

**Application of Spectroscopic Methods in
Molecular Structure Determination
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**Lecture – 02
Nuclear Magnetic Resonance Spectroscopy
Principle and Application in Structure Elucidation**

Hello, welcome to the second module on the course on Application of Spectroscopic Methods in Molecular Structure Determination. In this module, we will consider Nuclear Magnetic Resonance Spectroscopy or the NMR spectroscopy. We will consider the basic principle behind this particular spectroscopy technique.

Nuclear Magnetic Resonance Spectroscopy is a very powerful tool it is very widely used in this structural elucidation problem of organic, organometallic and inorganic complexes. It is an indispensable tool in the chemistry laboratory, whenever a student makes a compound a new compound immediately rushes into the nuclear magnetic resonance spectroscopy laboratory to record the NMR spectrum. The wealth of information that one gets from the NMR spectrum is invaluable in structure solving problems.

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HISTORICAL PERSPECTIVE

Discovery of NMR phenomenon in 1945

**Purcell, Torrey and Pound – Harvard University, USA
Bloch, Hansen and Packard – Stanford University, USA**

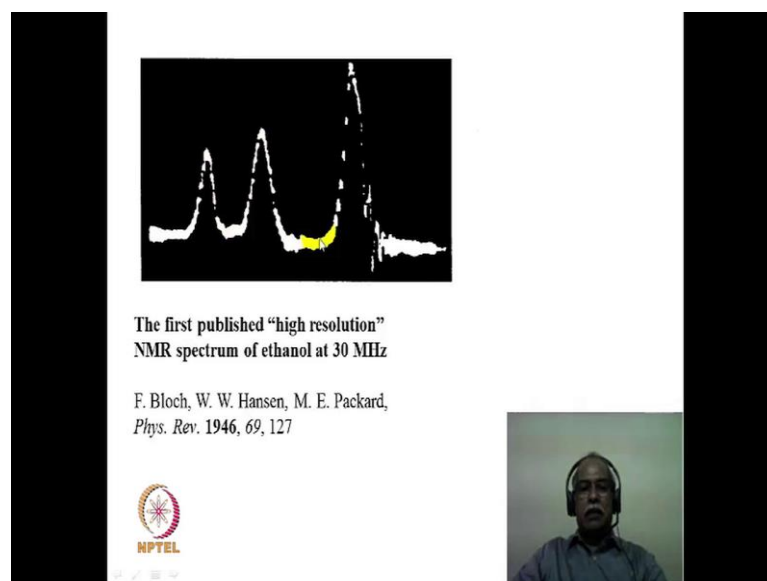
When ethanol was placed between pole pieces of an electromagnet and irradiated with electromagnetic radiation it absorbed radiation in the radio frequency region. When the magnetic field was turned off, NO absorption was observed.

**Purcell and Bloch –
Nobel prize in Physics – 1952
for the discovery of NMR.**



Now, from the Historical Perspective, the phenomenon of Nuclear Magnetic Resonance was discovered in the year 1945 by two groups working independently; one at the Harvard University and another at the Stanford University. Purcell, Torrey and Pound, they were working at Harvard University; Bloch, Hansen and Packard were working in the Stanford University. The experiment they performed was very simple; they place the sample of ethyl alcohol between pole pieces of an electromagnet and irradiated the sample with the electromagnetic radiation. What they observed was that the sample absorbed the electromagnetic radiation in the radio frequency region, when the magnet was turned on; when the magnet was turned off there was no absorption of the electromagnetic radiation. From this experiment, they concluded that there are actually studying a magnetic property of the sample. Purcell and Bloch were awarded the Noble prize in physics in 1952 for the discovery of the NMR phenomenon. Now NMR phenomenon was developed into a NMR spectroscopy and now it is very widely used for the structure determination.

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The first published "high resolution"
NMR spectrum of ethanol at 30 MHz

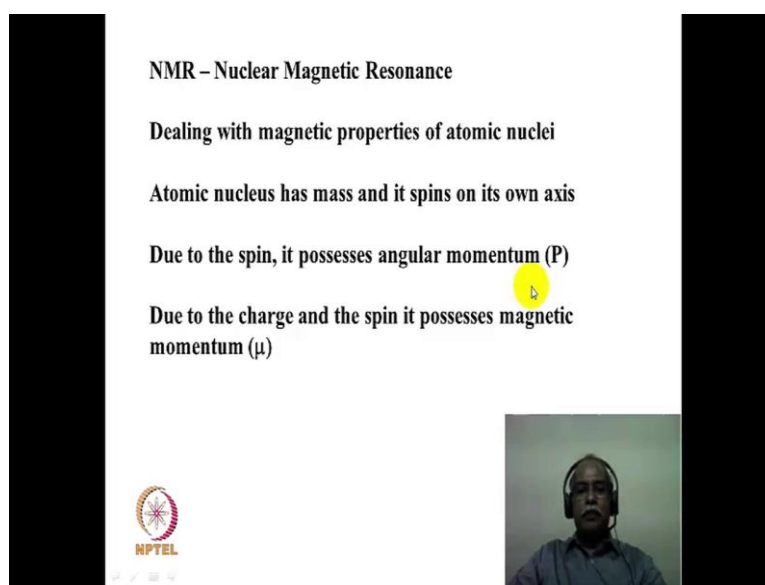
F. Bloch, W. W. Hansen, M. E. Packard,
Phys. Rev. 1946, 69, 127

