Implementation Aspects of Quantum Computing

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Lecture – 13
Basics of NMR

We are discussing about quantum computer and what we have looked at is; mainly what is the difference from being a classical computer.

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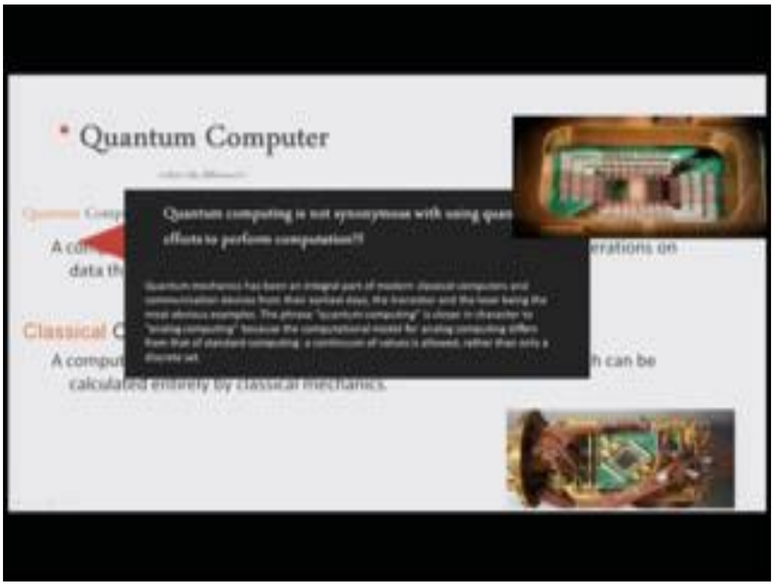

Quantum Computer

Quantum computing is not synonymous with using quan effects to perform computation!!

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Classical C

A comput h can be calculated entirely by classical mechanics.

Quantum computer is of a Multi-state variant, a computer that uses quantum mechanical phenomena to perform operations on data through devices such as super position and Entanglement. On the other hand Binary Classical Computer is the one that uses voltages flowing through circuits and gates, which can be calculated entirely by classical mechanics.

However quantum computing is not synonymous with using quantum effects to perform computation quantum mechanics has been an integral part of modern classical computers and communication devices from their earliest days. The transistor and the laser being the most obvious examples; the phrase quantum computing is closer in character to analog computing because the computational model for analog computing differs from that of standard computing; a continuum of values is allowed rather than only a discrete set. These are the basic essence that we have disclosed until now.

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Pioneers

We went through the pioneers who dreamt of quantum computers in electrical realities. First of them we mentioned was of Richard Feynman, Now will learn it from (Refer Time: 01:54) in 1980, he was the first among a few who began to investigate the generalization of conventional information science concepts to quantum physical processes considering the representation of binary numbers in relation to the quantum state of 2 state quantum systems.

In other words simulating quantum systems not with conventional computers, but with other quantum systems constructed for this purpose. In 1985 David Deutsch published a theoretical paper describing a universal quantum computer proving, that if 2 state systems could be made to evolve by means of a set of simple operations any such evolution could be produced and made to simulate any physical system. These operations came to be called quantum gates as they function similarly to the binary logic gates in classical computers.

In 1994 Peter Shor proposes a method using Entanglement of qubits and super position to find the prime factors of an integer a rather valuable process as many encryption systems exploit the difficulty in finding factors of large numbers the RSA algorithm for example, in principle his algorithm would far surpass the efficiency of any known computer when executed on a quantum computer; Shor's discovery proves quite instrumental in provoking a storm of research both by physicist and computer scientist.

These are the basic points that we have looked into we have looked into the bits or the basic idea behind this computing.

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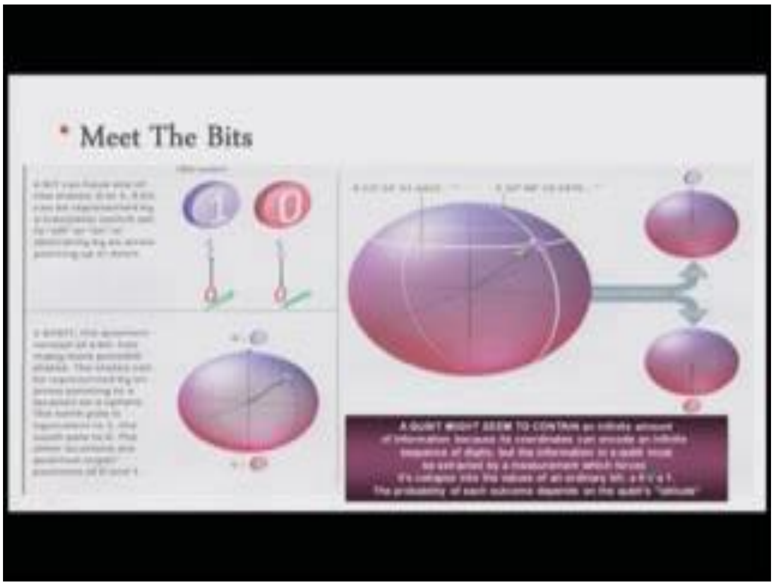

- Meet The Bits

We have met the bits as data carriers a bit can have one of the 2 states, 0 or 1. A bit can be represented by a transistor switch set to off or on or abstractly by an arrow pointing up or down.

A qubit on the other hand is the quantum version of a bit has many possible states, the states can be represented by an arrow pointing to a location on a sphere the north pole is equivalent to 1, the south pole is equivalent to 0. The other locations are quantum super positions of 0 and 1. So, that is how it is a continuous variable approach where as in classical mechanics it is one of the 2 values, 0 or 1. A qubit might seen to contain an infinite amount of information because its coordinates can encode an infinite sequence of digits, but the information in a qubit must be extracted by a measurement which forces it is collapse into the values of an ordinary bit a 0 or a 1. The probability of each outcome depends on the qubits latitude.

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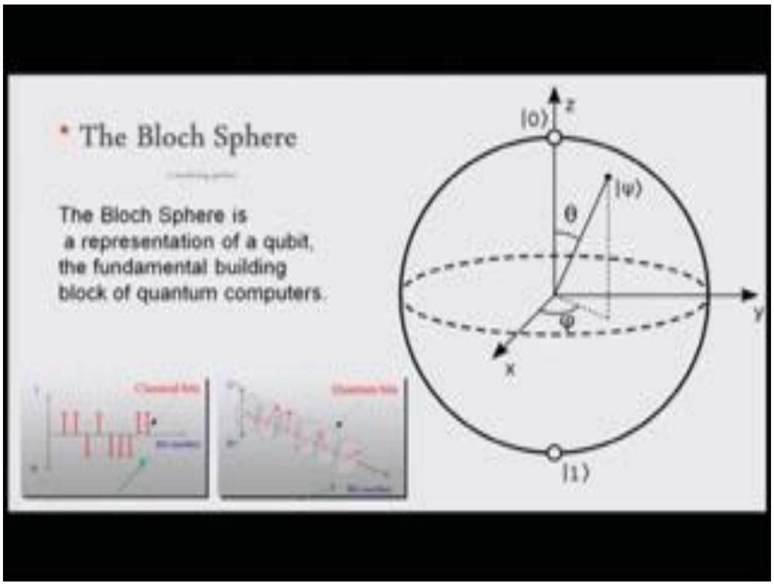

- The Bloch Sphere

The Bloch Sphere is
a representation of a qubit,
the fundamental building
block of quantum computers.

Finally in order to visualize the qubits we invoke the Bloch sphere. The Bloch sphere is a representation of a qubit the fundamental building block of quantum computers as we just mentioned. This is the sphere in which the arrangement of the qubit can be anywhere the classical bits keep having their singular values between 0 and 1 depending on how they are these are the classical bit representations whereas, the quantum bits will have continuous variables that they can assume at any point of time; however, whenever you look at it it is going to be one or the other as we just mentioned.

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- Entanglement

Entanglement is the ability of quantum systems to exhibit correlations between states within a superposition.

“ **Spooky Action At A Distance —> Einstien**

When two particles become entangled, their identities merge: their collective state is precisely determined, but the individual identity of each of the particles has disappeared. The entangled particles behave as one, even when separated by a large distance.

—> Professor Ronald Hanson

The key thing which has been utilized is the quantum information exchange part which is the Entanglement the other part of super position is also been used, but here the Entanglement is the one which is important for quantum information exchange it is the ability of quantum systems to exhibit correlations between states within the super position. It is almost like spooky at a distance which was (Refer Time: 06:34) Einstein mentioned because of his famous EPR paradox when 2 particles become entangle their identity is merged, their collective state is precisely determined, but the individual identity of each of the particles has disappeared; the entangled particles behave as one even when separated by large distance and so is the idea that whenever you actually measure one of the entangled state the other one is automatically determined.

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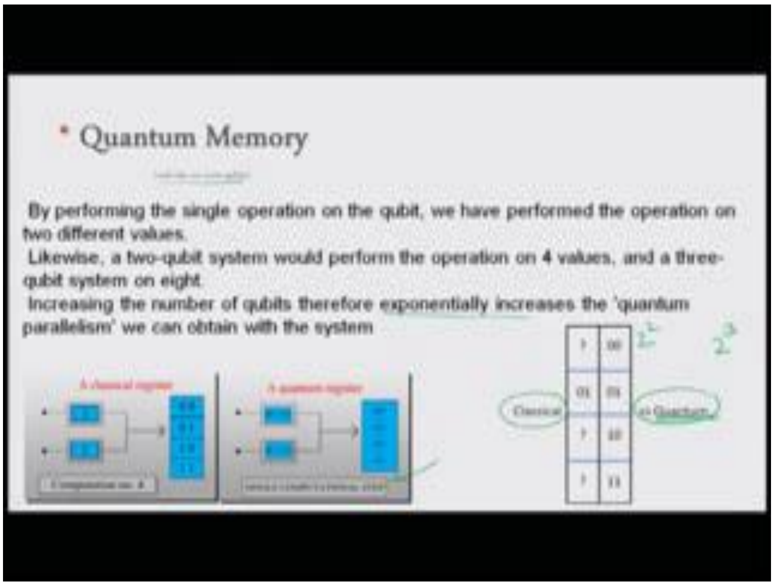

• Quantum Memory

By performing the single operation on the qubit, we have performed the operation on two different values.

Likewise, a two-qubit system would perform the operation on 4 values, and a three-qubit system on eight.

Increasing the number of qubits therefore exponentially increases the 'quantum parallelism' we can obtain with the system

The concept of having qubits also leads to Quantum Memory by performing the single operation on qubit; we have performed the operation on 2 different values likewise a 2 qubit system would perform the operation on 4 values and a 3 qubit system on 8, 2 to the power 3 goes by 2 to the power number the classical one; however, only is able to do one at a time whereas, the quantum one does all at the same time increasing the number of qubits therefore, exponentially increases the quantum parallelism we can obtain with the system. So, that is illustrated here and that is the advantage which we get by using a single computational step for quantum bits or qubit we can get lot parallelism which is in the exponential order.

