One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis

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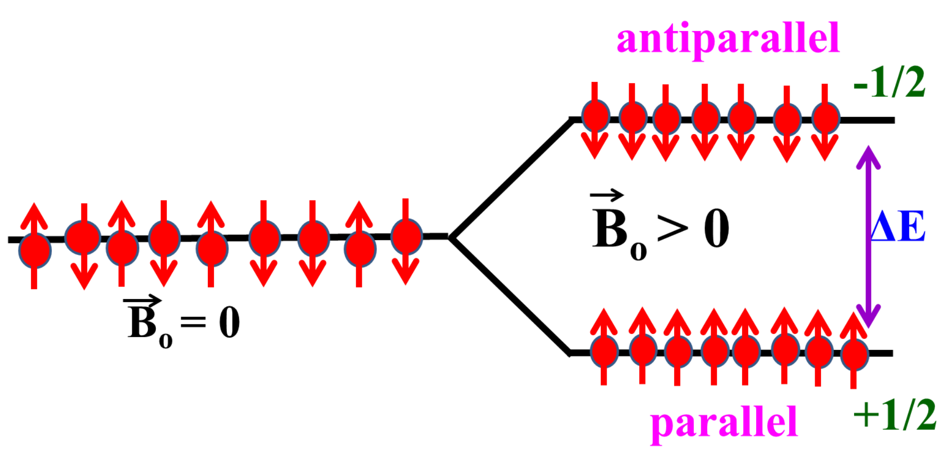
Lecture 02 - NMR spin physics-I

Welcome all of you. In the last class, I gave general introduction to nuclear spin and how to arrive at the nuclear spin quantum of the nucleus based on the simple empirical formula depending upon atomic mass and atomic number of different elements. I also discussed about two important quantum numbers; spin quantum number I and the magnetic quantum number m. And I said they are related to each other; they are quantized and I also discussed m depends upon I; for particular value of m we have different quantization directions which takes the value from -I to +I in steps of 1. For example, for spin half nuclei we have two possible orientations; minus half and plus half. And we also worked out what is the magnitude of this quantization direction; what is this magnitude of spin angular momentum also we worked out. And I said there is a magnetic moment mu because we can treat spin of nucleus as a tiny magnet.

This magnetic moment μ is dependent on what is called gyromagnetic ratio of the given nucleus. This is constant for a given nucleus, and is different for different nuclei. And I said even though proton and carbon have same I and same m; I is equal to half m equal to minus half and plus half, the gammas are different because it depends upon mass. As a consequence magnetic moment μ is different. Since μ is different we can study independently. Individually these two can be studied. So, that is what I said for any element of the periodic table if you look at, the gamma is different. As a consequence every element of the periodic table can be studied. So, long as the nucleus possesses a spin, it can be individually studied by NMR this is what I discussed last time.

Now, we will go further today and I will introduce what is called Zeeman interaction. What is the Zeeman interaction? What is the basic requirement of NMR is the interaction of the magnetic moment μ with the static magnetic field, ie. the external magnetic field. It is the huge magnetic field which is static and denoted as B_0. The magnetic moment μ of the nucleus should interact with this. So, the nucleus spin quantum number I must be non-zero. That is what I said. I told you μ depends upon this I and if I is equal to 0, I worked out and showed you in the last class, μ is 0. Since μ is 0 there is no NMR. That means I must be present to detect NMR. That is the reason why for the nucleus whose is spin is 0, there is no NMR. That is what we discussed and this is what I showed you last time and also again I am writing μ is equal to gamma into h cross I into I plus 1. And the interaction of μ with B0. As soon as you put the nuclear spin inside the external static magnetic field, what is going to happen? The nuclear spins start aligning with the static magnetic field. Initially they are all randomly oriented; there is no preferred orientation direction of the nuclear spins. As soon as you put them in the external magnetic field they start aligning with the static magnetic field. Then how do they align? Some of them align in the direction of the field, some of them align in the direction opposite to that of the field. These are the preferred orientation directions and the energies of interactions for both these orientations are different. If the spins are aligned in this direction it has one type of energy; if the spins are aligned in the direction opposite to magnetic field, it has different energy. And these two energies are different; and in fact we can calculate these two energies. In the absence of the magnetic field these two energies states are not separated; they are degenerate states, in the absence of the magnetic field. As soon as you put it in the magnetic field then there is a removal of degeneracy. The energy levels get separated out for both spin half or orientation in the direction of the field; and the orientation in the direction opposite to that of the field. Both get separated out. And you can also understand from Boltzmann distribution more spins are aligned in the direction of the magnetic field than are opposing it. This is a Boltzmann requirement; a Boltzmann distribution. This is what is going to happen and this method of way of separation of the two energy states is called removal of degeneracy by the interaction of the magnetic movements with the external magnetic field. It is called Zeeman effect.



