Advanced NMR Techniques in Solution and Solid – State

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Module -1
Introduction to NMR
Lecture - 01

Hello everyone, welcome all of you for this course on advanced NMR techniques in solution and solid state. I am Professor Suryaprakash and was also the chairman, just recently retired from NMR Research Center, Indian Institute of Science, Bangalore. So, we will be interacting together for the next couple of week. I always welcome all of you to talk to me or correspond with me in the email given in the first slide. Most of the time I will be able to respond to your queries if there are any. We will start with this course. The fiirst thing is there is a prerequisite for this course on 1 and 2 dimensional NMR spectroscopy for chemists which was given last year.

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Pre-requisite
Course on One and Two Dimensional NMR
for Chemists

Not Mandatory but Advantageous

It was again a 12 week course and of course it is being rerun now, and, I think this course if you have attended it is well and good. It is a prerequisite I would say, although it is not mandatory but it is advantageous. The reason is, in the first 1 or 2, first week or at least one and a half weeks I will be covering some of the fundamentals which I introduced in the last course.

Though not in detail, to some extent I will be covering right from fundamentals of NMR spectroscopy, and about NMR parameters, analysis of the spectrum of proton and other varieties of hetero nuclei. And some of the things you would have already exposed to this in the previous course. Nevertheless, I will slightly give a brief introduction to many of these things before we go to the advanced topics.

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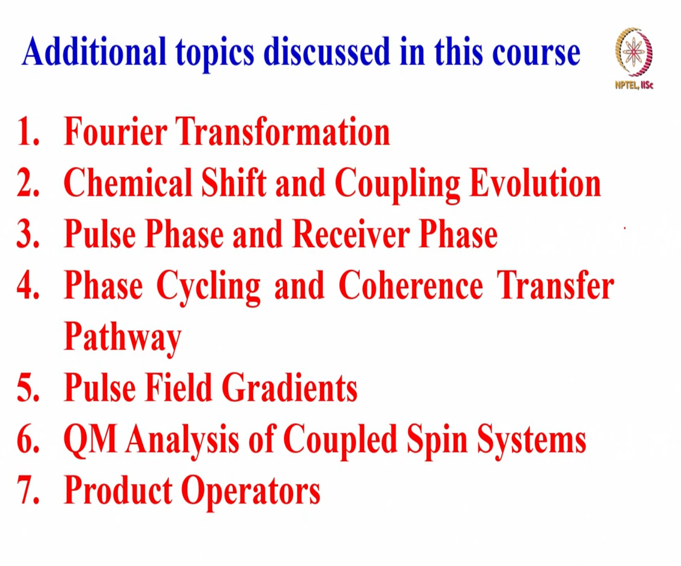

The question is what are the advanced topics which I am going to cover in this course. In this course, I am introducing Fourier transformation which is one of the essential prerequisites for NMR spectroscopy. It is an essential mathematical tool which we always use; in variably you require this. And I will be talking about Fourier transformation, and of course in the last class I discuss about chemical shift and coupling evolution which I am also going to introduce this time. But I am going to tell you something about how it evolves in different pulse sequences or when you apply pi pulse in different axes what is going to happen? So, in that connection I am going to discuss about pulse phase and receiver phase. I will be talking about phase cycling and coherence transfer pathways; how do you select the coherence transfer pathway? And how do you do the phase cycling.

Then I will introduce pulsed field gradients, how can we use pulse field gradients to select coherent pathway. While analyzing the spectrum of coupled spins especially the proton spectrum, it is possible to analyze the first order way, first order analysis, it is feasible in most of the weakly coupled spin systems. But of course, there is also a quantum mechanical way of getting the chemical shifts and coupling constants in addition to intensities of the transitions.

So, I will be introducing quantum mechanical analysis of coupled spin systems, if not for all the spins, at least for 2 couple spin system. I will try to introduce AX, AB and A2 spin systems. I also want to introduce product operators and this product operators are very useful, with this product operator you can understand how the magnetization evolves at different parts of the pulse sequences. As you know NMR is full of pulse sequences, the varieties of 2 dimensional and 3 dimensional pulse sequences, both homonuclear and heteronuclear. And if you have the knowledge of product operators you will be able to understand how the magnetization evolves in different pulse sequences, at different points of the pulse sequences.

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And continuing further I will also be introducing relaxation mechanisms, which I guess last time I tried to introduce, but I could not complete because of lack of time. So, this time I will be talking about relaxation mechanisms, T1 and T2 measurements, nuclear overhauser effect concepts, pure shift NMR, multiple quantum NMR, and I also would like to talk about high resolution NMR spectroscopy in solids, where I will be introducing magic angle spinning, cross polarization and multipulse techniques. All these things, of course may not be the same order, depending upon how we are progressing with the course I will be taking up many of these advanced additional topics in this course. Now let me start with the basic concepts of NMR spectroscopy. This is the benefit of those people who are attending this course, who did not attend my previous course where I was giving fundamentals of varieties of things in NMR including analysis of the spectrum. But I would like to quickly introduce, in couple of classes, the basic concepts. Well let us start with spin angular momentum and magnetic moment. These are the 2 important concepts which we require to understand NMR spectroscopy.

