NMR Spectroscopy for Chemists and Biologists
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Lecture No. 28
Density Matrix description of NMR – II

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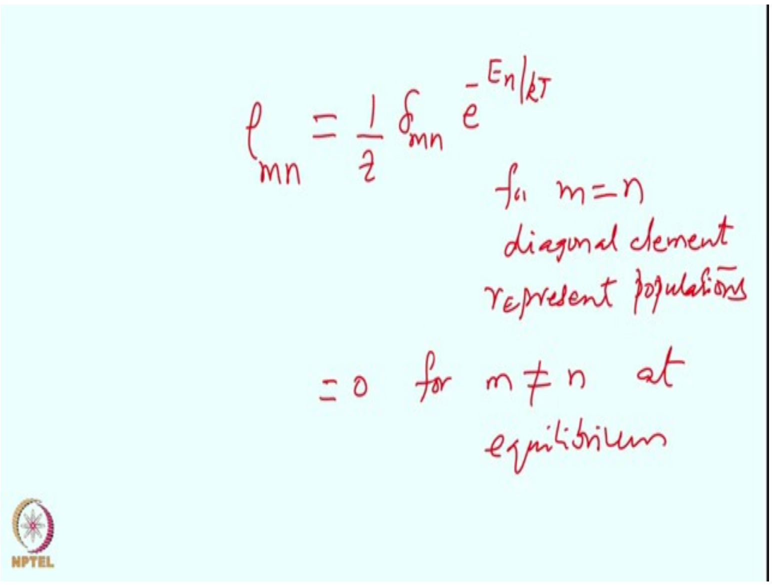

$$\rho_{mn} = \frac{1}{Z}\delta_{mn}\, e^{-E_n/kT}$$

for $m=n$

diagonal element

represent populations

$= 0$ for $m \neq n$ at

equilibrium

Let us continue to the discussion of density matrix we wrote the equation for the density matrix mn^{th} element of density matrix as by the following equation

$$\rho_{mn} = \frac{1}{Z}\delta_{mn}\, e^{\left(\frac{-E_n}{kT}\right)}$$

where E_n is the eigen value of the state n and δ_{mn} is Kronecker delta and for $m=n$ this will be the diagonal element. So, diagonal element and this then will represent the populations. Off diagonal elements are 0 at equilibrium, at thermal equilibrium. This will be 0 $m \neq n$ at equilibrium. And we also wrote in the previous class an operator form of density, for the density operator we derived an equation.

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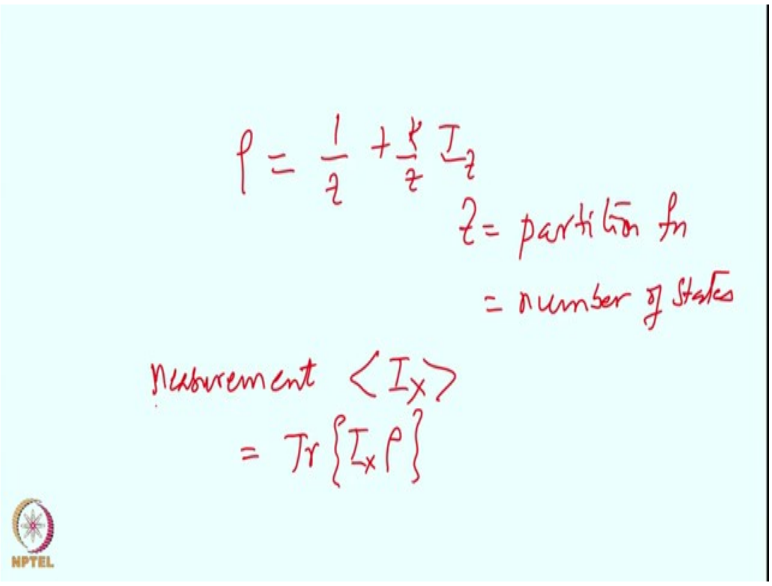

$$\rho = \frac{1}{Z} + \frac{K}{Z} I_z$$

Z = partition fn

= number of states

measurement $\langle I_x \rangle$

$= Tr\{I_x \rho\}$

We wrote the density operator, equation for the density operator

$$\rho = \frac{1}{Z} + \frac{K}{Z} I_z$$

Where I_z is z magnetization and this Z is the partition function, and this represents the number of states. Now we also wrote earlier when we make a measurement, let us say if we want to measure x magnetization then we also derived earlier that we have to calculate the expectation value of this operator which represents the x magnetization and that is equal to

