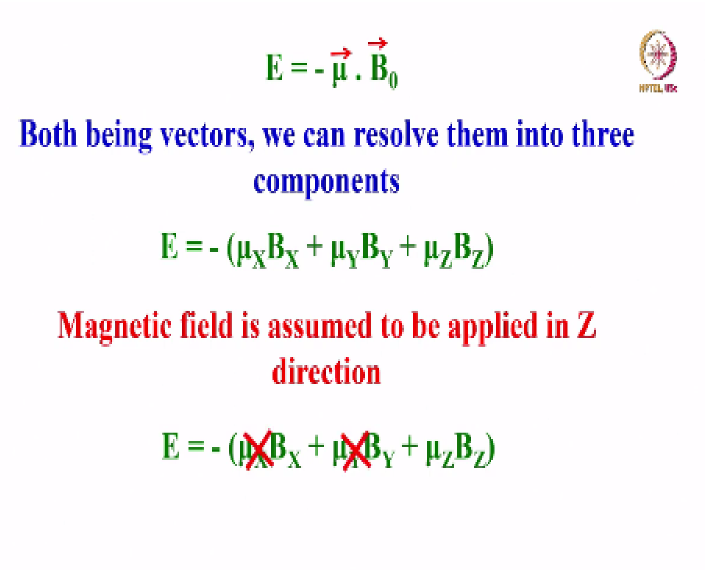

So, we continue for that both are vectors μ is a vector B_0 is a vector and we can resolve them into 3 components, in x y and z directions. So, it can be written as E = -(μx Bx + μy By + μz Bz). We always assume magnetic field is applied in the direction the magnetic field z axis, z direction is the direction μz we apply the magnetic field. So, as a consequence, we can remove x component, and y component. They will go to 0.

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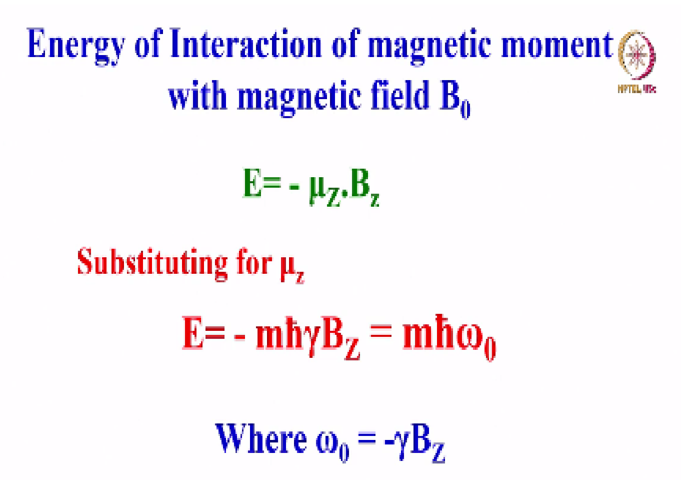

And we are left with only E = - μz x Bz. This is the energy of interaction of the magnetic moment with the magnetic field B_0. Now substitute for μz. We already worked out what is μz. μz = m into h cross into gamma; that is what we worked out already. Substitute that; and this can be equated to m into h cross into omega naught. What I did? Gamma into Bz; I equated it and I replaced by a term called omega naught, an angular frequency, where minus sign is also included. omega naught = minus into gamma Bz is the term. So, I replace omega naught, by minus gamma into Bz and this is the energy of interaction.

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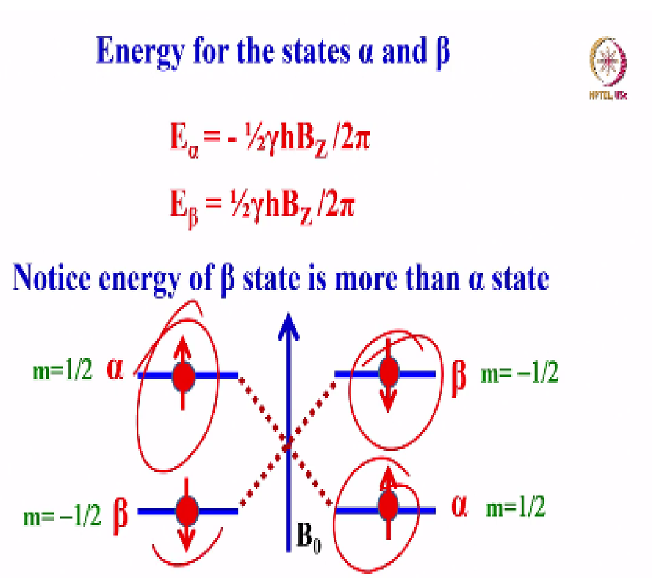

Now, energy for 2 spin states alpha and beta I can resolve them. I can find out Ealpha energy for the alpha state; you can write it as m is equal to half. Go back in the previous equation, see m is equal to half there. So, m is equal to half and minus half you put it, minus half into gamma h cross Bz over 2 pi. Instead of h cross I have written h over 2 pi, beta is same; half into h Bz over 2pi. Please remember the change here alpha is plus half state because energy is minus it is minus. And beta is minus half state because the minus $\mu.B_0$; it becomes positive. So, E beta is positive and E alpha is negative. So, notice because of that energy state of beta is more than that of the alpha state and in the absence of the magnetic field, if I write this as the alpha state and this as a beta state; as soon as you put in the magnetic field, this is the energy state beta, which has higher energy than that of the alpha state. So, remember this is up and this is down and before the magnetic field; this is alpha and this is beta.

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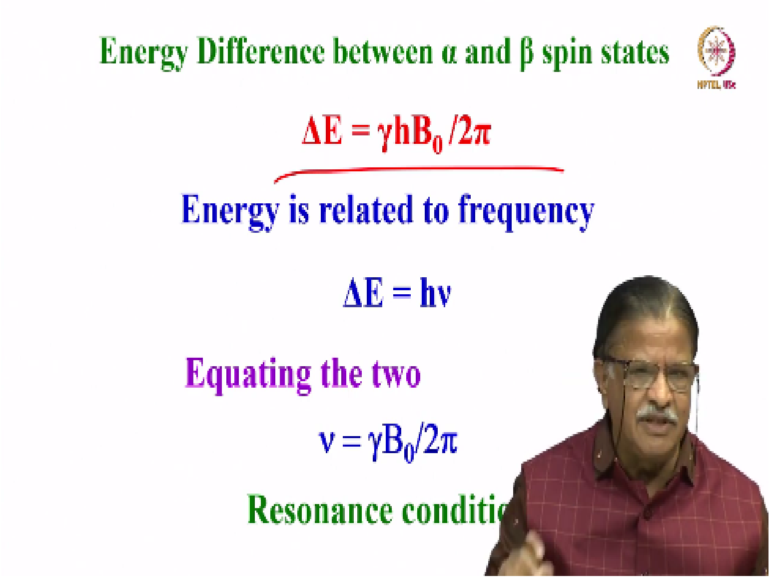

Now, find out the difference in the energy between alpha and beta spin states; delta E = gamma into h into B_0 over 2 pi. Now, you all know in atomic physics you would have studied; energy related to frequency, Delta E = h into μ. Now, you equate these 2; and do some mathematical rearrangement, then he can find out and show that ν = gamma into B_0 over 2 pi; the famous equation of NMR. Please remember, this is called a resonance condition.

It is a beautiful equation, which is responsible for giving several Nobel Prizes in NMR. So, this is resonating condition ν = gamma into B_0 over 2 pi. This must be in your fingertips all the time.