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Now, here the very first spectrum of ethyl alcohol published using a 30 megahertz NMR spectrometer corresponding to roughly 0.7 Tesla of magnetic field strength. This is a very unresolved spectrum in today's standard; nevertheless, from the historic perspective it is the very important discovery. Now, when we look at the spectrum you see three different peaks in the NMR spectrum and if you look at the structure of a ethyl alcohol there is CH

3 group, there is a CH₂ group and OH group. So, one can assigned these peaks corresponding to one for the CH₃ that is this particular peak here and one for the CH₂ which is this particular peak here and one for the OH. In fact, if one measures the area under this three peaks, it will correspond to 3 is to 2 is to 1 corresponding to the CH₃ CH₂ and OH. So much of wealth of information was available right at the first intense of recording the first very NMR spectrum of ethyl alcohol sample.

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NMR – Nuclear Magnetic Resonance

- Dealing with magnetic properties of atomic nuclei
- Atomic nucleus has mass and it spins on its own axis
- Due to the spin, it possesses angular momentum (P)
- Due to the charge and the spin it possesses magnetic momentum (μ)

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The slide features a central text area with a yellow mouse cursor pointing to the text 'Due to the charge and the spin it possesses magnetic momentum (μ)'. At the bottom left is the NPTEL logo, and at the bottom right is a small video inset showing a man wearing a headset.

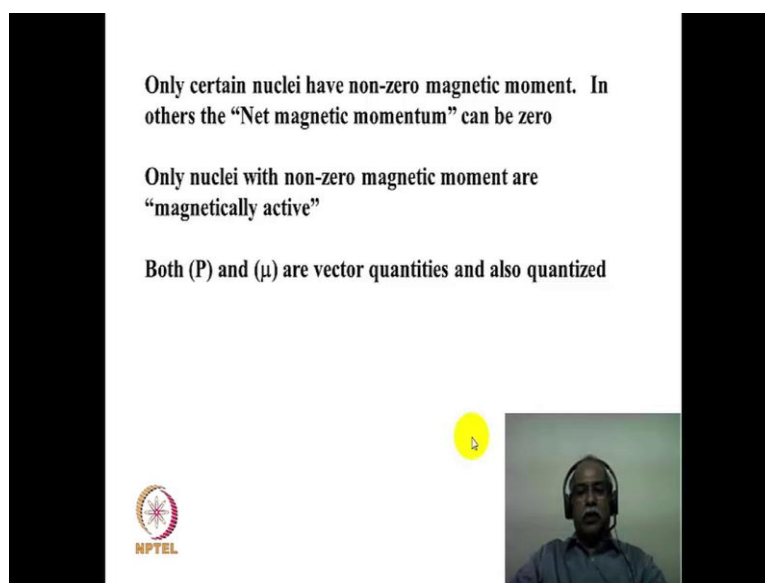
Now, let us look into some properties of the nucleus in terms of what is useful for nuclear magnetic resonance spectroscopy. Now we are dealing with magnetic properties of the atomic nuclei as evident from the NMR experiment. Atomic nucleus has both mass and it also spins on its own axis, because of a spinning mass, it has an angular momentum; because of a spinning charge, it also possesses magnetic momentum. And these two parameters are essential parameters for the NMR experiment the angular momentum is given the symbol P and the nuclear magnetic momentum given the symbol μ .

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Only certain nuclei have non-zero magnetic moment. In others the “Net magnetic momentum” can be zero

Only nuclei with non-zero magnetic moment are “magnetically active”

Both (P) and (μ) are vector quantities and also quantized






Only certain nuclei have non-zero magnetic moment. Other words, “Net magnetic momentum” can also be zero in certain other nuclei. Only nuclei with non-zero magnetic moment are “magnetically active” and those are the nuclei, which are useful for the purpose of Nuclear Magnetic Resonance Spectroscopy. In other words, those nuclei whose magnetic momentum is zero cannot be useful or is not useful for the purpose Nuclear Magnetic Resonance Spectroscopy. Both these quantities namely the angular momentum and the magnetic momentum are vector quantities and according to quantum chemistry there are quantized in nature.

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The ratio of magnetic momentum to angular momentum is called “Gyromagnetic ratio”.

It is very characteristic of a given nuclei. It is a constant for a given nucleus.

