Fundamentals of Spectroscopy
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Lecture 47
NMR Spectroscopy – 1

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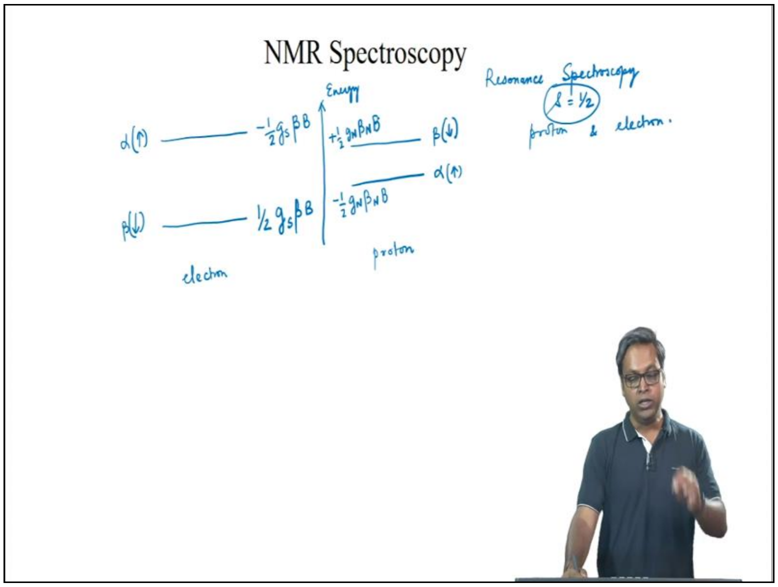

NMR Spectroscopy

Hello all, welcome to the lecture in the last two lectures we discussed resonance spectroscopy and compared the spin and the associated magnetic properties for two spin half systems or spin s equals half, so we compared 2 spin half particles one is proton and the other is electron. So, we saw that in the presence of an externally applied magnetic field B the schematic energy levels of the spin States of a spin half particle can be drawn as so let us say this is my energy axis and here on the left side we are drawing the electron on the right side we are drawing the energy level of the protons.

So, we have this two spin states for the electron the beta spin state or the down spin is of lower energy and alpha or the up spin is of higher energy. And the energy for this beta is half gs beta B and for alpha its minus half gs beta B. For proton we discussed in the last lecture that the energy difference between these two states are much smaller than what we see for electrons. And the other difference is here the lower energy state is the Alpha state which is half spin and the higher energy state is the beta state which is downstream.

So, the energy for this alpha state is half gN because we are talking about nuclear thing here gN beta NB and this is plus half gN beta NB.

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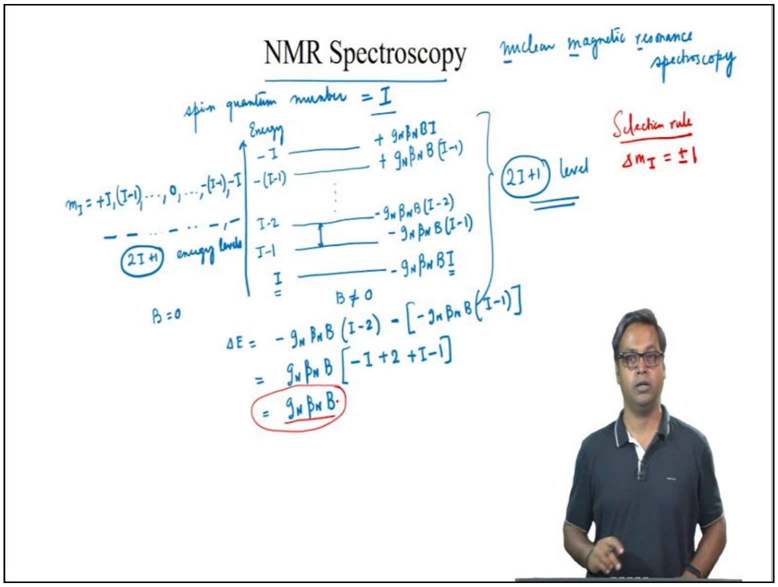