¿ $Tr\{I_x \rho\}$

We have derived this equation earlier.

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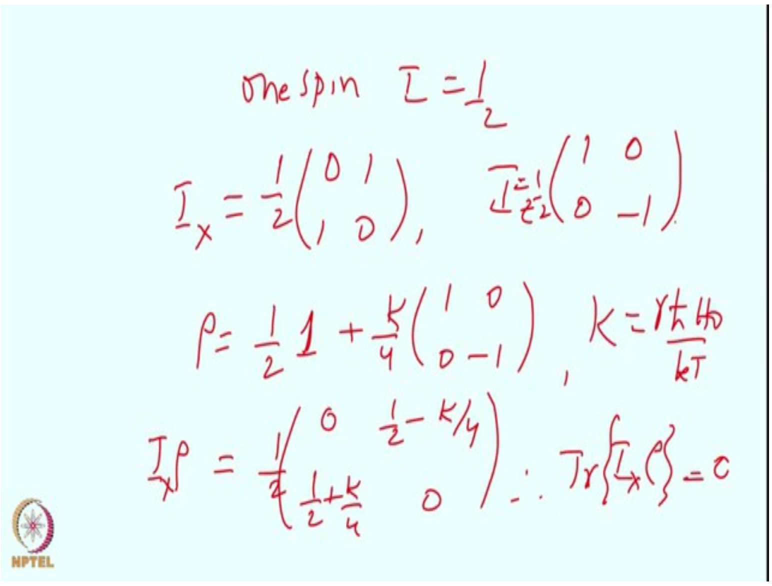

One spin $I = \frac{1}{2}$

$$I_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad I_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\rho = \frac{1}{2}1 + \frac{K}{4}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad K = \frac{\gamma\hbar H_0}{kT}$$

$$I_x\rho = \frac{1}{2}\begin{pmatrix} 0 & \frac{1}{2} - K/4 \\ \frac{1}{2}+\frac{K}{4} & 0 \end{pmatrix} \therefore Tr\{I_x\rho\} = 0$$

Let us take example here for one spin-system. $I = \frac{1}{2}$, we have, we derived this expression in a matrix representation of the I_x operator is equal to

$$I_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, I_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

And therefore, the density operator for this

$$\rho = \frac{1}{2}1 + \frac{K}{4}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, Where, K = \frac{\gamma\hbar H_0}{kT}$$

So, now putting this together you calculate

$$I\rho = \frac{1}{2}\begin{pmatrix} 0 & \frac{1}{2} - \frac{K}{4} \\ \frac{1}{2} + \frac{K}{4} & 0 \end{pmatrix} Therefore\, Tr\left|I_x\rho\right| = 0$$

Therefore there is no x magnetization in the equilibrium state. This also we have said earlier when we defined a thermal equilibrium off diagonal elements are 0 and so this is mathematically shown here that the x magnetization is 0 at equilibrium condition.