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

Resonance Frequencies vary linearly with the magnetic field

So, what is that you are going to observe here? If I take the resonating condition; ν is the frequency; gamma is the gyromagnetic ratio for a given nucleus; B_0 is a magnetic field. 2 is constant, pi is constant. We know the value of pi, everything is constant. gamma is constant, 2 is constant, pi is constant effective the magnetic B_0 constant, that means, for a particular value of B_0; the frequency is constant. It means, if I double the magnetic field, the frequency gets doubled, it shows the resonance frequency vary linearly with the magnetic field. That is an important condition. So, ν varies linearly with the magnetic field B_0.

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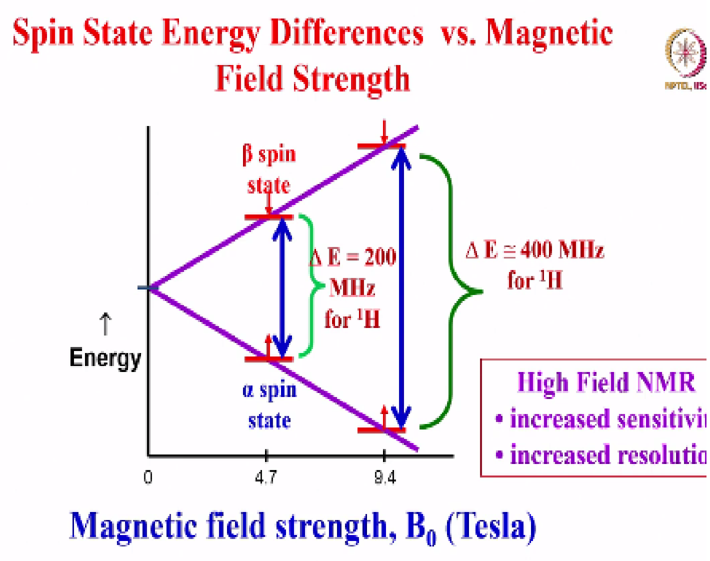

So, this can be seen like this, how does it affect the energy states; difference in energy for example. For a given magnetic field B_0, let us say; at 200 megahertz, which corresponds to 4.7 Tesla of the magnetic field and alpha beta are separated like this. And I can calculate the energy; this turns out to be 200 megahertz. Now, I will double the magnetic field; go to 9.4 Tesla, what is going to happen is you can see that the energy separation gets doubled. And if you calculate the difference in the energy, it turns out to be delta E = 400 megahertz.

So, double the magnetic field resonant frequency gets doubled. Most important concept here you should remember; higher the magnetic field, higher the sensitivity and higher the resolution. That is why we always want to go to higher and higher magnetic field so that we get better resolution and better sensitivity in NMR.

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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

The resonating frequencies at different magnetic fields strength can be given like this. For different magnetic fields strength, you can see for example, 200 and 400 is exactly double. The 200 and 800 you can see exactly 4 times; you can find out so, this varies linearly. Now, the question is where does NMR Spectroscopy appear in the electromagnetic spectrum? You all would have seen electromagnetic spectrum starting from x-ray or gamma ray, up to radio frequency region; in the different regions of the electromagnetic spectrum you see different types of spectroscopy; different molecule spectroscopy can be studied. Now, the question is where does NMR come in the electromagnetic spectrum? We can find out.

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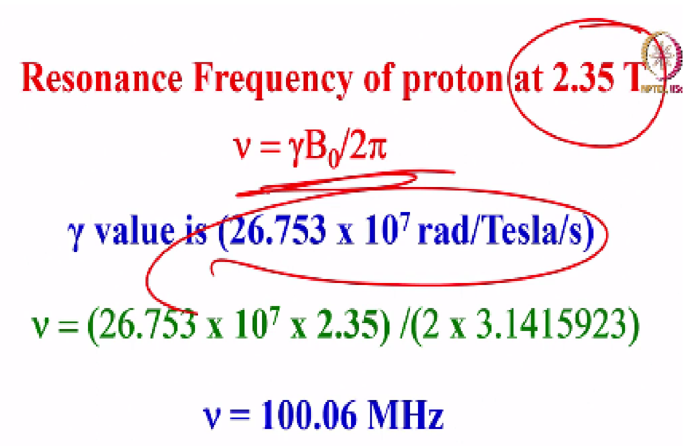

Now, in the resonating condition I have put; let us take the magnetic field as 2.35 Tesla and substitute in this equation. I know 2 and I know pi, I know gamma for proton whose value is given here is 26.752 into 10 to the power 7 radians per Tesla per second; and substitute this value; do simple calculation, take your calculator and calculate. It turns out to be 100 megahertz. ν the resonant frequency of protons at 2.35 Tesla is around 100 megahertz.

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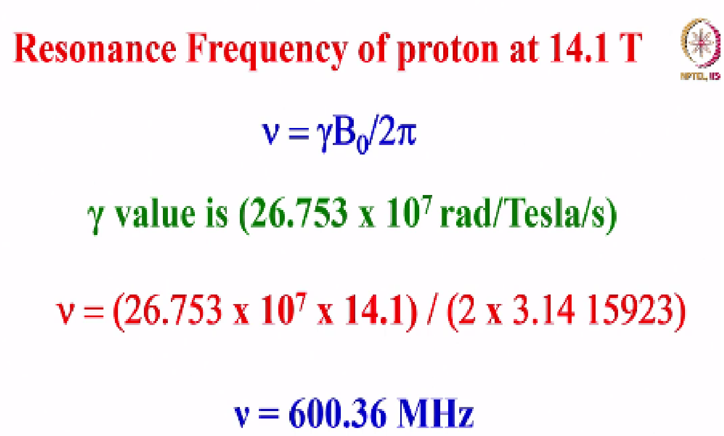

Now, what happens if I increase the magnetic field? I changed it from 2.35 to 14 Tesla, then again put these values everything remains same; only magnetic field is different; gamma, 2 Pi are same. You substitute this value it is turns out to be 600.36 megahertz. So, that means, you change the magnetic field by 6 times, from 100 megahertz it became 600 megahertz. So, like that it is linearly varying.

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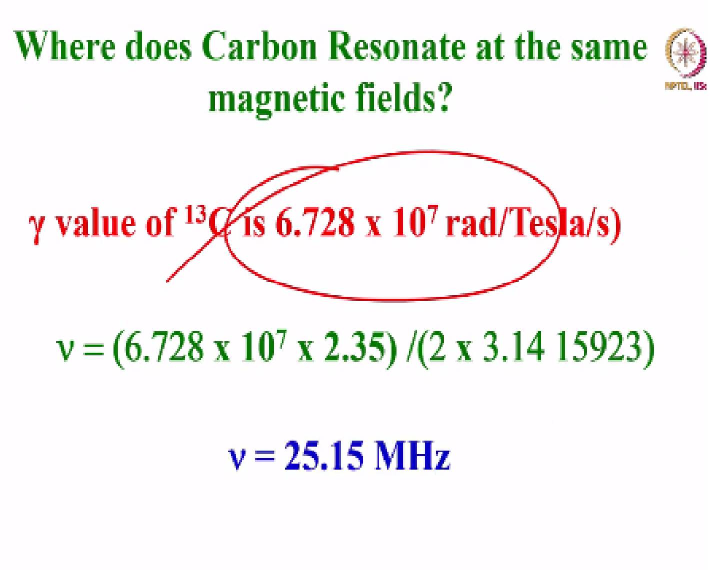

Now, what will happen to the different nucleus like carbon. This is as far as the proton is concerned, because I substitute for the gamma of protons. Now, where does carbon comes in same magnetic field. The gamma value of carbon is 4 times less than that of the proton; remember is 6.72; unlike in the case of proton it was 25 point something, I wrote earlier. So, gamma is 4 times less. That means, ν is also 4 times smaller; that means in the proton it was 100 megahertz, now, it is 25 megahertz, 4 times smaller.

