One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture No -2
Spin Angular Momentum and Magnetic Moment

Welcome back. So in the last class I started giving you some historical perspectives of NMR spectroscopy and gave you some information about its utility in various branches of Science, and I also mentioned the names of the pioneers who contributed significantly, many Nobel laureates for this NMR Spectroscopy. Of course we have to know that, so we should know who are the pioneers, who made NMR what it is today. So that is what we discussed and also I discussed about spin angular momentum and how we can get empirically by knowing the atomic mass and atomic number.

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How to arrive at the value of Nuclear Spin?

^{1}H Single Proton, Spin is 1/2

^{2}H Single Proton and Single Neutron
Neither of them are paired [Each spin ½]

Nuclear spin of ^{2}H is 2 x 1/2 = 1

What will do today, is that we will continue further and see how we can arrive at the value of nuclear spin based on the alignment of protons and neutrons within the nucleus. Of course empirical rule is one way. Just to make you familiar, you should know how we can get. If I say it is half, just because I know atomic mass and atomic number we can work out. But there is way to get it also in different way. If I take Proton, I mean, the proton means hydrogen atom.

Please remember in NMR jargon when we say hydrogen atom, we colloquially say it is proton. It means not we are talking about proton of the nucleus. Of course that is what we are mentioning, that is what we are referring to. Colloquially if there is a hydrogen atom in a molecule we say we are dealing with proton. That means we have only one proton in it and by practice colloquially we say for hydrogen atom as a proton.

So if you look at hydrogen atom it has single proton in the nucleus. What the spin of proton I said, it is half. So no question of any discussion on that. It is only one proton and it is established experimentally its spin is half. Now let us take deuterium, it has single proton and single neutron. There is no pairing, none of them are paired they are single. Each them are unpaired single spin. Each of them are single and each has spin half. Now joined this, combine this. What is the total nuclear spin of deuterium. 2 into half, each of them have spin half, so 2 into half, it is one. I am just taking them together for the total spin. So the total spin is one.

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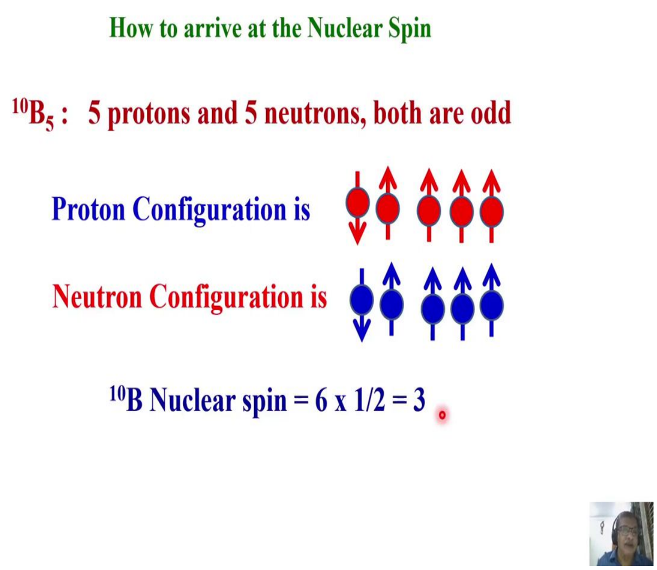

so spin of deuterium is one. Now let us look at what is the spin of boron 10. See the atomic mass is 10 and atomic number is 5. So, in the nucleus of boron 10, we have 5 protons and 5 neutrons, both are odd numbers. Now, let us see what is the configuration. How they get paired. Of course it is similar to your atomic theory where you can find out how the electrons are paired, etc. You all know atomic theory. Exactly similar to that. Of course more details are there. I am not going into details, for which you need to understand lot more about nuclear physics. But simply I am giving you how you have to find out the configuration. From the configuration how will you arrive at the spin. The proton configuration is given like. There are 5 protons, first two are paired, the remaining 3 are unpaired. Why they are unpaired, why these 2 are paired and why these are unpaired, more details you can see in the nuclear physics, Ok no problem, but you just take my word.

Similarly neutron, 5 neutrons are there, it is an odd number. First 2 are paired other 3 are unpaired. So, what is the total spin of boron? 6 into half. they are unpaired remains. you must always count unpaired ones, You should always count unpaired protons and unpaired neutrons. You should always take into account the unpaired protons and unpaired neutrons and then work out the total spin. So, 3 unpaired protons and 3 unpaired neutrons together there are 6, and total spin of each of them is half, so the total spin is 3. Boron 10 has spin 3. It is an integer number. That is what you get from your table which I gave you earlier.

