Fundamentals of Spectroscopy

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Lecture 46
Resonance Spectroscopy - Introduction 2

Hello all welcome to this lecture. So, in the last lecture we have been deriving lots of different equations on angular momentum. So, now you might wonder why are we deriving all these different equations, but we know spectroscopy is all about transitions between two different levels. So, we will see during this lecture that in the absence of this magnetic field or the externally applied magnetic field the energy levels will be degenerate.

But when there is an interaction or the torque that happens that is J cross or mu J cross B so that kind of lifts the degeneracy so the presence of this external magnetic field lifts the degeneracy. So, the energy levels will no longer be degenerate and some transition can take place or there will be some energy difference between these two levels. So, to understand this properly we need to understand very importantly, we need to understand angular momentum.

So that is the reason we have been talking about angular momentum that is the spin angular momentum as well as the properties of angular momentum in general. So, in the last lecture, what we saw, we saw this Jz that the z component of the angular momentum is constant.

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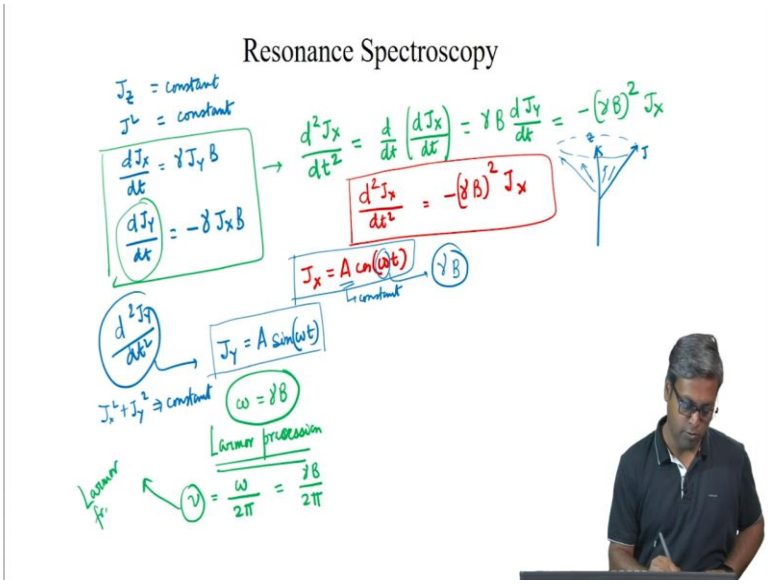

And also J squared is constant and the two other expressions we got was dJx dt equals gamma JyB and dJY dt equals - gamma Jx B. Now from these two equations one for dJx dt and one for dJy dt, we can write let us say we say d square J x or d 2J x dt 2 so this we can write as d dt of dJx dt. So, this is gamma B times d Jy dt and if we put the value of dJy by dt what we get is minus gamma B whole squared Jx.

So, if we write this final expression again, we can write d 2 J x dt 2 equals -gamma B whole squared Jx. So, this as you can see is a differential equation and the solution to this or one of the solution to this differential equation is Jx equals A cos omega t. So here this A is a constant and this Omega equals gamma B. So, similarly, if we look into let us say d2 Jy dt2 from here we can get Jy equals A sin omega t. so, this is because in the last lecture we saw that Jx squared + Jy squared is constant.

So, now we have Jx equals A cos Omega t and Jy equals A sine omega t and because cos squared theta + sine square theta equals 1 if we do Jx square + Jy squared then it will be a constant, that is a square. So the main important thing is what does this equation imply? This implies that the vector J precesses along the surface of a cone in other words let us say this is my z axis and this is my angular momentum vector J, so the J, precesses along the surface of a cone and it precesses with an angular velocity.

So, the angular velocity if we denote the angular velocity by Omega then, Omega equals gamma B. And this precision that means this J that is précising along the surface of a cone, this precision is known as Lanmor precession. And because it is rotating there is a frequency associated to it and we know the frequency nu is related to Omega by Omega by 2 pi. So, we can write nu equals gamma B by 2 pi where nu is the Lanmor frequency.