Gyromagnetic ratio = $[\gamma] = (\mu)/(P)$



The ratio of the magnetic momentum to the angular momentum is what is refer to us the “Gyromagnetic ratio”. Gyromagnetic ratio is a fundamental constant of a nucleus; it is a constant for a given nucleus. The ratio namely mu by P is called gamma, which is a gyromagnetic ratio. This is an important parameter in the case of Nuclear Magnetic Resonance Spectroscopy.

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Sort by spin Sort by frequency **NMR Periodic Table** Sort by receptivity Sort by abundance




PARAMETERS FOR: ^1H

Spin = 1/2
Natural abundance = 99.985%
*Frequency factor = 1.000
Magnetogyric ratio = 26.7522
Relative nu vs. ^1H = 1.00
Relative nu vs. ^{13}C = 5.67×10^4
Shift range = -25 to +12 ppm
Shift reference: (CH₄)
 ΔS (TMS)

NUCLEAR SPIN, I

H	X	I = 1/2	X	I = 1/2 and I > 1/2	He																	
Li	Be	X	I > 1/2	B	C	N	O	F	Ne													
Na	Mg			Al	Si	P	S	Cl	Ar													
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe					
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn					
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt														
									Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
									Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

http://www-usr.rider.edu/~grushow/nmr/NMR_tutor/periodic_table/nmr_pt_frameset.html



Now, let us look into certain resources that are available in the internet. In the internet, there are quite a lot of resources available as for as nuclear magnetic resonance spectroscopy is concerned. I am highlighting two such examples in this particular lecture. The first one is from this particular website; when we go to this website, it gives you an interactive periodic table. In the interactive periodic table, if you click on any particular element and look at on the left-hand side this particular bar here, it tells you very valuable information regarding the parameters that are useful for the nuclear magnetic resonance spectroscopy. It tells you the spin of the particular nucleus, the natural abundance its availability in nature for example, the frequency factor the gyromagnetic ratio and so many other parameters are listed on the left-hand side bar of these particular slide.

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The screenshot shows a periodic table with a sidebar on the left that provides detailed information for a selected element. Below the table is a URL: <http://www.bruker-nmr.de/guide/eNMR/chem/NMRnuclei.html>. The NPTEL logo is visible in the bottom left corner, and a video feed of a man wearing a headset is in the bottom right corner.

Group	I	II	IIIa	IVa	Va	VIa	VIIa	VIIIa	IX	X	XI	XII	IIIb	IVb	Vb	VIb	VIIb	VIIIb
Period																		
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lr	
7	Fr	Ra	Ac	Th	Pa	U	Np	Pu	A	B	C	D	E	F	G	H	I	J
**Lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lr	
**Actinides			Ac	Th	Pa	U	Np	Pu	A	B	C	D	E	F	G	H	I	J

Now, if you go to another website; this is by the company Bruker which manufactures the nuclear magnetic resonance spectrometers. This is also an interactive periodic table; if you click on any particular element, then the screen pops up with the information that is relevant to the NMR experiment.



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NMR Periodic Table
Hydrogen NMR

PHYSICAL PROPERTIES

Isotope	Natural Abundance (%)	Nuclear Spin (I)	Magnetogyric ratio (10^{-10} rad/T*s)	Quadruple moment (10^{-28} Q/m ²)	Resonance frequency (MHz) at 11.744T (500 MHz for ¹ H)	Relative sensitivity (¹ H=1.00)	Absolute sensitivity (¹ H=1.00)
¹ H	99.98	1/2	26.7519	0	500.000	1.00	1.00
² H	1.5*10 ⁻²	1	4.1066	2.8*10 ⁻³	76.753	9.65*10 ⁻⁶	1.45*10 ⁻⁶
³ H	0	1/2	28.535	0	533.317	1.21	0

<http://www.bruker-nmr.de/guide/eNMR/chem/NMRnuclei.html>




For example, it lists all the isotopes that are magnetically active; they are natural abundance in cases where they isotope is synthetic isotope of course, the natural abundance will be zero. The nuclear spin, the Gyromagnetic ratio; if there is a quadruple moment, it also lists the quadruple moment; it also tells you the resonance frequency with reference to proton being a 500-megahertz resonance frequency; it also tells you about the sensitivity with reference to proton as a source. These are kind of information which are very useful. So, one can identify in the periodic table what are the various elements that are present in terms of its property related to nuclear magnetic resonance.