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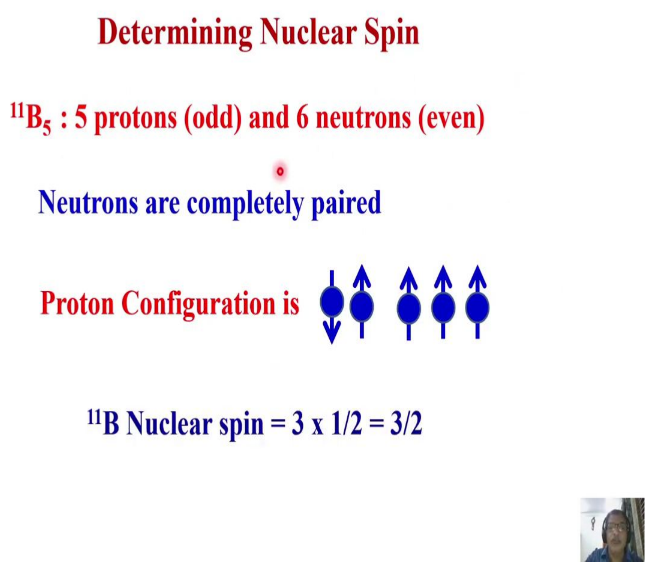

For determining nuclear spin, we can go for boron 11. It is the other isotope of boron. There are 5 protons and 6 neutrons. The neutrons are completely paired; an even number. Proton configuration is of course we saw in the previous example 2 are paired and 3 are unpaired. So, as far as neutron are concerned completely they are paired you do not have to worry. There are 3 unpaired protons. As a consequent boron-11 nuclear Spin is 3 into half, that is 3 / 2. See boron 10 spin is 3; boron 11spin is 3 / 2. This is what you could get from that table I gave you by empirical rule.

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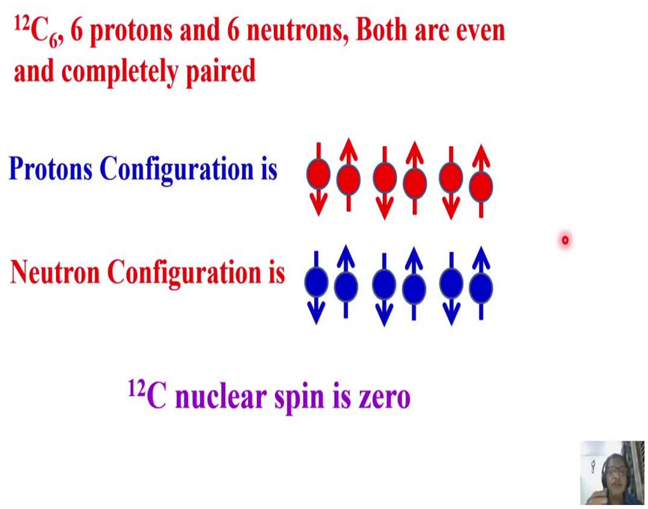

Now carbon 12 we will see. It is another thing, we always say carbon 12 spin is 0. that is what we saw, both numbers atomic mass and atomic number both are even. The spin of carbon 12 is 0 why? Look at this one, both of them has 6 protons and 6 neutrons. They are completely paired, or there is no unpaired proton in the configuration. Proton paring configuration if you see, there is no unpaired proton. Similarly there is no unpaired neutron. All protons and neutrons are completely paired. So, what is the total spin of carbon 12? 0. There is no unpaired protons and unpaired neutrons.

