Advanced Quantum Mechanics with Applications
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Lecture – 14
Applications of NMR, time evolution of Magnetic Moments

So, we are going to look at the principles physical principles behind NMR; we will work out so, called theory of NMR alright.

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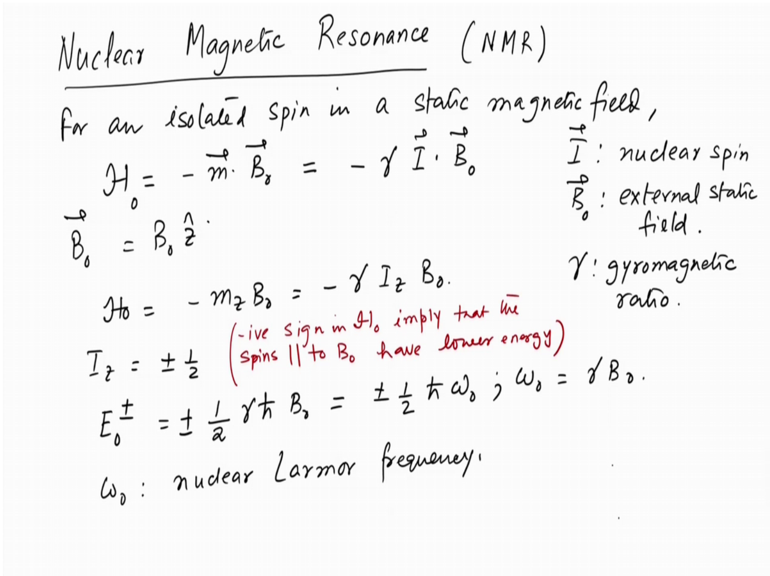

So, let us talk about a single spin. So, for an isolated spin in a static magnetic field; static means which is not changing with time that is a time independent magnetic field, the Hamiltonian we will write it like this is equal to let us write it with H 0, it is m dot B 0. We had probably used H earlier for the magnetic field just to avoid any confusion between the Hamiltonian H and the magnetic field H, we have now resorted to this notation of writing it as B 0 ah, but they are related Bs and the Hs are related by B equal to mu H where mu is the permeability of the material.

So, this can be written as minus gamma and I dot B where I is actually the nuclear spin. So, I is a nuclear spin vector and of course, so this is B 0 where B 0 is the external static field. So, this and of course, gamma is called as a gyromagnetic ratio and ah; so if B 0 is taken in the z direction. So, let us write B 0 is equal to B 0 z cap in which case only the z component of the nuclear spin survives because of the dot product. And we can write down the Hamiltonian as a minus m z B 0 which is equal to a minus gamma I z and B 0.

So, if we assume that I z equal to plus minus half that is we are talking about the nuclear spins being half. So, the z component of the nuclear spin is plus half or minus half we get 2 energies corresponding to the plus minus sign. And we will write it just here as a half; so, these are the Eigen values of the Hamiltonian. So, it is half gamma h cross B 0 which can be written asplus minus half h cross omega 0, where omega 0 is the basically the Larmor frequency ah. And because we are talking about in the nuclear case; so, this is called as a nuclear Larmor frequency.

So, omega 0 is called as a nuclear Larmor frequency. So, let us just have a quick recap what we have done we are talking about a single isolated spin in a static magnetic field. The magnetic field is applied in the z direction which gives rise to a Hamiltonian, which is minus gamma I z B 0 and I z is equal to plus minus half; we are talking about the nuclear spin having value which are plus half or minus half.

So, the energy Eigen values corresponding to these values of I z are given by plus minus I half h cross omega 0 there is a plus minus sign that I have missed. So, plus minus h cross half h cross omega 0, where omega 0 is a gyromagnetic ratio multiplied by the external magnetic field and this omega 0 is called as a Larmor frequency.

Now, the electrons which a surround the nucleus because of their motion; they actually screen the external magnetic field and it produces a magnetic field B prime which opposes this external magnetic field B 0. So, we will can write this as let me just write this because this is important ah.

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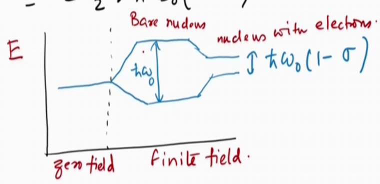
The electrons which surround the nucleus, because of their motion, they screen the magnetic field B_0 and produces B' in a direction opposite to B_0.