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Basic theory of NMR Spectroscopy

Nucleus should be magnetically active –
non-zero magnetic momentum

According to quantum mechanics angular momentum
can have only certain fixed values (*eigen* states)

$P = (m)(h/2\pi)$ where m is the magnetic quantum number of the
nucleus In the presence of an external
magnetic field (m) can have
($2I+1$) values, 
namely (+ I), ($I-1$), ($I-2$),.....(- I)
where (I) is the spin quantum
number of the nucleus



Now, we will deal with the very basic theory; non mathematical way of describing the theory of NMR spectroscopy, nucleus should have a non-zero magnetic momentum. In other words, it should be magnetically active first of all for the experiment to be consider for the NMR spectroscopy. According to quantum chemistry, angular momentum can have only certain fixed values which are given by P is equal to $m h$ by 2π , where m is the magnetic quantum number of the nucleus. Now the magnetic momentum the magnetic quantum number can have in the presence of an external magnetic field different values corresponding to $2 I$ plus 1 values; namely plus I , I minus 1, I minus 2 all the way to minus I where I is the spin quantum number of the nucleus.



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Allowed orientation of spin angular momentum I in external applied magnetic field

For $I = \frac{1}{2}$, two states are possible ($+\frac{1}{2}$) and ($-\frac{1}{2}$)

For $I = 1$, three states are possible ($+1, 0, -1$)



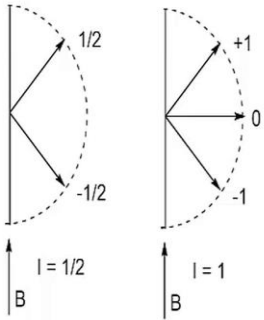
For $I = \frac{3}{2}$, four states are possible ($\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$)



For example, if we consider I is equal to half then the number of spin quantum they allowed orientation of spin angular momentum I in an external magnetic field is what is described here. For a spin of half, you can have a possibility of plus half and minus half; for a spin of one for example, you can have the possibility of plus 1, 0 and minus 1. In accordance with this particular rule, which tells you the number of magnetic quantum numbers that are possible in the presence of an external magnetic field. Now for a spin of 3 by 2, you can have 3 by 2, plus half, minus half and minus 3 by 2.

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Quantization of spin angular momentum in an external magnetic field B for spin $\frac{1}{2}$ and spin 1 nuclei



Picture really it is represented in this particular format this is the direction of the applied magnetic field, then a spin half nucleus can have two states, two spin states namely minus of spin states which is the ground state and plus half spin state which is the excited state. In the cases of a spin 1 nucleus, it can have three different orientation or three different values. The minus one state is the ground state then you have the first excited state, which is the 0-state and the plus 1 state which is the higher excited state. Now quantization of spin angular momentum is what we are taking about in this particular case the presence of an external magnetic field this is what is known as the Zeeman splitting in the NMR terminology.

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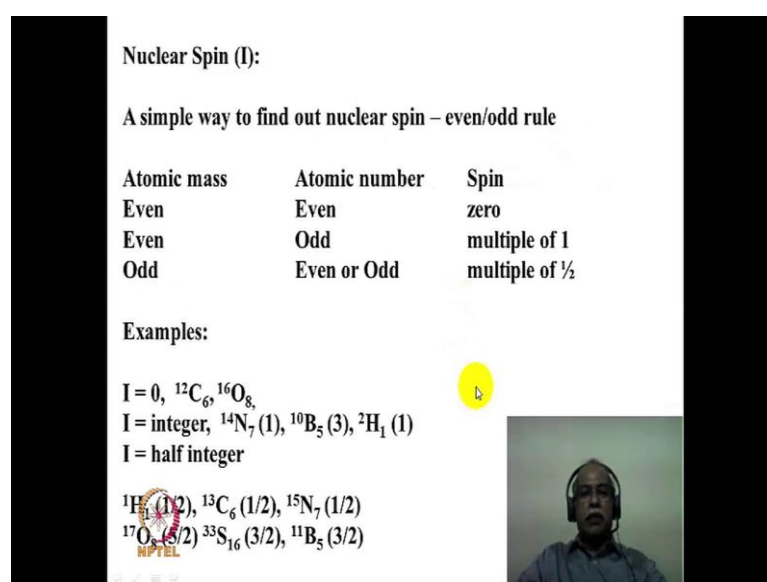
Nuclear Spin (I):

A simple way to find out nuclear spin – even/odd rule

Atomic mass	Atomic number	Spin
Even	Even	zero
Even	Odd	multiple of 1
Odd	Even or Odd	multiple of $\frac{1}{2}$

Examples:

$I = 0$, $^{12}\text{C}_6$, $^{16}\text{O}_8$
 $I = \text{integer}$, $^{14}\text{N}_7(1)$, $^{10}\text{B}_5(3)$, $^2\text{H}_1(1)$
 $I = \text{half integer}$
 $^1\text{H}_1(1/2)$, $^{13}\text{C}_6(1/2)$, $^{15}\text{N}_7(1/2)$
 $^{17}\text{O}_8(3/2)$, $^{33}\text{S}_{16}(3/2)$, $^{11}\text{B}_5(3/2)$