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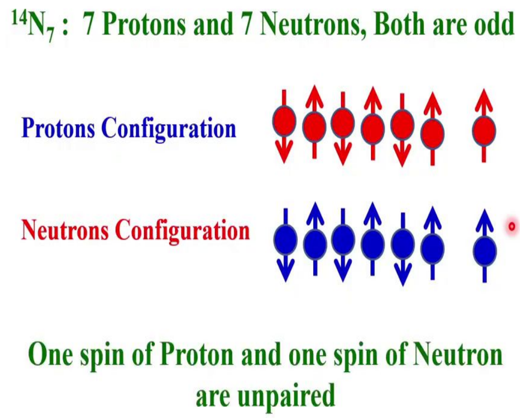

Nitrogen 14, I am giving you another example to make you more familiar. 7 protons and 7 neutrons both are odd numbers. Now let us see the configuration, proton configuration, six of them are paired only one Proton is unpaired. Similarly, neutron configuration; 6 are paired and one is unpaired. So how many are unpaired in the nucleus? one proton and one neutron. Now take this thing together for the two unpaired, one proton and one neutron. The total spin of Nitrogen 14 is 1. So the Spin of ^{14}N is 1.

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Basics of NMR Spin Physics

With that, of course, I give you some examples workout. Do this exercise, take any isotope of an element in the periodic table. Of course do not get a bigger one, because then for your configuration , you have to start working out. It is going to be a huge exercise. Something simple you can take like silicon or lithium like that. Find out what is the spin of lithium, ok lithium 6, lithium 7 by this configuration. How they will get align, you will know. You can use table to find out or you can also use a method of configuration how they get paired to get the spin of the nucleus. That is an important concept to understand. Now if you want to understand the NMR spectroscopy, you must know the basics of NMR physics. Without that you cannot understand NMR. But you need to understand some Mathematics, some spin physics. But I will try to minimize mathematics as much as possible. I will not frighten you by giving high funda mathematics, high level mathematics. But whatever is required basically, I will make it as simple as possible take carry all of you with me. But these are the important concepts you must know, if you want to know NMR spectroscopy.

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There are Two Quantum Numbers associated with the spin angular momentum (P) of the nucleus. These two quantum numbers determine its properties

Spin Quantum Number (I)

All the Nuclei with Spin Angular Momentum have a magnetic moment with constant magnitude and direction. This is determined by

Magnetic Quantum Number (m_I)

Now, if I look at the angular momentum P which is the represented as P of the nucleus. There are 2 Quantum numbers associated with that. For a nucleus if you have a spin angular momentum P there are 2 quantum numbers associated with that, and these 2 quantum numbers define its properties, properties of angular momentum. Remember for the nucleus, spin angular momentum if it is there, it is associated with the 2 quantum numbers.

These two quantum numbers define the properties of this P. Ok. What are they? One is a spin quantum number I, ok and all the nuclei with spin angular momentum have a magnetic moment also. This is the spin quantum number that is one of the quantum number after 2. Second remember all the spin angular momentum of all the nuclei also have magnetic moment. Again it is a vector, which has a magnitude and direction. And that magnitude is constant and direction is also defined, you can define the direction. What is this? This is magnetic quantum number given by m and m is related to I. If I know spin quantum number I, I know what is magnetic quantum number m. That is why I have written as m subscript I. Please remember spin angular momentum P of the nucleus is associated with these 2 quantum numbers. Spin quantum number I and magnetic quantum number m which depends upon what is I? And these 2 numbers will define the properties of angular momentum.

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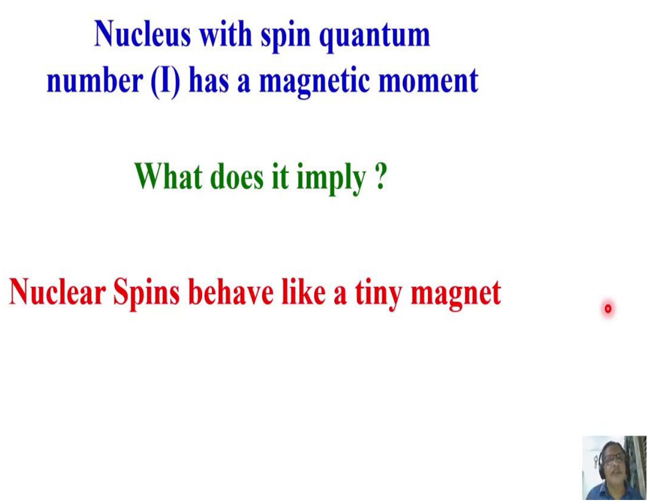

Now let us look at nucleus spin quantum number I, when I say it is a magnetic moment, we should understand what does it imply? What do you mean by telling a material has a magnetic moment? Nucleus with spin quantum number I has a magnetic moment. It implies that nuclear spin behaves like a tiny magnet. You know that, when you have magnet you can get a magnetic moment.