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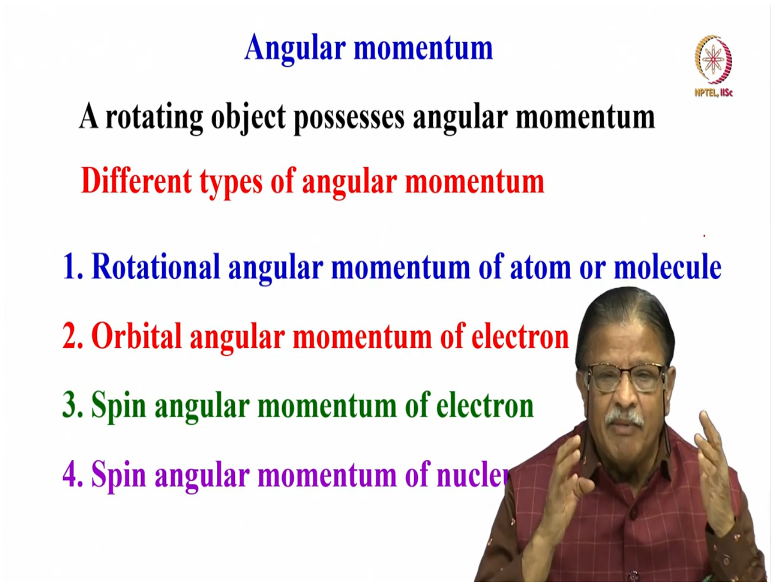

Let us start with angular momentum. A rotating object possesses angular momentum. Different types of angular momentum you can think of, especially when we look at rotational angular momentum of atom or molecule itself, orbital angular momentum of electron, spin angular momentum of electron and also the spin angular momentum of nucleus itself. Varities of angular momentum we can think of.

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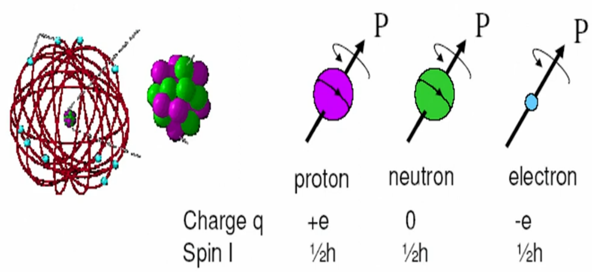
Spin angular momentum of subatomic particles



Let us focus on the spin angular momentum of subatomic particles or in other words elementary particles. There is a subtle difference between these two. But let us not worry about it. Look at it if we consider an atom, we have proton, neutron and electron. All the 3 are present. Protons and neutrons are present in the nucleus, electrons are surrounding them. But if you look at this slide you will see protons and electrons have charges which are opposite in sign. Neutron has charged 0. But all the 3 particles have spin angular momentum I, which is half, half is the spin angular momentum for all these fundamental particles.

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Spin is a quantum mechanical concept. There is no good classical analogy

It is not, produced by rotation of the particle. It is an intrinsic property of the particle (is always there, even at 0 K)

Then why it is called spin ?

It is described by equations treating angular momentum (P) and it is a vector

Now what is a spin? Spin is a quantum mechanical concept, there is no classical analogy for it. It is not produced by the rotation of the particle. It is an intrinsic property of the particle, that means it is always there, always present even at absolute 0 K. You cannot question why it is there, it is there, it is there and we have to accept it. So, spin is nature's gift for us. Then the question is why do we call it a spin? if it is not produced by rotation of the particle.

Because it is described by equations treating angular momentum which is P and it is a vector. So, this is the reason why we call this spin angular momentum as spin although classically we talk about rotation of the particle about its own axis and varieties of things we talk, but in reality it is because it is treaded by the equations governing spin angular momentum, hence it is called a spin.

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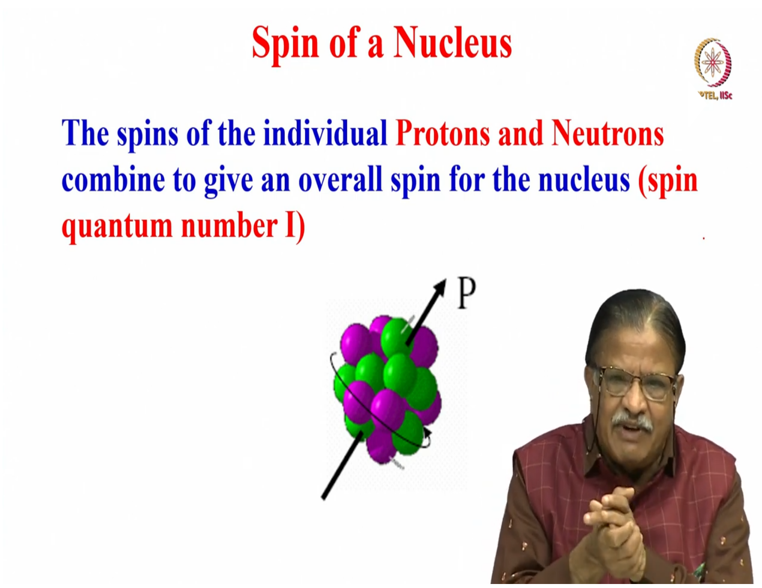

Now will let us look at the spin of a nucleus. The spins of individual protons and neutrons combine to give an overall spin for the nucleus which is called spin quantum number I of the nucleus itself, not individual particles. It is the total spin angular momentum of the nucleus. In the diagram what I have shown we have green bars and a magenta color balls. You can consider one of them as protons, others as neutrons. So, they somehow assemble the nucleus in such way, they pair themselves, and give us to total spin angular momentum for the nucleus itself.

