One and Two Dimensional NMR Spectroscopy for Chemists

Prof. N. Suryaprakash
NMR Research Centre
Indian Institute of Science- Banglore

Lecture No -3
Interaction of Spins with the Magnetic Field

Welcome back. So, in the last two classes we started understanding some fundamental spin physics required for understanding NMR spectroscopy especially one and two-dimensional NMR and its applications. In the last class I introduced to you about spin angular momentum P whose direction I said was quantized along Z axis P_Z. I also said P_Z is equal to m into h cross, m is the magnetic quantum number.

This magnetic quantum number I, am sorry m, depends upon spin quantum number I and takes the values from minus I to plus I. So, these defines the directions of quantization. The quantization is defined by number minus I to plus I. Now if you want to know the quantization directions for spin half, we got minus half and plus half only two. Similarly, for spin one the quantization directions were -1, 0 and 1.

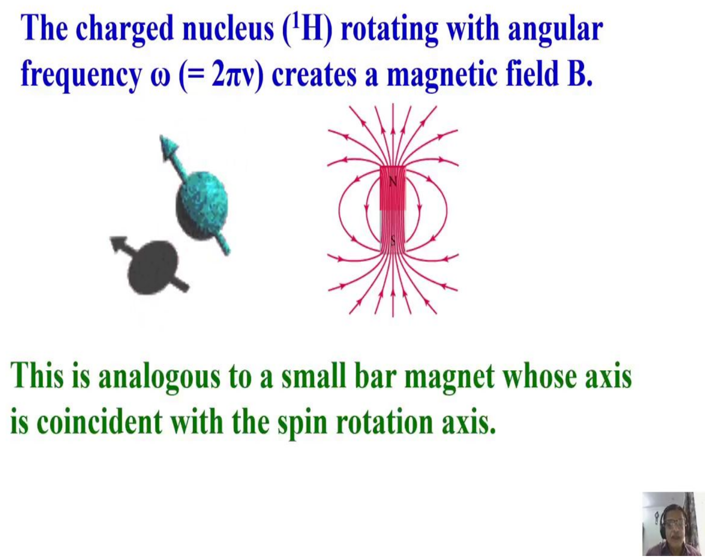
We also found out the angles of the directions of these vectors of the quantization directions. we also worked out the angles and we got their magnitudes.

(Refer Slide Time: 01:52)

Nuclear Magnetic Moment (μ)

From today we will go further and I introduce another parameter magnetic moment μ.

(Refer Slide Time: 02:03)



This is defined as μ. We will start like this, what is nuclear magnetic moment. If you have a charged nucleus rotating with some angular velocity omega which I know is equal to 2Pi into frequency ν, then it creates a magnetic field. You know that, charged nucleus rotating with angular velocity gives a magnetic field. Let us say this charged nucleus as spin which is rotating spin undergoing precision. So it has to create a magnetic field. So it is analogous to a small bar magnet with two poles, north and South Pole. So, that means you can interpret this spin as a small dipole. A small tiny magnet. This is analogous to the bar magnet whose axis is coincident with the spin rotation axis here. Now as a consequence we can say nuclear spin behaves like a tiny magnet.

(Refer Slide Time: 03:14)

Nucleus spin behaves like a tiny magnet

Thus it has a magnetic (dipole) moment (μ)

μ is a vector

When I say nuclear spin behaves like a tiny magnet, we can define magnetic moment also and .since it is a dipole, having two poles north pole and south pole. Similarly, it is analogous to a small bar magnet, this spin has a dipole moment. It is called magnetic dipole moment which is represent μ. And μ is a vector. Remember I am introducing few terms. First we started with the angular momentum P, we found the Z component of that P_Z which was equal to m into h cross, m is magnetic quantum number which depends upon spin quantum number I, which I said is m_I.

I is equal to let us say the spin of the nucleus, then m_I means magnetic quantum number goes from minus I to plus I. So, those were the three times. Now this is a magnetic moment μ is another term I am introducing. Please do not get confused with the terms that I am repeatedly using and changing. so μ is vector.