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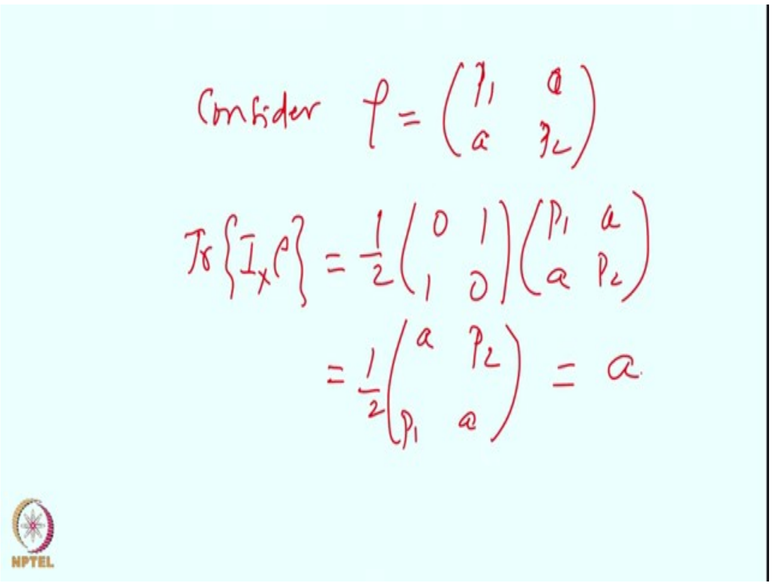

Consider $\rho = \begin{pmatrix} P_1 & a \\ a & P_2 \end{pmatrix}$

$Tr\{I_x \rho\} = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} P_1 & a \\ a & P_2 \end{pmatrix}$

$= \frac{1}{2}\begin{pmatrix} a & P_2 \\ P_1 & a \end{pmatrix} = a$

Now suppose, for example you are dealing with a non-equilibrium state and that often comes when you do various kinds of manipulations. You can create a density matrix which has off diagonal elements which are non-zero. In earlier cases you notice that the density matrix had off diagonal element 0.

So, now we consider a matrix

$$\rho = \begin{pmatrix} P_1 & a \\ a & P_2 \end{pmatrix}$$

so we said these are the populations here density matrix has off diagonal elements are the populations and we somehow consider a situation where the off diagonal element here are non-zero but are equal to a. Now, what will be the consequence of this?

Now if I want to calculate the trace again of

$$Tr\{I_x \rho\} = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} P_1 & a \\ a & P_2 \end{pmatrix}$$

so this will turn out to be

¿ $$\frac{1}{2}\begin{pmatrix} a & P_2 \\ P_1 & a \end{pmatrix} = a$$

Now you see there is the trace is non-zero. Therefore, there is net *x* magnetization. In this situation. Therefore, the density matrix represents the complete situation about the system.

You have the diagonal element which have populations and the off diagonal elements will represent the transverse magnetization.

Same thing will happen *y* as well. So you may create various kinds of situations and how does these things occur, how do these things occur? This will happen as the result of various kinds of manipulations you might do with your experimental sequence, then it will become necessary for us to actually calculate the density operator and then we can make the measurement.

So, the density operator calculation that will be dependent on time, if you are making a pulse sequence where lots of pulses are applied and this go as function time along the time axis. So therefore, we need to consider and calculate the evolution of the density operator with time.

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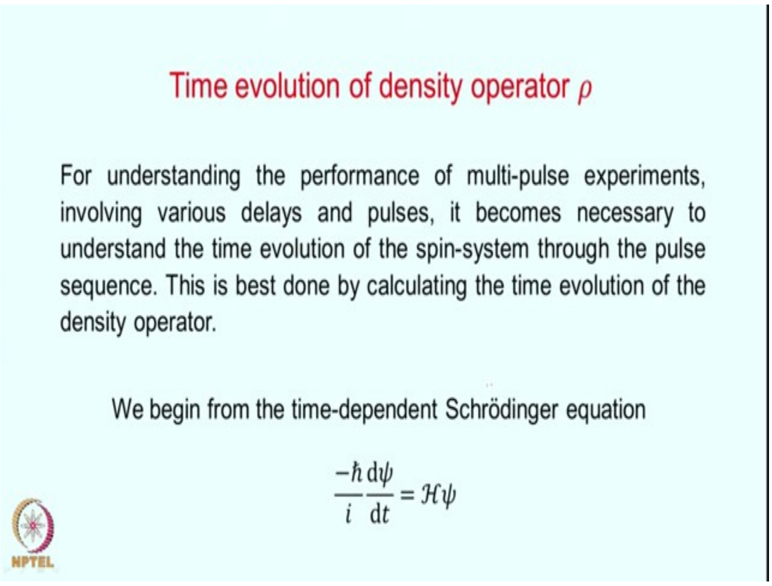