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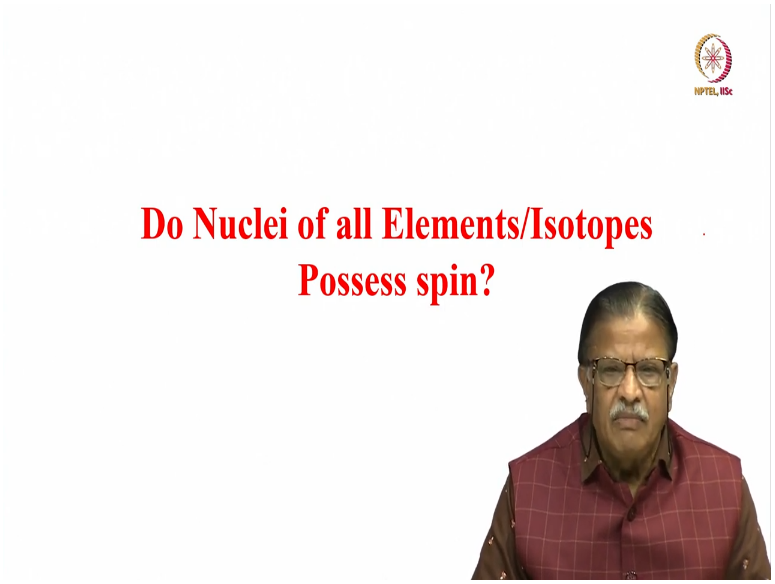

Then one can ask a question, do all the nuclei of all elements or isotopes of elements possess spin? We need to answer this question.

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Empirical rule to Predict NMR Activity of a Nuclear Spin

Atomic Mass	Atomic Number	Examples of Nuclei	Total Nuclear Spin	NMR Active
Odd	Odd / Even	$^{1}H_{1}$, $^{13}C_{6}$, $^{15}N_{7}$, $^{31}P_{15}$	Half integers 1/2, 3/2, 5/2	YES
Even	Odd	$^{14}N_{7}$, $^{2}H_{1}$, $^{10}B_{5}$	Integers 1, 3	YES
Even	Even	$^{12}C_{6}$, $^{16}O_{8}$, $^{32}S_{16}$	Zero	NO

Of course, there is an empirical rule to predict the NMR activity of a nuclear spin. If you look at this table which is given, there are actually 5 columns and 4 rows and in each of them we have written some of the properties like atomic mass, atomic number and verities of examples of the nuclei. And in the fourth column you see the spin angular momentum of that particular nucleus or particular element or isotope of an element.

And the last column tells you whether such nuclei are NMR active or not. Start with the second row. What it says, if you take an atomic mass of any given nucleus, if that is odd number, and its atomic number can be odd or even, does not matter. For example you take proton, proton is nothing but the hydrogen atom, in NMR jargon we call it as proton. It has atomic mass one atomic number is one both are odd numbers. Look at carbon 13, its atomic mass is 13 which is odd number, whereas the atomic number is 6 is even number, it does not matter. So, long as atomic mass is add such type of nuclei exhibit total nuclear spin angular momentum, which can be expressed as half integers; meaning their spin values could be 1/2, 3/2, 5/2, etc. As you see in the last column it says, YES. That means such type of nuclei are NMR active nuclei, you can detect NMR with such nuclei. Go to the third row with atomic mass is even; atomic number is odd. Example like nitrogen 14, deuterium and boron 10. Nitrogen 14 atomic mass is an even number, well atomic number is an odd number, it is 7. And such type of nuclei do possess spin angular momentum but their values or integer numbers. Their values of spin are; 1, 3, 4 like that. Again such nuclei are NMR active. Come to the last row when atomic mass is even number and atomic number is also even. For example carbon 12, atomic mass is 12, atomic number is 6 both are even number. There are 2 other examples I have given there. Such nuclei with a total spin angular momentum 0, such nuclei are NMR inactive. They are not NMR active; they are called NMR silent nuclei.

You cannot detect NMR of carbon 12 or oxygen 16. This is very important thing to understand whether a given element or isotope of an element; whether it possess a spin or not, you can understand from an empirical rule given in this table.

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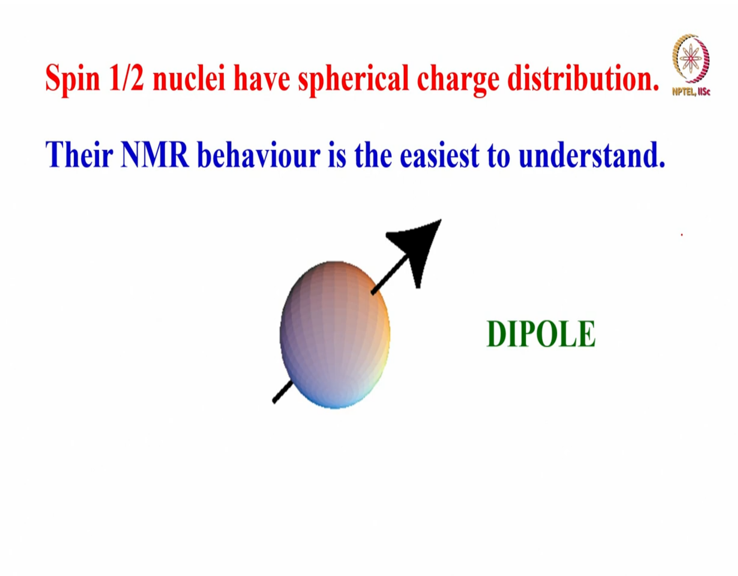

Next we will look at spin half nuclei. That is what most of the time we are covering in this course. We do not go to nuclei which are greater than spin half. Occasionally one or two we may touch upon, but most of the time in this course we cover spin half nuclei. And such nuclei are very easy to understand, their NMR behaviour is very easy to understand. Whereas if you go to the nuclei with more than spin half they are very difficult to understand.

Remember the spin half nuclei always have spherical charge distribution. The charge distribution of these nuclei are always spherical. And we call them as dipoles that mean it has 2 poles; positive charge and negative charge. So, it can be treated like a tiny magnet. so spin half nuclei are called dipoles.