$B' = \sigma B_0$ $\quad$ σ : spins for each chemically different nuclei

$B_{eff} = B_0(1-\sigma)$: effective magnetic field.

$\mathcal{H}_0 = -m_z B_0(1-\sigma) = -\gamma I_z B_0(1-\sigma)$

$E_0^{\pm} = \pm \frac{1}{2}\gamma\hbar B_0(1-\sigma) = \pm \frac{1}{2}\hbar\omega_0(1-\sigma)$.



The electrons which surround the nucleus because of their motion; that is the motion of the electrons, they screen the magnetic field B 0 and produces a B prime in the opposite in a direction opposite to B 0. So, B prime is equal to call it as sigma B 0 where sigma is the basically the; denote the spins for each chemically different nuclei ok.

So, for a given nuclei sigma has a value say if it is a spin half nuclear spin nuclear spin half then its equal to half. But there is a possibility that there are a number of nuclei may be present in given situation and these correspond to the different spins of the different chemically different nuclei. So, the Hamiltonian takes a form; so, basically before that let us talk about the B effective. So, B effective takes a form which is B 0 1 minus sigma that is the effective magnetic field. And so the Hamiltonian takes the form which is H 0 is minus m z B 0 1 minus sigma and so, it is written in terms of the nuclear spin as gamma I z 1 minus sigma and so on.

So, in presence of an external magnetic field B 0; a proton in a molecule will actually experience a magnetic field that is given by this quantity which is known as the B effective. And the corresponding energy values; so, let us call that as E 0 plus minus that is the way we have talked about; is half gamma h cross B naught 1 minus sigma which is simply equal to plus minus half h cross omega. So, your omega naught is what we have used. So, let us write it as omega naught and 1 minus sigma and. So, this is the energy spectrum that comes out and if you are look at the spectrum; then we let us try to. So, this is the line 0 field and this is finite field and this is of course, the energy E.

And now this is ah; so there is without field there is no splitting now in presence of the field there is this splitting and then in presence of the screening. So, there is this it comes down and it comes down like this. So, this is h cross omega naught and this is h cross omega naught 1 minus sigma. So, basically this is bare nucleus just write this. So, this is bare nucleus which is what we have worked out and this is nucleus with electrons nucleus with or in presence of the electrons ok. So, of course, with at 0 field there is no splitting and as soon as a field is applied for the bare nucleus; they split into these 2 values which we have shown here which are plus minus half h cross omega naught.

So, this is minus half h cross omega naught this is plus half h cross omega naught. And then in because of the screening by the electrons these they sort of reduce the splitting reduces and this has a the top one has the value which is plus half h cross 1 minus sigma and the lower one has a value which is a plus minus half h cross omega 1 minus sigma.

And so, there is basically there is a negative sign in the Hamiltonian and let us write this that. So, let us we can write it here the; so here the negative sign in Hamiltonian in H 0 imply that the spins parallel to B 0 have lower energy; lower energy compared to what? Lower energy compared to the spins which are aligned anti parallel to that of B 0.

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In an NMR experiment, we probe the system with an oscillating magnetic field perpendicular to the static field, say applied along $\hat{x}$ axis.

$$\mathcal{H}_1(t) = -\vec{m}\cdot\vec{B}_1(t) = -\gamma\vec{I}\cdot\vec{B}_1(t)$$

$$= -\gamma I_x B_1 \cos\omega t$$

To compute the transition frequency, one uses fermi's golden rule. The matrix elements are given by,

$$V_{fi} \propto \langle\phi_f|\mathcal{H}_1(t)|\phi_i\rangle$$

f : final state

i : initial state

$$I_x = \frac{1}{2}(I_+ + I_-).$$

$$V_{fi} = \gamma B_1 \langle\phi_f|(I_+ + I_-)|\phi_i\rangle$$

So, in the simplest NMR experiment we prove the system with an oscillating magnetic field with an oscillating magnetic field, which is perpendicular to the static field. And in particular it say applied in the x axis, along the x axis and which has a form now this is an RF field and it is not a static field it depends on time in a sinusoidal manner. And this is equal to minus m and a B 1 t dot and this is equal to minus I the nuclear spin dotted with this RF field. Now since B 1 is in the x direction; so, the x component of the nuclear spin survives and one gets Hamiltonian of this form.