So to understand, to it implies me, if I say any nucleus spin I it also has magnetic moment m. As a consequence we can say all the nucleus spins behave like a tiny magnet. Every nuclear spin is a tiny magnet. Imagine if I take small amount of sample to study NMR in an NMR tube. Let us say 1 ml, you can find out how many atoms are there in a given sample by using a Avagadro number. And each of them has so many tiny magnets. Remember millions and millions of tiny magnets will be there because we can treat every nuclear spin as a tiny magnet.

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The magnitude of this Nuclear Spin Angular Momentum (P) is given by Spin Quantum Number I

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

ħ is the planck's constant (h), divided by 2π

$$\hbar = h/2\pi$$

Next what is the magnitude of this nuclear spin angular momentum? I said nuclear spin angular momentum it has a magnitude also. What is the magnitude of the spin angular momentum that is given by spin quantum number I. Because as I said, its properties is decided by two Quantum numbers I and m magnetic quantum. That is what I said. Now if you want to find out the magnitude of P, it is given by this expression h cross into square root of I into I + 1.

Now what is I? What is h cross? h cross is of course nothing but the Planck's Constant. You all know h, divided by 2 Pi. Planck's Constant divided by 2 Pi is called h cross, that is put here. So, P is the angular momentum and its magnitude is given by this and I is the spin quantum number. All are known now. You do not have to get confused. all these parameters, P and I, everything is known.

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Component of Angular Momentum along the axis of magnetic field, Z, is governed by

Magnetic quantum number m

$$P_Z = m\hbar$$

Another thing, we say in quantum mechanics, a component of angular momentum along the axis of magnetic field Z is governed by magnetic quantum number m. See it is angular momentum is again a vector quantity. It is also get quantized at a particular direction in a magnetic field and I am taking P_Z direction, quantized direction and the Z component of this P_Z is given by what is called mh cross. What is m? m is the magnetic quantum number. Remember I told you already m is the magnetic quantum number which depends upon I. That is what wrote m_I, the total Z component of the angular momentum depends upon m and it given as P_Z equal to mh cross.

All the things you can derive. But remember you no need to go into more details. This is a concept you must know that Z component of the angular momentum, that is along the direction P_Z is given as mh cross.

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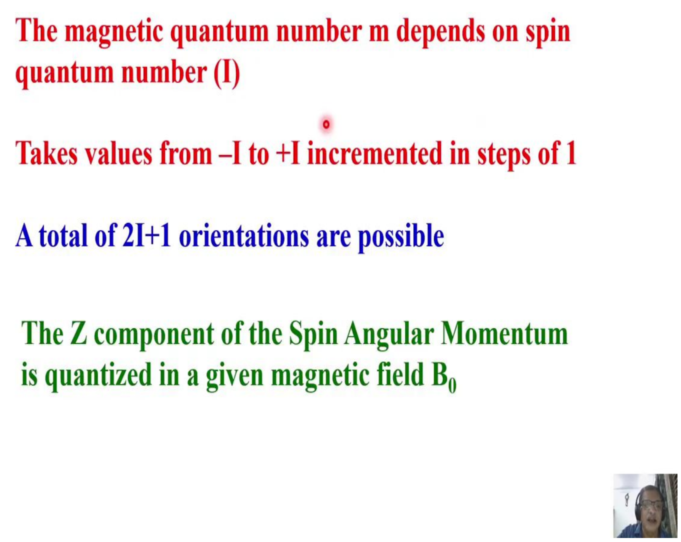

The magnetic quantum number m, I said depends upon I; how does it depend upon I? There is well established rule given, the magnetic quantum number m always takes the value of I from - I + I incremented in steps of 1. Please understand. If I know I that is spin quantum number, for example spin quantum number of protons is half, what is minus I, since I is half then minus I minus half, and plus I is plus half. So it will go from minus half to plus half, it is in steps of 1.

The magnetic quantum number m depends upon I which can go from –I to +I in steps of 1. So, as a consequence how many orientations are possible? There are 2I + 1 possible orientations. So, If I want to find out what is magnetic quantum number m which I said $m_{I,}$ that it defines the orientation of m based on I, and there are totally 2I+1 orientations possible for any given spin I. Z component of the spin angular momentum, means is always quantized in a given magnetic field, $B_{0.}$ That is what I said, Z components is quantized. It is not continuous, it is discrete quantized, and these directions are defined by the number of orientations, and are given by $m_{I,}$ which goes form –I to +I in steps of 1.