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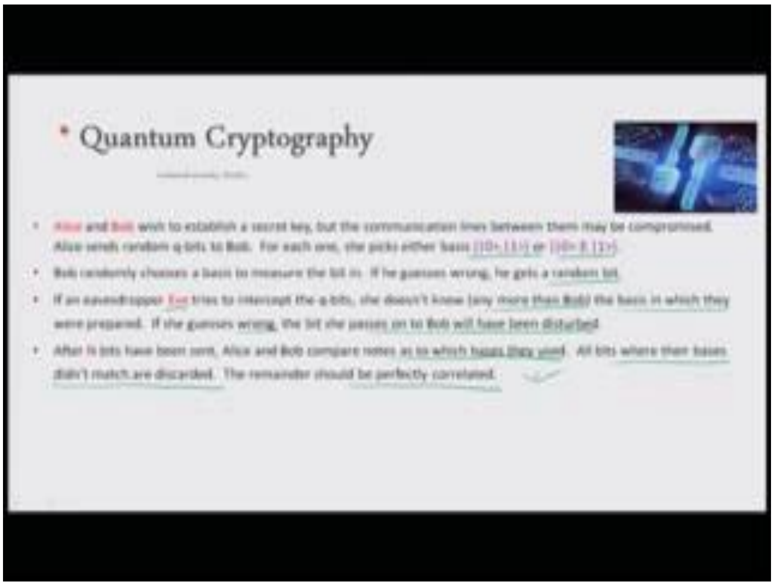

Quantum Cryptography

We have also explored the idea of Quantum Cryptography which where we use the idea 2 members Alice and Bob, which is typically used the names who wish to establish a secret key, but the communication lines between them may be compromised Alice and random qubit to Bob for each one she picks either basis 0 1 or 0 plus minus 1, Bob randomly chooses a basis to measure the bit in it, if he guesses wrong he gets a random bit if an eavesdropper eve tries to intercept the qubits; she does not know any more than bob the basis in which they were prepared, if she guesses wrong the bit she passes on to Bob will have been disturbed, that is how the compromise is caught. After N bits have been sent Alice and Bob compare notes as to which basis they have used all bits where their basis did not match are discarded the remainder should be perfectly correlated and this is the basis behind Quantum Cryptography.

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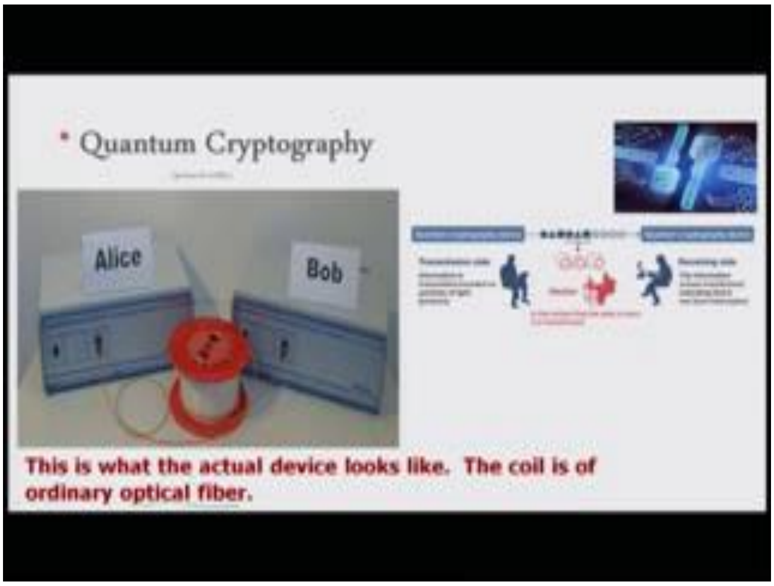
- Quantum Cryptography

This is what the actual device looks like. The coil is of ordinary optical fiber.

This was the pictorial features in which this is how the actual set up looks like with a fiber optic device, you can have one set send information to the other set and do this; this has been actually done in reality by using ordinary optical fibers across large distances. So, this is the reality of the concept right now.

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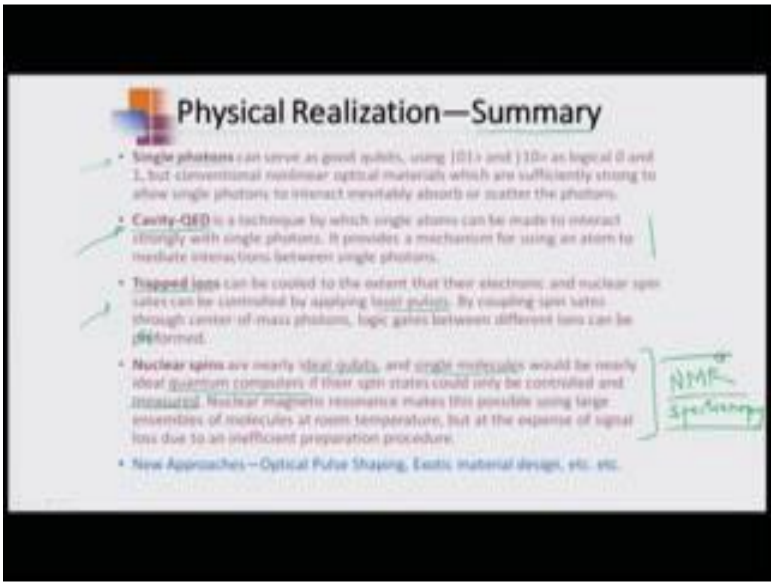
Physical Realization—Summary

- **Single photons** can serve as good qubits, using |01> and |10> as logical 0 and 1, but conventional nonlinear optical materials which are sufficiently strong to allow single photons to interact inevitably absorb or scatter the photons.
- **Cavity-QED** is a technique by which single atoms can be made to interact strongly with single photons. It provides a mechanism for using an atom to mediate interactions between single photons.
- **Trapped ions** can be cooled to the extent that their electronic and nuclear spin sates can be controlled by applying laser pulses. By coupling spin sates through center-of-mass photons, logic gates between different ions can be performed.
- **Nuclear spins** are nearly ideal qubits, and single molecules would be nearly ideal quantum computers if their spin states could only be controlled and measured. Nuclear magnetic resonance makes this possible using large ensembles of molecules at room temperature, but at the expense of signal loss due to an inefficient preparation procedure.
- New Approaches—Optical Pulse Shaping, Exotic material design, etc. etc.

NMR
Spectroscopy

In terms of information exchange the other aspect of physical realization which I summarize here are based on the principle that attempts have been made in terms of qubits, which have been single photons which can serve is good qubits using 0, 1 and 1, 0 as logical 0 and 1, but conventional non linear optical materials which are sufficiently strong to allow single photons to interact in a inevitably absorb or scatter the photon that is the problem, but this one way cavity QED is a technique by which single atoms can be made to interact strongly with strong photons. It provides a mechanism for using an atom to mediate interactions between single photons. This is another approach which has been use which is cavity QED trapped ions can be cooled to the extent that they are electronic and Nuclear Spin states can be controlled by applying laser pulses by coupling spin states through center of mass photons logic gates between different ions can be performed, that is the third case.

The Nuclear Spins are nearly ideal qubits and this is by far one of the early demonstration successfully which has been done in quantum computing; where and single molecules in this case would be nearly ideal quantum computers if their spin states could only be controlled and measured Nuclear Magnetic Resonance makes this possible using large ensembles of molecule at room temperature, but at the expense of single loss due to inefficient preparation procedure.

However, this is a very popular technique because there is already a large aspect of NMR spectroscopy, which exist which is a routine technology which is applied for identifying molecules and so, this spectrometer is a readily available machine which has been utilized for quantum computing. There are many more newer approaches involving other kinds of approaches, but for this class today we will be focusing on NMR spectroscopy right from the beginning of the principle of NMR Nuclear Spins and all of that.

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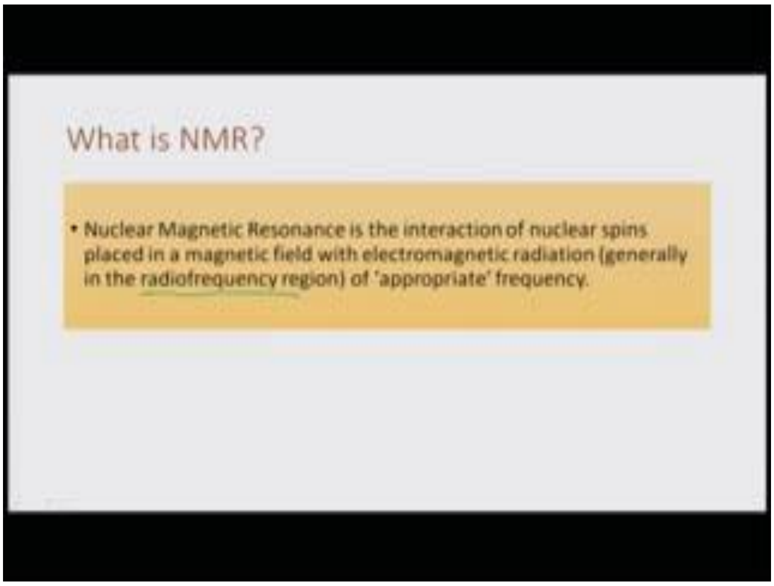

What is NMR?

- Nuclear Magnetic Resonance is the interaction of nuclear spins placed in a magnetic field with electromagnetic radiation (generally in the radiofrequency region) of 'appropriate' frequency.

Let us begin that part today. What is NMR as I just mention Nuclear Magnetic Resonance is the interaction of Nuclear Spins placed in a Magnetic Field with electromagnetic radiation in this particular case generally it is the radio frequency region of appropriate frequency that is what we will be looking at.

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NMR

- Based upon quantum mechanical magnetic properties of atomic nucleus
- All nuclei that contain odd numbers of protons or neutrons have an intrinsic magnetic moment due to a property called spin
- nuclear spin can be either aligned [illegible] or anti-aligned [illegible]
- Under an externally applied static magnetic field, a spin will precesses about the axis of the field. This precession movement generates an oscillating field that can be measured and provides information on the state of the spin. In turn, by externally applying an oscillating (RF) magnetic field to a spin, the spin will gradually move from state up to state down, or vice versa

It is based up on quantum mechanical magnetic properties of atomic nuclei all nuclei that contain odd numbers or protons or neutrons, have an intrinsic magnetic movement due to a property call spin of the atom. Nuclear Spin can be either aligned or anti aligned. So, we can have this as 0 state or 1 state. Under an externally applied static Magnetic Field a spin will precise about the access of the field. This Precession movement generates an oscillating field that can be measured and provides information on the state of the spin interned by externally applying and oscillating RF Magnetic Field radio frequency Magnetic Field to a spin, the spin will gradually move from state up to state down 0 or 1 as we called or vice versa.

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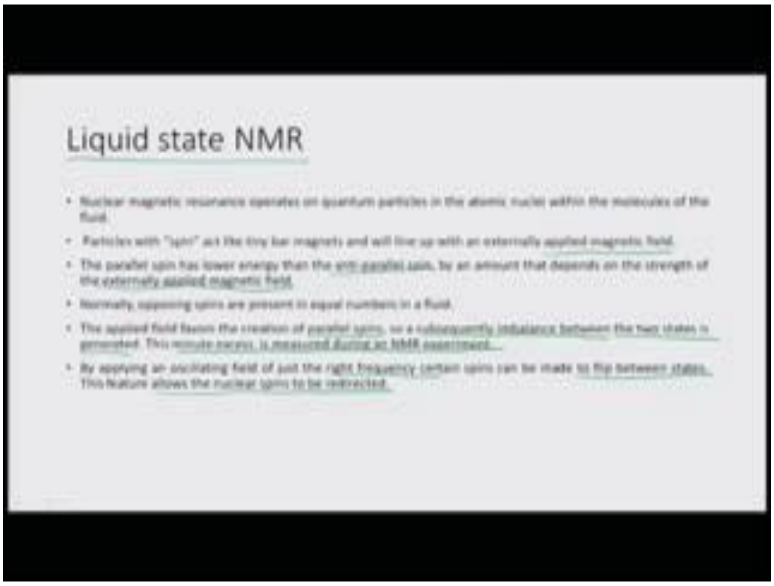

Liquid state NMR

- Nuclear magnetic resonance operates on quantum particles in the atomic nuclei within the molecules of the fluid.
- Particles with "spin" act like tiny bar magnets and will line up with an externally applied magnetic field.
- The parallel spin has lower energy than the anti-parallel spin, by an amount that depends on the strength of the externally applied magnetic field.
- Normally, opposing spins are present in equal numbers in a fluid.
- The applied field favors the creation of parallel spins, so a subsequently imbalance between the two states is generated. This minute excess is measured during an NMR experiment.
- By applying an oscillating field of just the right frequency certain spins can be made to flip between states. This feature allows the nuclear spins to be redirected.