So, in order to compute the transition frequency let us see what we can do about that ah. So, basically we talk about ah; so in presence of a time dependent magnetic field, there will be transition from one state to another state. So, that is between the accessible states there will be a transition and we wish to compute the transition frequency between these states. And so that one can use Fermi’s golden rule and which the matrix elements are given by V f i; f corresponds to a final state and i corresponds to an initial state.

So, V f i that becomes equal to which is proportional to say you are not writing it exactly because this would include a number of things; such as density of states and so on which we are immediately not very concerned about. So, this is proportional to a phi f and my H 1 t and a phi i and so on. So, this is the transition matrix element now as it is written here is proportional H 1 is proportional to I x ah. So, one knows that I x can be written as a half of I plus I minus in which case V f i is equal to a gamma B 1.

And a phi f and a I plus a I minus and a phi i; so, that is the matrix element that we want to compute. Now you note that the integral is only non zero when phi f and phi i are magnetically different which means that their quantum numbers are differ by 1 unit. Because otherwise, there will be no overlap between phi f I plus between phi f and phi i or I minus between phi f and phi i.

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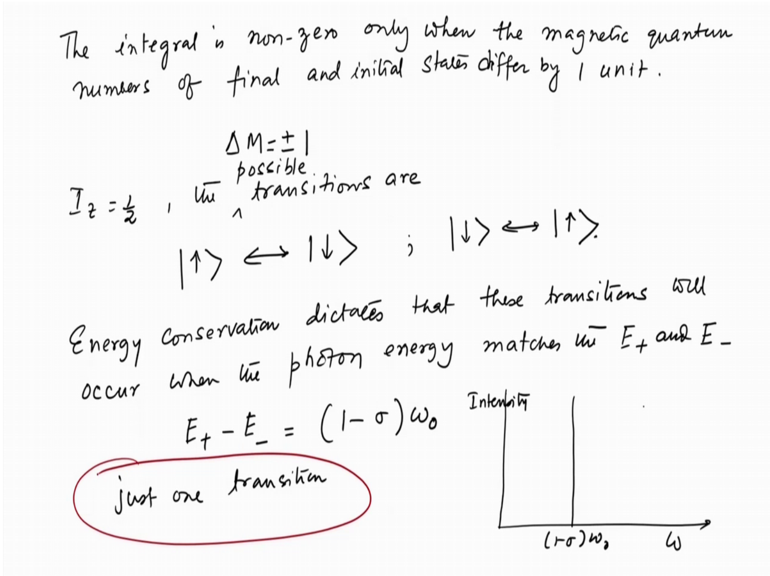

So, the integral is non zero only when the magnetic quantum numbers of final and initial states differ by 1 unit. So, what I mean to say is that delta M, which is the magnetic quantum number that should differ by plus 1 or minus 1 depending upon whether we are operating it by I plus or I minus ah.

So, since we have I z equal to half ah. So, that 2 the possible transitions are between the up going to down and the down similarly going to up and vice versa. Further the energy conservation dictates that the transition will take place when the photon energy matches the energy difference between the E plus and the E minus states. These transitions will occur when the photon energy matches the energy difference between E plus and E minus ok. So, here one can easily see that E plus minus E minus equal to 1 minus sigma omega 0. So, if we do this experiment we should get one frequency in the spectrum corresponding to this. So, which means that our intensity versus energy or frequency. So, this is intensity is at this value which is given by 1 minus sigma omega 0 and so on; so, just one transition.

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Two points may be noted :

(i) Had we chosen the RF field parallel to the homogeneous field, trivial transitions will occur. $|\uparrow\rangle \rightarrow |\uparrow\rangle$, $|\downarrow\rangle \rightarrow |\downarrow\rangle$.

$$V_{fi} \propto \langle \phi_f | I_z | \phi_i \rangle.$$

(ii) For $S = 3/2$ nucleus for $\hat{x}$ RF field, $|\frac{1}{2}\rangle \leftrightarrow |\frac{3}{2}\rangle$

$|-\frac{3}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle \leftrightarrow |\frac{1}{2}\rangle$,

All these transitions will occur at the same frequency.