(Refer Slide Time: 04:31)

Magnetic Moment (μ) is proportional to Spin Angular Momentum (P)

$$\mu = \gamma P$$

γ is gyromagnetic ratio: A constant for a given nucleus (SI Unit of γ is radian per second per tesla, i.e. rad.s^{-1}.T^{-1})

Substituting for P in μ

$$\mu = \hbar\gamma\sqrt{I(I+1)}$$

If I is zero, no magnetic moment !!!

The magnetic moment μ is proportional to the angular momentum P. Remember the magnetic moment is proportional to angular momentum P and the proportionality constant is given by a term called gamma. gamma is gyromagnetic ratio. It is a constant for a given nucleus, gamma is constant for a given nucleus and it has some units. In the SI unit gamma is expressed as radian per second per tesla. We see the unit of gamma, radians per second per tesla. So, please remember the magnetic moment which I just now introduced the term, is proportional to spin angular momentum by a constant proportionality constant gamma.

Now we knew what is P. I worked out, P we also got P is equal to h cross into root of I into I + 1. Remember the first slide in the last class before last class, when I introduced magnetic as angular momentum P. I worked out and I said P is equal to h cross into root of I into I + 1. Substitute for that P in this equation now. Now this μ becomes μ is equal to h cross into gamma into I into square root of into I + 1. All I did is that I substituted for P in this equation, that is all.

Now what happens if I is equal to 0. Then μ becomes 0, there is no magnetic moment. Remember magnetic moment is important. When you have a magnet you have a magnetic moment. Because as you go ahead I will tell you the interaction of the magnetic moment with the external field is required to observe NMR. That means if I = 0, μ= 0, no magnetic moment. no NMR, for that we come later.

(Refer Slide Time: 06:35)

γ values have been experimentally determined

For proton, its value is 26.753 x 10^7rad T^{-1} sec^{-1}

For carbon-13, its value is 6.728 x 10^7rad T^{-1} sec^{-1}

Now coming back to gamma, gamma is a constant for a given nuclei, gamma values have been experimentally determined. For example, for proton its value is 26.753 into the 10 to the power of 7 radians per tesla per second. Remember this value. Very often we require this. Similarly, for carbon 13 isotope, the value of gamma is 6.728 into 10 to the power of 7 radians per tesla per second. You may also notice one small, interesting thing here. The gamma of carbon is nearly 4 times smaller than that of protons.

Gamma of proton divided by 4 is nothing but the gamma of carbon, approximately. This keep it in mind, I need to stress upon this again because I will be using this term very often in the subsequent classes.

(Refer Slide Time: 07:39)

Angular Momentum (P) is quantized

Thus magnetic moment (μ) is also quantized along Z direction in the presence of an external magnetic field

$$\mu_Z = \gamma P_Z = \gamma \hbar m$$

Its value also depends on magnetic quantum number m

Now angular momentum P, I said is quantized and μ is also a quantized, because angular momentum is a vector, we calculated its component along Z axis and we had a quantization direction also. So, as a consequence μ is also quantized, along z direction. In the presence of an external magnetic field, like P is quantized, P is related to μ; so we have just now worked out here remember μ is equal to gamma into P, because P is quantized μ is also quantized.

So we can write P_Z component we knew we worked Z component with angular momentum P_Z is equal to h cross into m. Now if I have to get a μ_Z component, it is simply equal to gamma into P_Z because μ is equal to gamma into P. The Z component is similarly μ_Z is equal to gamma into P_Z. All we have to do is to substitute for P_Z which is h cross into m, that we have been working out. We calculated P_Z magnitude everything, remember, earlier.

It is nothing but μ_Z into gamma into h cross into m. Its value also depends on the magnetic quantum number m. So, the next conclusion is, we introduce the term μ, the magnetic quantum number, which when we were understanding angular momentum, we came to know that it depends upon magnetic quantum number m. So, the magnetic moment depends upon magnetic quantum number m. μ is a magnetic quantum number. It depends, upon I am sorry, magnetic moment μ is a magnetic moment. It depends upon magnetic quantum number m, please understand. We have come to some level where you understood angular momentum P was quantized, we got the Z component of angular momentum which was quantized. We understood the direction of quantizations and then afterwards we introduce the term μ.