This is the basic idea behind NMR. So, let us actually go into a little bit more detail how to look at it and the more important part is the liquid state NMR. So, in liquid state NMR operates on quantum particles in atomic nuclei within the molecules of the fluid. Particles with spin act like tiny bar magnets and we line up with an externally applied Magnetic Field, the parallel spin has lower energy than the anti parallel spin by an amount depends on the strength of the externally applied Magnetic Field. Normally opposing spins are present in equal numbers in a fluid. So, that the system is magnetically neutral.

The applied field favors the creation of parallel spins so, a subsequently imbalance between the 2 states is generated. This minute excess is measured during an NMR experiment. So, this is the basic idea behind this principle that we are going to have this outside applied field, which is going to create is slight excess of the spins which are aligned favorably with respect to those which are anti parallel so as to create this situation and this minute excess is going to be the one which will be measure through NMR by applying an oscillating field of just the right frequency certain spins can be made to flip between states, this feature allows the Nuclear Spin to be redirected and this is the principle behind this NMR.

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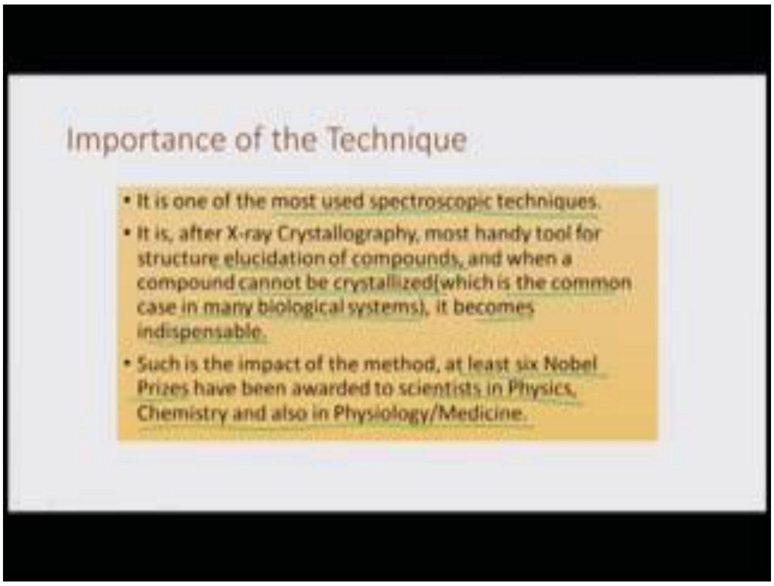

Importance of the Technique

- It is one of the most used spectroscopic techniques.
- It is, after X-ray Crystallography, most handy tool for structure elucidation of compounds, and when a compound cannot be crystallized(which is the common case in many biological systems), it becomes indispensable.
- Such is the impact of the method, at least six Nobel Prizes have been awarded to scientists in Physics, Chemistry and also in Physiology/Medicine.

So, the Importance of the Technique as I already mentioned, this is one of the most used spectroscopy technique. It is after X-ray Crystallography, most handy tool for structure elucidation of compounds and when a compound cannot be crystallized which is the common case in many biological systems, and it becomes indispensable. That is one of the reasons of the celebration at the advantage of NMR over many other techniques. Such is the impact of the method at least 6 Nobel prizes have been awarded to scientists in physics, chemistry and also physiology medicine in this field of NMR.

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- The Nobel Prize in Physics 1943 – Otto Stern, USA – Discovery of magnetic moment of proton
- The Nobel Prize in Physics 1944 – Isidor I. Rabi, USA – Discovery of resonance method for recording the magnetic properties of atomic nuclei
- The Nobel Prize in Physics 1952 – Felix Bloch, USA and Edward M. Purcell, USA – Methods for nuclear magnetic precision measurements.
- The Nobel Prize in Chemistry 1991 – Richard R. Ernst, Switzerland – Methodology of high resolution NMR.
- The Nobel Prize in Chemistry 2002 – Kurt Wuthrich, Switzerland – Determining 3-D Structure of biological Macromolecule in solution by NMR Spectroscopy
- The Nobel Prize in Physiology/Medicine 2003 – Paul C. Lauterbur, USA and Peter Mansfield, U.K. – Discoveries concerning MRI.

Here are these 6 the Nobel Prize in physics in 1943 was due to the discovery of magnetic moment of proton to Otto Stern from US. The Nobel prize in physics in 1944 to professor Rabi in USA discovery of resonance methods for recording the magnetic properties of atomic nuclei Nobel Prize in Physics in 1952 to Fellix Bloch, the Bolch equation US and Edward W. Purcell US for Methods of nuclear magnetic Precession measurements. Nobel Prize in Chemistry in 1991 to Richard R. Ernst, Switzerland for the Methodology of high resolution NMR; Nobel Prize in chemistry in 2002 Kurt Wuthrich, Switzerland for Determining 3-D Structure of biological Macromolecules in solution by NMR spectroscopy Nobel Prize in Physiology/Medicine in 2003 to Paul L Lauterbur and Peter Mansfield, UK one from US, discoveries concerning MRI. So, these are the 6 which has still come in the field of NMR for this field.

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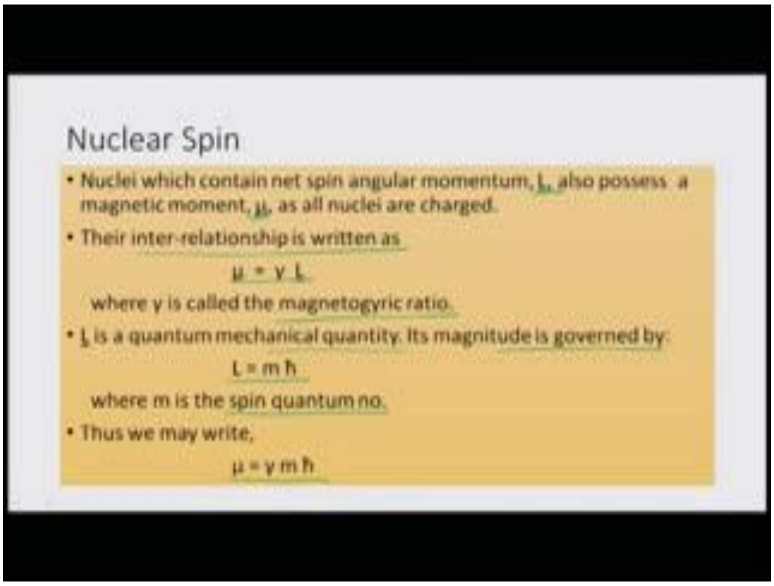

Nuclear Spin

- Nuclei which contain net spin angular momentum, L, also possess a magnetic moment, μ, as all nuclei are charged.
- Their inter-relationship is written as

$$\mu = \gamma L$$

where γ is called the magnetogyric ratio.
- L is a quantum mechanical quantity. Its magnitude is governed by:

$$L = m \hbar$$

where m is the spin quantum no.
- Thus we may write,

$$\mu = \gamma m \hbar$$

What is this Nuclear Spin? Nuclei which contain net spin angular momentum L, also possess a magnetic moment mu, as all nuclei are charged. Their inter-relationship is written as mu is equal to gamma L, where gamma is called the magnetic magneto gyric ratio or gyro magnetic ratio whichever way you want to put it. L is a quantum mechanical quantity its magnitude is governed by: L is equal to m h cross as the quantum mechanical, where m is the spin quantum number. So, you may write mu is equal to gamma m h cross.

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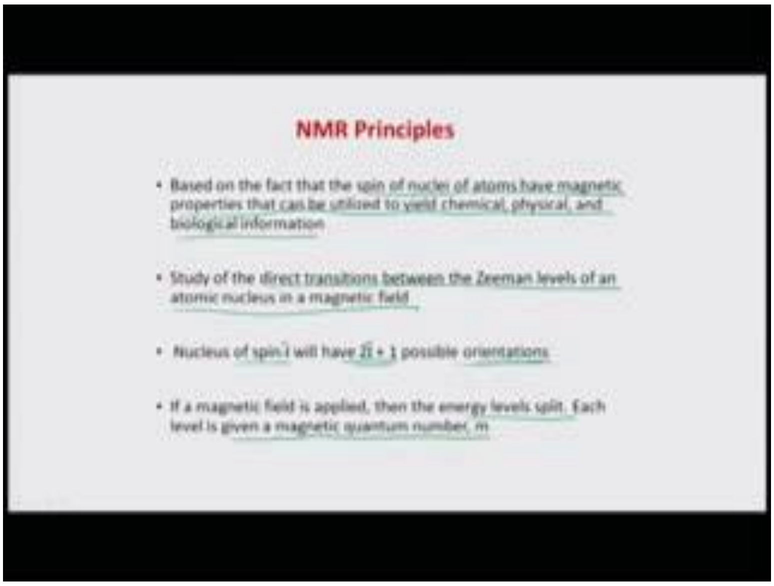

NMR Principles

- Based on the fact that the spin of nuclei of atoms have magnetic properties that can be utilized to yield chemical, physical, and biological information
- Study of the direct transitions between the Zeeman levels of an atomic nucleus in a magnetic field
- Nucleus of spin I will have 2I + 1 possible orientations
- If a magnetic field is applied, then the energy levels split. Each level is given a magnetic quantum number, m

So, as far as the NMR Principles go based on the fact that the spin of the nuclei of atoms have magnetic properties that can be utilized to yield chemical, physical and biological information as I have just mentioned. Study of the direct transitions between the Zeeman levels of atomic nuclei in a Magnetic Field; Nucleus of spin i will have 2 i plus 1 possible orientations. If a Magnetic Field is applied, then the energy level split. Each level is given a magnetic quantum number m.

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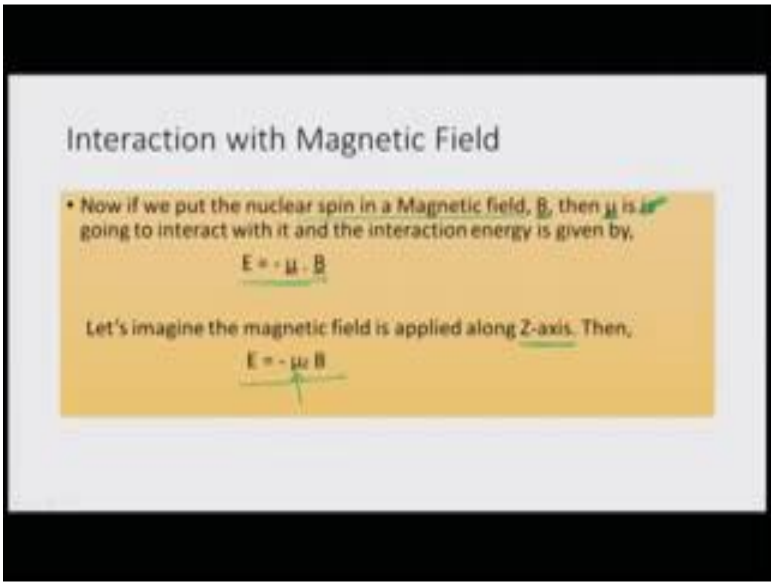

Interaction with Magnetic Field

- Now if we put the nuclear spin in a Magnetic field, $\underline{B}$, then $\underline{\mu}$ is going to interact with it and the interaction energy is given by,

$$E = -\underline{\mu} \cdot \underline{B}$$

Let's imagine the magnetic field is applied along Z-axis. Then,

$$E = -\mu_z B$$

When a Magnetic Field is applied there will be interaction and if we put them nuclear magnetic spin on Magnetic Field B, then mu is going to interact with it and the interaction energy is given by, e is equal to minus mu dot B. Let us imagine the Magnetic Field is applied along the Z or Z direction. Then, e is equal to minus mu z that component times B.