Depending on their "chemical" environment, different protons will be shielded differently resulting in a Spectrum -

So, here it is important to note 2 points. So, had we chosen the RF field parallel to the homogenous field or the isotropic field rather the static field, then there will be some trivial transitions between up and down because I z has matrix elements between states which have magnetic quantum numbers to be same which means delta M to be equal to 0. So, this will be having trivial transitions will occur such as up to up and down to down and so on.

So, such that your V f i is proportional to a phi f I z and a phi i; second thing for a larger nucleus with a larger spin value. So, say for S equal to 3 half nucleus for x direction RF field, the allowed transitions are minus 3 by 2 to minus half and of course, there are a minus half to plus half and a plus half to plus 3 by 2 and so on ah; however, there will be no direct transitions from minus 3 by 2 to half or minus 3 by 2 to plus 3 by 2 and so on. So, all these transitions will occur at the same frequency; so depending on the environment; I am writing it as chemical environment which means presence of different chemically different nuclei; different protons will be shielded differently resulting in a spectrum let us show the spectrum.

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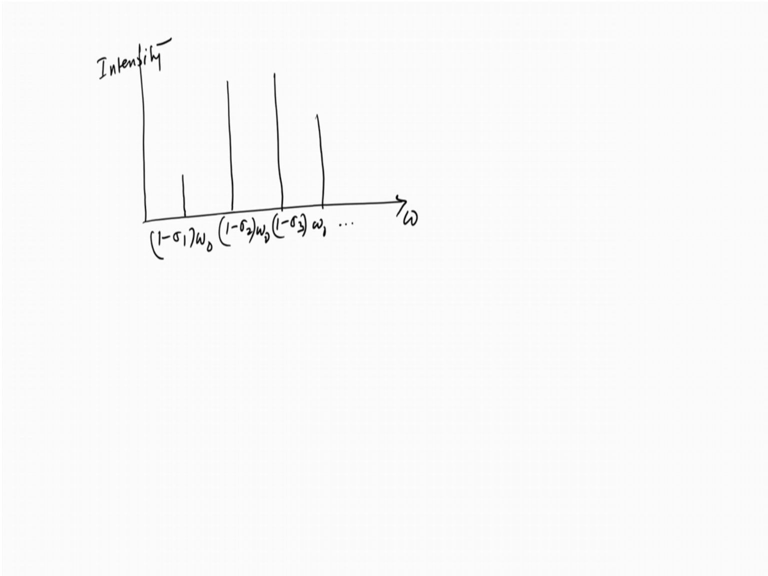

So, so it will be; so this is the again the intensity and this is a omega which is frequency. So, we will have it like this and then like this then like this, then like this and so on. So, which are at 1 minus sigma 1 omega 0, 1 minus sigma 2 omega 0, 1 minus sigma 3 omega 0 and so on ok. So, these are different peaks that one gets let us now get into another interesting topic which is spin dynamics and in presence of pulsed signals.

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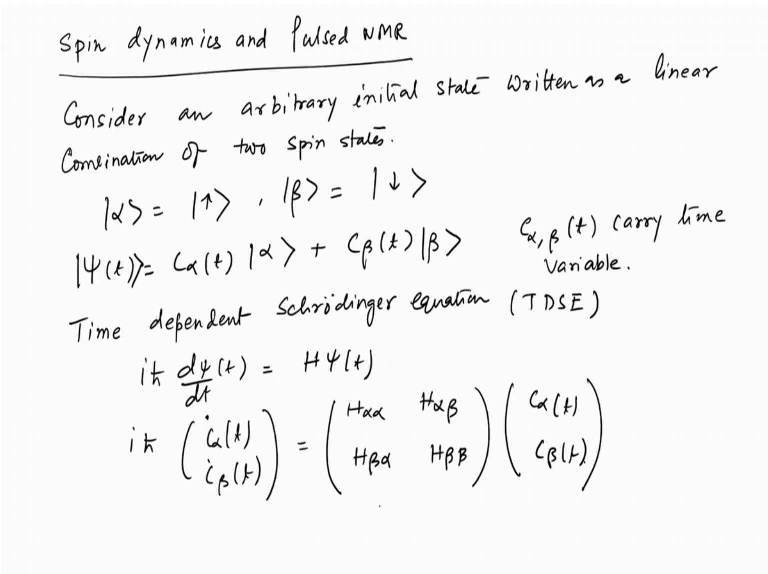

So ok; so one of the appealing aspect of NMR is that one can exactly a workout virtually any property that we are interested in knowing.