Now, for spin half nuclei we can work out by simple mathematics. E equal to minus μ dot B_0; μ is the magnetic moment and B_0 is the static magnetic field.

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

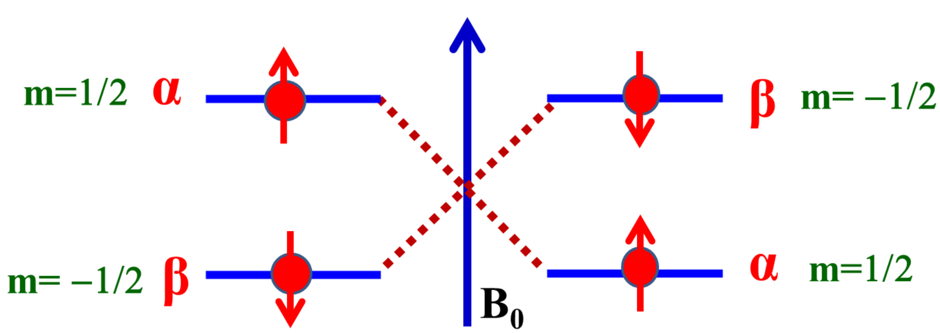
In the absence of the magnetic field, B_0 is equal to 0; you can see all the spins are oriented in random, there is no preferred orientation. Both orientations in the direction of the field; up and down both the spin states are not separated. They are degenerate stated. You cannot separate them out in the in the absence of the magnetic field; when B_0 is equal to 0. Now, as soon as I put it in the magnetic field which is nonzero then what is going to happen is there is a separation of the energy states. One correspond to minus half other correspond to plus half. This is for the anti parallel orientation; this is for the parallel orientation. This is the orientation in the direction of the field. This is the orientation in the direction opposite to that of the field. And when there is a separation of the energy you can find out what is the energy difference That means, we can find out what is delta E; and you all know once it is this thing as I told you there are more spins in the direction of the field than in the direction opposite to the field. There is small excess population of the nuclear spins in the state alpha, which is equal to plus half. And this is called the removal of degeneracy. Now energy of interaction of the magnetic moment with the magnetic field we can calculate.

How do we do that? E equal to minus μ dot B_0 That is an equation, a general equation written. You can ask me a question why did I write negative? E the energy is always positive; but it is to ensure that the spins oriented in the direction of the external magnetic field has lower energy. That is the assumption, that is the reason why deliberately E has been put negative sign. So interaction energy is given by μ dot B_0. Both are vectors, it is a dot product of the vectors. This is the energy of interaction of magnetic moment for two different spin states. E is equal to plus half and minus half; For E alpha and E beta we can work out the energy like this.

$$E_\alpha = - ½\gamma h B_Z /2\pi$$

$$E_\beta = ½\gamma h B_Z /2\pi$$

One is minus half gamma H Bz over 2 pi; other is plus half gamma Bz over 2 pi. Notice the energy of the beta state here is more than the alpha state. Of course you know why because E equal to minus mu dot B_0, mu dot B_0 I told you. So since minus is there, E beta state is minus into minus half, is plus half. As a consequence always we see that as soon as you put it in the magnetic field; this is the higher energy state m equal to minus half; this m equal to plus half is the lower energy state.