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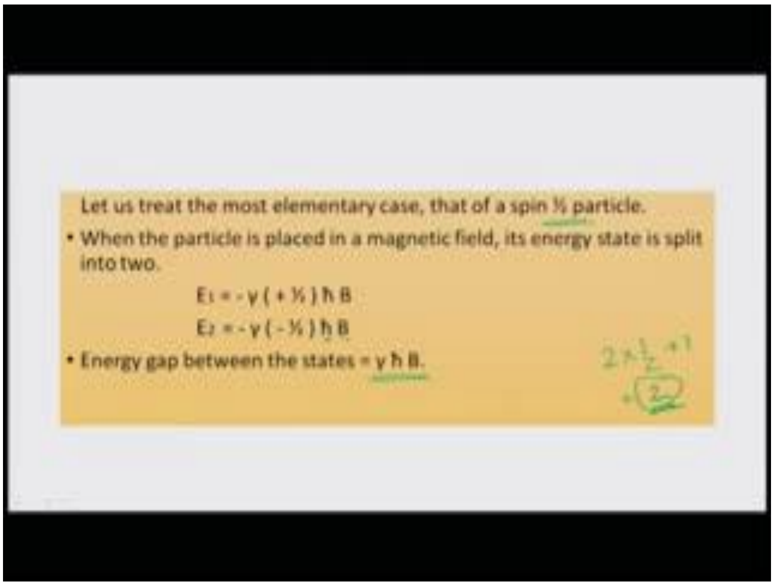

Let us treat the most elementary case, that of a spin ½ particle.

- When the particle is placed in a magnetic field, its energy state is split into two.

$$E_1 = -\gamma(+½)\hbar B$$
$$E_2 = -\gamma(-½)\hbar B$$

- Energy gap between the states = $\gamma \hbar B$.

$2 \times \frac{1}{2} + 1$
$= \boxed{2}$

Let us treat the most elementary case, first that is of the spin half particle. That is the most elementary case because 2 times half plus 1 is equal to 2 possibilities, that is the minimum possible case there are 2 particular cases; when the particle placed in the Magnetic Field its energy state is split in to 2 E 1 is equal to minus gamma plus half h cross over h cross B or E 2 is minus gamma minus half h cross b. So, these are the 2 different possibilities energy gap between these states are therefore, going to be gamma h cross B is the separation between these.

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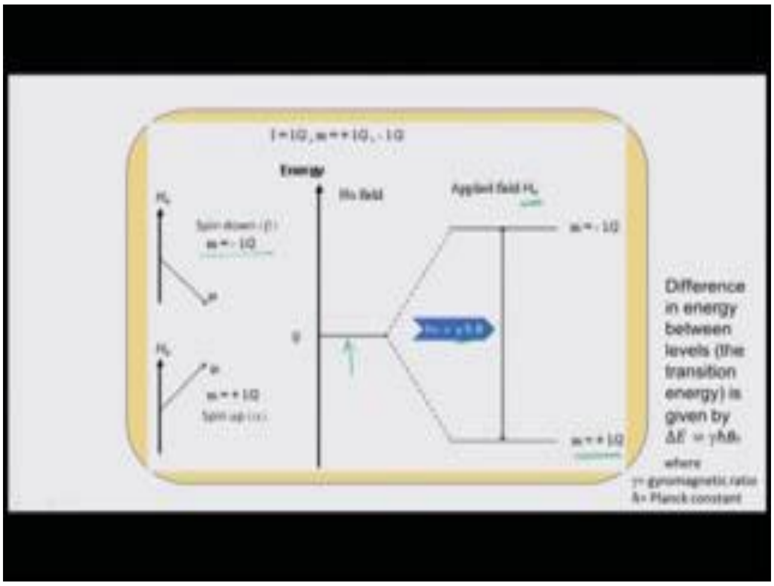

Difference in energy between levels (the transition energy) is given by $\Delta E = \gamma \hbar B_0$

where

γ= gyromagnetic ratio

ħ= Planck constant

So, this is how it looks, you have the interaction either as a spin down case, where the field is going to be counter towards the direction or it could be spin up; now the field is going in the up direction the Magnetic Field. One is more favored than the others so, the energy lowering for the spin up case is makes it go at the bottom whereas, the other one interacts with a little bit of to gain a little bit more energy. When there is no field there is no separation between these 2 magnetic cases, they are the same, but when the applied Magnetic Field h 0 is provided then h 0 or B which ever notation we take, then there will be a separation of the 2 which will be according to the energy gap which is gamma h cross B. The sensitivity of the technique would depend on these few parameters.

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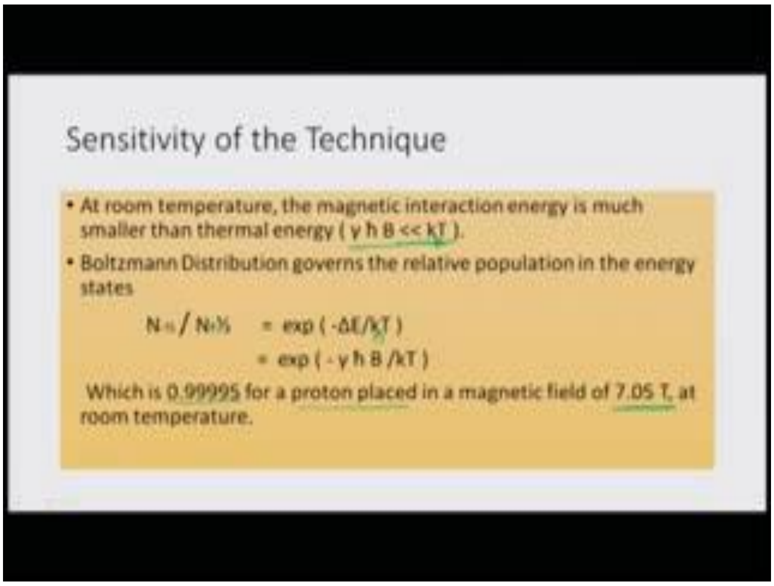

Sensitivity of the Technique

- At room temperature, the magnetic interaction energy is much smaller than thermal energy ($\gamma \hbar B << kT$).
- Boltzmann Distribution governs the relative population in the energy states

$$N_{-\frac{1}{2}} / N_{+\frac{1}{2}} = \exp(-\Delta E/kT)$$
$$= \exp(-\gamma \hbar B/kT)$$

Which is 0.99995 for a proton placed in a magnetic field of 7.05 T, at room temperature.

At room temperature, the magnetic interaction energy is much smaller than the thermal energy. Which means that gamma h cross B is much much smaller than k B T; k B is Boltzmann constant here. The Boltzmann distribution governs the relative population in the energy states, n minus half over let say n plus half. It will be given by exponential minus delta E over k B T, which is equal to exponential minus gamma h cross B over k T. This is going to be as small as 0.99995 for a proton placed in a Magnetic Field of 7 Tesla at room temperature. It is a very small entity; we were talking about a very small entity.

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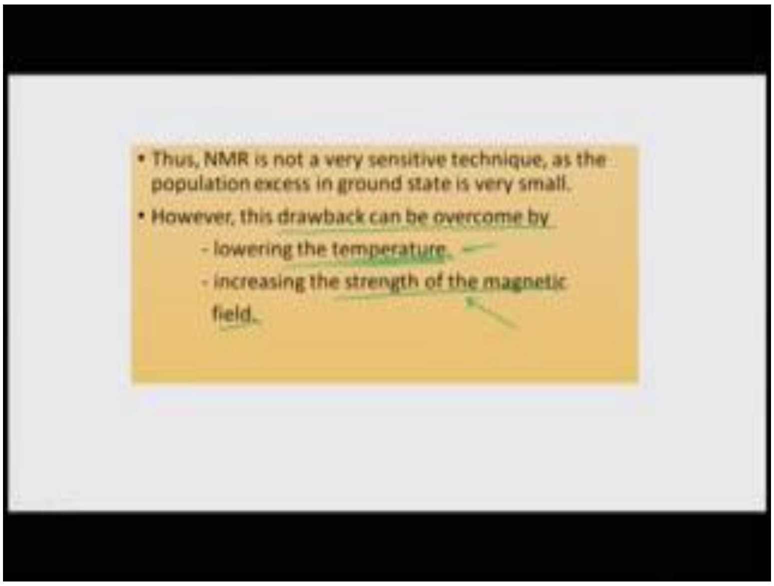

- Thus, NMR is not a very sensitive technique, as the population excess in ground state is very small.
- However, this drawback can be overcome by
  - lowering the temperature.
  - increasing the strength of the magnetic field.

NMR is not a very sensitive technique, that way as the population excess in the ground state is very small. However, this drawback can be overcome by lowering the temperature or increasing the strength of the Magnetic Field because as you can see this gap depends on the temperature concerned and the Magnetic Field strength.

Let us see how you can go ahead about this. We can essentially these experiments are done in both the cases where in one case the temperature, the spectrometer essentially operates at a low enough temperature and it increases the strength of the and it is also operating at a very high Magnetic Field strength. Many a times temperature cannot be worked on because you want the state of the matter not to change that is why.

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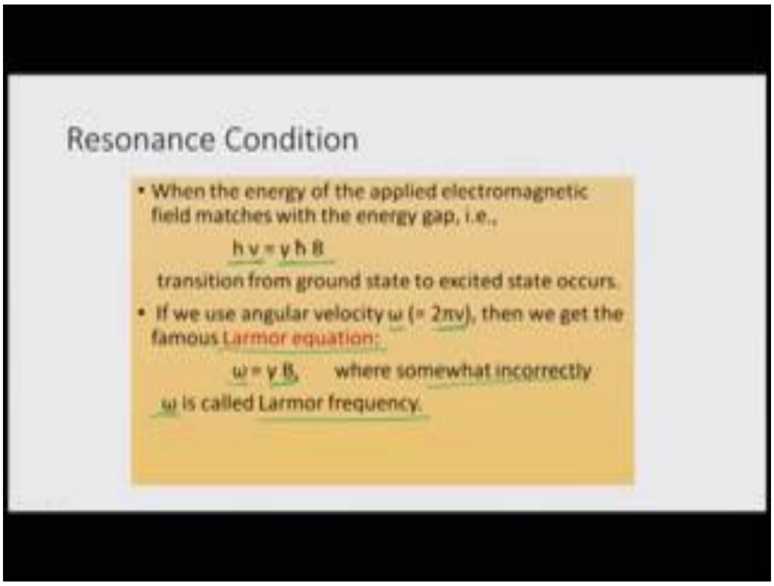

Resonance Condition

- When the energy of the applied electromagnetic field matches with the energy gap, i.e.,

  $h\nu = \gamma \hbar B$

  transition from ground state to excited state occurs.
- If we use angular velocity ω (= $2\pi\nu$), then we get the famous Larmor equation:

  $\omega = \gamma B$, where somewhat incorrectly ω is called Larmor frequency.

The other important part here is the Resonance Condition. When the energy of the applied electro Magnetic Field matches the energy gap, though gap that we mentioned gamma h cross B and we have applied the electro Magnetic Field h nu then the transition occurs from the ground state to the excited state. If we use angular velocity omega, which is 2 pi nu; then we get the famous Larmor equation: which is omega is equal to gamma B, where somewhat incorrectly omega is called the Larmor frequency although, it is basically an angular velocity, but anyway it is call the Larmor frequency. This omega is called the Larmor frequency that is because it was discovered by Larmor.