NMR Spectroscopy

nuclear magnetic resonance spectroscopy

spin quantum number = I

Selection rule

$\Delta m_I = \pm 1$

$m_I = +I, (I-1), \ldots, 0, \ldots, -(I-1), -I$

$\boxed{2I+1}$ energy levels

$\boxed{2I+1}$ level

$$\Delta E = -g_N \beta_N B (I-2) - [-g_N \beta_N B (I-1)]$$
$$= g_N \beta_N B [-I+2+I-1]$$
$$= g_N \beta_N B$$

So, in today's lecture we will focus on nuclear magnetic resonance spectroscopy or if we take the acronyms NMR, so we have NMR spectroscopy. So, in general for a nucleus with spin quantum number equals I the Zeeman levels and the corresponding energy levels can be shown as so let us say again this is our energy axis. So, when B equals 0 that means there is no externally applied magnetic field the mI can take values because the spin quantum number is I so mI can take values plus I then I can write I - 1 dot dot dot 0 is one value if it can take.

Then minus of I - 1 and -I so all these energy levels that correspond to this mI equals I, mI equals – I, so all these energy levels are degenerate. So, in total there are 2I + 1, energy levels which are degenerate but when we apply an external electric field that is B is not equal 0 that degeneracy will be lifted. So, let us draw the different non degenerate energy levels now. So, the lowest energy level has mI equals I so the energy is gN beta N BI and this I comes from mI this value come I and there is a minus sign.

Then for I - 1 it will be minus gN betaN B times I - 1 for I - 2 it will be gN beta N B times I - 2 so we will have this all these different levels and for minus of I - 1 it will be -g N beta N B but this minus minus becomes positive so it becomes plus I - 1 and the topmost level which has the highest energy there mI equals – I. So, this is +gN beta N B times I so in total there are 2I + 1 levels but when V0 equal to 0 then these levels are non degenerate.

So, now if we look into the energy difference between any two successive levels we can see let us take this levels I – 1, I - 2 so the energy difference or Delta E is given by -gN beta N B times I - 2 - g N beta NB times I -1. So, if we take g N beta NB common then we have -I + 2 + I -1 so this becomes gN beta NB so we can see the gap between two successive levels is given by gN beta NB and the selection rule is Delta m I equals + -1. So, this selection rule states that the transition will only take place between two successive levels because the difference between two successive levels the energy difference is given by gN beta B.

So, we can say that this nu equals gN beta NB by h so if this frequency matches with the frequency of light there will be a transition from the lower level to the upper level.

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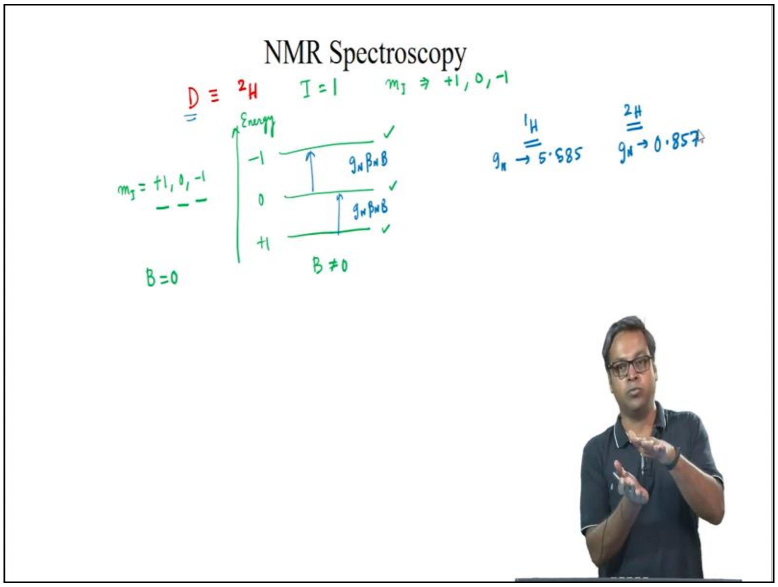

NMR Spectroscopy

So, for example if we take dotron so we present dotron as D we can also write this as 2 H for this case I equals 1. So, for dotron we can draw a schematic energy level diagram and look into the possible transitions. So, if we draw this for I equals 1 this is my energy axis. So, for I equals 1 m I can take the values of +1 0 -1 so when there is no external magnetic field then the mI values or the states are all degenerate so this is +1 0 -1 and all these energy states are degenerate.