So, in particular we can get a picture of the dynamics of the spin in presence of an external magnetic field. So, this will give a qualitative picture that on what we can extract or make out from an NMR spectrum and also served as a basis for the modern day pulsed NMR experiments. So, consider an initial state written as a linear combination of is 2 spin states. And we are specifically talking about spin half particle because we talking about 2 spin states. And this can be written as say alpha is written as up and beta is written as down and so on.

So, the superposed state is written as psi t equal to C alpha t alpha plus a C beta t and beta; remember that the time dependencies are all carried by the coefficients and the basis states which are alpha and beta are same all the while. So, C alpha and beta carry a time dependence ok. So, the time dependence a; are the dependence carried by coefficients C alpha and C beta. So, let us write down the Time Dependent Schrodinger Equation and we call it TDSE; Time Dependent Schrodinger Equation is written as i h cross d psi dt, this is equal to H psi t. So, this a I h cross C alpha dot because the time dependencies are on C alpha and C beta only.

So, this is equal to H alpha; H alpha beta and H beta alpha H beta. So, it is clear that H is written in the alpha beta basis and this is C alpha t and a C beta t. So, this is nothing, but the Schrodinger equation which is we call it as TDSE.

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For a spin in a static field,

$$\mathcal{H} = -\hbar\omega_0(1-\sigma)I_z = -\hbar\tilde{\omega}_0 I_z \qquad \tilde{\omega}_0 = \omega_0(1-\sigma)$$

$$= \begin{pmatrix} -\hbar\tilde{\omega}_0 & 0 \\ 0 & \hbar\tilde{\omega}_0 \end{pmatrix}$$

Putting in TDSE.

$$i\hbar \begin{pmatrix} \dot{c}_\alpha(t) \\ \dot{c}_\beta(t) \end{pmatrix} = \begin{pmatrix} -\hbar\tilde{\omega}_0 & 0 \\ 0 & \hbar\tilde{\omega}_0 \end{pmatrix} \begin{pmatrix} C_\alpha(t) \\ C_\beta(t) \end{pmatrix}$$

$$i\hbar\dot{c}_\alpha(t) = -\frac{\hbar\tilde{\omega}_0}{2} C_\alpha(t) \Rightarrow C_\alpha(t) = e^{i\tilde{\omega}_0 t/2} C_\alpha(0)$$

$$i\hbar\dot{c}_\beta(t) = \frac{\hbar\tilde{\omega}_0}{2} C_\beta(t) \Rightarrow C_\beta(t) = e^{-i\tilde{\omega}_0 t/2} C_\beta(0)$$

For simplicity one can assume $C_\alpha(0)$, $C_\beta(0)$ are real.

So, for a spin in a static field H is equal to minus h cross omega 0 1 minus sigma and I z which can of course, get values which are or acquire values which are plus half or minus half. And let us write this down as minus h cross omega 0 tilde I z where omega 0 tilde is equal to some renormalized frequency omega 0 1 minus sigma.

So, if I write I z with 1 and minus 1 as the diagonal elements; I will get a minus h cross omega 0 0 0 h cross omega 0 and so on. So, that is the Hamiltonian; it is easy to diagonalize such a Hamiltonian or put it into the in the time dependent Schrodinger equation. So, it is i h cross C alpha and C beta both with the dot if you are unable to see the dot please look at it carefully ah. So, this is equal to minus i h cross omega naught 0 and h cross omega naught and this is C alpha t and C beta t and so on.

So, if you open this up this actually reduces to uncoupled equations and the uncoupled equations are i h cross C alpha dot t equal to minus h cross omega naught by 2 C alpha t ah; with the solution that C alpha t becomes equal to exponential i omega naught tilde I mean t by 2 C alpha 0. And for the other one it is i h cross C beta dot; so this is h cross omega tilde by 2 C beta t and again solving it will one gets at exponential minus I omega naught t by 2 C beta 0. So, these coefficient C alpha and C beta; they denote the time evolution of each of the spin component up and down components with time.

So, how they evolve with time ah; so for simplicity you can actually assume C alpha 0 and C beta 0 to be just numbers which means that they are real values ok. In which case the magnitude of C alpha t and C beta t ah; they remain constant and one requires only a phase factor to describe these coefficients ok. So, let us see a few properties and see how they are relevant to us.

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Some properties.