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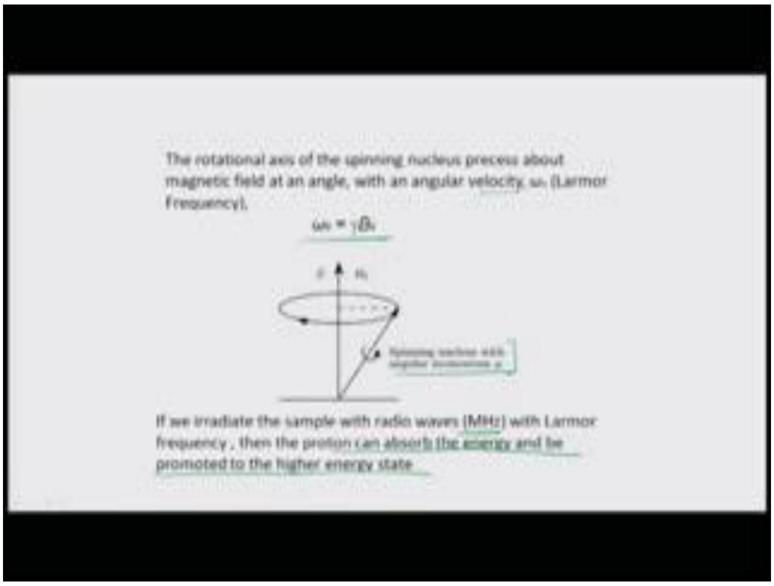

The rotational axis of the spinning nucleus precess about magnetic field at an angle, with an angular velocity, ω_0 (Larmor Frequency).

$\omega_0 = \gamma B_0$

If we irradiate the sample with radio waves (MHz) with Larmor frequency , then the proton can absorb the energy and be promoted to the higher energy state

The rotational axis of the spinning nuclei precesses about Magnetic Field at an angle with an angular velocity omega Larmor frequency.

Here is just spinning nucleus with an angular momentum mu and so, omega naught is equal to gamma B naught. if we irradiate the sample with radio waves of Mega Hertz radiation with Larmor frequency, then the proton can absorb the energy and be promoted to the higher energy state. That is the principle that I just mentioned earlier it is shown pictorial here.

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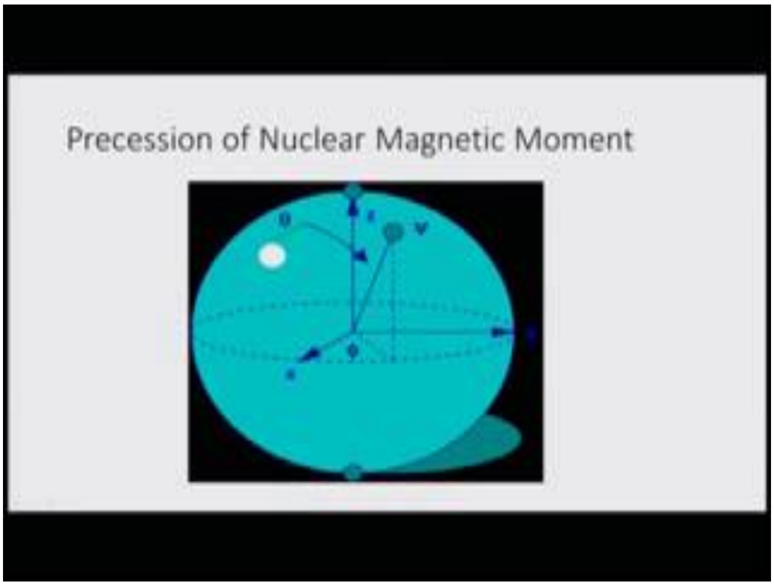

Precession of Nuclear Magnetic Moment

The Precession of the nuclear magnetic moment sort of looks like this; this is my angle theta, this is along the z axis as we mentioned is our Magnetic Field working and the Precession is by this particular spin particle which is precessing around that and there are 2 angles set with it one is the Azimuthal angle and the other one is the (Refer Time: 24:56) angle theta and phi and we can see what is going on with this.

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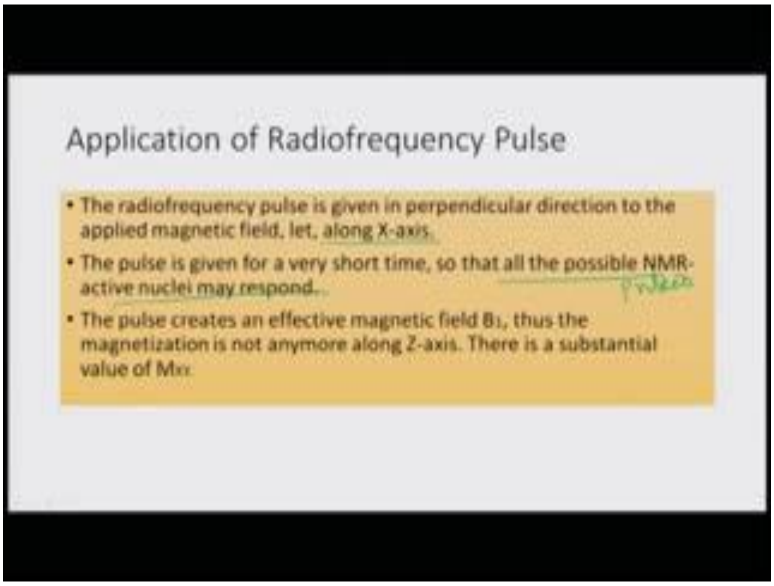

Application of Radiofrequency Pulse

- The radiofrequency pulse is given in perpendicular direction to the applied magnetic field, let, along X-axis.
- The pulse is given for a very short time, so that all the possible NMR-active nuclei may respond.
- The pulse creates an effective magnetic field B_1, thus the magnetization is not anymore along Z-axis. There is a substantial value of M_{XY}

By Application of the Radio frequency Pulse which is given at perpendicular direction to the applied Magnetic Field, this is along the X axis. The pulse is given for a very short time so, that all possible NMR active nuclei may respond. This is one of the important parts of pulsed NMR. This is one of the most important developments in the part of NMR because unless you use pulsed NMR it is very difficult to get the nuclei to respond properly.

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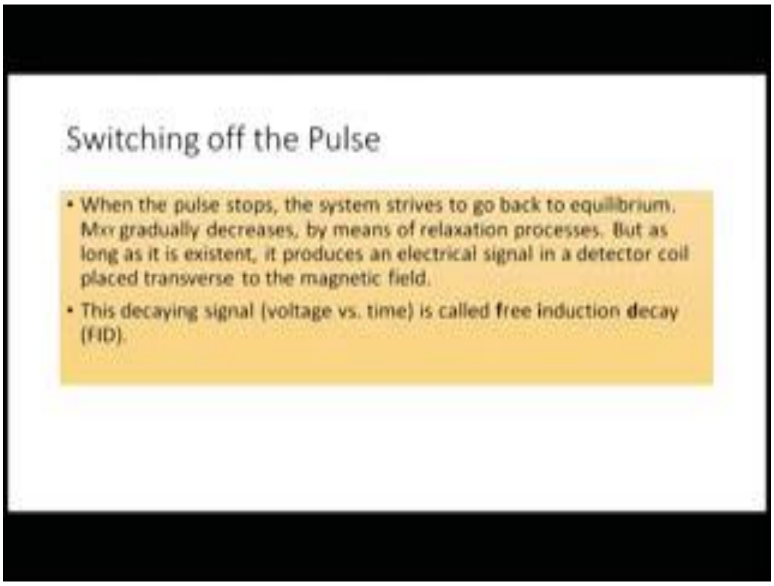

Switching off the Pulse

- When the pulse stops, the system strives to go back to equilibrium. M_{XY} gradually decreases, by means of relaxation processes. But as long as it is existent, it produces an electrical signal in a detector coil placed transverse to the magnetic field.
- This decaying signal (voltage vs. time) is called **free induction decay** (FID).

If you are going to excite one nuclei at a time it is extremely difficult to get the right frequency and be able to apply that. Instead a short pulse in time a lot of frequency are available and all possible NMR active nuclei would respond the pulse creates an effective Magnetic Field B 1 thus the magnetization is not any more along the z axis there is a substantial value of m of X Y, there is an X Y plane application because of this applied radio frequency pulse.

When the pulse stops, the systems tries to go back to equilibrium m X Y gradually decreases by means of relaxation processes, but as long as it exists it produces an electric signal in a detector coil placed transversely to the Magnetic Field. This decaying signal voltage versus time is called free induction decay or FID.

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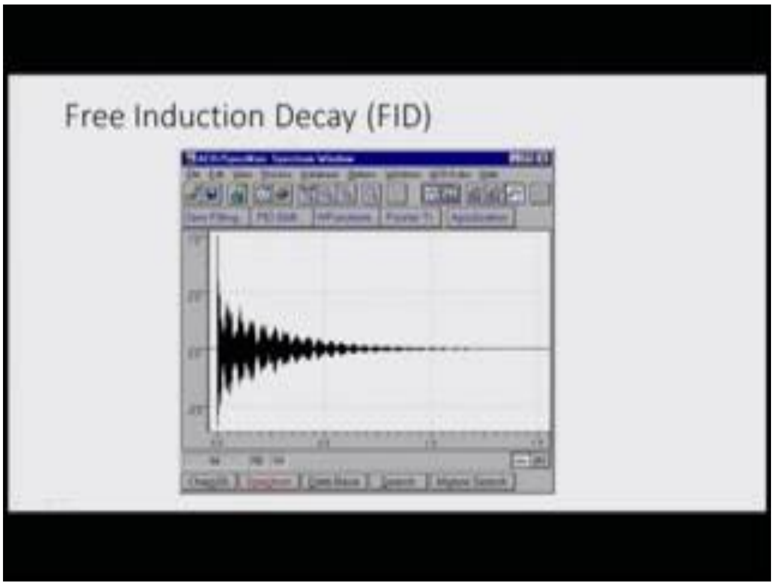

Free Induction Decay (FID)

An FID signal sort of looks like this; there is this voltage which with time goes down because of the relaxation process and this is what is essentially captured as a result of this applied RF field.

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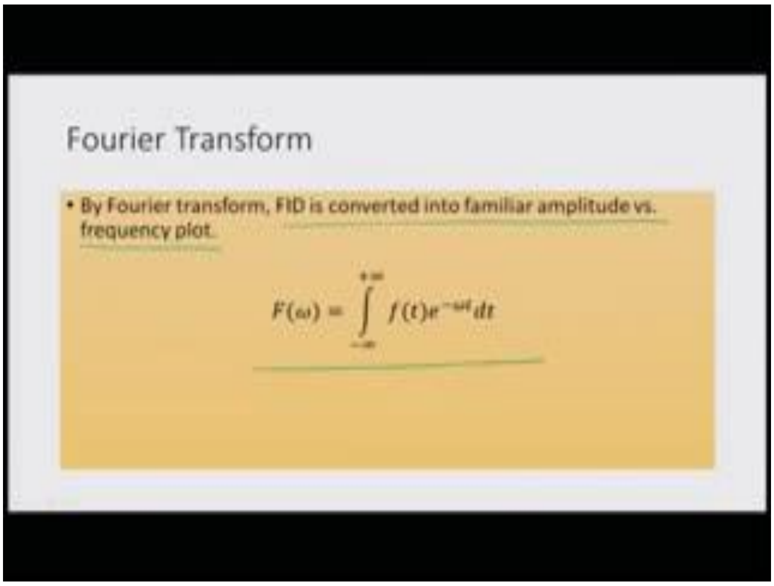

Fourier Transform

- By Fourier transform, FID is converted into familiar amplitude vs. frequency plot.

$$F(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt$$

By Fourier Transform FID is converted into the familiar amplitude versus frequency plots and this is how this Fourier transform works.