But when we apply an external magnetic field the degeneracy is lifted and we have here +1 0 and -1 so thus we can see we have 3 energy levels corresponding to mI equals +1 mI equals 0 and mI equal to -1 and so there are two possible transitions. Since the two energy gaps are equal because in both cases the energy gap is g N beta NB and this other case also it is gN beta N times B. So, only one signal will be observed.

However the frequency of the absorbed radiation for this dotron will be different from that of a proton that is 1 H and this is because there is a difference between the gN values of the proton and the dotron. So, for 1 H or the proton the gN value is 5.585 and for dotron that is to H the gN value is 0.857 so because the gN value is much smaller for dotron the energy gap or the energy spacing is also much smaller for dotron as compared to proton.

Thus under the condition of proton resonance the dotron resonance will not take place. So, now let us look into the experimental setup of NMR.

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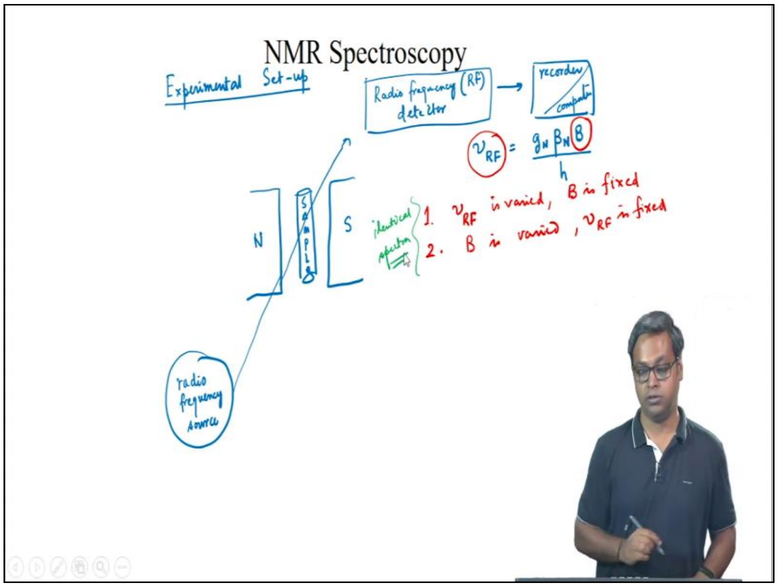

NMR Spectroscopy

Experimental Set-up

$$\nu_{RF} = \frac{g_N \beta_N B}{h}$$

identical spectra
1. ν_{RF} is varied, B is fixed
2. B is varied, ν_{RF} is fixed

So, we will look into the experimental setup, so let us say we have our sample here so this is sample and this external magnetic field is being applied using this magnet. So, we have the North Pole here and the South Pole of the magnet or the right side and as we know we need radio frequency light. So, what we need is a radio frequency light source so let us say this is our radio frequency light source.

And the light passes through the sample and then what we need is a radio frequency or radio frequency which we can in short write as RF. So, we need a radio frequency detector. So, it will detect that light after it passes for the sample and whatever the signal is being detected actually this is being recorded by a recorder or we can say our computer. So, the frequency of the RF is given by g N beta NB by h. So, we can see this expression the gN beta NB by h equals nu RF has two parameters one is the nu RF and the other is the external magnetic field that is B.