(i) $$\langle I_z(t) \rangle = \begin{pmatrix} C_\alpha^*(t) & C_\beta^*(t) \end{pmatrix} \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} \begin{pmatrix} C_\alpha(t) \\ C_\beta(t) \end{pmatrix}.$$

$$= \frac{\hbar}{2} \left[|C_\alpha(t)|^2 - |C_\beta(t)|^2 \right].$$

$$= \frac{\hbar}{2} \left[C_\alpha^2(0) - C_\beta^2(0) \right].$$

The z component of spin does not change with time.

So, properties such as the expectation value of I z that is the z component of the nuclear spin. So, this is I z t it is C alpha star t C beta star t; then the Hamiltonian or sorry the not the Hamiltonian, but I z operator which is 0 minus h cross by 2 and then C alpha t and C beta t.

So, this will simply be equal to h cross by 2 C alpha t mod square minus C beta t mod square. So, this is equal to h cross by 2 and since C alpha t and C beta t; the mod square would simply be the values which are the values at t equal to 0 and so on. So, it tells you that the z component of spin does not change with time; so what happens to the x component?

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$$(ii)\quad \langle I_x(t)\rangle = \begin{pmatrix} C_\alpha^*(t) & C_\beta^*(t)\end{pmatrix}\begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0\end{pmatrix}\begin{pmatrix} C_\alpha(t) \\ C_\beta(t)\end{pmatrix}$$

$$= \frac{\hbar}{2}\left[C_\alpha^*(t) C_\beta(t) + C_\beta^*(t) C_\alpha(t)\right]$$

$$= \frac{\hbar}{2} C_\alpha(0) C_\beta(0)\left[e^{-i\tilde{\omega}_0 t} + e^{i\tilde{\omega}_0 t}\right]$$

$$= \hbar\, C_\alpha(0) C_\beta(0) \cos\tilde{\omega}_0 t.$$

$$(iii)\quad \langle I_y(t)\rangle = -\hbar\, C_\alpha(0) C_\beta(0) \sin\tilde{\omega}_0 t.$$

$$\tilde{M}(t) = \left(\langle I_x(t)\rangle, \langle I_y(t)\rangle, I_z(t)\right)$$

The projection of M(t) onto the magnetic field direction is constant, while perpendicular motion traces out circular path.

That is this quantity which is equal to a C alpha t ah; C beta t and 0 h cross by 2 h cross by 2 0 and a C alpha t C beta t and so on.

So, this is equal to h cross by 2 and when I multiply this. So, this becomes equal to C alpha star t C beta t plus C beta star t and C alpha t and this is again equal to h cross by 2 C alpha 0 C beta 0 and exponential minus i omega tilde t plus exponential i omega tilde t which is nothing, but the cosine twice of cosine. So, that 2 goes away and one gets a h cross C alpha 0 C beta 0 andsin as sorry what is it? Cosine of omega naught tilde t ah; similarly one can actually get that for the y component ah. So, i y of t is equal to minus h cross C alpha 0 C beta 0 sin omega naught t.

So, the x and y component oscillate with time while the z component remain constant and they would be oscillating with a shielded Larmor frequency omega naught. And the; so the magnetization vector which is given by M t which is this I x t; I y t and I z t no need to write and we are writing the components I z t that is the vector ah. This vector actually processes about the magnetic field the z component is fixed ah; so the projection on the z axis is fixed, but the x and y component they ah. So, the perpendicular motion of the magnetic field it traces out a circular path about the direction in which the magnetic field is applied ok.

So,the projection of M t onto the magnetic field -[dire]ction is constant while perpendicular motion traces out circular path; circular path about the field axis magnetic field axis ok. So, have a look at it once more I z is independent of time it is a constant; the I x goes as cosine omega t and the I y goes as sin omega t. Omega means the omega naught tilde which we are talking about as the shielded Larmor frequency. So, this is basically the pulsed NMR; so, one gets the magnetization the components of the magnetization.

And one may actually want to study that how these components of the magnetic moment or the magnetization that evolve with time. And may actually want to plot it on a something like the a block vector or a block sphere; which is called as a stroboscopic plot which we will not show it here. So, this is by and large the theory of NMR in which people have this great amount of literature that exists on this particular field ah.

You can have a look at any of those literatures or many books also talk about NMR; we had given a very brief introduction to NMR as an application to the ongoing quantum mechanics course that we have been doing.