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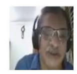
Possible Orientations of angular momentum for different Spin Quantum Number I

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, what are the possible orientations we can think of for angular momentum P for different spin quantum number I. We will take examples. I am talking about I spin of the nucleus and angular momentum P is there, and we find out what are the possible orientations. Angular momentum orientations, possible orientations are given by m_I. So, now for spin half nuclei there are 2 orientations, minus half and plus half. Of course in steps of 1. If you take minus half and then add one, you will get plus half.

So only two quantization directions, there are only 2 orientations. For spin half there are only two quantization directions. For spin 1 there are 3 orientations, 3 quantization directions, because start with -I, that is -1 add 1, it is 0, and add 1 it is 1. So, from –I to +I there are only 3 orientations for spin one nuclei. There are 3 quantization directions. For spin 3/2 there are 4 orientation, starts with -I, -3/ 2 then add 1 then it will become -1/2, then add 1, it will be come, + 1/2 and finally add another 1, it will become +3/2. There are 4 possible quantization directions, 4 possible orientation of angular momentum which is quantized along Z axis. You can work out like this for any spin quantum number I of the nucleus.

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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 positive values of m_I : the spin angular momentum orients in the direction of the field

For negative values of m_I : the spin angular momentum orients opposite to the direction of the field

So the quantized orientation direction we understood, for spin half nuclei it is 2, then what is the quantization direction? There are 2 possible orientations which has directions, two quantization directions, what are these? What do you mean by plus half direction? What do you mean by minus half directions? This is positive value of m_I that is positive value of half, spin angular momentum orients in the direction of the field, and this spin angular momentum orients in the direction of the field.

For spin angular momentum which is for negative values of m_I, so positive value of mI it is in the direction of the field. Same thing if it negative it is in the direction opposite to the magnetic field. There are 2 orientations for spin half, this way and this way. Remember this concept we will be using it very often to understand that degeneracy of the spin system, etc. as you go ahead. Ok so spin half nuclei there are two possible quantization directions of your m_I, plus half in this direction it is a magnetic field let us say Z axis, as the direction of the magnetic field. So one of the orientation directions is in the direction of the field and the other quantization direction is in the direction opposite to that of the field.

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The two spin states (m_I) of spin ½ nuclei are |+½> and |-½>

They are called 'spin-up' ↑ and 'spin-down' ↓

Conventionally spin up state is denoted as α and spin down state is denoted as β

And the one which is in the direction of the field is called spin up and other one is called spin down. There are 2 orientations, spin up and spin down. That is also represented as plus half and minus half states. So, spin half has 2 possible quantization states. Ok, 2 possible orientations along Z direction. So, they are plus half and minus half, spin up and spin down states, and colloquially or conventionally in NMR jargon the spin up is defined as alpha and spin down that state is denoted as beta. Please remember alpha and beta are the spin up and spin down states nothing, but plus half and minus half states. Is it clear, the 2 spin states of spin half, plus half and minus half, this is spin up and this is spin down, or alpha state and beta state. These are terminologies which are in use.

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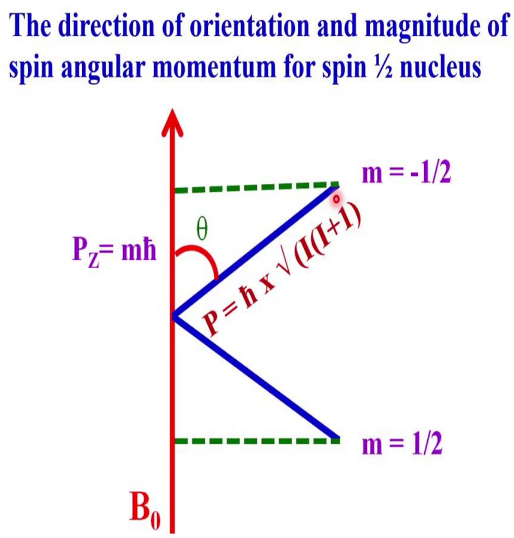

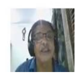

Now let us calculate the directions of orientation and magnitudes of the angular momentum for spin half nucleus. I said, it is quantized and have 2 directions. Spin angular momentum, I said Z component is quantized and it is given by mh cross. Remember I wrote a equation P_Z is equal to mh cross. What is m? what is m is equal to; m depends upon I, +I to –I. So for spin half nucleus, we have 2 orientations, minus half and plus half. Now let us find out orientation direction and its magnitude. And I said it orients in the direction of the field, and in the direction opposite to the field. But it does not mean always perfectly aligned along the field. In fact although we say in the direction the field, it is making an angle theta. The orientation, the direction of orientation of the component along these 2 quantization directions make an angle theta.