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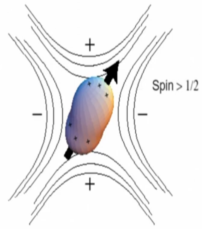
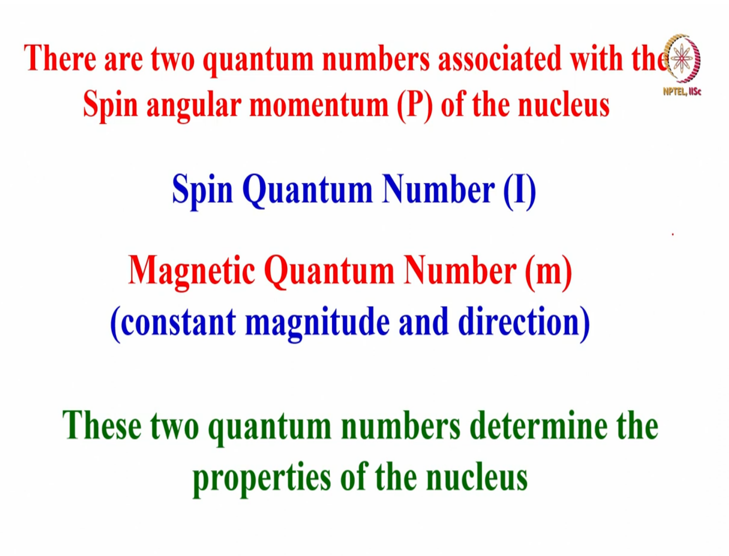
Nuclei with spin > ½ have non-spherical charge distribution. They are called quadrupolar nuclei



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

Whereas the nuclei with spin greater than half have non-spherical charge distribution. They are not spherical, they are called quadrupolar nuclei. As you can see there are 4 poles here there are 2 plus, plus charges and minus, minus, unlike dipole just 2 charges positive and negative. Here quadrupoles have 2 positive charges and 2 negative charges. And such nuclei are very difficult to understand by NMR, not impossible it is difficult compared to spin half nuclei.

The quadrupolar nuclei have electric quadrupole moment and as we go ahead I will tell you this quadrupolar interaction in NMR is electric in nature. Whereas all other interactions you can think of, like dipolar interaction, all other things you come across at a later stage, which we are going to discuss are all magnetic in nature. But only thing is a quadrupolar interaction is electric in nature.



So, with this let us start with some fundamentals of NMR spin physics. There are 2 quantum numbers which are associated with the spin angular momentum. I told you about the spin angular momentum of the nucleus, there are 2 quantum numbers associated with that one is the spin quantum number, other is a magnetic quantum number. And this magnetic quantum number m has a constant magnitude and also direction. It is has vectorial properties, and these 2 quantum numbers determine the properties of the given nucleus.

So, if I consider a nucleus if I want to find out the spin angular momentum; I need to know spin quantum number and I need to know its magnetic quantum number. If I know this then I can define the properties of this nucleus.

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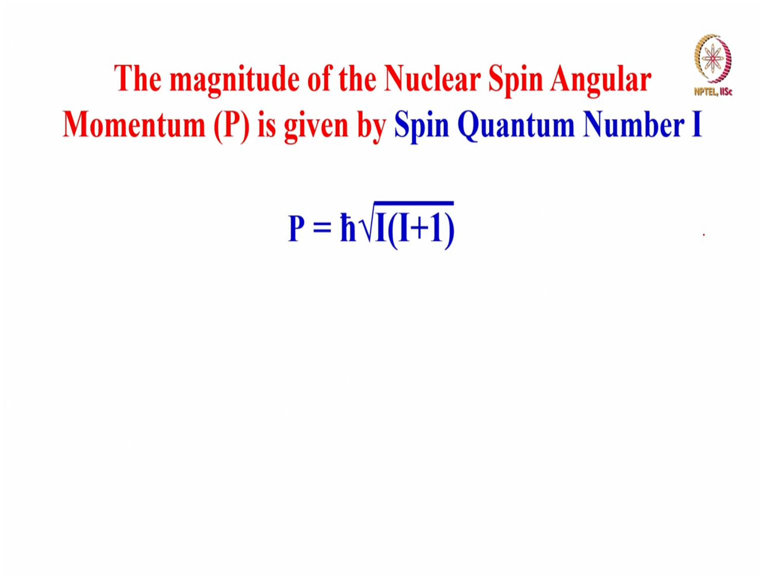

So, we can also calculate the magnitude of the nuclear spin angular momentum P; and it is given by spin quantum number I by a simple equation; P which is h cross into root of I into I + 1. I is the spin quantum number, h cross is the Planck's constant h divided by 2π and p is spin angular momentum.

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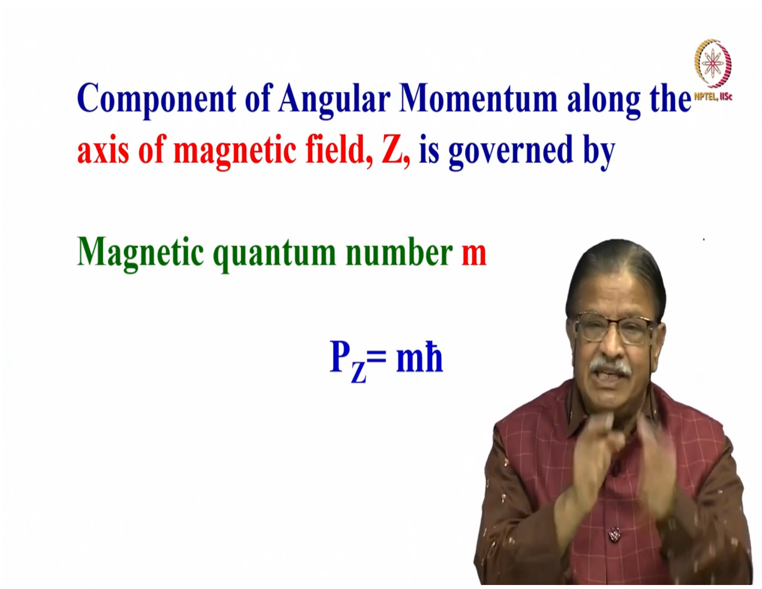