Now, there is a easy way to find out what is the nuclear spin of a given nucleus, this is called the odd even rule. This is a highly empirical rule, which as now basis in terms of theoretical basis or anything. It is a very mnemonic kind of methodology to determine the spin of a given nucleus. This is purely based on atomic mass and atomic number. When the atomic mass and the atomic number are even, the spin is always zero. When, the atomic mass is even and the atomic number is odd, the spin will be multiple of one. And when the atomic mass is odd and the atomic number is either even or odd then the spin will be multiple of half. The examples are shown here. For example a spin of zero would correspond to a carbon-12 nucleus the isotope-12 of carbon. Isotope-16 of oxygen for example, they all have net magnetization of zero and they are not very useful in the



NMR experiment. When I is equal to integer the examples are nitrogen 14 for example, it has a spin of 1, boron-10 for example, has a spin of 3 and deuterium has a spin of 1.

The half integer nucleus very useful nuclei and this is what we would be considering for the rest of the lecture in this particular course. Proton has a spin half carbon-13 although it is a low abundant isotope of the carbon; it has a spin half nitrogen-15 has a spin half; oxygen-17 has a spin half 5 by 2; boron-11 for example, has spin of 3 by 2. So, this is a very simple hematology to find out what is the spin of a nucleus based on the odd even rule of that atomic mass and atomic number.

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Properties of some common NMR nuclei:

Nucleus	Spin	γ (rad T ⁻¹ s ⁻¹)	Natural abundance (%)
¹ H	½	26.7	99.9
² H ₁	1	4.107	0.015
¹³ C ₆	½	6.72	1.10
¹⁹ F ₉	½	25.18	100
³¹ P ₁₅	½	10.84	100
²⁹ Si ₁₄	½	-5.32	4.67



Here, we list some interesting properties of common NMR nuclei. For example, proton, deuterium, carbon-13, fluorine-19, phosphorus-31 and silicon-29; these are the most widely often used nuclei as far as the NMR experiments are concerned. Most of them are spin half nuclei with exception of deuterium, which has a spin half 1. The gamma which is the gyromagnetic ratio is mentioned here and the gyromagnetic ratio is a measure of the sensitivity of the nucleus as far as the NMR experiment is concerned. Higher the value of the gyromagnetic ratio, the more sensitive the nucleus would be. For example, if you take proton which is a gyromagnetic ratio of 26.7 with a natural abundance of 99.9 percent. And consider fluorine which has a very similar gyromagnetic ratio roughly 25 or so with a natural abundance of 100 percent, these two nuclei will have similar sensitivity

in sense of the NMR experiment. For two reason one the gyromagnetic ratio is nearly the same; and secondly, the natural abundance is for 100 percent, which is also nearly same for example for this two nuclei.

On the other hand, if you take carbon and proton, carbon has roughly one-fourth of the gyromagnetic ratio and it is not bad actually that is only one-fourth, but what is even words is the natural abundance is it about one percent is the magnetically active isotope of carbon namely carbon-13, the remaining 99 percent of cause is carbon-12 which is not useful for the purpose of NMR experiment. So, both the gyromagnetic ratio as well as natural abundance play a very vital role in terms of the sensitivity of that particular nucleus for the NMR experiment.

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NMR of spin $\frac{1}{2}$ nuclei, namely proton and carbon-13

In the absence of external magnetic field the magnetic moment vectors will be randomly oriented

In the presence of applied external magnetic field (B_0) two orientations are possible, namely $(+1/2)$ and $(-1/2)$




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From now on, we will devote ourselves to the NMR of spin half nuclei namely the proton and the carbon-13. In the absence of an external magnetic field, the magnetic moment vectors will be randomly oriented; however, in the presence of an external magnetic field, according to quantum mechanics, they will have finite values they take up two orientations which are conventionally represented as plus half and minus half.

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The two orientations, one aligning with external field (-1/2) and another opposing the external field (+1/2), differ in energy.

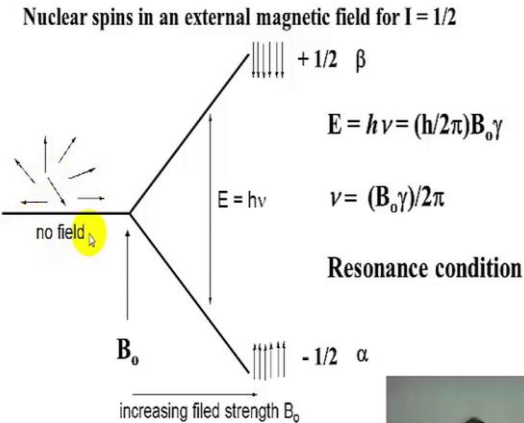
The energy difference depends on the strength of applied magnetic field



The two orientations, corresponds to one aligning with the external magnetic field namely minus half another one opposing the external magnetic field which is plus half, and they differ in energy. The energy difference depends on the strength of the applied magnetic field.