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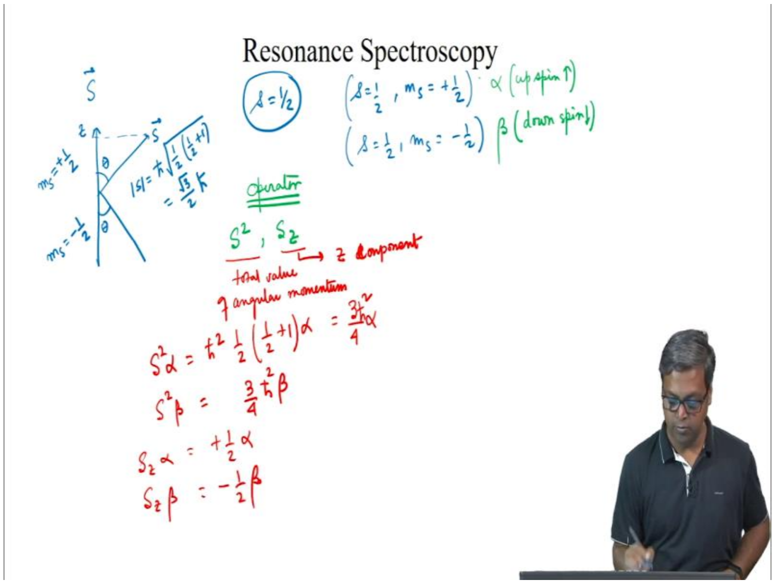

For electrons or any other spin half system or spin 1/2 particle there are two possible orientations of the S vector or this angular momentum vector, the spin angular momentum vector. So, if we draw it, this is my z direction and let us say, this is my spin angular momentum vector, so it can have two different orientations and the magnitude is given by h cross root over 1/2 times 1/2 plus 1 so that is root 3 by 2 h cross but the projection, in other words, the m s is +1/2 in one case and m s equals -1/2 in the other case and this is because s equals 1/2.

So, for s equals 1/2 we have two spin states one is s equals 1/2 m s equals +1/2. So, this is one spin state and the other is s equals 1/2 m s equals minus, so the first one is known as alpha but the half spin and the second one in is known as beta or the down spin. So, any observant in quantum mechanics has a corresponding operator. So, we are talking about quantum mechanics here because as I had mentioned in the last lecture spin has no classical analog.

So, for electron spin the relevant operators are s squared and s z. So, this s square defines the total value of angular momentum and this s z determines the z component. So, this s square alpha is h cross squared then 1/2 times 1/2 plus 1 alpha. So, this is 3 by 4 Alpha. So, similarly we have h cross squared here, so similarly, A squared beta equals 3 by 4 h cross squared beta and for the sz case is z alpha equals +1/2 alpha and is sz beta equals -1/2 B.

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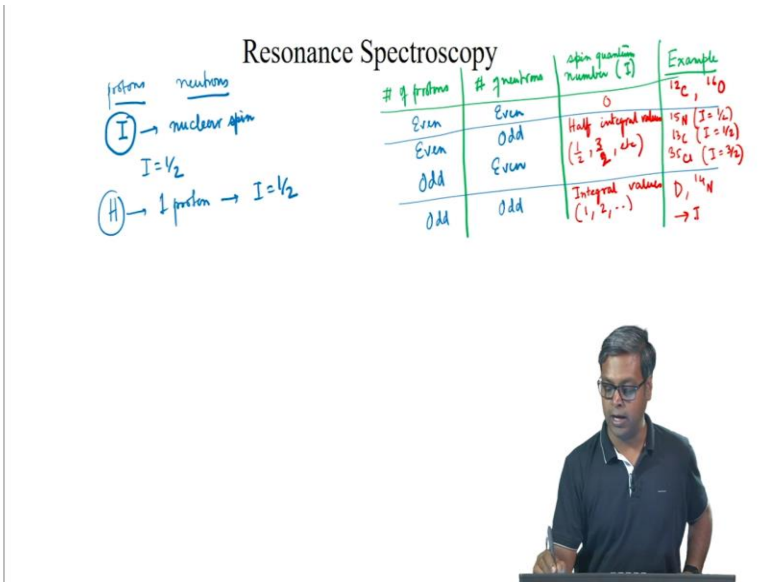

So, like spin or electrons are other elementary particles. For example, if we think about protons or neutrons, so these elementary particles also possess spin. For nuclear particles, the spin is denoted by I or I denotes nuclear spin for both protons and neutrons. They are characterized by I equals 1/2. So, nucleus of, let us say, hydrogen atom is the simplest case because hydrogen atom only has one proton.