We know μ is equal to gamma into P. That was the equation I gave you because μ is proportional to angular momentum, proportionality constant is gamma. Since this is quantized μ_Z is also a quantized. The Z component of magnetic moment is also quantized and that quantization, as I said depends upon magnetic quantum number. So, simply you understand magnetic moment, the direction of quantization again depends upon magnetic quantum number. That is the conclusion that you must remember.

(Refer Slide Time: 10:27)

Gyromagnetic ratio depends on charge and mass of the nucleus

$\gamma = e/2mc$

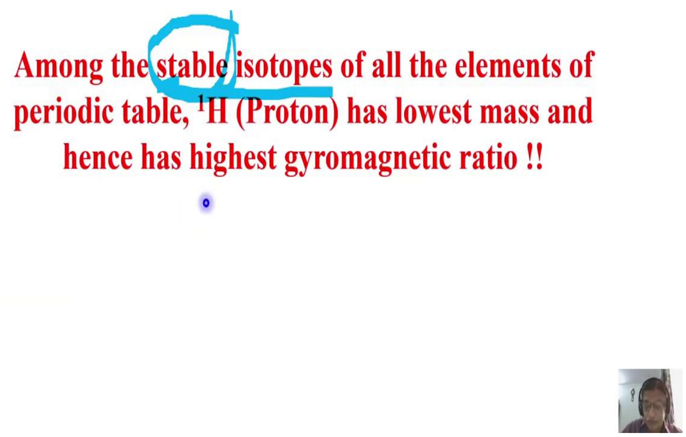
e is charge and m is mass

Nuclei with higher mass have lower γ !!

We introduced the constant of proportionality called gamma, what does gamma depend on? how do you get the value of gamma? Of course gyromagnetic ratio you can work out, it depends on the charge and mass of the nuclei. If you know gamma it is equal to e over 2 into m c, e is a charge, and m is mass, ofcourse you know c. So, now simply you can understand from this equation, a logic, that nuclei with higher mass has lower gamma.

Remember mass comes in the denominator of this equation, as you go to higher and higher nuclei in the periodic table mass keeps on increasing, gamma value keeps coming down. It is a very important parameter, remember gamma. The nuclei with higher mass always have lower gamma. Remember in one of the previous slides I showed gamma for proton was 26.75 into 10 to the power of 7 radians per tesla per second. When I showed for carbon; it was 4 times less because carbon 13 mass is higher than that of proton, as a consequence gamma was 4 time less.

(Refer Slide Time: 11:47)



Now you understand among all the stable isotopes of elements in the periodic table, the proton that is a hydrogen atom, has the lowest mass and has the highest gyromagnetic ratio. Please remember my statement, I use this statement that stable isotopes. why I use the stable isotopes? You can consider tritium that is a different, tritium the isotope of hydrogen is something different. That is an unstable isotope, it has a different gamma. I will not go into the detail. But please understand that has a higher resonating frequency compared to that of proton. But among all the stable isotopes, proton has the lowest mass and has the highest gyromagnetic ratio.

(Refer Slide Time: 12:49)

γ is the constant for a given nucleus

Different nuclei have different γ

$$\mu_Z = \gamma P_Z = \gamma\hbar m$$

μ_Z has different values for different nuclei, even though they have

Same Spin Quantum Number (I)
Same Magnetic Quantum Number (m)

And gamma is the constant for a given nucleus, that is known, and different nuclei have different gamma. I said gamma is only constant for a given nucleus and different nuclei and different isotopes have their different masses, as a consequence gamma has to be different. The different nuclei have different gamma because of their mass. Now if you go by this equation μ_Z is equal to gamma $P_{Z,}$ is also equal to gamma into h cross into m.

μ_Z has different values for different nuclei, even though they have the same spin quantum number I, and same magnetic quantum number m. please understand this, do not get confused μ_Z is equal to gamma h cross m, that is what I wrote earlier also when we substitute that for $P_{Z,}$ which is equal to h cross into m. we know what is μ_Z. Now m depends upon I, that means consider two nuclei, let us say it has same I and it may have a same magnetic quantum number because I is same.

But μ_Z can still be different. μ_Z has different values for different nuclei even though I is same and m is same.