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Nuclear spins in an external magnetic field for $I = 1/2$





$E = h\nu = \frac{h}{2\pi} B_0 \gamma$

$\nu = \frac{B_0 \gamma}{2\pi}$

Resonance condition

increasing field strength B_0



This is diagrammatically represented in this particular slide. If you look at the side where

there is no magnetic field, the magnetic field is applied here on wards and in this side there is no magnetic field. In the absence of a magnetic field, the magnetic moment vectors which are represented by these arrows are randomly oriented. As soon as the magnetic field is applied, energy level is set up for example, for the ground state and excited spin state the two state that corresponds to the minus half and the plus half state of the spin of the nucleus. And this energy gap is essentially corresponding to $h\nu$. And you can see certain population in the ground state and certain population in the excited state.

Now this is the equation that governs the basic NMR experiment. This frequency or this energy gap essentially is directly proportional to the applied magnetic field; it is also directly proportional to the gamma, which is a gyromagnetic ratio. So, these are the two parameters on which this energy gap; in other words the energy separation between the ground state and the excited state depend upon. The equation is simplified; in other words the ν which is the resonance frequency corresponds to B_0 which is the applied magnetic field and gamma which is the gyromagnetic ratio of the given nucleus. So, for you can from this equation, you can easily figure out that for every nucleus where the gamma is different, the frequency will be different for a given magnetic field strength. In other words, two nuclei which have different gamma values will resonate at two different frequencies under the same identical magnetic field strength. In other words, there are no two nuclei which were resonated the same frequency under a given nuclear magnetic fields strength, because the gamma is going to be different for the two nuclei.

You can also see from this figure as the field strength increases, this is the increasing field strength of the magnetic field, as the field strength increases the energy also increases the energy gap also increases essentially indicating that this is directly proportional to the frequency or the energy is directly proportional to the field strength. So, with increasing field strength of course, the energy gap also keeps increasing. The resonance condition essentially corresponds to matching this frequency to this particular expression when the energy corresponds to the ultra-magnetic radiation which corresponds to the expression here is satisfied then the resonance occurs in other words absorption of energy will take place. This is typically the energy gap is such that typically the frequency that is necessary for this transformation from the lower spin state to the upper spin state corresponds to the radio frequency region of the electromagnetic

spectrum.

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Distribution of nuclear spins:

Maxwell Boltzmann distribution

$$N_{\alpha} / N_{\beta} = \exp(-\Delta E / kT)$$

N_{α} / N_{β} is the population ratio of the excited state to the ground state



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Once you set up the alpha and beta state are the minus half and the plus half state which is shown here for example, this is lower energy spin state and this is the higher energy spin state. Once you set up these energy levels then one can easily calculate using the Maxwell Boltzmann distribution law. The population ratio between the excited state and the ground state which is governed by the exponential to the minus delta E by k T, where k is the Boltzmann constant and T is the temperature at which the population difference or the population ratio is calculated. The N_{α} , N_{β} is the population ratio of the excited state to the ground state of the two spin states that we are talking about.

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B_0 (T)	ν (MHz)	ΔE (J)	N_α / N_β	T °C
2.35	100	6.7×10^{-26}	17 ppm	17
4.70	200	22.5×10^{-26}	57 ppm	17
7.0	300	33.5×10^{-26}	85 ppm	17
2.35	100	6.7×10^{-26}	28 13	-100 +100



Now, this table tells us the results from the calculation of the alpha, beta state population ratio with respect to the magnetic field strength and the corresponding resonance frequency of the NMR spectrometer. And in terms of the energy gap between the alpha and the beta spin state or the plus half and the minus half spin state is shown in this particular column here. And essentially when the information is plugged into the Maxwell Boltzmann distribution function one gets the result of the excess population or the population ratio to the alpha to the beta population ratio is shown here. As you can see here, NMR is not a very sensitive technique because both the states are equally populated only a very small fraction of the order of ppm is the excess population that is present in the ground state comparison to the excited state. At around room temperature also which is about 17 degrees calculation temperature that is shown here.

But what is important is as you increase the field strength going from 2.35 Tesla magnet to about 7 Tesla magnet, in other words from a 100 megahertz NMR spectrometer through a 300 megahertz NMR spectrometer the population gradually increases which means the sensitivity should also increase. Because now you have more population in the ground state for to be excited to the excited state spin state of the systems. So, essentially this tells us that with increasing frequency of the NMR spectrometer because of the axis population being higher the sensitivity also goes up. Now what is the effect of temperature you can for example, measure the NMR spectrum at minus 100 or you can

measure it at plus 100, the NMR spectrometer you can cool to the probe can be cool to minus 100 or plus 100, and the measurement can be made.