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^{13}C resonance at the magnetic field of 14.1Tesla

$$\nu = (6.728 \times 10^7 \times 14.1) / (2 \times 3.14\,15923)$$

$$\nu = 150.98 \text{ MHz}$$

Same thing for example, for 14.1 Tesla, you substitute; it turns out to be 150 megahertz. There it was 600 megahertz for proton, for carbon it is 150 megahertz. So, gamma is the one which is dictating the resonating frequency. So what is the resonating frequency for different nuclei? You can find out by different gammas.

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

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

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

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

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

So, that means, you can calculate in a reverse way also, let us say I have protons and they I do not know the spectrometer frequency, I record the NMR spectrum. I know it resonates at 300 megahertz, then if you ask me what is the magnetic field? what was the magnetic field at which we got the resonance of 300 megahertz. Do the reverse calculation ν = gamma B naught over 2 pi. So, B naught become 2 pi ν over gamma.

Substitute the value of 2 pi, and then frequency of 300 megahertz and then gamma is 26.753 into 10 to the power 7 radians per Tesla per second. And you calculate, teh magnetic field is 7.04 Tesla. So, all the time we are dealing with the magnetic field in Tesla; for different magnetic fields starting from 2.35 Tesla, I showed you we keep on increase the magnetic field and resonating frequencies are always coming in megaHertz region.

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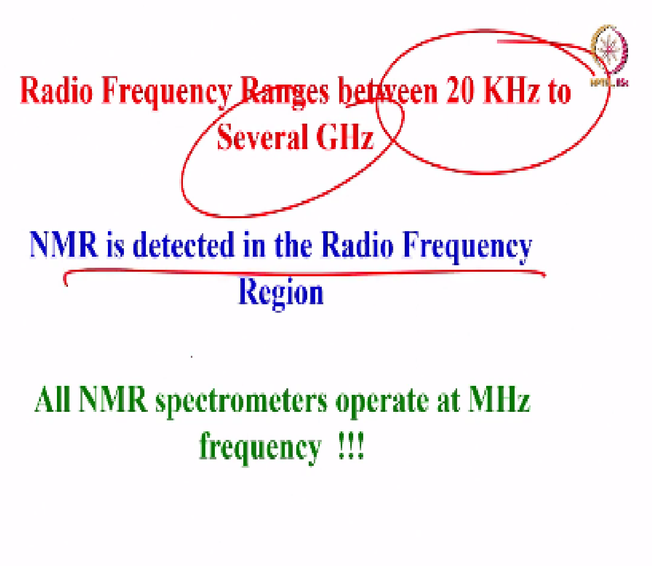

This is where the problem comes. The radio frequency range, always go between 20 kilohertz to several gigahertz, what is the frequency we calculated for different nuclei now? for protons, it was 100 MHz, 600 Megahertz, carbon 25 MHz and 150 megahertz; that is within this range. That means, the resonating frequency or the NMR always comes in the radio frequency region; because the radio frequency ranges between 20 kilohertz to several gigahertz.

And we calculate the resonating frequencies; we saw for example, it was between 20 kilohertz to several gigahertz; we can see that NMR is detected in the radio frequency region. So, that is why all NMR spectrometers operate at megahertz frequency, which is the radio frequency region.

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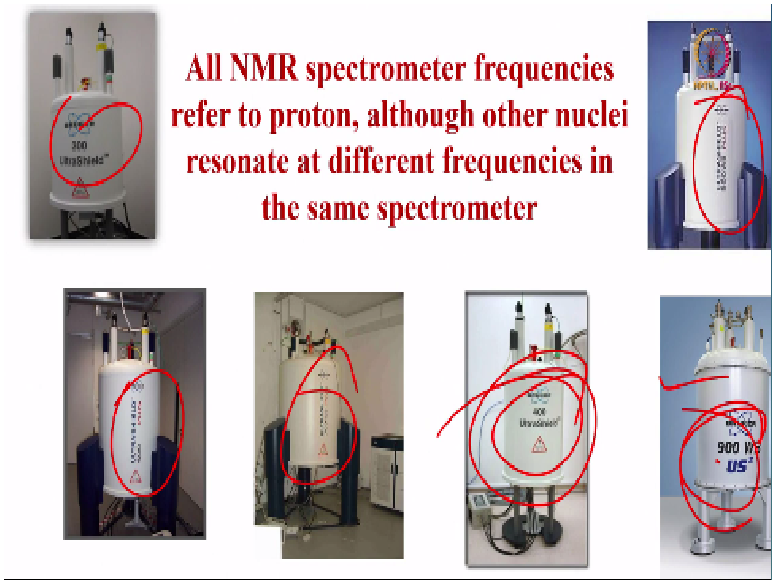

You go to NMR spectrometers, any laboratory where you have NMR spectrometers, you will see a big, you know a sort of cylindrical objects like that, they are called strong magnets, you can see it is 300 magahertz here; and you can see here for example, 500, 400, 900 megahertz. All these numbers are written here, what are these numbers? They are the resonating frequencies of protons in the corresponding magnetic field given there.

For example, if I say 900 megahertz; in this magnetic field, the protons resonates 900 megahertz In this magnetic field, the protons resonate at 400 megahertz. So, all spectrometers are referred to the protons frequency in a given magnetic field. So, that is what you please remember they all come in the radio frequency region.

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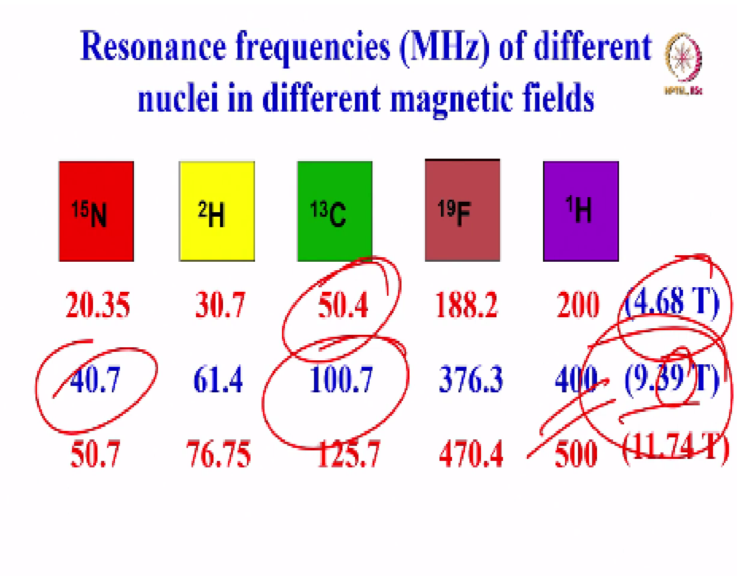

So, resonance frequencies of different nuclei in different magnetic fields, let us see. We can see proton, nitrogen, carbon, fluorine, varieties of nuclei you can see. Let us see, I have a 4.68 Tesla magnetic field, proton comes at 200 megahertz, fluorine comes at 188.2 megahertz. Similarly, carbon comes at 50 MHz and nitrogen comes at 20.35 megahertz; all in megahertz range. Why? Because the gamma is different so, you know that I told that gamma of carbon is 4 times smaller. So, at 200 megahertz, at 4.68 Tesla, proton has a resonanting frequency of 200 megahertz. Carbon is 4 times smaller, 50 megahertz, nitrogen is 20 that is 10 times smaller. So, that means, gamma of nitrogen-15 is 10 times smaller than that of proton. So at 4.68 Tesla these are the resonating frequency of different nuclei. Now, what happens if I change the magnetic field see from 4.68 I changed to 9.39; the proton resonates at 400 MHz and then similarly, carbon-13 is doubled, and these get doubled; everything get doubled because I change the magnetic field into double. Of course, you start to exactly double, check. It gets multiple by 2, there is some multiplication mistake do not worry, it should have been 9.36. So, similarly utilize 11.74 Tesla you can see different resonating frequencies are different. So, at different magnetic field different nuclei, we have different resonating frequencies, all can we individually studied. Now, let me give you some classical analogy.