(Refer Slide Time: 14:20)

What Makes ^{1}H and ^{13}C Different?

Both have spin quantum number (1/2)
Both also have same magnetic quantum numbers
(-1/2 and +1/2)

What about γ

$$\gamma = e/2mc$$

$$\mu = \gamma P$$

^{1}H and ^{13}C have different magnetic moments !

I will give an example now consider proton and carbon 13. Why they are different? because as far as the spin quantum number is concerned, the I spin quantum number, is same. Both are spin half nuclei. What is magnetic quantum number for both of them? m. That is minus I to plus I it will take. Both have same magnetic quantum numbers. Then what makes it different? I said μ_Z is different for different nuclei, that is because, remember gamma is different due to mass. As a consequence μ is different. That is what makes proton and carbon different because of their masses. So, what is different is although two nuclei proton and carbon have same spin quantum number, same magnetic quantum number, their gammas are different consequent to different masses.

As a consequence what happens, μ is different because gamma is different. μ is equal to gamma into P. so μ is different. So, carbon 13 and proton have different magnetic moments. It is a very important point. They have different magnetic moments.

(Refer Slide Time: 15:41)

Characteristic Properties of Selected NMR nuclei

Isotope	Natural Abundance	Spin (I)	Magnetic Moment (μ) in units of nuclear magnetons = $5.05078 \cdot 10^{-27}$ JT^{-1}	Gyromagnetic ratio (in units of 10^7 rad T^{-1} sec^{-1})
^{1}H	99.984	1/2	2.7927	26.753
^{2}H	0.0156	1	0.8574	4.107
^{11}B	81.17	3/2	2.6880	8.584
^{13}C	1.108	1/2	0.7022	6.728
^{17}O	0.037	5/2	-1.8930	-3.628
^{19}F	100.0	1/2	2.6273	25.179
^{29}Si	4.700	1/2	-0.5555	-5.319
^{31}P	100.0	1/2	1.1305	10.840

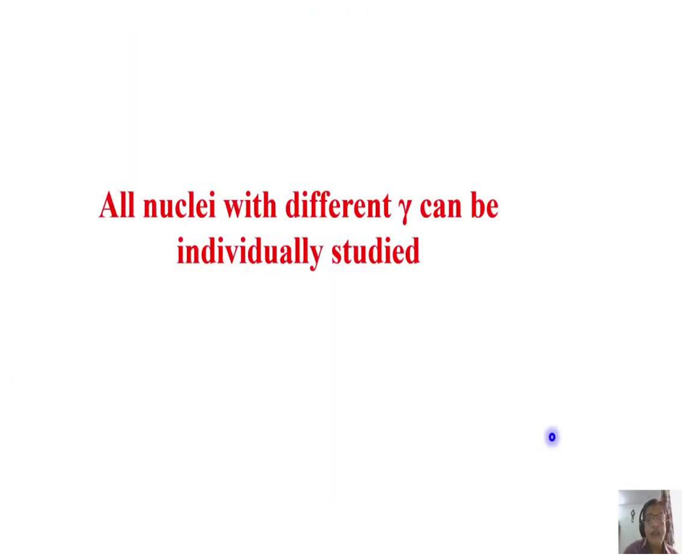
So let see some characteristic of the nuclei. I have made a list here. Let us go through a couple of them. There are five columns and several rows. I have put several nuclei with different properties. Concentrate on proton. That is the hydrogen isotope I am considering as proton. The natural abundance is 99.98 almost 100%, close to 100%. It is spin half nuclei. its magnetic momentum is calculated already. we know how to calculate experimentally, but its gyromagnetic ration gamma is 26.75 into 10 to the power of 7 radians per tesla per second, that I have been repeating I told you earlier also.

Now look at the same thing for deuterium. It has a very small abundance 0.0156. spin is 1 and gamma you see is much, much smaller. About 6.5 times smaller than that of proton. And look at carbon 13, this is another nuclei which is extensively studied by chemists and biologists. Everybody, all of us study apart from proton, carbon, nitrogen and others that are very favorable nuclei for us. That is interesting. Look at this natural abundance of carbon, 1.108. Again the spin is equal to half, but gamma is nearly 4 times smaller than that of proton.