And if I just take the spin angular momentum or angular momentum, I can find out the component of it along Z axis; and it is governed by what is called a magnetic quantum number m. What is the magnetic quantum number? I will tell you, it depends upon the z component the angular momentum P, is given by m into h cross. It is quantized. See the angular momentum along the Z axis is always a quantized, and it is given as Pz equal to m into h cross. What is m? It is a magnetic quantum number which depends upon I, the spin quantum number which we are going to discuss that.

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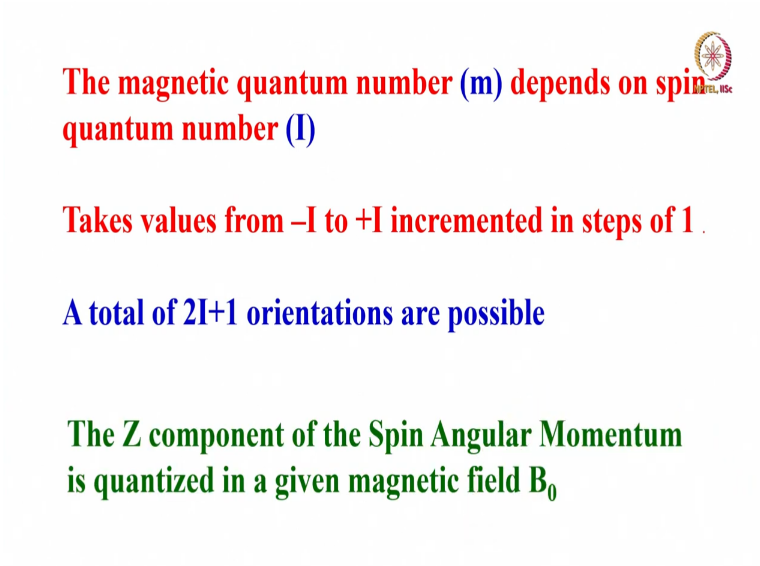

So, the magnetic quantum number depends upon spin quantum number, and how it depends the value of m goes from – I to + I incremented in steps of one. For example, I say spin is equal to 1 start with – I; - 1 increment by 1, 0 and then 1. So, – I to + I how many we can have? there are 2I + 1 possible orientations. Depending upon I the magnetic quantum number can have 2I + 1 possible orientations. And the Z component of the spin angular momentum is quantized in a given magnetic field B_0.

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Possible Orientations of angular momentum for different Spin Quantum Number I

For spin ½ nuclei, there are 2 orientations: -1/2 and 1/2

For spin 1 nuclei, there are 3 orientations: -1, 0 and 1

For spin 3/2 there are four orientations : -3/2, -1/2, 1/2 and 3/2

Now we can find out what are the possible orientations for different spin quantum number I. For example I take spin half nuclei. There are 2 orientations for spin half nuclei, which correspond to minus half state and plus half state. you can find out m goes from – I to + I there are only 2 possible orientations minus half and plus half. For spin half nuclei there are 2 orientations. For spin 1 nuclei, as I told you earlier there are 3 possible orientations – 1, 0 and 1. What about spin 3 / 2? There are 4 orientations such the – 3/2, -1/2, 1/2, 3/2; there are 4 possible orientations.

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Quantization directions of magnetic quantum number m_i

For Spin ½ nuclei, m_I can take 2 values, +1/2 and -1/2

For m_I +½ : The spin angular momentum orients in the direction of the field

For m_I (–½) : The spin angular momentum orients opposite to the direction of the field

Now we can find out the quantization directions of the magnetic quantum number. I know what is the magnetic quantum number I can find out the quantization direction also. This for example for spin half nuclei since m_I can take only 2 values as I said, plus 1/2 and – 1/2, for m_I which is equal to +1/2 the spin angular momentum orients in the direction of the field, for m_I equal to -1/2 the spin angular momentum orients opposite to the direction of the field.

But here you should know in the direction of the field means, not exactly aligned along the field, it makes an angle theta which you can understand if you go more into the details of this which I covered in the last course. So, I am not going to touch upon those things.

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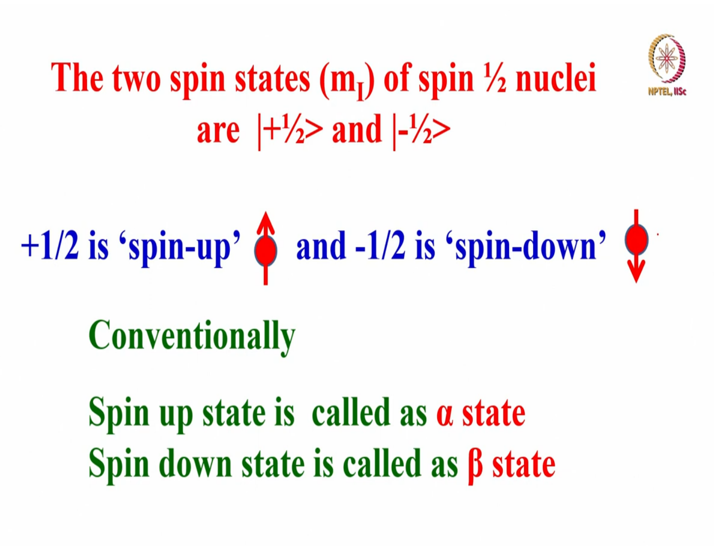

But please remember we can find out the angle theta at which these orientations are frozen. We can find out those things. Let us consider 2 spin states for spin half nuclei m_I plus half and minus half. The plus half is called a spin-up state. The nuclear spin is in the direction oriented parallel magnetic field; minus half spin down-state. And conventionally spin-up state is called the alpha state and spin-down state is called the beta state.