So, if I have a hydrogen atom which has only one proton in that case, the hydrogen nucleus will have I equals 1/2. But other nuclei consist of both protons and neutrons. So, due to existence of spin both proton and neutron possess angular momentum or magnetic moment which are vector quantities. So, for a nucleus we have a resultant vector representing the angular momentum or magnetic moment.

So, we can draw a table and so we can understand the value of I as a combination of the number of protons and number of neutrons. So let us in one column we say number of protons and then we have number of neutrons. Then, let us say, we have spin one term number which is denoted by I and finally we will look into examples where we can find these scenarios. So, the first scenario is both the number of protons and neutrons are given. There are other scenarios, we can have number of protons, even number of neutrons or number of protons odd, number of neutrons even.

And then there is a last scenario where in both cases the number of protons and number of neutrons are odd. So, we will divide this into three parts. So, we will see that when both are even I equals 0 when both are odd. I can take integral values or we can say I equals 1, 2 etcetera. But in the case when either the number of proton is odd and the neutron is even, or the neutron is odd proton is even, the I can take 1/2 integral values.

So, the values of I can be half 3 by 2 etcetera and now let us go to the examples. So, for I equals 0 the example is 12 carbon or 16 oxygen and for the half integral values we have examples in N 15 in this case, I equals 1/2. Similarly, for 13C, I equals 1/2 but let us say if we have 35 chlorine CL, then, I equals 3 by 2. And for this odd-odd case where you have integral values of I then diotorium or let us say 14 nitrogen in those cases, I equals 1. So, the magnetic moment of a nucleus is denoted by mu N.

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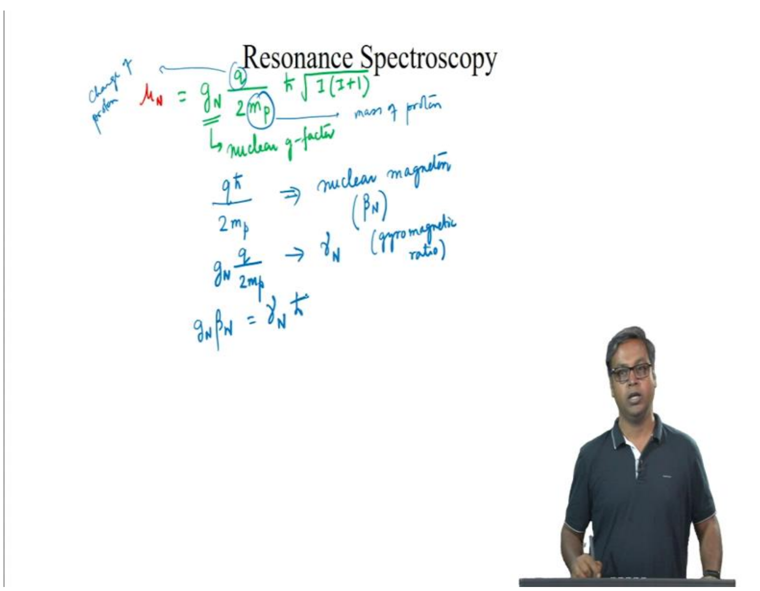

And now we should remember when we are talking about spin, we said the magnetic moment was denoted by mu s, where s stood for spin and now here n stands for nucleus. So, we can write mu N equals g N q by 2 m P h cross root over I times I + 1. So, you can see, we can find the analogy of what we talked about in the last lecture about spin, that is about the electron spin and now, we are talking about the nuclear spin. So, here this gN is known as the nuclear g factor and this q is the charge of proton and mp is the mass of proton.

And again we can write this q h cross divided by 2 mp, this is known as the nuclear magneton. So, we saw four electron spin, we define something as Bohr Magneton, in case of nucleus, we have nuclear Magneton. So, it is denoted by beta but we have beta sub N, N stands for nucleus or nuclear. As in the case of this electron we can also define g n q by 2 mp as gamma N where this is the gyromagnetic ratio and like we saw in the last lecture, we can write g sub N beta N equals gamma sub N h cross.