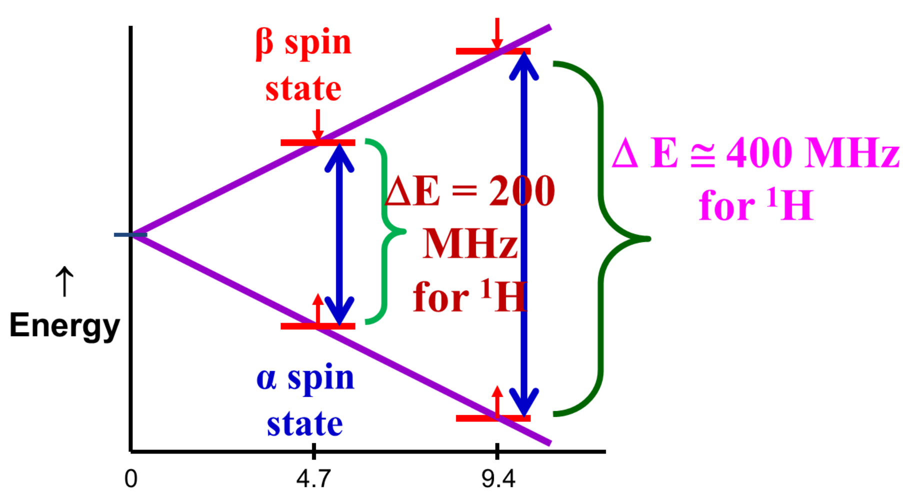


This is what is going to happen so as soon as you put the spins in the magnetic field. So this is the energy separation this is the energy of each of these two spin states; E alpha and E beta. When I calculate the energy of each of these two states; I can calculate the difference in the energy ΔE.

$$\Delta E = \gamma h B_0 / 2\pi$$

Simple equation; from the previous equation you can calculate. Of course you all know energy separation is related to frequency; H nu; equate these two now. Then what will happen when equating these two and do some simple jugglery you will find out nu is equal to gamma into B_0 over 2 pi. This is a important equation of NMR called the resonance condition where nu is equal to gamma B naught and over 2 into pi. This is the resonance condition. This basic equation is the one which is responsible for seeing NMR signal and this is the equation which has given four noble pressures in NMR, a simple equation. So the research carried out in this NMR spectroscopy is based only on this equation, a basic equation; the n resonance condition, gave four noble prizes. So this is what is the basic resonance equation and as you can see here υ is a constant for a given nucleus. I told you 2 is a constant pi is a constant and of course magnetic field you can keep yourself constant; there is no need to vary it. That means frequency is constant. Now I will double the magnetic field what will happen? This will get doubled because other three parameters remain same. That means the resonance frequency is varies linearly with the magnetic field. If I have a magnet and I get the resonating frequency for a given nucleus I calculate for a particular spin for a like proton or carbon, or nitrogen, whatever it is; and if I double the magnetic field simply the resonating frequency I have to double it. That is what happens; the resonance frequency gets doubled by linearly changing the magnetic field.

And this is what



happens; the energy level gets separated out because the frequency gets doubled. The frequency is related to energy separation; as a consequence when we double the magnetic field; the energy difference also gets doubled. This is what happens. For example, at a given magnetic field 4.7 tesla this is alpha state and beta state I calculate the energy difference and let us say this is the 200 MHz, I calculate. I simply double the magnetic field go to 9.4 tesla. See what is going to happen now; the ΔE is equal to 400 MHz. Now just doubling the magnetic field 4.7 to 9.4 the energy separation became double and the resonating frequency also doubled. There are few advantages of this; as we go ahead I will tell you. When you increase the magnetic field you have increase the sensitivity and you also have increased resolution. So, when you are doing the NMR, the peaks if you are seeing the NMR resonance at higher and higher magnetic field get dispersed. There are certain advantages of sensitivity and resolution as we go ahead further we will discuss these things.