Since the expression, the population difference or the population ratio is inversely proportional to the exponential of temperature, it is also effects the population difference. At low temperature, you have a higher population compare to higher temperature where, you have a lower population. For example, because of the inverse relationship of the population ratio to the temperature of the system. So, it is advantage is to measure the NMR spectrometer lower temperature compare to higher temperature; however, you can see here the advantage gained by this experiment is not so high, it is only about twice as much of sensitivity increase as in the higher temperature for example. So, one always apt for increasing the frequency of the spectrometer are going to the higher and higher resolution spectrometer where the sensitivity is also higher.

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**Higher the magnetic field strength –
higher the sensitivity and resolution**

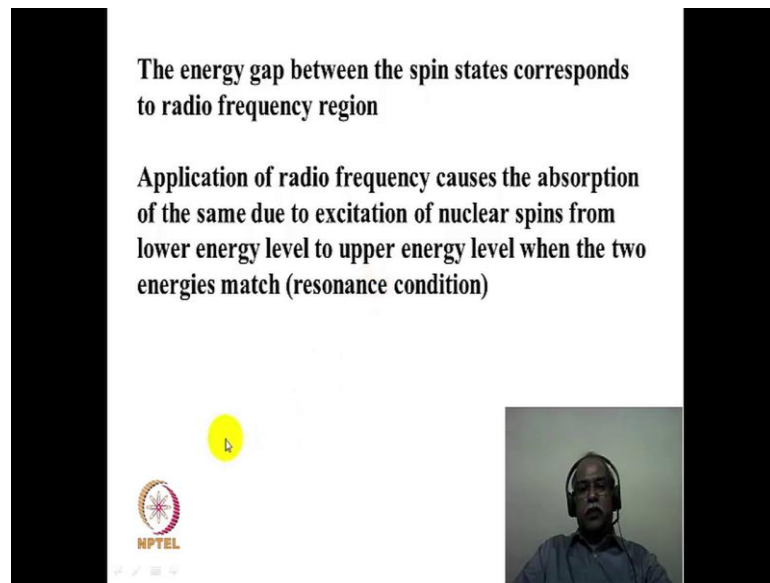
**Lower the temperature –
higher the sensitivity**

**A 500 MHz NMR instrument is more sensitive
as well as more resolving than a 60 MHz NMR
instrument**

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So, to conclude the earlier slide, we will say that higher the magnetic field strength higher will be the sensitivity as well as the resolution. We will come to the resolution part a little later; let us for the time being, confine ourselves to the sensitivity part. Lower the temperature the higher the sensitivity; in other words, a 500 megahertz NMR instrument is more sensitive as well as more resolving than a 60 megahertz NMR instrument.

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The energy gap between the spin states corresponds to radio frequency region

Application of radio frequency causes the absorption of the same due to excitation of nuclear spins from lower energy level to upper energy level when the two energies match (resonance condition)

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As I mentioned earlier, the energy gap between the spin states corresponds to the radio frequency region. So, application of radio frequency essentially causes the absorption of the same due to the excitation of nuclear spins from lower energy level to the upper energy level when the two energies match. In other words, the energy which is applied and the energy gap of the two spins state and this is what is known as the resonance condition. And this resonance condition essentially is when the frequency matches the energy gap the absorption of the energy takes place and the spins which are in the lower spins state get excited to the higher spin state.

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Classical description of NMR

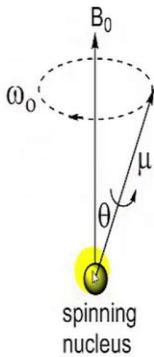
The net magnetization of the sample is sum of all individual nuclear magnetic moments.

The interaction of magnetic field with nuclear magnetic moment induces the nuclear magnetic moment to precess about the applied magnetic field with certain frequency called Larmor frequency



In the classical description of NMR, one can think about a nucleus, which is possessing around the magnetic field that is being applied. In other words, the net magnetization of the sample is sum of all individual magnetic moments. The interaction of the magnetic field with nuclear magnetic moment induces the nuclear magnetic moment to precess about the applied magnetic field with certain frequency called Larmor frequency.



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Precessing spin about the applied magnetic field direction