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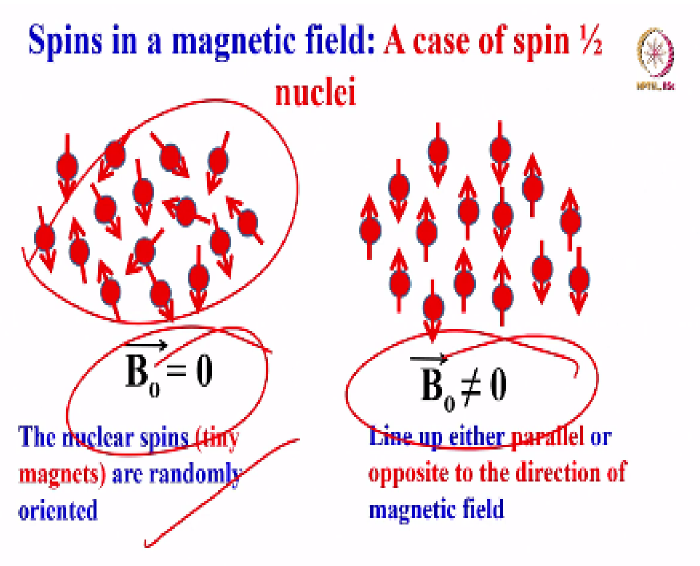

Classical analogy is like this. Of course, this normally nobody uses but I am just telling for the sake of making people understand. Let us consider an ensemble of spins; put in a given magnetic field. Consider the case of spin half nuclei. If the magnetic field is 0, look at it all the spins are randomly oriented; there is no preferred alignment of the spins. Every possible orientation you can think of. On the other hand, you put them in a magnetic field the here random orientation is there as soon as you put it in a magnetic field, which is nonzero, very strong and homogeneous magnetic field; that is very important. Then you see, spins are aligned here, some in the direction of the field; some in the direction opposite to the direction of the magnetic field. This is called the removal of degeneracy. Some spins are up, and some spins down. So, this is a classical analogy of what we discussed with a quantum mechanical concept, ie. the separation the energy levels. The same thing in the classical analogy, we can say the spins which have different types of orientations in the absence of the magnetic field, and have two possible alignments in the magnetic field.

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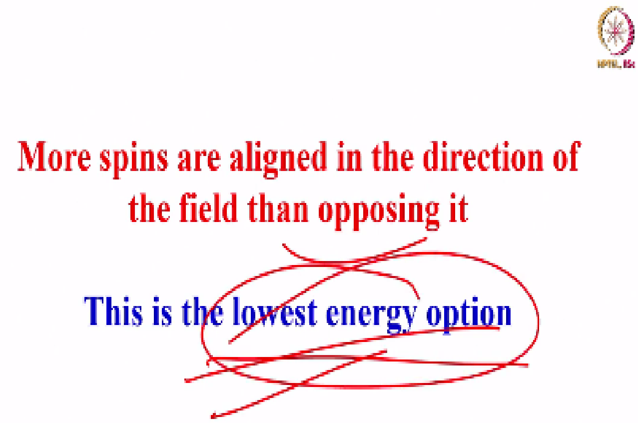

So, an another important concept we should know here is that, more spins are aligned in the direction of the magnetic field than opposing it. Something strange right? it is true, it is because of the Boltzmann population distribution. You will understand when we go to the Boltzmann population ratio; we will calculate and see the more spins are always aligned in the direction of the magnetic field than opposing it. And this is the lowest energy option; Remember, in this lowest energy option more spins should be in the direction of magnetic field than opposing it.

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And once you put the sample in the magnetic field, we also have what is called a classical phenomena which we understood. There are 2 forces acting in the spins in the magnetic field. One the large static external magnetic field, which ensures that the spins are oriented in the direction of it, aligned with it or opposite direction of it. But the spin angular moment wants to keep it spinning at a restricted orientation. Quantum mechanically we calculated the magnitude and also theta. You know cos theta I told you, calculated. It turns out to be 54.7 for μ equal to plus half was found out. It wants to be in a particular restricted orientation; and what will happen? because of this there exists a sort of a torque, it is a tug of war, of course between these spins. Then what happened the spins will start undergoing precession, it is called precession; a circular motion around the magnetic field direction. This is a magnetic field, it starts going in the direction of the magnetic field, undergoing precession like this. This is called Larmor precession.

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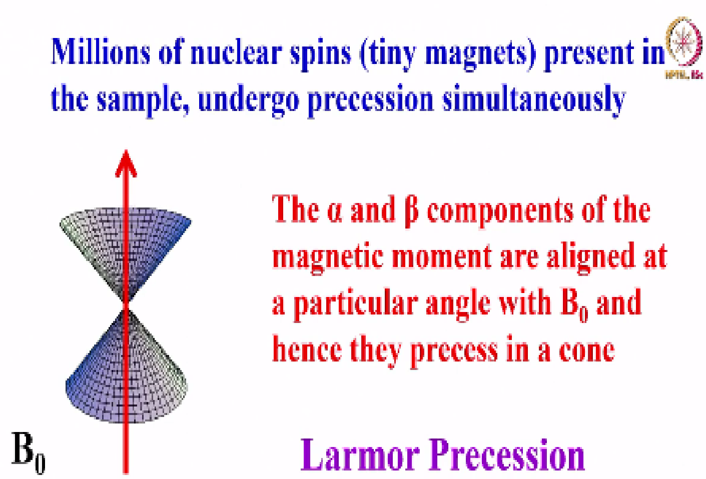

So, this is how it happens; the spins which are orientated in the direction the magnetic field spins which are oriented in the direction opposite to the magnetic field; like a cone these millions and millions of tiny magnets which are present in the sample start undergoing precession, simultaneously. And alpha and beta components form 2 different types of cones like this. And this type of precession is, as I said, is called the Larmor precession. Then you may ask me a question; ok, they are undergoing rotation, that is called precession. What is the frequency of precession? how fast they are rotating.