This is a simple table. Look at in this column we have a magnetic field, put here in this column, the resonating frequency look at it at 100 megahertz the resonating frequency magnetic field is 2.3487 tesla.

B_o (In Tesla)	MHz
1.4092	60
2.3487	100
4.6974	200
7.0461	300
9.3950	400
11.7435	500
18.7898	800
23.4870	1000

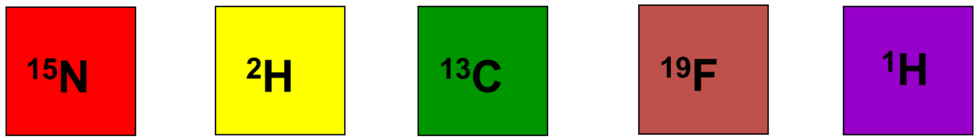
Remember magnetic field is always expressed in tesla; one tesla means 10000 gauss; very strong magnetic field; in fact very very strong magnetic field. Now I double the magnetic field 2.3 become 4.6; already you go to 200 MHz. In fact what I am going to do is I am going to increase it 8 times 2.34; I make it 18.78. You see the resonating frequency became 8 times larger. This is basically what is going to happen. So, resonating frequency varies linearly with the external magnetic field. With this now I want to tell you one thing, where does NMR spectroscopy appear in the electromagnetic spectrum. Remember in the very first slide I showed you the electromagnetic spectrum; and I said NMR spectroscopy appears in the radio frequency region; correct? let us understand this, whether it is true or not. We will calculate ourselves I know the resonating equation, the resonating condition; I know all the other parameters. I will fix the magnetic field as 2.35 tesla and I know what is the gamma value for proton it is 26 point something into 10 to the power of 7 radians per tesla per second. I plug in all these values into this equation and then calculate what is the resonating frequency. It turns out to be 100 MHz, which is the radio frequency region. Now I will double the magnetic, I will increase the magnetic field to a large value. I go to 14.1 tesla; plug in this value. All other parameters remain same, I am not changing it. If I plug in the value for all of them and work out you will see resonating frequency is now 600 MHz. For a given magnetic field of 2 point something it was 100 megahertz; now when it is 14.31 Tesla it is 600 MHz. What about carbon in this magnetic field? where does carbon resonate? I know proton resonates in two different magnetic field at 100 MHz and 600 MHz, I calculated. Now where does carbon come? put the value of carbon gamma that is 6.725; all other parameters remain same; only gamma is different. I plug in those values and calculate at 100 MHz of the proton where the magnetic field is going to be 2.35 tesla; the resonating frequency is 25. 15 MHz.

Remember for this magnetic field proton was resonating at 100 MHz. The gamma of carbon is 4 times smaller; as a consequence the resonating frequency of the carbon is 4 times smaller. Same thing; now go to the higher magnetic field where we calculated for proton that was we got 600 MHz; but now for this if you plug in the value of gamma for carbon it turns out to be 150 megahertz. So that shows for all these nuclei with two examples which I took NMR is coming in the MHz frequency range, which is in the radio frequency region. That is why NMR comes in the radio frequency region; because the radio frequency region from small few of megahertz to few gigahertz. As a consequence we are going to observe NMR in the radio frequency region.

Now let us do reverse engineering, let us say I have protons in a given molecule which in a given magnetic field resonating at 300 MHz. Now if I ask you what is its magnetic field strength? of course we can calculate it, what we will do is plug in this value; earlier you plugged in value for B_0 and calculated what is the resonating frequency. Now I know the resonating frequency I have to calculate B_0. Rerearrange this equation now plug in the values for 2 pi nu; what is the resonating frequency 300 megahertz I know the value of gamma calculated for example for a certain value for this 300 MHz. B_0 turns out to be 7.04 Tesla. See we know how to calculate the magnetic field strength when I know the resonating frequency of a particular nucleus. I can calculate at what magnetic field the experiment was done or in other words if you tell me what is the magnetic field strength you have, I can tell you different nuclei will resonate at which frequency; that is what are the frequencies at which different nuclei will resonate. That is what I can detect, I can calculate. Okay so what is the radio frequency range? it goes from 20 kilohertz to several gigahertz. Where did we calculate the resonating frequency of proton and carbon for different magnetic fields they were all in megahertz. As a consequence I am telling you NMR is detected in the radio frequency region this is what I said in the very first slide; when I showed the slide where electromagnetic spectrum are shown, and I asked a question where does NMR comes and I said is RFregion and this is what it is. We can confirm it because now we know the resonating condition; we know gamma, we know υ_0. We can plug in the values and get the resonating frequency and these are all in the radio frequency region.