Please remember the rest of the course wherever possible I will be using alpha state, beta state alpha alpha, beta beta, varieties of terms I will be using. Always remember when I consider spin half nuclei, alpha is spin-up state and beta is spin-down state.

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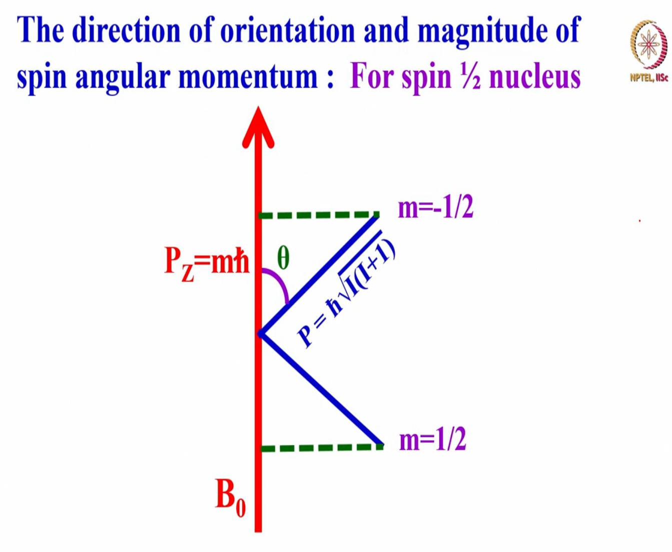

Now the direction of the orientation and magnitude of the magnitude of the spin angular momentum for a spin half nucleus can be found out by a simple equation. Of course, as I told you it is making an angle theta and if I consider spin angular momentum P; I told you in the previous slide which equal to h cross into root of I into I +1. Now the z component is also quantized which I said also Pz = m into h cross. Now you know, 2 sets has the rectangle triangle and I can find out what is the opposite side, and I know what is theta.

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Directions of Orientation of Spin Angular Momentum

For m = 1/2

$$\cos\theta = \frac{m\hbar}{\hbar\sqrt{I(I+1)}} = \frac{1/2}{\sqrt{3/4}}$$

$\theta = 54.7^0$ with respect to Z-axis

For m = -1/2

$\theta = 54.7^0$ with respect to -Z-axis

(125.3^0 with respect to Z axis)

So, I can find out theta knowing these things; and if I find out cosine of the angle theta which is given by mh cross over h cross in the square root of I into I + 1. This is for magnetic quantum number m equal to half. I am substituting all these values and calculated. You can find out what is the angle theta? Theta turns out to be cosine inverse of half over root of ¾, which if you calculate turns out to be 54.7 degree with respect to Z axis. This is for m equal to plus half.

What happened for m equal to minus half state? Again you can put these parameters and find out it is same 54.7 degree but in the direction opposite to the magnetic field. That is in the -Z axis; towards -Z axis or another words if you consider from +Z axis it is 125.3 degrees or 54.7 degree from -Z axis. So, with this let me introduce a new term called nuclear magnetic moment mu.

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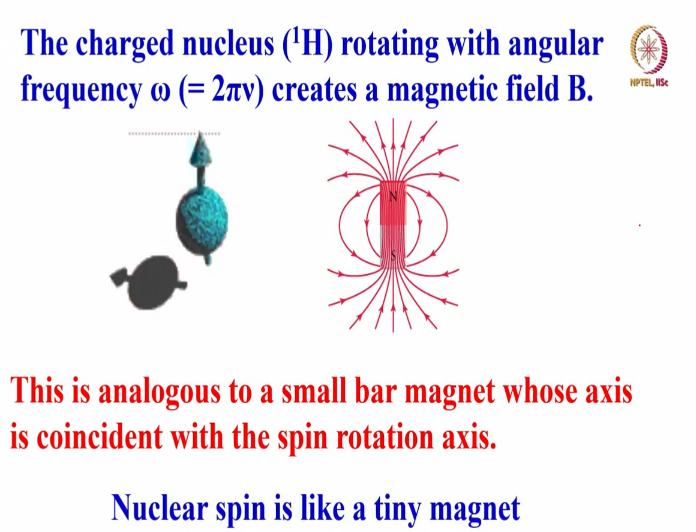

Now if I consider the charged nucleus, the charged nucleus rotating with angular frequency omega; which is given by 2 pi into mu, it creates a magnetic field B and this is the way this nucleus will be, let us, say undergoing spinning. It is the charged nucleus. Then it generates a magnetic field. It can treated like a tiny bar magnet. As I told you spin half nuclei are dipoles. It can be treated like a small tiny bar magnet; it is analogous to that; where the axis of the magnet is coinciding with the spin rotation axis. So, nuclear spin is like a tiny magnet.