Next abundant spin, which is favorable to study is fluorine. Look at fluorine 100% abundance, spin half nuclei and look at the gyromagnetic ratio, almost close to that of proton. And please understand, look at this thing, because I am going to tell you later this gamma is a very important parameter for defining the sensitivity of the nuclei and abundance is another thing which is also important in detecting the signal. That is why I am stressing on these two columns.

Natural abundance and gyromagnetic ratio and of course spin is an important thing. So, that is why I have concentrated on the deuterium, carbon and fluorine, all the three nuclei. So, which is the nuclei with higher gamma apart from proton, next is fluorine. Among the nuclei which are well studied, which is generally in demand, apart from proton, afterwards more investigated is carbon 13, which is spin half gamma is 4 times smaller. Let us keep this point in mind. Of course, some of the times biological studies and in some other studies phosphorus is also extensively investigated. Again it is 100% abundant, spin half nuclei. But you see, the gamma is nearly 2.5 times smaller than that of protons. These are some of the interesting nuclei; proton, carbon, fluorine, phosphorus and sometimes for inorganic molecules and others, you can study silicon also no problem.

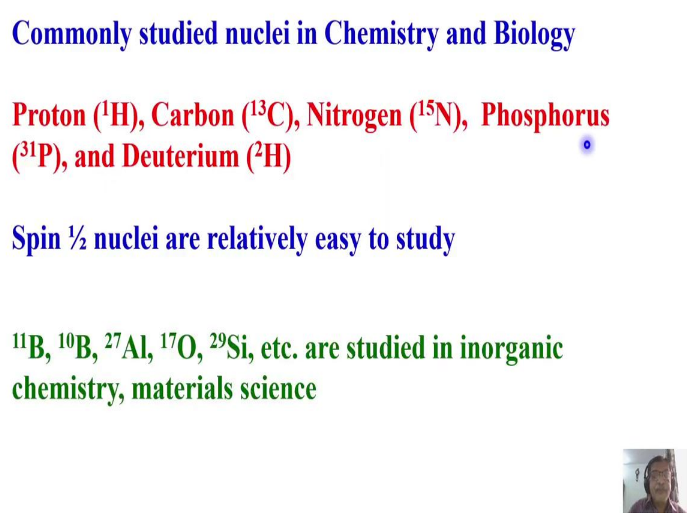
(Refer Slide Time: 18:58)



What I wanted to say here is, they all have different gammas. Though fluorine and proton have nearly equal values, but there is a difference, no problem for us. That small difference is enough. What it means is all nuclei with different gamma can be individually investigated, all nuclei in the periodic table if you look, they have different gamma and they can be individually studied. What does it mean?

In the periodic table of elements you can see lot of elements, in every element at least there is one isotope which has spin I and that all these elements have different gammas. So, everything can be individually studied, the whole periodic table can be studied by NMR, individually.

(Refer Slide Time: 19:54)



But if you look at the commonly investigated nuclei in chemistry and biology are proton, carbon, nitrogen, phosphorus. All are spin half nuclei and this is abundant this is highly abundant. Of course, these two are less abundant spin, but more explored. These two are very well utilized. And of course deuterium in many examples of hydrogen deuterium exchange studies, etcetera and direct detection also we use. This has spin 1.

So spin half nuclei are relatively easy to study. Spin half nuclei are very easy to study. Remember I always stress upon this, our main focus of this course is to study and understand spin half nuclei. Spin one nuclei or spin greater than half are all quadripolar nuclei, like 11B, boron 10, aluminum, oxygen, silicon and many of them are studied in inorganic chemistry and in material science, they require. People do extensive studies on boron, silicon, aluminium studies in borosilicate , aluminum silicate glasses and zeolites.

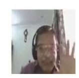
Varieties of materials are there where such nuclei are also used to study their properties, structure, conformation, etc. That is also there, but they are all spin greater than half, of course except silicon. And here these nuclei are most often used in chemistry and biology, except deuterium, all are spin half nuclei. Please remember this, extensively we use it, when you analyzing the spectrum later, many of this example I will take.