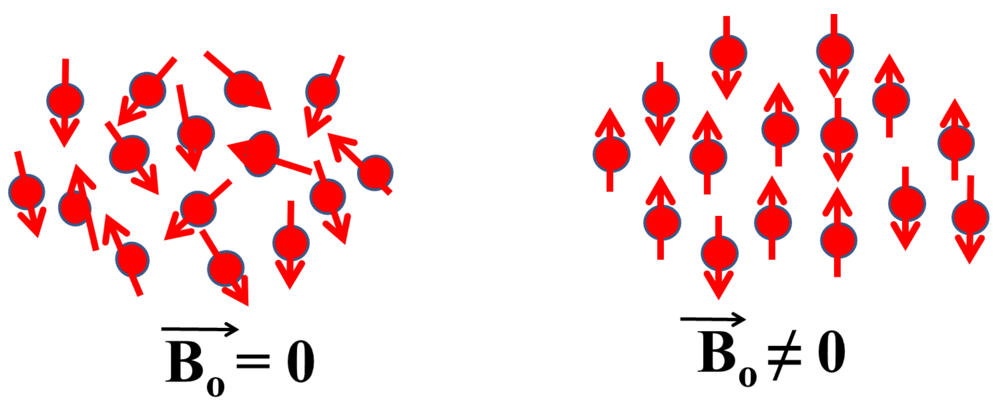
Okay now if you look at it if you go to any NMR laboratory you will see big cylinders like this; okay big big cylinders like this? what are these things? if you see, look at it there are some numbers written here; 400, 700, 600, what do this mean? what do this refers to? this is the resonating frequency of protons. These cylindrical materials what you see in any NMR lab; are huge magnets, strong magnets and if I say 400 here, that means in this magnetic field proton is resonating at 400 megahertz. In this magnetic field proton is resonating at 900 megahertz. This is what you have to understand. When you go and see in different NMR laboratories, you see different cylinders like this, with a number written on it. That is the spectrometer frequency at which protons are detected in a given magnetic field. This is the magnetic field and you should know the strength of this because you know what is the resonating frequency, that is what it is. And the highest magnetic field currently available for doing NMR is 28.2 Tesla, whose cost is close to 20 million dollars; very very huge. But only hardly some three or four such spectrometers are available in the world. It is very difficult to afford and also to purchase these things; so hardly some three four laboratories. It is just to give you an idea, the present-day world we can go up to 28.2 Tesla magnetic field where we can get the resonating frequency of protons at 1.2 gigahertz; huge magnetic field and resonating frequency is very huge. And this magnetic field strength, remember is nearly 6 lakh times stronger than that of the Earth's magnetic field. The Earth's magnetic field is only 50 micro Tesla and this is 28.2 Tesla.

What is one Tesla, it is equal to 10,000 Gauss. If you calculate this thing, it is going to be huge value. Okay so now we understood that NMR resonating frequency is in the radio frequency region, we know we calculated the resonating frequency in a given magnetic field for both proton and carbon. At two different magnetic fields, we calculated. Now let us see what is going to happen if you look at this.