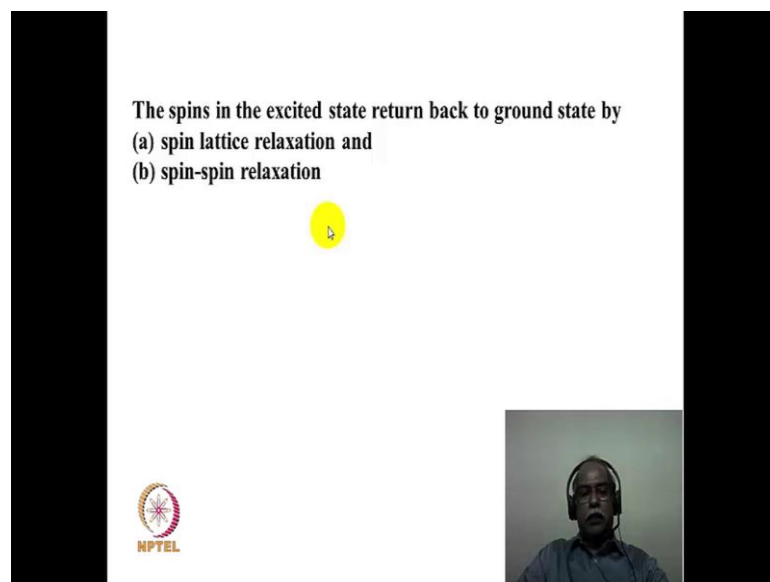
ω_0 – Larmor frequency

spinning nucleus



This is better explained using a diagram for example; this is a spinning nucleus, spinning on its own axis. When an external magnetic field is applied in this direction namely this B_0 is the external applied magnetic field. It starts to precess around the axis of the external magnetic field and this precession frequency is what is known as the Larmor frequency. When the precession frequency and the applied radio of frequency match each other, there is a spin flipping that take place in other words the spin that is aligning with external magnetic field flips to the spin which is oppose to the external magnetic field. In other words, the plus minus half state spin goes to the plus half state are the alpha state goes to the beta state as the case maybe.

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The spins in the excited state return back to ground state by
(a) spin lattice relaxation and
(b) spin-spin relaxation

NPTEL



Now, once these spins reach the excited state, they will have to come back to the ground state to attain the equilibrium population. This is essentially happening by two mechanisms; one is the spin lattice relaxation, where the excess energy is actually transformed or to the medium and to the surroundings which is the lattice in this particular case. Or it can also transfer the excess energy to another spin which is known as the spin-spin relaxation essentially. These are the two mechanistic features by which an excited spin state can come back to the ground state in the case of NMR spectroscopy.

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$$\nu = (B_0 \gamma) / 2\pi$$

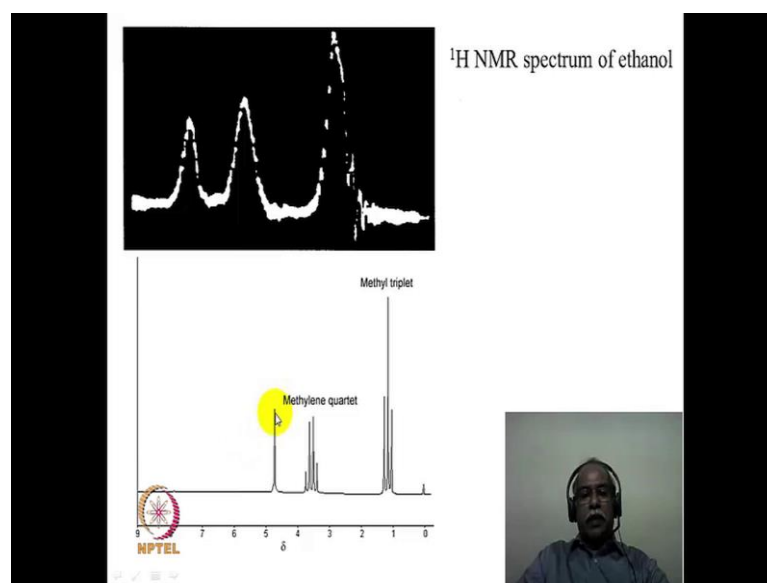
From the above equation one infers that all the hydrogen nuclei in a molecule, say ethanol should have the same resonance frequency, irrespective of its chemical nature, at a given magnetic field.

But this is not true. Hydrogens in different chemical environment give different resonance frequencies in the NMR.



Now, from the above equation; one infers that all the hydrogen nuclei must come to the same frequency. For example, if we consider all the hydrogen nucleus in a molecule, gamma is essentially same for all of them and B_0 which is the applied magnetic field is also same. So, all the hydrogen in a molecule should essentially confined to a single frequency which is governed by this equation, but this is we know that this is not true because different hydrogens in a molecule come under different frequencies, hydrogens in different chemical environment give different resonance frequencies in the NMR. And for example, if you take the ethyl alcohol spectrum itself, you know the OH hydrogen comes at a difference frequency compare to for example, the CH 2 hydrogen which comes at a different frequency and finally, the CH 3 hydrogens coming at a different frequency.

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In fact, if we look at the higher resolution NMR spectrum, it is not only that the three different frequencies are obtained that is also certain spectral features which we call us multiplets creeps into the picture, which essentially gives us the valuable information regarding the structure of an ethyl alcohol. We will consider the final aspects of the spectrum of ethyl alcohol, we will introduce the concept of chemical shift and we will also introduce the concept of spin-spin coupling in the next lecture. So, to summarize in this particular lecture, we have looked at what is an NMR phenomenon, how the NMR spectroscopy was developed from that phenomenon and what is basic principle behind the NMR spectroscopy; these are the things that we have covered in this particular lecture.

Thank you.