What is this angle theta? Find out, I also know this $P_{Z,}$ because this I know as mh cross, and I also know P is equal to h cross into root I into I + 1 that I mentioned earlier. I is spin half. I know I, I know h cross I can calculate what is P. I know P_Z, because it is equal to mh cross. m is equal to minus half and plus half are the only 2 orientations because it depends upon I. Now I can calculate theta for the that I must know what is this. Or I do not need to know if this and this also so I can calculate theta. Similarly, I can theta for this orientation and there is no difference between theta, this and this. One is this is theta positive, this is negative. This orients in the direction of the opposite to field. In the same angle it orients in the direction of the field. So, you can find out the angle theta, the direction of orientation.

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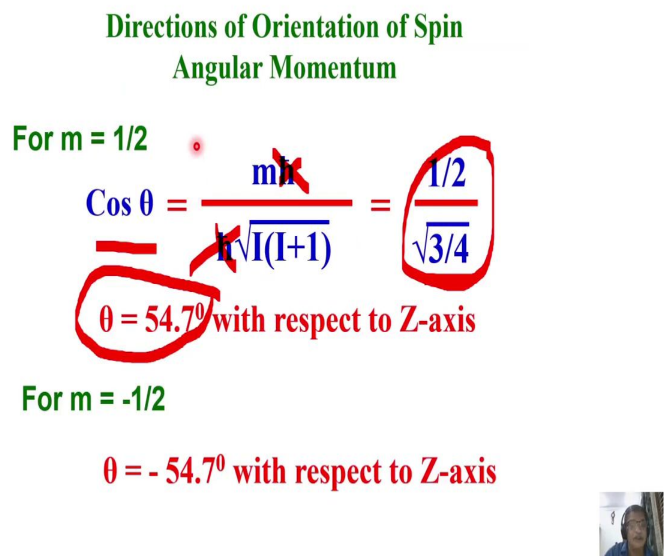

Let us do that, ok. For m half, find out cos theta is equal to mh cross over h cross into root of I into I + 1. Go back here, cosine of the angle theta is given by this side divided by this side. This is the trigonometry, the right angle triangle I am using. ok that is the idea. So I know cosine of the angle theta is divided by this. What is the value of m? Half. For m half, m is equal to half. What is I? h cross and h cross here. See this h cross and this h cross gets cancelled out. So you are left with m is equal to half and I is equal to half so it turns out be half over square root of 3 by 4. So this is the simple number plug it into the calculator. You get cosine of theta. Now find out Cos inverse of that. It turns out to be theta is equal to 54.7 degrees. Please remember, theta is 54.7 degree. Same way for m is equal to minus half, it is 54.7 degree in the direction opposite to the Z-axis. So, one of the orientations of spin angular momentum, one component of it is in the direction of the field corresponds to theta equal to 54.7.

Other is same angle in the direction opposite Z. These are 2 orientations. This one is +54.7, this is -54.7 with respect to this. ok this is what it is. we can work it out and we got this. So 2 angles we know, we understood magnitude also. We calculated the magnitude, and magnitude is given by this and we also know what is the angle theta.

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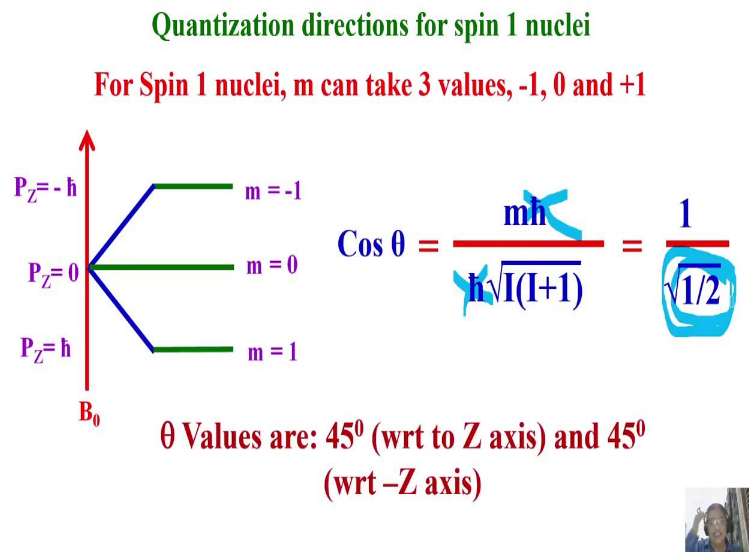