(Refer Slide Time: 21:37)

Interaction of nuclear magnetic moment with the External magnetic field is the basis of NMR

Nuclear Spin Quantum Number (I) Must be Non-Zero to Detect NMR

$$\mu = \hbar\gamma\sqrt{I(I+1)}$$



Next another important point I want to stress is the interaction of nuclear magnetic moment, that is μ, with the external magnetic field is the basis of NMR. Remember for NMR we require a very strong magnetic field. All you have to do for doing the experiment is, you have to take your sample put it in a magnetic field which is huge, whose strength is of the order several tens of Tesla; 10 tesla 15 Tesla or 20 Tesla, of that order. What is a Tesla, 1 Tesla is 10 to the power of 4 Gauss, very high magnetic field.

Such an external magnetic field is required for NMR. So, all you do is, take your sample for investigation put it in an external magnetic field. This external magnetic field is conventionally referred to us B_0, B subscript 0, it is referred to as B naught. Now what happens if it put your sample in the magnetic field. There is an interaction. Simply if you put the sample in a magnetic field you cannot get NMR. There is a reason for it, the reason is nuclear magnetic moment μ that we just now discussed, and it will interact with external magnetic field. And that is the basis of NMR. So, nuclear spin quantum number I must be non-zero to detect NMR. That is what we observe. μ depends upon magnetic quantum number m which depends upon I. just now you understood. So, I must be non zero we saw that when we calculated mu when I is equal to 0 we wrote μ is equal to gamma into root of I into I + 1. So, when I is equal to 0 μ is 0. That is what I said.

When a magnetic moment is zero, when I is 0 the magnetic moment is 0. When magnetic moment is 0 then such nuclei cannot interact with external magnetic field, please understand. So, μ must be non-zero. For that I must be nonzero. Then only we can detect NMR. So that is the reason why I said in the very first class, when I wrote the table to work out the spin of the nuclei based on the atomic mass and atomic numbers, I gave an example of carbon 12, whose spin is 0, I = 0, I said NMR inactive. That is the reason, I was 0.

So when I is equal to 0 μ is 0. When μ is 0 this nuclear magnetic moment cannot interact with the external magnetic field, as a consequence you cannot see NMR for carbon 12. Now this tells you that the spin must be present, I must be non-zero to see NMR.

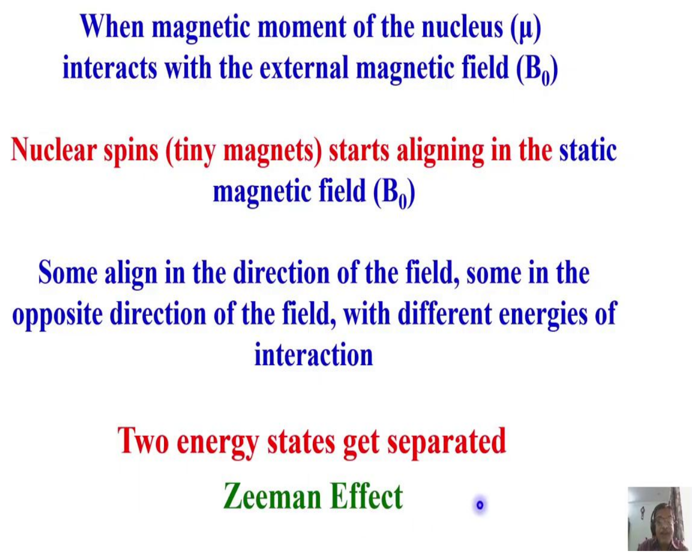
(Refer Slide Time: 24:47)

Different Nuclei with Different γ have different μ

They have different interaction strengths with the external magnetic field (B_0)

So, this is an important concept I hope you are understanding. Different nuclei with different gyromagnetic ratio of different μ. They all have different interactions strengths with the external magnetic field. So, since μ is different for different nuclei, because gammas are different, when the μ interacts with the external magnetic field, a strong magnetic field which you put it, they have different interaction strengths. As a consequence, interaction of the protons with the external magnetic field is different. Similarly, strength of interaction of carbon with the external magnetic field is different. So, this is what make the difference. As consequence you can observe nuclei individually, because their interaction strengths are different. If they were same then you would not have seen the NMR of different nuclei, so this is a beauty. Because gammas are different μ's are different, the interactions strengths are different with the external magnetic field. okay this is an important point.