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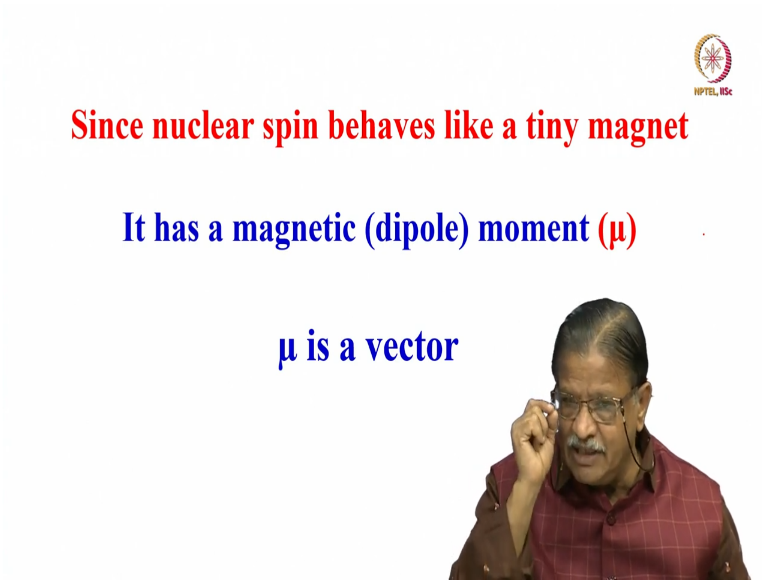

Now when we say since nuclear spin behaves like a tiny magnet. Whenever you have a magnet, you have studied in your school, we can define what is called a magnetic moment. Since a dipole, we can call it as a magnetic dipole moment, which is given as mu. We can define it we can find out these things. And this mu is a vector. Please understand, please you remember this mu is vector which we try to understand as we go ahead further.

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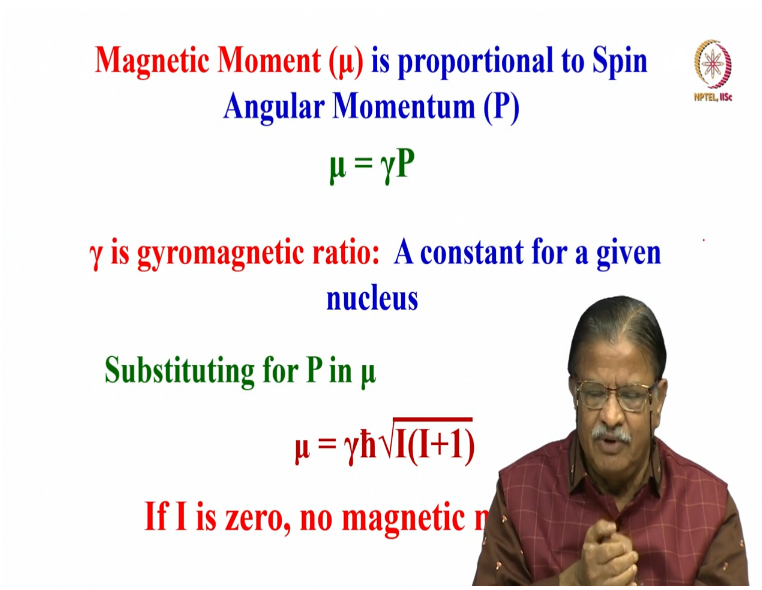

So, magnetic moment mu is proportionate to spin angular momentum P, mu = gamma into P, gamma is what is called a proportionality constant. It is called a gyromagnetic ratio; it is constant for a given nucleus. For different nuclei, the gamma is different and substitute for P in mu. I knew what is P, I already told you P = h cross into root of I into I + 1. You substitute that, then nu becomes gamma into h cross into root of I into I + 1.

Now what will happen if I is 0; the spin angular momentum is 0, mu is 0; that means magnetic moment is 0. And this you remember, this magnetic moment is very, very important. It should be present, that means spin should be present, only then the magnetic moment will interact with the external magnetic field. As I go further I will tell you, for observation of NMR. Thus I must be present, to see NMR.

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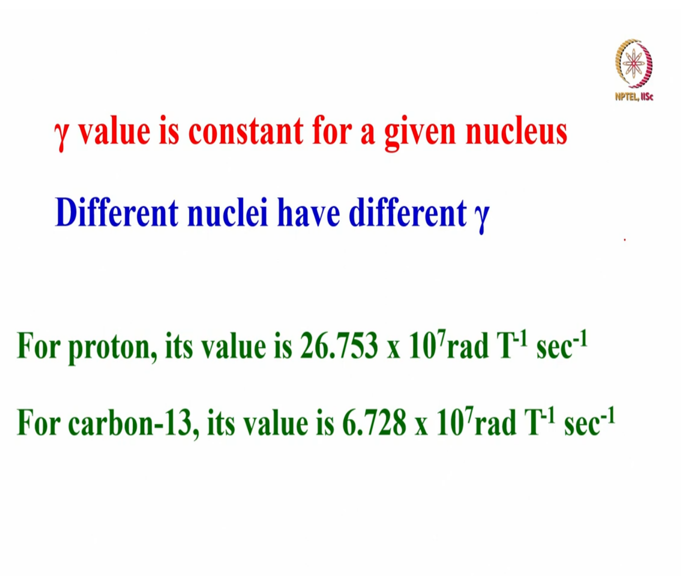

If I = 0 then no magnetic moment, no NMR. And gamma value is constant for a given nucleus, different nuclei have different gamma; and for example for protons its value is some number 26.753 into 10 to the power 7 radians for Tesla per second. Magnetic field is always expressed in Tesla, 1 Tesla is 10,000 Gauss. Similarly for carbon 13 its value is 6.728 into 10 to the 7 radians per Tesla per second. These values, for all the nuclei, these gamma values are known.

(Refer Slide Time: 26:07)

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

So, now interaction of different nuclei in the given magnetic field we can find out. Angular momentum P is quantized I told you, that means mu is also quantized; because mu and angular momentum are related to each other I already told you. So, mu is also quantized along Z direction in the presence of an external magnetic field. So, I would call mu = gamma into Pz, what is Pz? Pz = h cross into m; that is what I told you already.

So, z quantum of angular momentum is quantized which equal to h cross into m. So, its value also depends upon the magnetic quantum number m. So, the magnetic moment, mu its value depends upon magnetic quantum number m.