Now what is the quantization direction for spin 1 nuclei, can you understand, why not? For spin 1 nuclei m can take 3 values – 1, 0, +1. So, what are the quantization directions. 3 like this. We know P_Z is equal to mh cross, m is equal to -1. so –h cross m is equal to 0, P_Z is 0 here, m is equal to +1 P_Z is equal to h cross. Now calculate angle theta here. This is 0, this is 90 degree with respect to magnetic field, this is theta.

Now simply plug in these values. Cosine of theta for m is equal to 1, again in this case also take out this one. I am sorry, again this h cross and this h cross gets cancelled out and you are left with m which is one, I into I + 1 which is half into half + 1. ok half into half + 1, half + 1 is 3.4, there is some mistake made here, so you can find out. So this should be 3 by 4 ok there is a mistake. Anyway, please note this is not half this is I into I + 1 this has to be 3 by 4. Ok, plug in these values. I have written wrong here but I have correctly calculated the angle by plugging into the calculator. So this turn out be theta, for this is 45 degree, with respect to plus Z axis. This is 45 with respect to –Z axis. So, you calculate the angle theta for +1 0 -1 states.

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Quantization directions for spin 3/2 nuclei

For spin 3/2 nuclei, magnetic quantum numbers are

-3/2, -1/2, +1/2 and +3/2

Now in the same way work out the quantization direction for spin 3 by 2 nuclei. There are only 4 possible quantization directions -3/2, -1/2, +1/2, 3/2.

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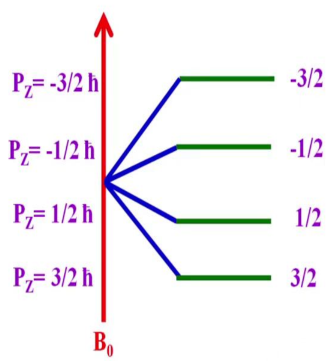

$$\cos\theta = \frac{m\hbar}{\hbar\sqrt{I(I+1)}} = \frac{3/2}{\sqrt{15/4}}$$

θ Values are: 39.23^0, 54.7^0 (wrt to Z axis) and 39.23^0 and 54.7^0 (wrt –Z axis)

Again I do not want to go to the details of that. ok plug in these values and then what is for m is equal to 3 by 2, it is 3/2 into 3/2 + 1, find out this number, plug into calculator to find out theta, theta values for these are 49.23 for this is 39.23 in the direction of the field and in the direction opposite to the field. Of course for this we already worked out, for plus half and minus half it is

54.7 both in the direction of the field and in the direction opposite to field. So that is what we have worked out. So now we can get magnitude and direction of orientations of all these.

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Ok now the next question is you have to understand another term I want to introduce, called nuclear magnetic moment. Well if I start discussing about is nuclear magnetic moment, I think it I have to take a lot of time. I cannot stop in between so what I am going to do is I will stop for the day. I have already introduced to you lot of things today, about spin angular momentum, direction of the quantization, how do you get their angle and how do you get their magnitude etcetera.

And what are the directions of orientations for spin half nuclei, spin 1nuclei, spin 3/2 nuclei. We calculated the angle theta magnitudes and everything. Please remember these things these are all important for the basic conceptual understanding of NMR. This spin physics is important and I also said for spin angular momentum P we have 2 quantum numbers, I and m, m depends upon I, is equal to m_I, goes to –I to +I. So based on that Z component of the angular momentum P which is quantized along Z axis is given as $P_{Z,}$ which is equal to $m\hbar$. m values are known, accordingly we calculated everything. This is the summary of what I said for today, in gist, in one or two sentences. We will continue further with some more concepts called magnetic moment, which is also essential and then we continue further about more understanding of the concepts from the next class.