I have a magnetic field at say 4.68 Tesla then if I say proton resonates at 200 MHz. Simply take the ratio of with gamma, if you know what is gamma. I can calculate fluorine comes at 188 MHz, the carbon comes at 50 MHz and 2H deuterium comes at 30 MHz and nitrogen comes at 20 MHz. These are the different resonating frequencies for different nuclei in a given magnetic field. Now change the magnetic field what will happen? I will increase it to 9.39 Tesla, then this correspondingly changes linearly because I double this so then you see keep on changing; 200 become 400 and keeps going like this; and I change it to some other value, increase it five times see now 200 became 500 this is fluorine 470 and nitrogen became 50 MHz. That means we can calculate the resonating frequency in any magnetic field for any nuclei. So in different magnetic fields, if you have different nuclei you can study and correspondingly the resonating frequencies are different. This is so far about little bit of understanding about resonating frequency and in different magnetic field strengths how we calculate the resonating frequency etcetera for different nuclei.

There is a classical analogy for this, which some of the people discuss in some chemistry books. What is this classical analogy? the classic analogy is very simple. I take the example spin half nuclei; as I told you spin half nuclei have only two possible orientations plus half and minus half.



In the absence of the magnetic field they are all randomly oriented. You see \there is no preferred orientation at all; they are all randomly oriented. As soon as I put them in a magnetic field these tiny magnets start aligning like this; you can see some are in the direction the field and some are in the direction opposite to the field. This is the magnetic field direction, they line up either parallel or opposite to the direction the magnetic field, as soon as I put in the magnetic field. And then what is going to happen? these two forces are there, which are acting on the nuclear spins in the magnetic field. One is the large magnetic field wants to pull it keep it aligned with that; and the spin angular momentum wants to keep at a restricted orientation. I told you know we can calculate the restricted orientation direction of quantization, we can calculate angle theta. I told you that is also fixed angle theta. At the same time the magnetic field wants to pull it towards it there are two forces acting. Then what is going to happen? it is like a tug of war, like a tug of war. There is going to be a torque created. As a consequence these two forces makes these nuclear spins to precess, that is to rotate around the magnetic field direction. This is called precession. This means rotation of a rotation rotating object is called precision, okay. So this starts rotating like this in a magnetic field. Now it looks like a cone which is opening upwards and cone opening downwards. The reason is for spin half nuclei you have two possible orientations; nuclear spins which are aligned like this, start rotating like this. The nuclear spins aligned like this start rotating like this.

As a consequence it appears like two cones, okay. This is what is happening and these two alpha beta components of the magnetic moment will have will have a particular quantization direction and start precessing in the magnetic field; because of the torque that is going to be produced due to two possible forces. This I explained and this is called Larmor precession. Remember this is called Larmor precession. Then the question you may ask me, okay they are precessing that is rotating at some speed, then what is the precession frequency? what is the speed at which they are rotating? what is the frequency of it? that you can work out. This is related to the magnetic field strength. Or in other words we calculated the energy separation between two energy states and then we got the resonating frequency, it is exactly the same. Okay the resonating frequency is the precession frequency and it is a Larmor frequency. It is nothing but the resonance frequency, the energy separation between two states if we calculate we know is the resonance condition; we can we calculate υ and υ is a resonating frequency which is also called Larmor precession frequency. So if I say Larmor frequency, remember it is nothing but the resonating frequency at a given nuclei in a given magnetic field. That is what it is. Now you may ask me a question what is the energy involved in this? see if you look at this energy, in this table there are so many things which are involved, here is a frequency, wavelength, radiation energy, for different type of spectroscopic techniques. But if you see the last column of it, you will see here radio frequency region energy is very very small.

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

Thus NMR spectroscopy falls in very very low energy region; very very low energy. compared to look at the gamma x-ray. They are 10 to the power of 8 here; 10 to the power of minus 7; 10 to the power of minus 3; several orders of magnitude smaller. so NMR spectroscopy is really a weak interaction energy; very very low energy region. Now I want to introduce one term called sign of the gamma. Remember I told you about precession frequency, the gamma is a gyromagnetic ratio for a given nucleus. Now this gamma has a particular sign. If I calculate them if I know the magnetic moment μ; if you know the angular momentum P; if both of them are the same sign then gamma is positive; if mu and P have opposite signs; gamma is negative; this is what it is. This is a magnetic moment, this is the nuclear spin angular momentum, if they have same orientation, it is positive sign; the gamma is greater than 0 positive. And now if they are opposite, that is angular momentum is like this, the spin angular momentum and the magnetic moment is like this; the opposite signs, then gamma is negative.