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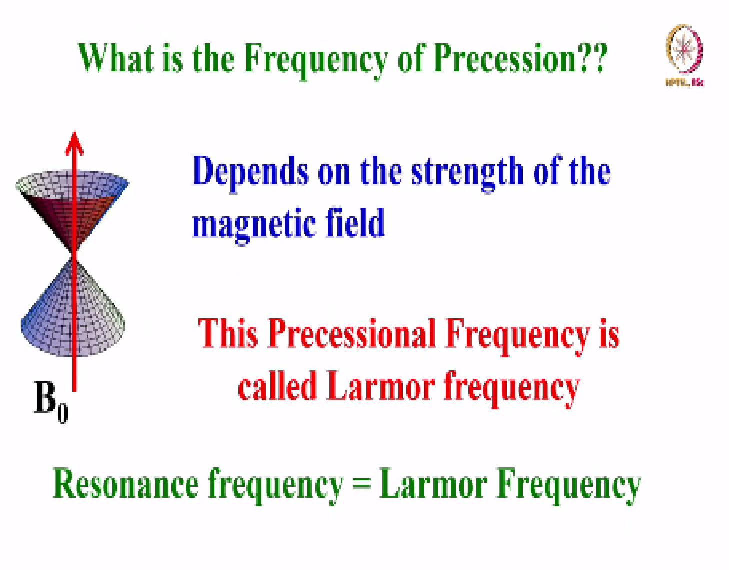

That depends upon the strength of the magnetic field. Larger the magnetic field you have, the precession frequency becomes larger and larger. Higher the magnetic field higher is the precessional frequency. If I increase the magnetic field they rotate very very fast. This precessional frequency is called Larmor frequency. Remember, we also calculated the resonance frequency; ν equal to gamma B naught over 2 pi.

I said it is the resonance condition; that frequency is the called resonance frequency; which is nothing but Larmor frequency. The frequency at which the nuclear spins are undergoing rotation or precession in a given magnetic field along the direction of the magnetic field is called Larmor precession.

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What is the energy involved ?

Radiation	Wavelength, λ (nm)	Frequency, ν (Hz)	Energy (kJ mol^{-1})
Cosmic rays	$<10^{-3}$	$>3 \times 10^{20}$	$>1.2 \times 10^{8}$
Gamma rays	10^{-1}–10^{-3}	3×10^{18}–3×10^{20}	1.2×10^{6}–1.2×10^{8}
X-rays	10–10^{-1}	3×10^{16}–3×10^{18}	1.2×10^{4}–1.2×10^{6}
Far ultraviolet	200–10	1.5×10^{15}–3×10^{16}	6×10^{2}–1.2×10^{4}
Ultraviolet	380–200	8×10^{14}–1.5×10^{15}	3.2×10^{2}–6×10^{2}
Visible	780–380	4×10^{14}–8×10^{14}	1.6×10^{2}–3.2×10^{2}
Infrared	3×10^{4}–780	10^{13}–4×10^{14}	4–1.6×10^{2}
Far infrared	3×10^{5}–3×10^{4}	10^{12}–10^{13}	0.4–4
Microwave	3×10^{7}–3×10^{5}	10^{10}–10^{12}	4×10^{-3}–0.4
Radio frequency	10^{11}–3×10^{7}	10^{6}–10^{10}	4×10^{-7}–4×10^{-3}

NMR spectroscopy falls in very low energy region

Now, the question is you may ask me what is the energy involved? See in the varieties of molecular spectroscopy techniques, in this table you can see it starts from cosmic rays, gamma rays, etc., you can see wavelength. frequency and energy. In the last column you see energy, the radio frequency comes in the last row at the bottom of the table. That means, look at the energy; some of the energy is very large; you know for example, gamma ray 1.2 into 10 to the power of 6 and it goes up to 10 to the power of eight; such a large interaction energy. Whereas, the radio frequency is at the end, only see 10 per minus 7 to 10 power minus 3. Very very weak interaction; the energy of interaction is very weak in NMR. The beauty is, this weak interaction is the strength of NMR. Because of this, you can understand, you can study the minute perturbations of the electronic charge distribution at the site of the nucleus can be very easily studied by using NMR. So, the weak interaction energy is actually the strength of NMR.

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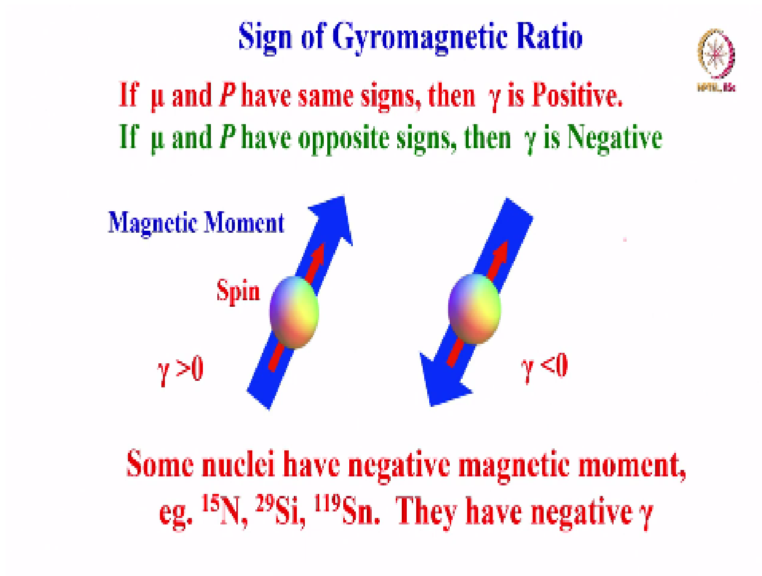

So, now with this I will introduce what is called sign of gyromagnetic ratio. I said we use a magnetic moment, and use the angular momentum. Both of them have the same sign, they can positive or negative signs. If both of them have the same signs, then gamma is positive. If both of them are opposite in signs, gamma is negative. So, how does it matter? See, if the magnetic moment and spin, both have the same signs, orient in the same direction, then the gamma is positive, if they orient in opposite directions, the gamma is negative. Some nuclei, for example, nitrogen 15, silicon-29, tin-119, all have negative gamma. You may ask me so what? positive or negative, it is a simple number, how does it matter if it is positive or negative? It has an importance as far as the precession is concerned.

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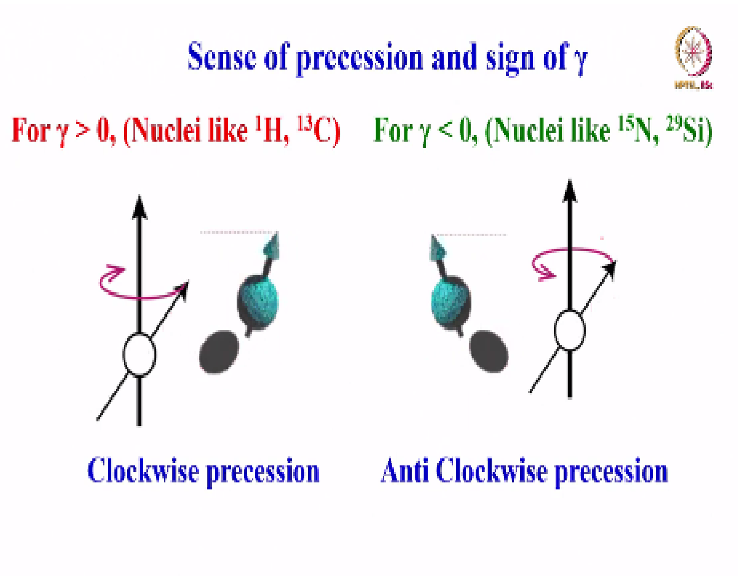

For example, the sense of precession changes with the sign of gamma. For example, for gamma greater than 0 it is rotating clockwise like this. For example protons, you put protons in the magnetic field they start rotating like this, in the clockwise direction. Similarly carbon also precess clockwise. All nuclei with gamma greater than 0, that are positive, rotate like this. Now, what about other nuclei with gamma less than 0. You see, now, they are rotating in the opposite direction; like nitrogen-15 and silicon-29. Their signs of gamma are different. Their sense of precession will be different. One is the clockwise precession and the other is the anti clockwise precession. These are very very important in NMR when you want to understand lots of things.