(Refer Slide Time: 25:50)



So, when magnetic moment of the nuclei interacts with the external magnetic field what happens, I said the interaction is essential, okay, magnetic moment of the nucleus is interacting with the external magnetic field. That is fine, so what happens? Next question. The important thing is the nuclear spins which are tiny magnets start aligning in the static magnetic field. Remember if I say nuclear spin, tiny magnet, magnetic moments, these are the same terms which we use interchangeably. Do not get confused at all.

If I say interaction of the magnetic moment is nothing but interaction of the nuclear spin, it is nothing but the interaction of the tiny magnet. All are changeable words, we keep using very often in NMR. Do not get confused, so the interaction of the nuclear spins or the magnetic moment means the nuclear spins start aligning with the static magnetic field or in other words magnetic moments start aligning in the magnetic field, you get the point. The nuclear spins start aligning in static magnetic. How do they align? Some align in the direction of the field, some in the direction opposite to the magnetic field. How should it happen? See we say interaction of magnetic moment in the external magnetic field has different energies for different nuclei, that is correct. But now I am telling you further, this magnetic moment μ have quantization directions that we observed.

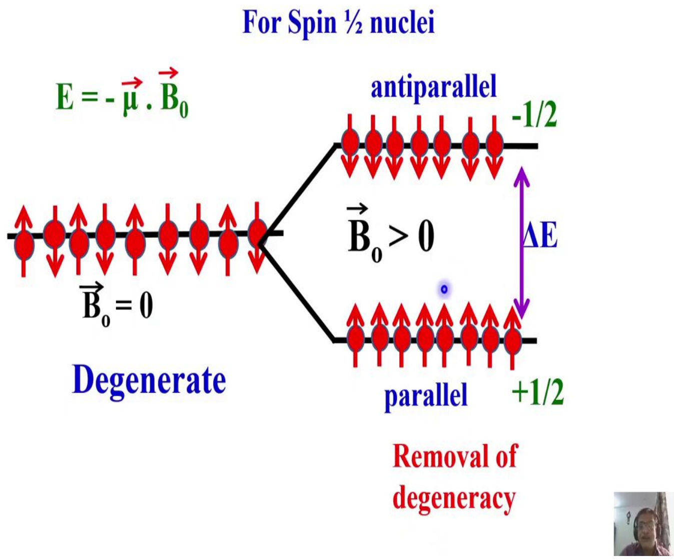
And what is happening is, some of the μ's orients in this direction, some orients in the opposite direction, and they have again different energies. you understand nuclear spins which align in this direction, in the direction of field, and those which align in the direction opposite to the field have different interaction energies. is it not NMR is very interesting to understand? We understood I because of μ, μ is because of m, m is because of I is there. And μ interacts with external magnetic field which is different for different nuclei because of different gamma.

But how it interacts, I said the nuclear spins starts aligning, because the quantization directions are known. As I said some orientation in this direction and some orients in the direction opposite to the field. of course, spin half nuclei I am considering and these further have different energies. Energy of interaction for the spin of the magnetic moment in the direction of the field is different from the energy of interaction the magnetic moment in the direction opposite to that of field.

So that means we have two energy states. When I say what happens because of interaction the magnetic moment with the external field, so what it interacts, how does it interact? This is the consequence of that interaction. The consequence of that interaction is these two energy states, which have two different energies for the orientation along the direction of the field and opposite to the direction of the field get separated out. This is called Zeeman effect, the very well known thing, all of you must have understood and studied in some spectroscopy.

This is called Zeeman effect. Zeeman effect is nothing but the interaction of the magnetic moment with the external field. It is largest interaction strength among all the external interactions including internal interactions apart from large quadrupole momentum of the nuclei. Among all the interaction strengths, especially external interaction, the Zeeman interaction has the largest strength.