So, we can vary either nu RF or B the experiment thus can be performed in either of the two ways number one is nu RF is varied but B is fixed or it can be done as B is varied but new RF is fixed. So, both these procedures whether we very nu RF and keep be fixed or nu vary B or keeping or a fixed both these procedures give identical spectrum. So, we will get identical spectrum from both these procedures.

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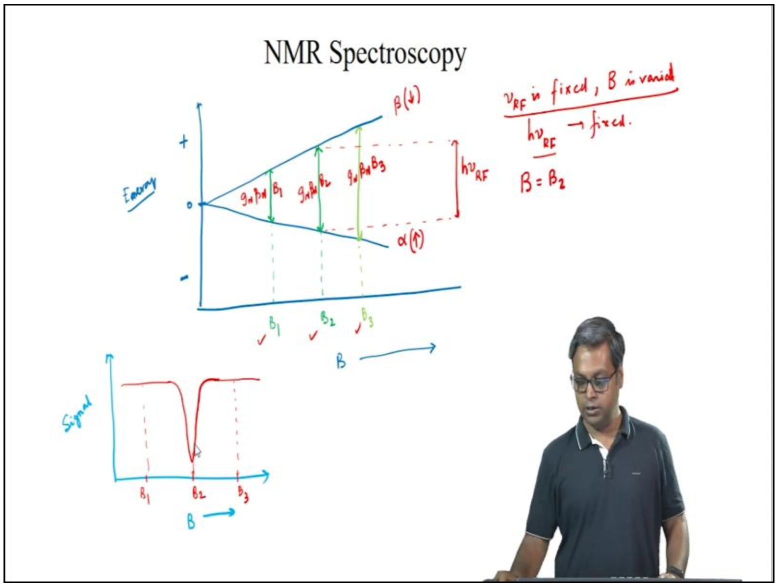

NMR Spectroscopy

ν_{RF} is fixed, B is varied

$h\nu_{RF} \rightarrow$ fixed.

$B = B_2$

So, the principal of the experiment can be understood if we draw the following figure. So, let us say we are drawing energy on the y axis so this is my energy, so this is my zero energy anything on top of zero is positive and anything below zero is negative. On the x axis we are plotting the magnetic field. So, when B equals 0 that means there is no external magnetic field both the energy levels or the energy states spin states are degenerate.

But as B increases the degeneracy is lifted, so at B equals 0 the both energies are 0. Now as B increases there is a difference in energy between the two states. So, let us say this is B 1, so this is the energy at B 1 energy difference which is given by gN beta NB 1. Now say this is my B 2 and this is energy differences at B 2 given by gN beta NB 2 and this is B 3 and the energy difference is given by gN beta NB 3.

So, as we have already stated the lower energy state is alpha which is the top spin and the upper energy state is beta which is down spin and let us say this energy difference at magnetic field equals B 2 is our h nu RF. So, out of the two different ways we have mentioned this is the example where this new RF is fixed but what we are varying is the external magnetic field or in other words then B is valid.

So nu RF is fixed that means h nu RF that is the energy is fixed. The energy gap at the magnetic fields B1, B2 and B3 are shown in this figure and as we can see the energy gap at B2 matches with h nu RF and hence the proton will resonate at B equals B2. So, if the signal at the detector is plotted versus B. So, let us say we plot the signal at the detector and so we have the signal on the y-axis and are plotting the signal against B.

So, we have B on the x-axis now let us look how the signal will look like. So, the sample will only absorb the nu RF at B equals B 2 so for B equals B 1 or B equals B 3 there will be no change in the nu RF. So, we can see the nu RF does not change it is flat but at B equals B 2 there will be a dip where the peak is at B equals B 2 and this is because due to the absence of the radio frequency because at B equals B 2 the radio frequency is absorbed and so whatever radio frequency goes to the recorder is less and that is why there is a dip and B equals B 2.