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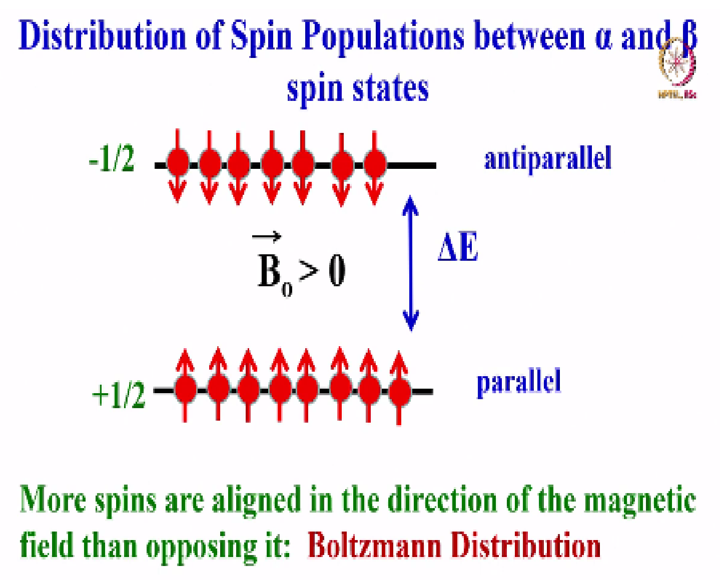

Now, I will introduce a term called population difference here. What is the population difference? The distribution has spin populations between alpha and beta spin states NMR is given like this, I told you there is energy separation in the magnetic field, for minus half plus half spin states, and we also calculated the difference in the energy Delta E. But, what happens is, there is a distribution law called Boltzmann distribution law.

According to which the more spins are aligned in the direction of the magnetic field than opposing it. It is a very important condition called Boltzmann distribution condition. NMR signal what you are going to detect here is the difference in this spin populations. If both of them are equal, what will happen? population difference is 0, that means you do not see signal. There must be a difference in population, only then you can see the signal.

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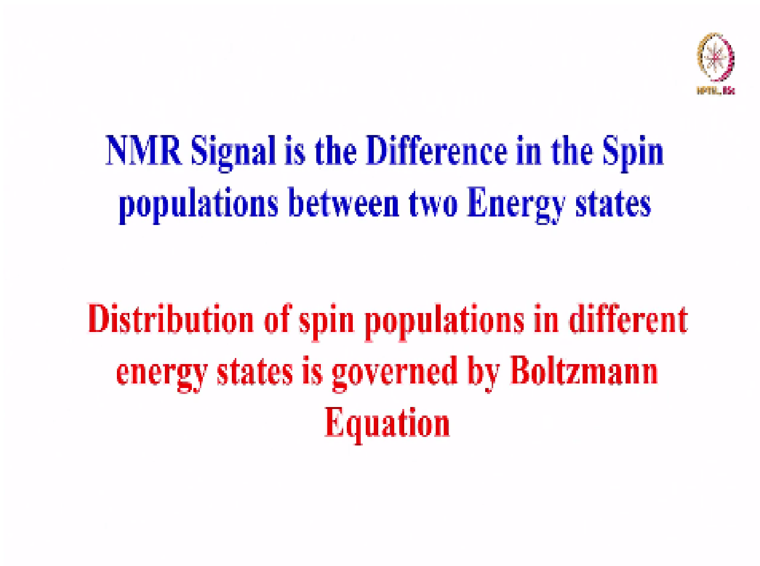

So, NMR signal is the difference in the spin populations between 2 energy states; but distribution has been population in different energy states is governed by what is called a Boltzmann equation.

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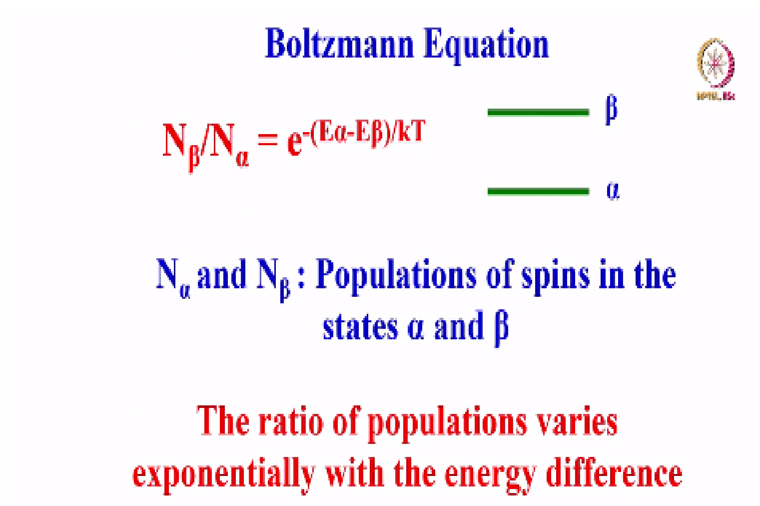

Which is given like this N beta over N alpha; beta and alpha are spin states, and the N beta and N alpha are spin populations in the alpha and beta spin states; and is given by an exponential law E = - (Ealpha - Ebeta) divided by kT. So, if you know the difference in the energy between alpha and beta spin states, if you know what is T, the temperature, k is a Boltzmann constant; you can find out what is the population difference.

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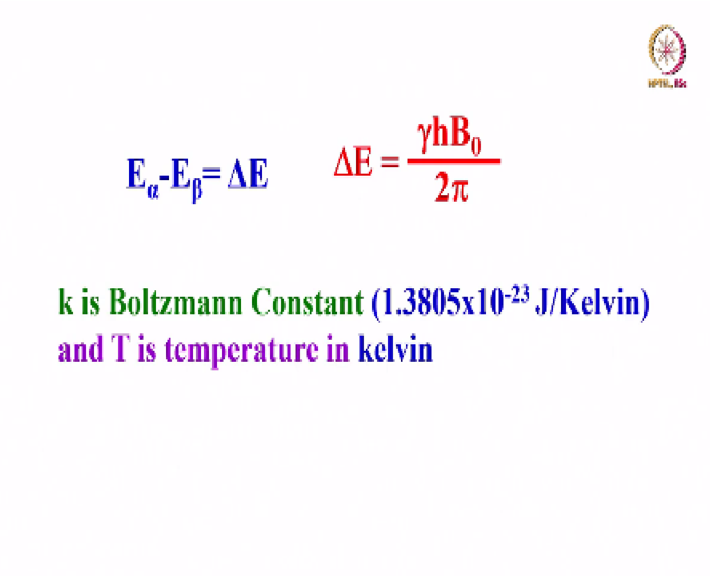

Very easy, I can do that. Ealpha and Ebeta, I know; I know what is deltaE, I know what is the Boltzmann constant, its value, I know what is the temperature T which is in Kelvin. I can calculate everything. So, with this now, let us see, what will happen to NMR sensitivity, can I calculate that?