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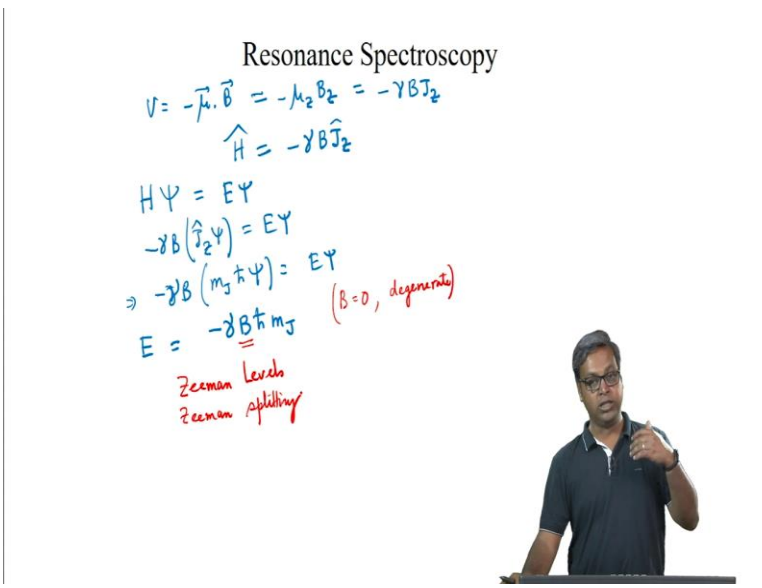

So, a magnetic dipole for a given orientation in a magnetic field, which is given by let us say B and which is along the z direction has this potential energy which can we can write the potential energy as V equals minus mu dot B and because B is in the z direction or along the z axis, we can write this as minus mu z B z, or again further we can write this as -gamma BJz but J the present an angular momentum vector.

So it can be either the spin angular momentum S or the nuclear angular momentum that is I. The Hamiltonian operator representing the interaction of an isolated spin will be H Hamiltonian will be - gamma BJ z. so, if Psi is the spin eigen function, so we know, we can write H psi equals E Psi in other words -gamma V times JZ psi equals E psi and Jz is J cos theta because there is the z component of the angular momentum.

So we can write this as -gamma P times mJ h cross psi equals E psi. In other words the energy E equals -gamma B h cross mJ. So, most importantly, we can see when V is 0, then, E is 0 or all the orientations of the spin vector has energy equals 0. In other words, when B is 0, then the energy levels are degenerate. But due to the application of an external magnetic field, different orientations have different energies.

Thus degeneracy has been lifted and different orientations belong to different energy levels. And these energy levels are known as Zeeman levels and the splitting of these energy levels is known as Zeeman splitting. So, now before we go into details of the spectroscopic techniques, let us now compare the spin and the associated magnetic properties in the 2 spin 1/2 particles. So, one is proton and the other is electron.

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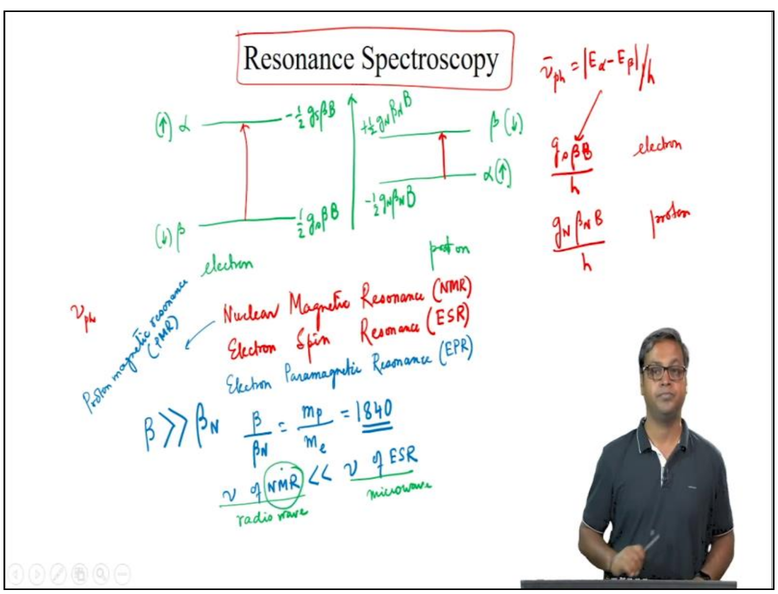

So we will make a table here to compare we have electron here and we have proton here. So, the first thing we can compare is the spin quantum number. So, in this case, we write s equals 1/2 and for proton we write I equals 1/2 Now, if we compare the angular momentum so here the modulus of s equals h cross root over s times s + 1. And here the modulus of I equals h cross root over I times I + 1.