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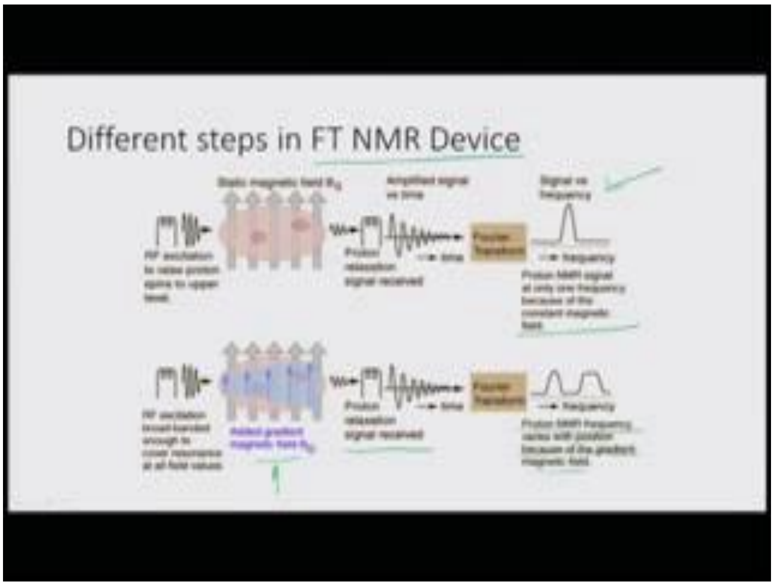

Different steps in FT NMR Device

The different steps in Fourier transfer NMR device are of this kind an RF excitation is used to raise the proton spins to the upper level has a static Magnetic Field, as a result of which proton is being provided this RF excitation in the states which is slightly differing. The proton relaxation process is now is going to happen now, the amplified signal versus time is been looked at then its Fourier transform and the signal versus frequency as is being generated; proton NMR signal at only one frequency because of the constant Magnetic Field.

Now, RF excitation broadband enough to cover resonance of all fields if you apply so, this is with one single frequency; now we add gradient Magnetic Field of (Refer Time: 28:08) proton relaxation signal receive, now if your Fourier transform then you will get the proton NMR frequency variation with position because the gradient of Magnetic Field is also applied so, these are various different ways of doing NMR. You can develop it to a point that you can do a lot of different applications to it.

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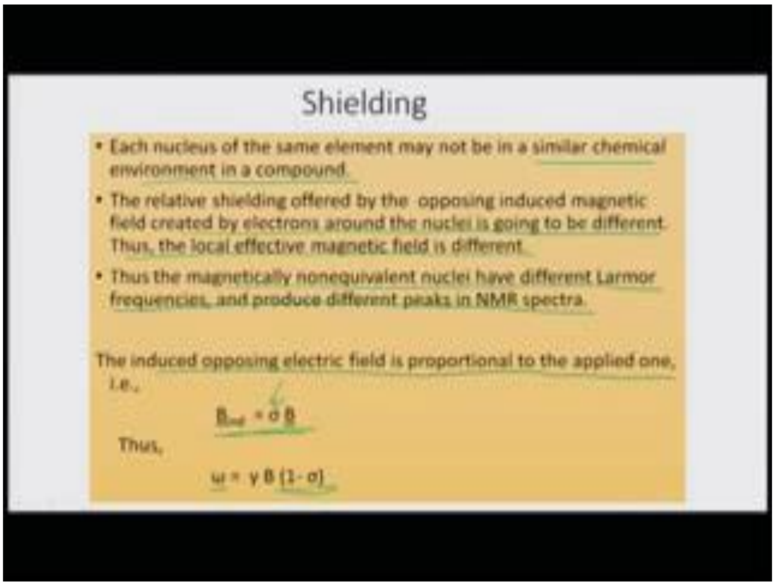

Shielding

- Each nucleus of the same element may not be in a similar chemical environment in a compound.
- The relative shielding offered by the opposing induced magnetic field created by electrons around the nuclei is going to be different. Thus, the local effective magnetic field is different.
- Thus the magnetically nonequivalent nuclei have different Larmor frequencies, and produce different peaks in NMR spectra.

The induced opposing electric field is proportional to the applied one, i.e.,

$$B_{ind} = \sigma B$$

Thus,

$$\omega = \gamma B (1 - \sigma)$$

.

Now, each nucleus of the same element may not be in a similar chemical environment in a compound now this is one of the most important parts of it being acting like a spectroscopy. The relative Shielding offered by the opposing induced Magnetic Field created by electrons around the nuclei is going to be different, thus the local effective Magnetic Field is different and that creates the spectra which are going to be different. The magnetically non equivalent nuclei have different Larmor frequencies and produce different peaks in NMR spectra. The induced opposing electric field is proportional to the applied one, that is induced B induced is equal to sigma this is the Shielding times the B the Magnetic Field and therefore, instead of seeing a Larmor frequency omega is equal to gamma B there is this part 1 minus sigma this Shielding constant which give raise to different values.

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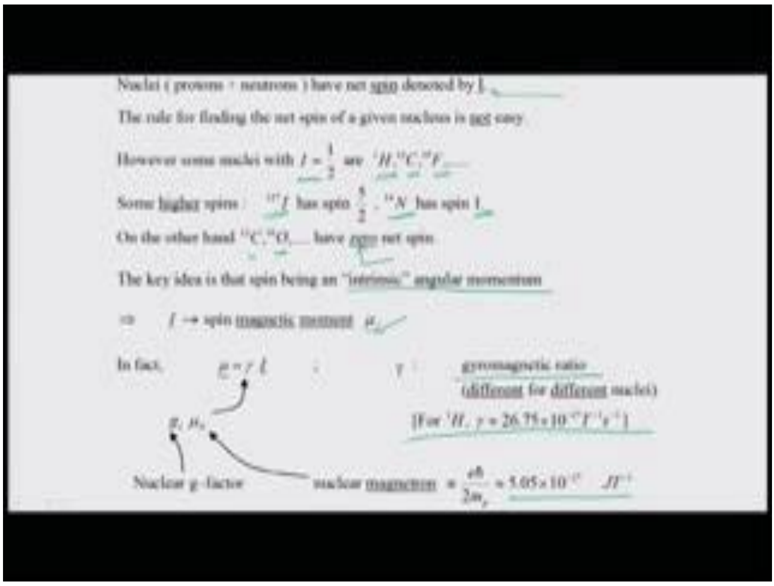

Nuclei (protons + neutrons) have net spin denoted by I

The rule for finding the net spin of a given nucleus is not easy

However some nuclei with $I = \frac{1}{2}$ are $^{1}H, ^{13}C, ^{19}F$ ....

Some higher spins : ^{127}I has spin $\frac{5}{2}$, ^{14}N has spin 1

On the other hand $^{12}C, ^{16}O$,.... have zero net spin

The key idea is that spin being an "intrinsic" angular momentum

$\Rightarrow$ $I \rightarrow$ spin magnetic moment μ

In fact, $\mu = \gamma I$; γ : gyromagnetic ratio (different for different nuclei)

[For ^{1}H, $\gamma = 26.75 \times 10^{7} T^{-1} s^{-1}$]

$g_I \mu_N$

nuclear magnetron $= \frac{e\hbar}{2m_p} = 5.05 \times 10^{-27}$ JT^{-1}

Now, in order to get to the more details of this problem and let us get into this in a little bit more detail; the nuclei which has both protons and neutrons have a net spin denoted by I, which we have already used until now the rule for finding the net spin of a given nucleus is not an easy task; typically it is based on the fact that it is an experimental value. You can sort of, you can measure the values; however, some nuclei with the spin value of half known are proton, carbon 13, fluorine 19 and so on and so forth. Some higher spin numbers are for example, iodine 127 which has a spin of 5 by 2; N 14 has a spin of 1.

On the other hand carbon 12, oxygen 16 have no spin there is 0 net spin the key idea is that spin is an intrinsic angular momentum property of the system that we are looking at. The spin magnetic moment therefore, corresponds to quantity mu which we were talking about and therefore, mu is related to the (Refer Time: 30:49) magnetic moment by gamma; which is the gyro magnetic ratio as we discussed before and this is different from different nuclei. So, mu is equal to gamma I and gamma can be written again in terms of the nuclear g factor g I times mu N, which is the nuclear magnetron value which is a constant for a given nuclei.

For proton for example, the gyro magnetic ratio is also given here 26.76 times ten to power minus 27 to the power per Tesla per second.

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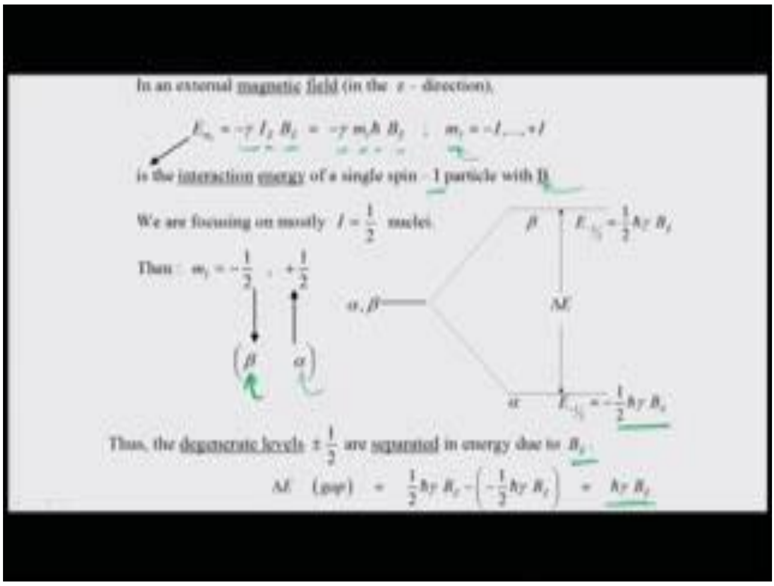

In an external magnetic field (in the z - direction),

$E_{m_I} = -\gamma I_z B_z = -\gamma m_I \hbar B_z$; $m_I = -I, \dots, +I$

is the interaction energy of a single spin - I particle with B

We are focusing on mostly $I = \frac{1}{2}$ nuclei.

Then : $m_I = -\frac{1}{2}$, $+\frac{1}{2}$

Thus, the degenerate levels $\pm\frac{1}{2}$ are separated in energy due to B_z

$$\Delta E \text{ (gap)} = \frac{1}{2}\hbar\gamma B_z - \left(-\frac{1}{2}\hbar\gamma B_z\right) = \hbar\gamma B_z$$

.

That is how the gamma and all these parameters are in an external Magnetic Field which is the (Refer Time: 31:40) direction as we discussed. The field is the interaction the E m I can be here we have defined it has the interaction energy of a single spin with I with acting on the Magnetic Field B. So, we get this value the interaction value is given by minus gamma terms I z B z because it is all in the z dimension minus gamma m I h cross B of z and m I is my magnetic spin coefficient and that can go anywhere from minus I to plus I. When we are focusing on the I equal to half this one is minus half and plus half only 2 values.

So, m I is equal to minus half and plus. As we had defined before the one which is interacting positively is the one which gets aligned, which is in the plus one dimension and that is alpha and the one which is of the other kind is the minus kind and it is called the beta. Alpha has lower energy than the beta and the gap is given by this value that we have done. Essentially its each of this values a minus half h cross gamma beta B z and the other one is E minus half is going to be half h cross gamma B of z. Thus the degenerate levels plus minus half are separated in energy due to the value of d to B z applied Magnetic Field along this z dimension. The energy gap therefore, is given by h cross gamma B z.