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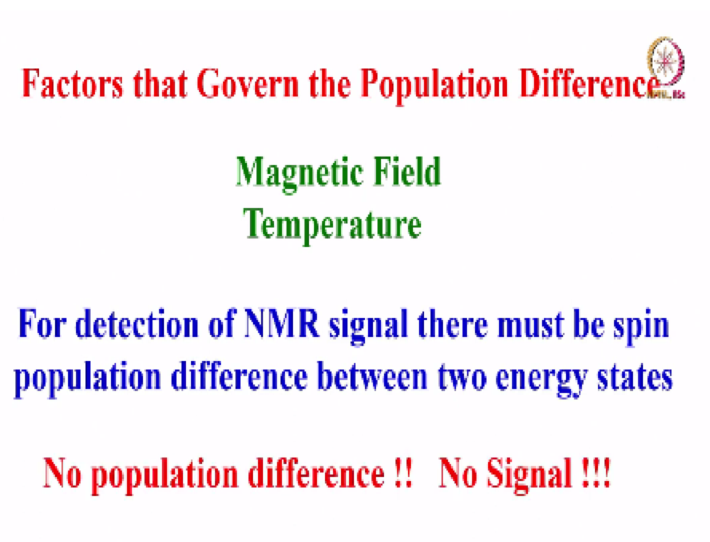

There are factors that govern the NMR population difference, one is the magnetic field, and the other is the temperature. For example, for detection of NMR signal there must be spin population difference, which I told you, when there is no population difference, I also said there is no signal. How the magnetic field and the temperature govern the population difference. Let us see that.

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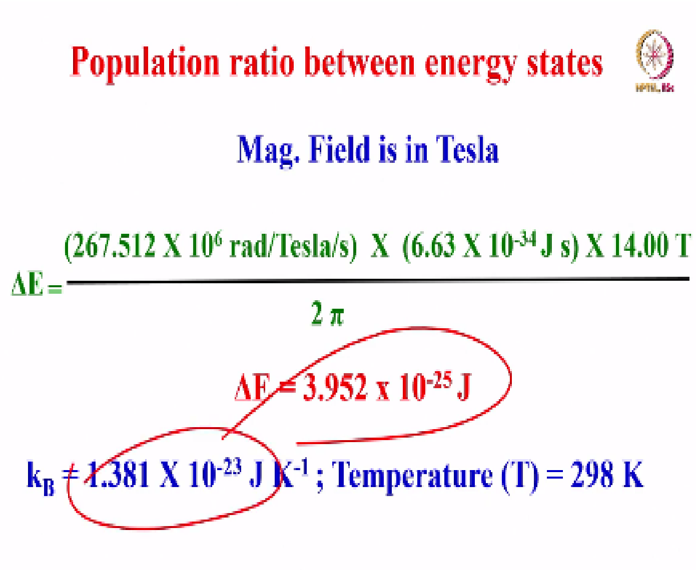

And this is the population difference Delta E, which I showed in the 2 slides before. I know what is gamma, I know what is Boltzmann constant, I know what is energy and I know the magnetic field. Simply substitute all these parameters in this equation. Calculate delta E. It turns out to be 3.952 into 10 to power - 25 joules. I know Boltzmann constant, I know the temperature, say ambient temperature 298 k; and in a given magnet field, which should be always in Tesla. say 14 Tesla.

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$$N_\beta/N_\alpha = e^{-(E\alpha - E\beta)/kT}$$

$$N_\beta/N_\alpha = \exp[-3.952 \times 10^{-25}\ J / (1.381 \times 10^{-23}\ J\ K^{-1} * T)]$$

$$N_\beta/N_\alpha = 0.999904$$

If you do that, what are you going to see. Calculate this, substituting this value and the population difference. If you calculate delta value, substitute in this. Now N beta / N alpha turns out to be 0.999904. What do you understand by this ratio? It is close to 1; 0.999904 that means, N beta over N alpha is almost equal to 1; which tells you the population difference between beta states and alpha states are almost identical, with negligible a small difference in populations.

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At Room Temperature

Eg: For 2 million proton spins in a 14 T Field at thermal equilibrium, at room temperature

The population ratio will be 0.999904.

β — 9,99,952

α — 1,000,048

And you can calculate this at room temperature. If I consider 2 million proton spins; and take a magnetic field that is14 Tesla. I calculated myself by putting into the equation and calculated population ratio turns out to be 0. 999904. Then I calculate how many spins are there in the alpha state. How many spins are there in the beta state.

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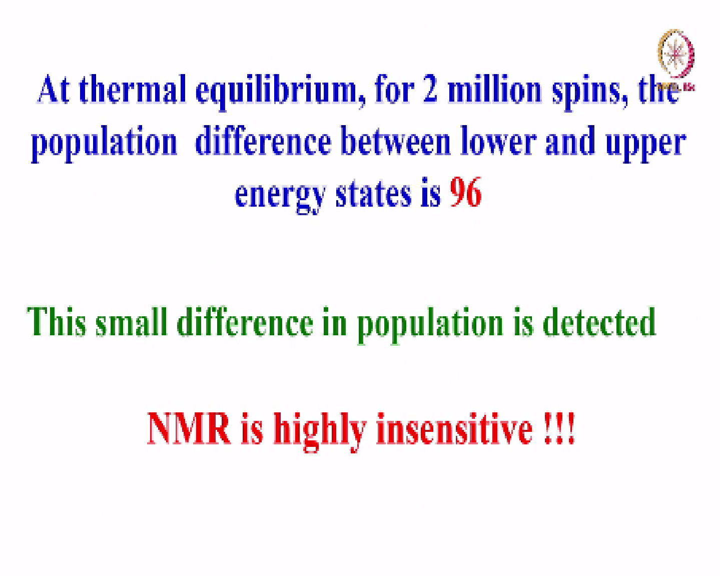

And I found out the difference. Difference is 96. My god, look at it. There are 2 million nuclear spins, I took as an example. And at the room temperature, in a given magnetic field of 14 Tesla, I found out the population difference is only 96. And that is what we have to detect, the difference in spin populations. The small population difference if we have to detect, what does it tell you? NMR is highly insensitive technique. Very very insensitive technique. And there is something which I want to tell you about sensitivity and the magnetic field. Now, let us see what happens if I change the magnetic field.

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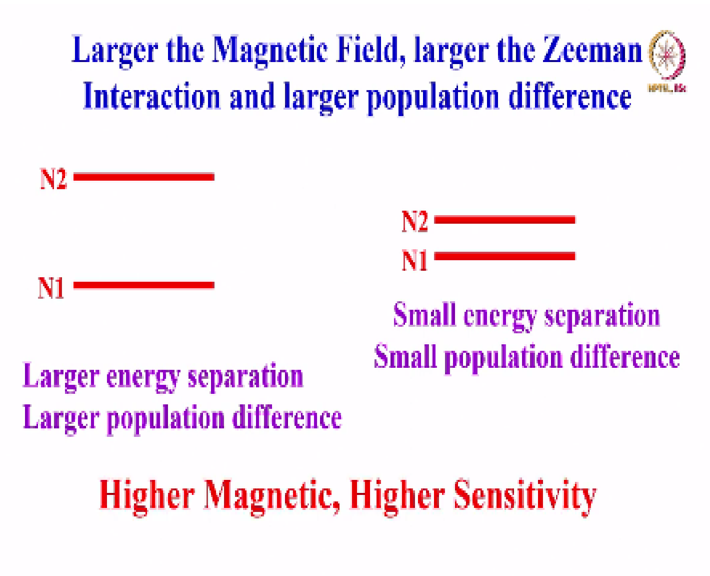

When I change the magnetic field I told you Zeeman interaction, which is the interaction of the magnetic moment with the magnetic field, which is larger. Larger the interaction, larger the population difference. That means, the energy separation becomes larger and larger if we increase the magnetic field. The smaller the magnetic field, smaller is the energy separation. So, larger the population difference means larger energy separation, smaller population difference means smaller energy separation.