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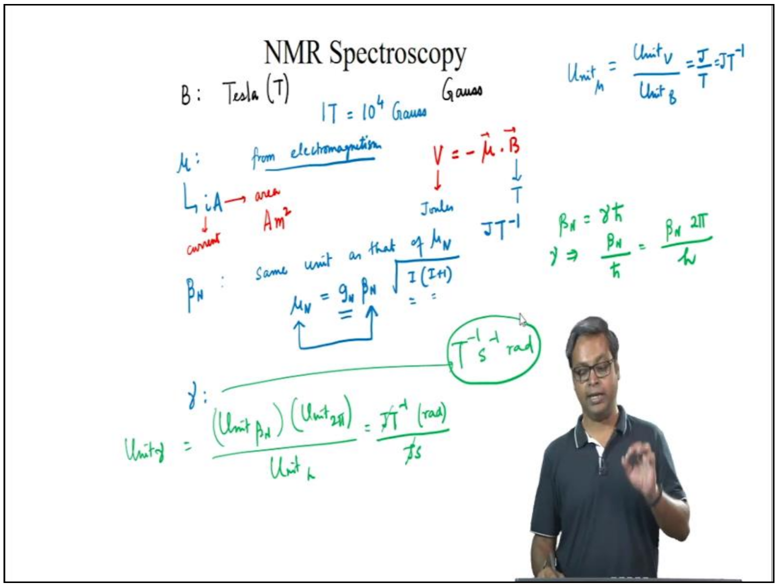

NMR Spectroscopy

B : Tesla (T) Gauss

$1T = 10^4$ Gauss

μ : from electromagnetism

$\hookrightarrow iA \rightarrow$ area

current

Am^2

$V = -\vec{\mu} \cdot \vec{B}$

Joules

T

JT^{-1}

$Unit_{\mu} = \frac{Unit_V}{Unit_B} = \frac{J}{T} = JT^{-1}$

β_N : same unit as that of μ_N

$\mu_N = g_N \beta_N \sqrt{I(I+1)}$

$\beta_N = \gamma \hbar$

$\gamma \Rightarrow \frac{\beta_N}{\hbar} = \frac{\beta_N 2\pi}{h}$

γ :

$T^{-1} s^{-1} rad$

$Unit_{\gamma} = \frac{(Unit_{\beta_N})(Unit_{2\pi})}{Unit_h} = \frac{\cancel{J}T^{-1}(rad)}{\cancel{J}s}$

So now let us look into the units so we have talked about different parameters we have talked about the magnetic moment the nuclear Magneton the magnetic field the gyromagnetic ratios. So let us look into all these units. So, let us start with B where B is the magnetic field. So, normally B is represented in the unit of Tesla which in short it is T or gauss and because there are two units there should be some relation.

So 1 Tesla equals 10 to the power 4 Gauss then let us come to mu or the magnetic moment so if you think in terms of electromagnetism or we can write from electro magnetism this mu is given by I times A where I is the current and A is the area so we can see the unit now is the unit of current times the unit of area that is ampere meter squared. However we can also write as we wrote in the last lecture that V equals - mu dot B so here V is the potential energy and because V is energy the unit of V is in Joule.

And as you have seen the unit of B is in Tesla. So, the unit of mu will be the unit of V divided by the unit of B which is Joule by Tesla or we can write joule Tesla inverse. Now let us move on to this Bohr Magneton that is beta N. So, beta N has the same unit as that of mu so it has same unit as that of mu or mu N that means the unit is Joule Tesla inverse and this is because this mu N can be written as g N beta N root over I times I + 1.

So g N is the nuclear g factor and I at the spin quantum numbers so we can see if we compare the units the units of mu N is the same as unit of beta N and finally let us go to gamma or the gyromagnetic ratio. So, we know this beta N is given by gamma h cross. So, we can write gamma as beta N by h cross or beta N 2 pi divided by h. So, the unit of gamma equals unit of beta N times unit of this 2 pi you are getting and the unit of h.

So this unit of beta N is jewel Tesla inverse then we have radians because it is 2 pi radians and h has the unit of Joule second so the Joule Joule cancels so it becomes the unit becomes here Tesla inverse second inverse Radian. So, the unit of gamma is Tesla inverse second inverse Radian.