So what? you may ask me a question okay gamma is positive gamma is negative, how does it matter for us? this matters because some nuclei which have a negative magnetic moment like this; some have positive magnetic moment. But those which have a positive magnetic moment precess in the direction opposite to that of the nuclei with negatige gamma.

For example if I have a proton; proton is rotating like this clockwise \ let us say, which has a positive gamma. Other nuclei like nitrogen-15, etc they rotate in the opposite direction because gamma is different so the direction of precession is different okay. But the resulting frequency remains same then you ask me a question how does it matter? its utility comes in many applications. If you know this only, you will understand. For example I want to do heteronuclear double quantum which I don't know whether I have time to discuss, we'll see at the end or the heteronuclear double quantum between proton and nitrogen one has a positive gamma other has a negative gamma they both precess in the opposite directions, so when the double quantum instead of adding it may get subtracted; it may become negative. We will discuss if there is a time later so these are all the consequences of precession of the nuclear spins either in the clockwise direction or in the anti-clockwise direction. So this is the concept which you have to know the sign of the gamma and the direction of precession is given like this. If the gamma is greater than 0 like proton and carbon, they are rotating like this in the clockwise. For gamma negative they are rotating in the opposite direction. Can you see the nuclear spins rotating both in the opposite directions? okay this is a clockwise precision this is anti-clockwise precision. this is the thing we should know, okay.

Now I will introduce a term called population difference what is the population difference? As I told you there are more spins aligned in the direction of the field than opposing it. This is because of the Boltzmann population distribution. That is a Boltzmann equation and this is equation is given by this the ratio of this spin population in beta and alpha states is given by this equation. It is an exponentially decaying function divided by K into T; K is the Boltzmann constant, okay. Now if I consider two energy states of a spin half nucleus, I have two orientations; plus half and minus half of states. There are number of spins like this there are more spins in this direction than in this direction. That all we know. This is anti parallel orientation this is a parallel orientation; fine. So now the advantage is there are more spins here, than here. If I take the difference between the nuclear spins, there is a population. If the number of spins in this state and number of spins in this state are exactly equal then we calculate the difference in spin population, it is 0. You will not see NMR. I will tell you as we go ahead further, there must be population difference to see the signal. Fortunately Boltzmann condition helps us to have more spins in the lower energy state than in the higher energy state, okay.

So with this we will have to discuss something about sensitivity of NMR. How do we detect the singal, what is sensitivity for different nuclei? what is selection rule ? how do we induce a resonance? This is little bit of discussion. So I think the time is up, I am going to stop here. What we discussed today, is about resonance condition, and then I have worked out what is resonating frequency for different nuclei in different magnetic fields; and we came to know that NMR comes in the radio frequency region; and if you know the resonating frequency we know how to calculate the magnetic field strength, and for different magnetic fields what is the resonating frequency for different nuclei we worked out. It simply linearly varies with gamma that also we understood. So with all these things we got an idea about what is happening for the nuclear spins in a given magnetic field. Then I calculated the energy difference and then frequency. We discussed the same thing using classical analogy. I said, it is nothing but the Larmor frequency, the precision frequency is called a Larmor frequency, which is nothing but the resonating frequency. And also we discussed something about positive and negative gamma of the nuclei. If the two nuclei have positive gamma negative gamma why it is positive negative I discussed one which has a positive gamma they precesss in same direction. If the two nuclei have opposite gamma, they precess in the opposite directions. In a given magnetic field one precess in the clockwise direction and the other precess in the anticlockwise direction. It is is an important term and all these have consequences. With this I am going to stop here. We will discuss something about NMR sensitivity how do you get the resonance, everything in the next class. Thank you very much