(Refer Slide Time: 26:45)

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 !!

So, the gyromagnetic ratio also depends on charge and mass of the nucleus. It is given by gamma which is equal to the e/2m into c. e is charge and m is mass and of course c is velocity of light. So, nucleus with higher mass have lower gamma, remember mass is coming in the denominator there. As the mass keeps increasing, the gamma value keeps coming down. So, the nucleus with the lower mass will have higher gamma.

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

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

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

So, if you look at this, we will go further. mu$_z$ we can say equal to gamma into Pz which is about a gamma into h cross into m; that is what I already explained. Now mu$_z$ has different values for different nuclei, because gamma is different, that is what I told you. So, for example some nuclei may have the same spin quantum number, I will be same. For example, I will be half when I is equal to half, magnetic quantum number m also should be same. Because it can take only for minus half and plus half; only 2 possible values. So, if I is same m is also same for different nuclei. Then what makes them different? What makes them different is the gamma.

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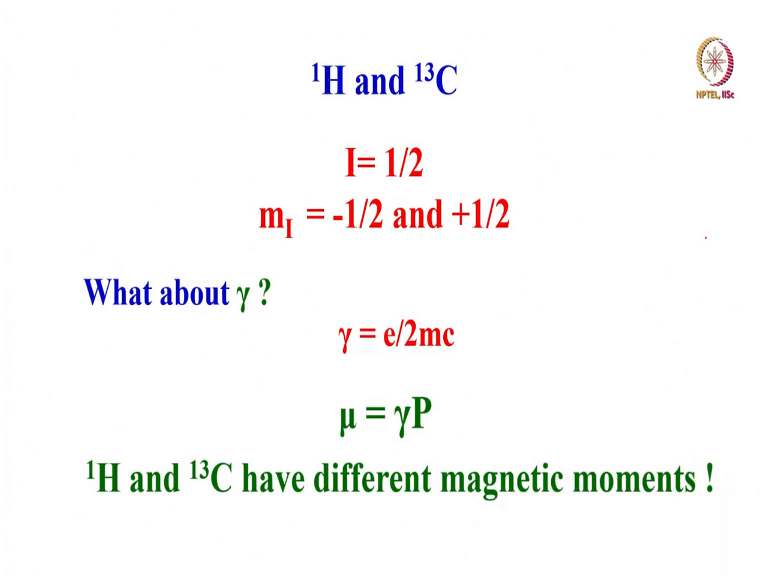

So, with this let us take an example of 2 nuclei proton and carbon 13. The carbon 13 isotope and proton, proton is hydrogen atom. I is equal to half for both of them. Spin is a half; when I say spin is half, I already told you, m_I is equal to minus half and plus half. There are 2 possible orientations. So, what about gamma? put the value for this in gamma, gamma = e over 2 into m into c. I is same, m is same, but what about mass? which is coming in the denominator? They are different. As a consequence if you go mu = gamma into P for proton and carbon 13 they have different magnetic moments, although they have same spin angular momentum, same spin quantum number, same magnetic quantum number, their magnetic moments are different because gammas are different that is the important thing. So, please remember all nuclei with a different gamma can be individually studied by NMR.

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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, these are the characteristics of some of the selected nuclei. If you go into the periodic table all nuclei at least one element of each nuclei can be studied by NMR. Some of the important nuclei which we study both in organic chemistry, biochemistry, biophysics or inorganic chemistry I have listed here. Look at this one for proton, the natural abundance is 99, spin is half, it is magnetic quantum number is 2.79 then its gyromagnetic ratio 26.75 into that unit which I have given in the top.

Look at the carbon 13 its spin is half; its abundance is 1.1, its gamma is 4 times less than that of proton. Similarly, as you go further some of the nuclei will have negative the magnetic moment, for example silicon-29. Look at silicon second row from the bottom its magnetic momentum is negative. So, gyromagnetic ratio is -5.3. All these parameters have some meaning unit. As we go ahead further will understand these things.

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Commonly studied nuclei in Chemistry and Biology

Proton (^1H), Carbon (^{13}C), Nitrogen (^{15}N), Phosphorus (^{31}P), and Deuterium (^2H)

Spin ½ nuclei are relatively easy to study

^{11}B, ^{10}B, ^{27}Al, ^{17}O, ^{29}Si, etc. are studied in inorganic chemistry, materials science

So, these are the things which we have to understand, but please remember commonly studied nuclei in chemistry and biology are proton, carbon, nitrogen 15, phosphorus 31. All of them are spin half nuclei. And also deuterium which is spin 1 nuclei. Spin half nuclei are relatively easy to study. And there are other nuclei like boron 11, boron 10, aluminum 27, oxygen 17 etc. These are studied in inorganic chemistry and material science etc.

I think now that time is up for the day, what I am going to do is I will stop here. So, what we did discuss today the fundamental concept of spin physics, about spin angular momentum, spin quantum number, magnetic quantum number, magnetic moment, how they are related to each other. We calculated the magnitude of possible orientations for spin half nuclei and we also found out the difference between 2 nuclei which have the same spin quantum number, spin magnetic quantum number, but they have different gamma which can be studied individually. And we also saw different properties of different nuclei which are based on the abundance, spin, gyromagnetic ratio and magnetic moment. Some of them positive magnetic moment, some of them negative magnetic moment. They have different meaning which I am going to discuss in the subsequent classes but these are the concepts which we understood.

Next we have to understand what happens if we take such type of nuclei and put it into the strong external magnetic field? what is going to happen? That is a new type interaction call Zeeman interaction which is the basis of study NMR. So, in the next class we will discuss Zeeman interaction and go further. Thank you very much.