(Refer Slide Time: 29:33)



Next we will understand, we will understand mathematically how these two are interacting. Consider spin half nuclei. I have 2 quantization directions, 2 orientations of the magnetic moment in plus half and minus half, okay. The interaction energy, I said there is a energy of interaction because magnetic moment interacts with $B_{0.}$ Both of them are vectors, μ is a vector, magnetic field is a vector and the interaction takes place and it is a dot product.

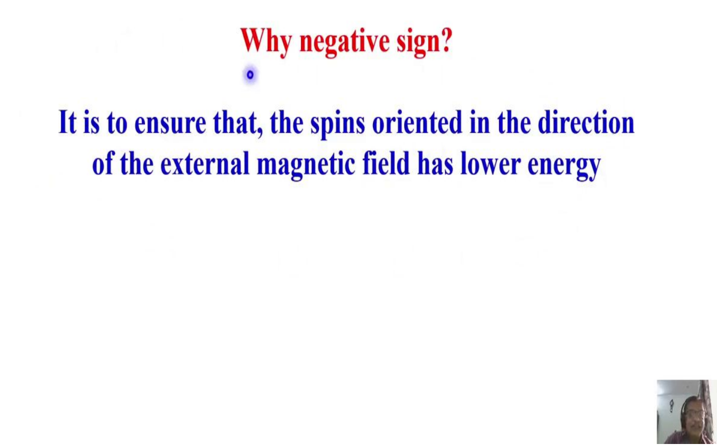
Now in the absence of this magnetic field all these orientations are random. There is no preferred orientation at all, preferred direction of orientation for any of these magnetic moments are nuclear spins is not there. There is no preferred orientation. Moment you put in the magnetic field what happens, ok before that let me tell you, when there is no preferred direction of orientation, all are equally probable, they are randomly distributed. That means these energy states are not separated out in the absence of the magnetic field.

That is why they are called degenerate states, degenerate means these energy states are not separated in the absence of magnetic field. There is no separation of energy states and they are called degenerate states. Now moment you put it in the magnetic field the degeneracy is removed that is what I said, the interaction energy in the direction parallel to the field and in the direction opposite to that of the field have different energies, as a consequence the spins orientation changes.

It is not randomly distributed as I said in the previous slide. There are some spins orienting in the direction of the field, some more into the direction opposite to that of the field. This is exactly what happens. This random distribution was there in the degenerate state. Now there is preferred alignment of nuclear spins, in the direction of the field, in the direction opposite to that of the field. This is called removal of degeneracy.

What happened now, when I put the magnetic moment in the magnetic field, the nuclear spin is magnetic moment, it interacted with the external field. As a consequence the energy states get separated out because of removal of degeneracy. This has one energy and this has one energy and the difference between this is called delta E that is the difference of energy.

(Refer Slide Time: 32:20)



Now if you understand here in this equation, I have put minus, the interaction energy. What do you mean by energy negative? why I put a minus? There is a reason for it, please understand. Reason is it is to ensure that spins are oriented in this direction of the external magnetic field has lower energy. Remember in this those spins that are oriented in the direction of the magnetic field, that is parallel to the magnetic field direction, have lower energy.

This is lower energy compared to this one, the higher energy state is the one where the spins orient anti parallel to the magnetic field. Lower energy is the one where the spins orient parallel to magnetic field.

To bring in this concept negative sign was put in this equation. You understand. Okay. Now, we can understand more about the energy of interaction and we can resolve them into different components and find out what is the energy for each of the states and get the energy difference between them calculate the energy difference between them and then calculate the frequency of that. Lot more things little bit of conceptual understanding is required.

We can do that. what I will do is. I will stop for the day. We will come back in the next class we will continue from this. Now we have understood in this class what is magnetic moment and how it interacts with external magnetic field, where the degeneracy is going to be removed because of the interaction of small these tiny magnets, nuclear spin , which I called as magnetic moments, with a big magnetic field, degeneracy gets removed.

Some orients in the direction of the field and some orients in the direction opposite to the field. And this interaction energy was given by E is equal to -μ dot B, it is a dot product, both are vectors and this is the general equation I gave. Now you calculate the energy for each of the orientations and get the frequency so that you know what is the frequency, and how we get NMR everything we will discuss in the next class.