So, that means, the magnetic field has a direct relevance as far as the Zeeman interaction and the population difference is concerned. It clearly tells me higher the magnetic field higher sensitivity.

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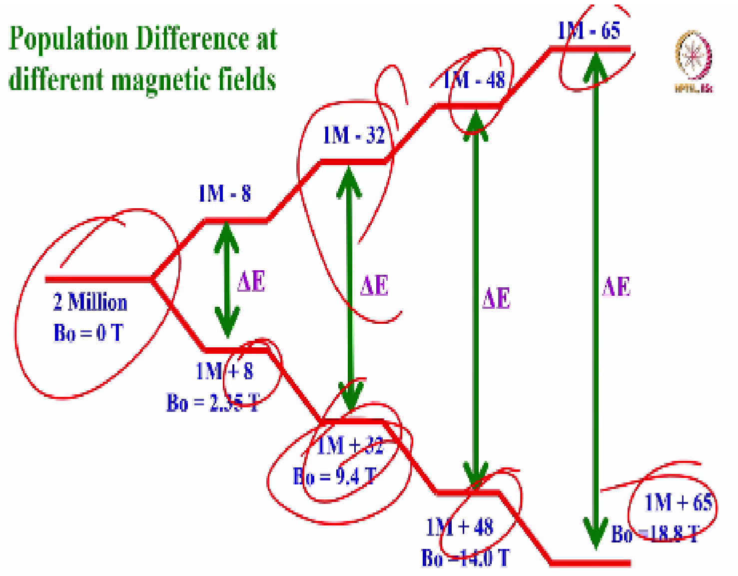

Population difference at different magnetic fields I have calculated. You can see that I started with 2 million spins in the absence of the magnetic field; B_0 = 0, states are degenerate; there is no separation of energy levels; all spins are in the same energy level, randomly distributed. Now at 2.35 Tesla there is a separation of the energy levels and the population excess is very small only 16. Here 64 when we change the magnetic field, 4 times larger; see here 32; whereas, I again increased further it becomes, 96. That is what we calculate for 14 Tesla. Now, even increase further also it became 130. What does it mean? you increase the magnetic field enormously upto 18.8 Tesla. Remember such a large magnetic field, to get homogenous magnetic field is not an easy job, it is very very challenging, and is not easy. Nevertheless, if you get it what gain we got? From 0, we could get only the difference in spin population of only 130. Is it a worthy exercise? Yes, even though it appears like this, in turn you will see there is a big gain in the sensitivity by go into higher magnetic field.

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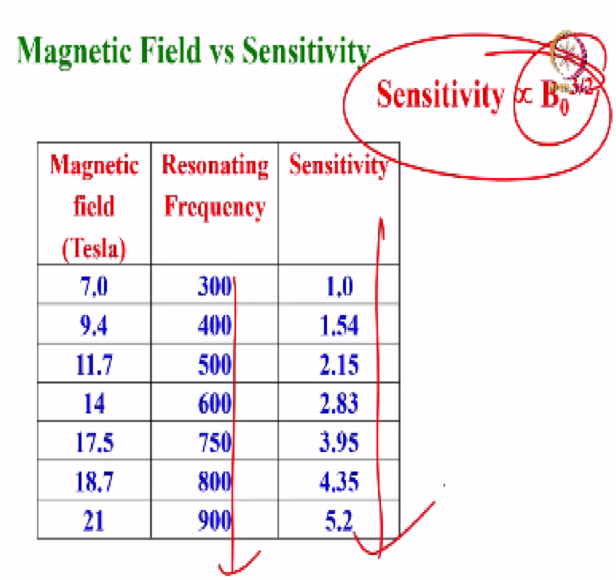

Magnetic field (Tesla)	Resonating Frequency	Sensitivity
7.0	300	1.0
9.4	400	1.54
11.7	500	2.15
14	600	2.83
17.5	750	3.95
18.7	800	4.35
21	900	5.2

So, higher the magnetic field you will see the sensitivity goes to the power of B_0 to the power of 3/2. B_0 is a magnetic field, the static magnetic field and the power of 3/2. You will see that, as I keep on increasing the magnetic field in this direction, the sensitivity keeps going up and up. And remember the sensitivity with respect to magnetic field is given by B_0 to the power of 3/2.

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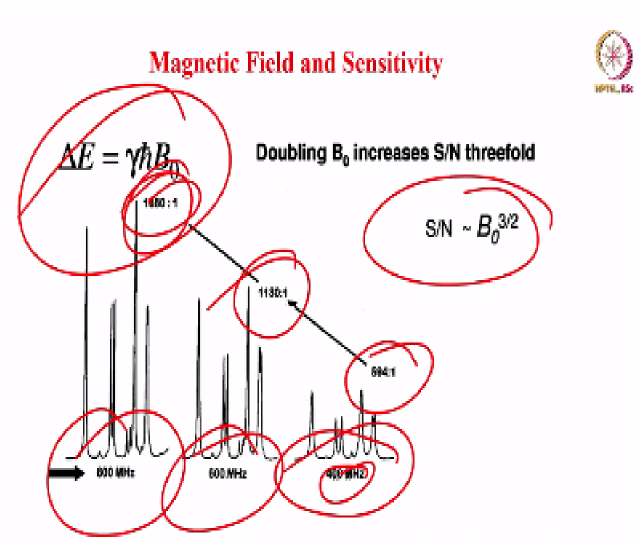

So, this is a spectrum which shows you as you keep on increasing the resonating frequency from 400 megahertz, 600 megahertz and 800 megahertz, you see the energy separation, you calculate, and the population ratio if you find out, I mean the signal to noise ratio, here to here, See here, it is about 600, the signal to noise ratio is about 1200, here is about 1700. So, by changing the magnetic field, you are increasing the sensitivity. So, higher the magnetic field, higher the sensitivity.

So, this is another important factor, the magnetic field, which governs the sensitivity of the detected NMR signal. So, now the time is up. I am going to stop here. But let me summarize what we discussed today. We started discussing about the interaction of the magnetic moments with the magnetic field, we calculated the energy, different energy states and equated it to find out the resonating condition ν = gamma in to B_0 over 2 pi also we worked out. And then we also gave the classical analogy, we calculated what is the Larmor precision frequency. And we found out in the given magnetic field what is the resonating frequency of a proton, what is the resonating frequency for the carbon at different magnetic fields and we found that they are all in megahertz range; and what is megahertz range? Radio frequency we know ranges from kilo hertz to gigahertz range. So, we understood NMR spectroscopy appears in the radio frequency region.

And if I know that the resonating frequency of protons in a given magnetic field, if I do not know the magnetic field, once I know the resonating frequency, because know gamma I can even calculate what is the strength of the magnetic field. And we knew and we calculated the population difference, the sensitivity of NMR is very, very low. And we saw by increasing the magnetic field the population difference can be enhanced, not enormously, but still it is sufficient enough to get the good signal to noise ratio.

So, sensitivity also depends upon the magnetic field, which in turn depends upon the energy separation, which increases energy separation. And we understood Boltzmann population ratio is the one which governs the population difference between 2 energy states. So, we understood NMR is insensitive technique. By increasing the magnetic field we can get the sensitivity. That is what we understood today. We will stop here and continue from in the next class. Thank you.