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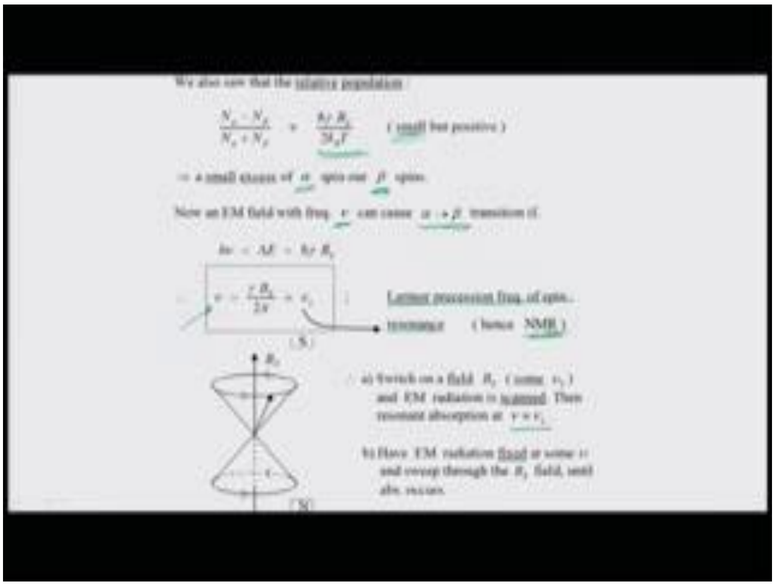

We also saw that the relative population :

$$\frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \frac{\hbar\gamma B_z}{2k_B T} \quad \text{(small but positive)}$$

⇒ a small excess of α spin over β spins.

Now an EM field with freq. ν can cause $\alpha \to \beta$ transition if

$$h\nu = \Delta E = \hbar\gamma B_z$$

$$\boxed{\nu = \frac{\gamma B_z}{2\pi} = \nu_L}$$

Larmor precession freq. of spin.

resonance (hence NMR)

a) Switch on a field B_z (some ν_L) and EM radiation is scanned. Then resonant absorption at $\nu = \nu_L$

b) Have EM radiation fixed at some ν and sweep through the B_z field, until abs. occurs.

.

We also saw that reality population, which is essentially an alpha minus N beta over N alpha plus N beta is given by h cross gamma B of z over 2 k B T which is small, but a positive value. A small excess of alpha spin over our beta spins because of the interaction advantage of the alpha over the beta.

Now, when an electro Magnetic Field with frequency nu is applied which can cause the transition alpha to beta; this will happen only when this matches the exact energy gap h nu is equal to delta E is equal to h cross gamma B of z. This particular case we will therefore, get the frequency to be gamma B z over 2 pi which is gamma L which is known as the Larmor Precession frequency of the spin resonance and therefore, it is for NMR, this is the resonance condition. It is Nuclear Magnetic Resonance because of this particular resonance condition. Whenever it is this particular case then it is a resonance case. Therefore, it switches on a field of B z which has some Precession value of nu L an electromagnetic radiation is scanned then the resonance absorption occurs at nu equal to nu l. On the other hand you can have an electromagnetic radiations fixed at some gamma value, some frequency nu and sweep through the B z field until absorption occurs; again which is a tough job because you want change the Magnetic Field continuously so on and so forth. Typically it is the other way around, where the as we have seen the frequency is possible to change abruptly by using a small paths of the radiation field.

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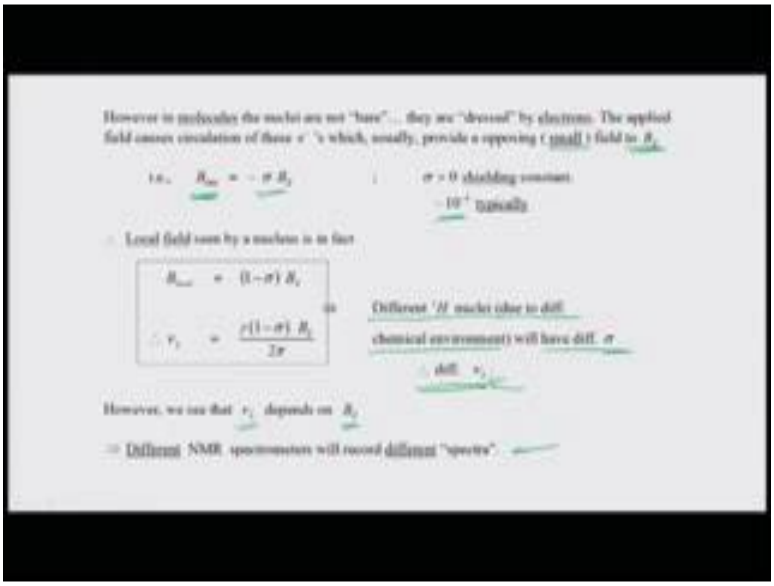

However in molecules the nuclei are not "bare"… they are "dressed" by electrons. The applied field causes circulation of these e^-'s which, usually, provide a opposing (small) field to B_z

i.e., $B_{el} = -\sigma B_z$; $\sigma > 0$ shielding constant

$\sim 10^{-5}$ typically

∴ Local field seen by a nucleus is in fact

$$\boxed{\begin{aligned} B_{local} &= (1-\sigma) B_z \\ \therefore \nu_L &= \frac{\gamma(1-\sigma) B_z}{2\pi} \end{aligned}}$$

⇒ Different ^1H nuclei (due to diff. chemical environment) will have diff. σ

∴ diff. ν_L

However, we see that ν_L depends on B_z

⇒ Different NMR spectrometers will record different "spectra".

However in molecules the nuclei are not bare, they are dress by electrons they applied field causes circulation of these electrons in which usually provides an opposing small field to B z. That is we have because of the electrons present in the molecule B of electron B electron, is equal to minus sigma B z. This sigma is just Shielding constant which is going to be 0 (Refer Time: 36:15) greater than 0; which is roughly 10 to the power minus 5 orders and that is the one for which we see a difference. Local field seen by nuclei is going to be in fact dependent on the sigma value. So, B local is equal to 1 minus sigma times B of z and different proton nuclei due to different chemical environment will have different sigma the Shielding and therefore, different nu L; however, we see that nu L depends on B of z different NMR spectrometers in that case would different, would record different spectra. This is not desirable when you are going to use the NMR is a spectrometer. So, what is done therefore is that at this point for a spectrometer a little bit of a different attitude is taken.

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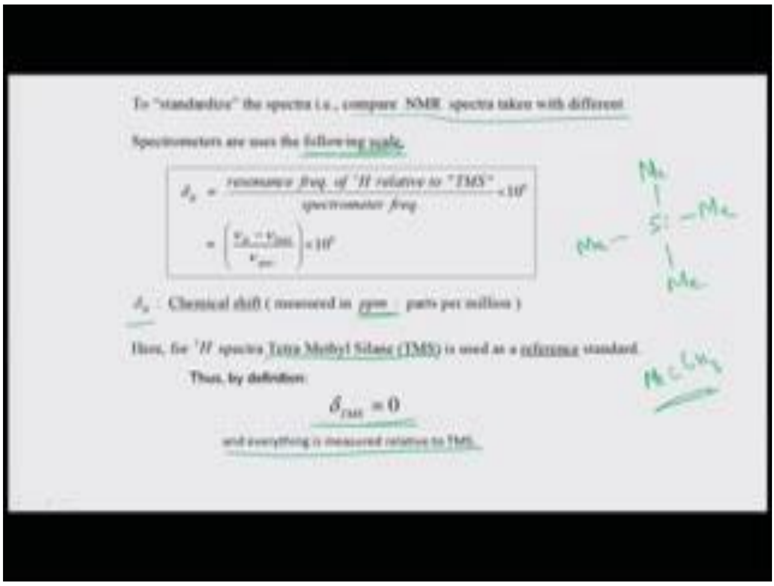

To "standardize" the spectra i.e., compare NMR spectra taken with different

Spectrometers are uses the following scale.

$$\delta_H = \frac{\text{resonance freq. of } ^1H \text{ relative to "TMS"}}{\text{spectrometer freq.}} \times 10^6$$

$$= \left(\frac{\nu_H - \nu_{TMS}}{\nu_{spec}}\right) \times 10^6$$

δ_H : Chemical shift (measured in ppm : parts per million)

Here, for ^1H spectra Tetra Methyl Silane (TMS) is used as a reference standard.

Thus, by definition:

$$\delta_{TMS} = 0$$

and everything is measured relative to TMS.

.

Standardization of the spectra is done by comparing NMR spectra will be done by different spectrometers and this is done by using a scaling factor. You basically define a scale for the NMR and a molecule called tetra methyl silane TMS, tetra methyl silane is used as a standard which has very low magnetic field effect because it is silicon and it has M e stands for CH3.

The protons in this particular CH3 group has as the least proton effect because it is the standard and therefore, it is with respect to this is measured with respect to resonance frequency or proton relative to TMS and the spectrometer frequency is the one which is being divided. When this scale is been used and this is written in terms of parts per million. So, 10 to the power of 6 is been multiplied we get something which is known as delta H which is the chemical shift. For proton spectra TMS is used as a reference standard and by definition TMS is taken as 0. It has the least changes and therefore, it considered as 0 and everything else is measured with respect to TMS.

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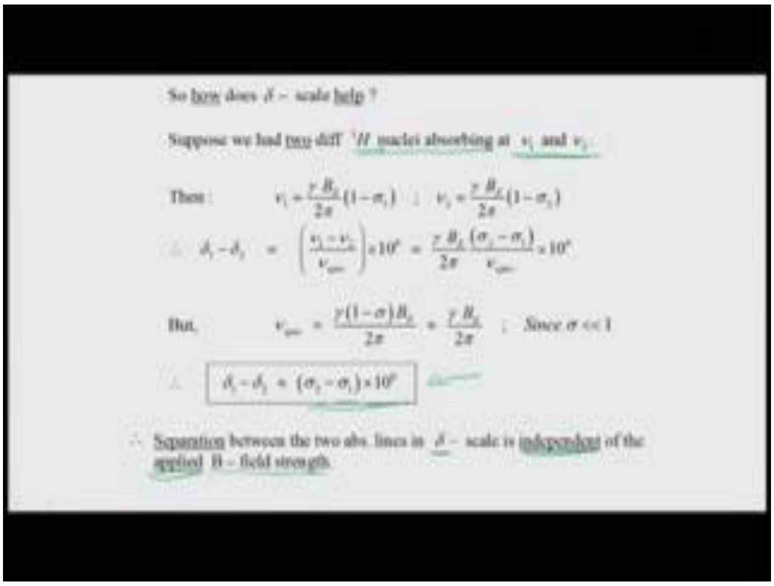

So how does δ – scale help ?

Suppose we had two diff ^1H nuclei absorbing at ν_1 and ν_2

Then : $\nu_1 = \frac{\gamma B_0}{2\pi}(1-\sigma_1)$; $\nu_2 = \frac{\gamma B_0}{2\pi}(1-\sigma_2)$

$\therefore \ \delta_1 - \delta_2 = \left(\frac{\nu_1 - \nu_2}{\nu_{spec}}\right)\times 10^6 = \frac{\gamma B_0}{2\pi}\frac{(\sigma_2 - \sigma_1)}{\nu_{spec}}\times 10^6$

But, $\nu_{spec} = \frac{\gamma(1-\sigma)B_0}{2\pi} \approx \frac{\gamma B_0}{2\pi}$; Since $\sigma << 1$

$\therefore \ \boxed{\delta_1 - \delta_2 = (\sigma_2 - \sigma_1)\times 10^6}$

$\therefore$ Separation between the two abs. lines in δ – scale is independent of the applied B – field strength.

That is the way the scale is defined when you are doing spectroscopy with NMR and when you define that this scaling essentially make sure that all the nuclear are going to be seen in the same way for the same molecule environment. Suppose we have 2 different proton nuclei absorbing at nu 1 and nu 2, then we can apply the standard that we have just done and what we find is that the difference of the 2 will be a value which will be as a result of the chemical shift difference will be as result of the Shielding of the 2, but the separation between the 2 absorption lines of the chemical shift scale is independent of the applied Magnetic Field, that is field strength and that is what exactly what we mentioned in the beginning, that we did not want the Magnetic Field to play a role on this because otherwise every instrument that you have will be different with respect to each other the NMR machine.