Now, we have also talked about something called magnetic moment. So, the magnetic moment that is mu s is given by gamma s and in proton we write this as mu N. N for the nucleus which given by gamma NI and also the gamma what we have here is given for the electron as gs times e 2m E and here for the proton we can write gamma N equals g N q times 2m p. Now, the value of g s and g N, they are not the same so g s is 2.002, on the other hand, g N is 5.585.

And also this mu s can be written as gamma then h cross root over s times s plus one or we can write this as g s beta root over s times s plus one in case of proton we can write mu n equals gamma n h cross root over I times I + 1 or we can write g n beta n root over I times I + 1 and for the Larmor precision of the frequency of Larmor precision so let us put larmor. So, for lammor precision we know that Omega larmor precision or the frequency that is nu larmor precision is given by gamma B by 2 pi or we can write as gs beta B by h.

And for the proton or the nucleus this nu lamnor position is given by gamma N V by 2 pi so this is g of N beta N be by h. So, we are talking about spin States so as we discussed there are two possible spin states so for the spin States there are two possible spin states one is alpha which is up spin and the other is beta which is down spin. Similarly for proton we have alpha which is up spin and beta which is down spin and the only difference is in case of alpha m s equals +1/2 and in case of beta ms equals -1/2.

So the energy now the here comes the important part for energy E of alpha is given by -1/2 g of s beta B and the for the energy of beta is given by 1/2 gs beta B, so we can write the same thing for the proton E alpha equals -1/2 g is beta B and E of beta equals 1/2 g s beta B but now comes the difference. So, in case of electrons the E of alpha is greater than E of beta and this is because for this case beta is negative.

But for protons this E beta is greater than E alpha because in this case beta is positive. So, when we talk about some energy difference that is Delta E given by modulus of E alpha - E beta this is g s beta B and this value is large we will see the reason and it is important to note that this energy or if we divide by energy by h we get the frequency this is exactly same as the larmor frequency and we will also talk about it in another in the next slide.

So for proton delta E we can write this is E alpha - E beta which is g n so this is g N beta with N B but this is small so in presence of an externally applied field we can draw the schematics of the energy levels of the spin states of a spin 1/2 particle. So, let us say this is my energy axis so for electron what we saw we have beta which is lower energy so this is down-spin alpha is higher energy top spin and so this is 1/2 gs beta B this is -1/2 gs beta B but for proton as I said the energy difference is less.

So here the energy difference will be less and another thing that is different here we have alpha which has less energy and beta has higher energy. So, here the energy is - half g N beta N B and here is +1/2 g N beta N B so a photon of frequency let us say the frequency of the photon is nu photon. So, this photon of frequency nu photon will induce a transition from the lower level to the upper one or we can say for the proton it will induce a transition from alpha to beta state and for electron it will induce a transition from beta to alpha state.

So and this transition will be induced when the energy of the photon becomes equal to the energy gap between these two levels. So, we can write this nu photon which is given by Delta E by h or modulus of E alpha - E beta by h so this will be g s beta B by h for electron and g N beta N this is B, B by h for proton. So, you can note that this nu photon or the frequency of light equals the frequency of the larmor position which I mentioned when I was making the table.

So this photon frequency equals the frequency of larmor precession of the spin system. So, since the frequencies match this is the resonance condition and that is why such a spectroscopy is known as resonance spectroscopy. So, for transition between nuclear Zeeman levels the spectroscopy is called nuclear magnetic resonance or NMR and for transition between electronic Zeeman levels the spectroscopy is called electron spin resonance or in other words ESR.

So NMR involving a proton is called proton NMR or proton magnetic resonance. So, we can write proton magnetic resonance or give or PMR and ESR is also known as electron paramagnetic resonance or EPR, so note that that the expression of frequency of absorb radiation contains the beta in other words the Bohr Magneton is for ESR and the nuclear Magneton is for NMR. But since beta or the Bohr Magneton is greater than greater than beta N or the nuclear Magneton this is because they are dependent on the mass of the proton and the mass of the electron.

So, we can write that beta by beta N equals mass of proton by mass of electron because they are inversely proportional and this is if you put the values we will get this mass of proton by mass of electron is 1840. So, in other words because beta or Bohr Magneton is much, much greater than nuclear Magneton. The frequency and the frequency is directly proportional to beta. So, the frequency of NMR is much, much less than the frequency of ESR.

If we do the actual calculation we can see that this nu of NMR comes in the radio wave region and the nu of ESR falls in the microwave region. So, this is where we will end today's lecture and in the next lecture we will start with NMR.