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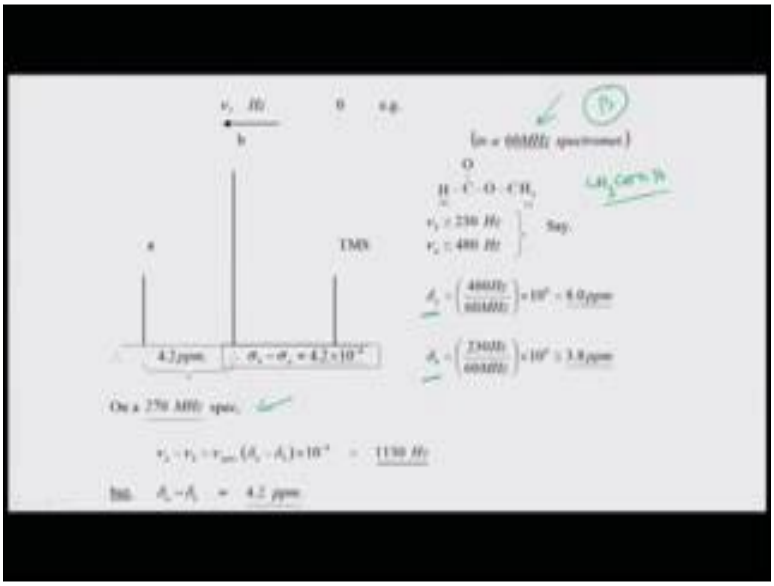

(on a 60MHz spectrometer)

On a 270 MHz spec.

1130 Hz

But $\delta_a - \delta_b$ = 4.2 ppm

Therefore, this is one of the scales which have been used all the time in NMR to make sure that this is how it works. Here is an example of the case of a molecule. So, this it is CH3, COOH molecule. It is an acetic acid, on a 60 Mega Hertz spectrometer when this acetic acid is being measured say you get some numbers like that and you can calculate and how these 2 different values will show up in terms of chemical shift.

However, if you should put that in the same on a 270 Mega Hertz machine you will find that though the individual values are different; the ultimate the separation will remain the same. 4.2 ppm is the separation which is the same whether you are using a 270 Mega Hertz machine or you are using a 60 Mega Hertz machine.

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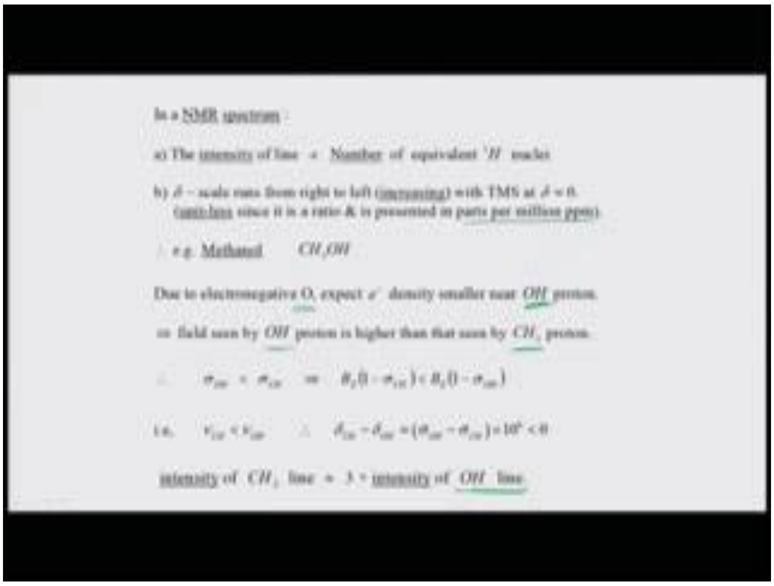

In a NMR spectrum :

a) The intensity of line ∝ Number of equivalent ^1H nuclei

b) δ – scale runs from right to left (increasing) with TMS at $\delta = 0$.
(unit-less since it is a ratio & is presented in parts per million ppm).

∴ e.g. Methanol CH_3OH

Due to electronegative O, expect e^- density smaller near OH proton.

⇒ field seen by OH proton is higher than that seen by CH_3 proton.

∴ $\sigma_{OH} < \sigma_{CH}$ ⇒ $B_0(1-\sigma_{CH}) < B_0(1-\sigma_{OH})$

i.e. $\nu_{CH} < \nu_{OH}$ ∴ $\delta_{CH} - \delta_{OH} = (\sigma_{OH} - \sigma_{CH}) \times 10^6 < 0$

intensity of CH_3 line = 3 × intensity of OH line

Now, this 270 and 60 Mega Hertz are the values related to the applied Magnetic Field and that is how it becomes a standard (Refer Time: 40:48) system. In a NMR spectrum therefore, the intensity of the line is; however, proportional to the number of the equivalent protons that you have the delta scale runs from left to right with respect to increasing with the TMS at delta given to as 0 and it is unit less since it is a ratio and is presented in parts per million.

For example, in methanol you can find out that due to the electro negative nature of the oxygen the electron density is smaller nears the OH proton. So, the field seen by OH proton is higher than that seen by CH3 proton and so, this gives raise to the expected value of what we see the intensity of the CH3 line is roughly going to be 3 times the intensity of the OH line and this is how we can find out how this goes we can do all the example cases of this.

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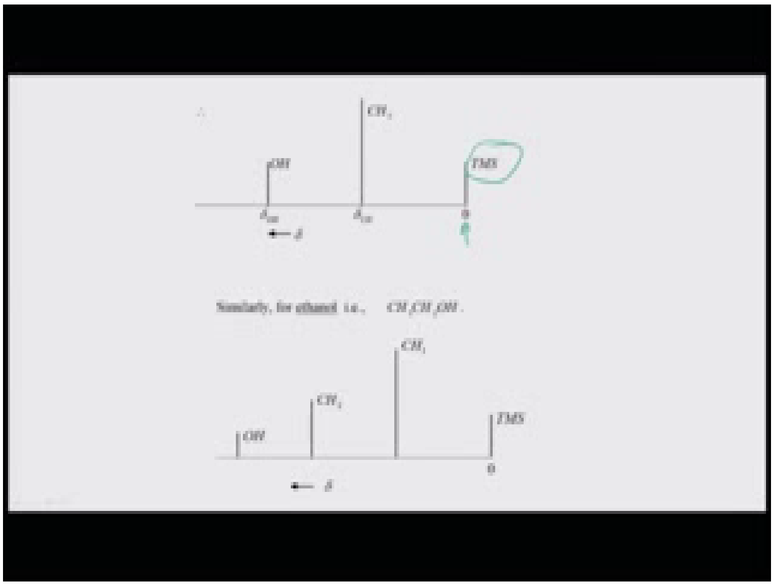

Similarly, for ethanol i.e., CH_3CH_2OH .

This how the NMR spectrometer works and this is an example of how this looks like the standardization level is set as 0 and with respect to that it shows how much more the Shielding is. So, those with a lot of Shielding will be moving basically when the proton is going to have its electron cloud removed from it it will go further away from the TMS or the starting point further away and those which have lesser of that effect that they will be closer to the TMS values and therefore, you can see that CH3 lies protons lies closer to TMS than OH and similarly you can have this ethanol which will be CH3, CH2 and OH again, once again it will be 3 is to 2 is to 1 kind of ratio in terms of heights which is what we see here it was 1 is to 3 because it is the number of protons which have been looked at; however, there is one effect which we can qualitatively describe due to spin spin coupling now that is something which is the next part of the story here.

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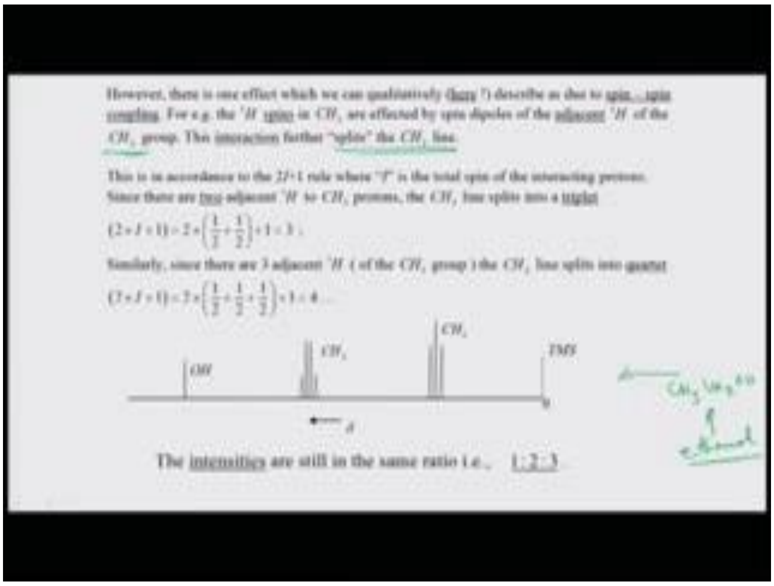

The intensities are still in the same ratio i.e., 1:2:3

Now, for example, the proton spins in CH3 are effected by spin dipoles of the adjacent protons of the CH2 group this interaction further splits the CH3 line in the.

In these cases. When it is done at very low Magnetic Field then you would not see these spins spin effects, but when you go on to higher Magnetic Field then each of them will have other effects and that is what happens they have spin spin couplings and this is in accordance to the 2 I plus 1 rule; where i is the total spin of the interacting protons since there are 2 adjacent proton to CH3 proton for ethanol the CH3 lines splits in to a triplet, similarly there are 3 adjacent protons of c h 3 group the c h 2 lines split in to a quartet and this is how they all look in case of CH3, CH2, OH ethanol.

The intensities follow the same ratio which is 1 is to 2 is to 3, the total intensities. That is how they come the intensity peaks follow the binomial form and we can use the pascal's triangle to predict them as follows.

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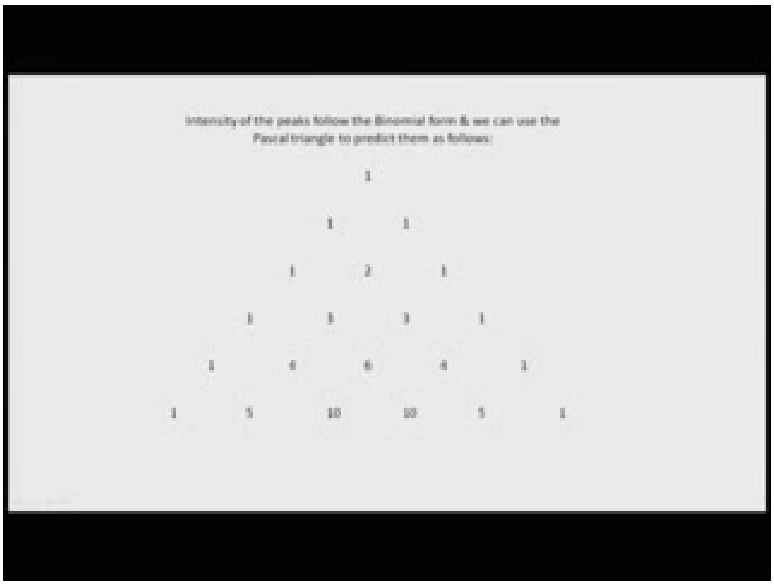

Intensity of the peaks follow the Binomial form & we can use the Pascal triangle to predict them as follows:

1

1 1

1 2 1

1 3 3 1

1 4 6 4 1

1 5 10 10 5 1

This is the basic idea behind the spectroscopy which is also been used very heavily in terms of the NMR, what we have discussed here in the beginning was that we would like to use this very sensitive technique to go ahead and see how we can make this into a way where it can be use for quantum computing. This was the basic to sort of make the connection to how and the device which has Nuclear Spins that can be connected to measuring very sensitively although the measurement as we can see initially was not very large, but could be enhanced by many other ways that is what is been discussed here until now. In the next class we will be discussing how it can be utilized now for quantum computing.

Thank you.