Time evolution of density operator ρ

For understanding the performance of multi-pulse experiments, involving various delays and pulses, it becomes necessary to understand the time evolution of the spin-system through the pulse sequence. This is best done by calculating the time evolution of the density operator.

We begin from the time-dependent Schrödinger equation

$$\frac{-\hbar}{i}\frac{d\psi}{dt} = \mathcal{H}\psi$$

So, how do we do this? This will require framework where we can calculate the time evolution of the density operator. So this is what we are going to discuss in the next few minutes. So for understanding the performance of multiple experiments, it becomes necessary to understand the time evolution of the spin-system through the pulse sequence and this is best done by calculating the time evolution of the density operator.

So for this we begin from the time dependent Schrödinger equation, see this time dependent Schrödinger equation describe how there state evolves with time and that is equation is given in this manner.

$$\frac{-\hbar}{i}\frac{\mathrm{d}\psi}{\mathrm{d}t} = \mathcal{H}\psi$$

Where, $\mathfrak{H}$ is the Hamiltonian describing the system containing all the interaction and ψ is dependent on the time. So evolution of psi tells you how the system is evolving with time.

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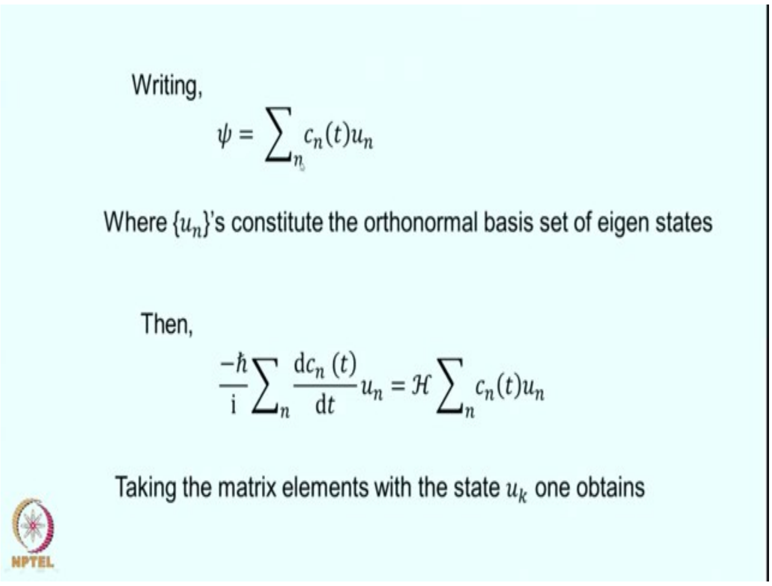

Writing,

$$\psi = \sum_n c_n(t)u_n$$

Where $\{u_n\}$'s constitute the orthonormal basis set of eigen states

Then,

$$\frac{-\hbar}{\mathrm{i}}\sum_n \frac{\mathrm{d}c_n\,(t)}{\mathrm{d}t}u_n = \mathcal{H}\sum_n c_n(t)u_n$$

Taking the matrix elements with the state u_k one obtains

So to achieve this let us write the wave function psi as before as superposition of various state function eigen states the $C_n(t)$ are co-efficients and un are your eigen states. They constitute an orthonormal basis set as we defined before. Now, let us substitute this in the Schrödinger equation we get

$$\frac{-\hbar}{\mathrm{i}}\sum_n \frac{\mathrm{d}c_n\,(t)}{\mathrm{d}t}u_n = \mathcal{H}\sum_n c_n(t)u_n$$

Now it takes matrix elements of this which is the states u_k.

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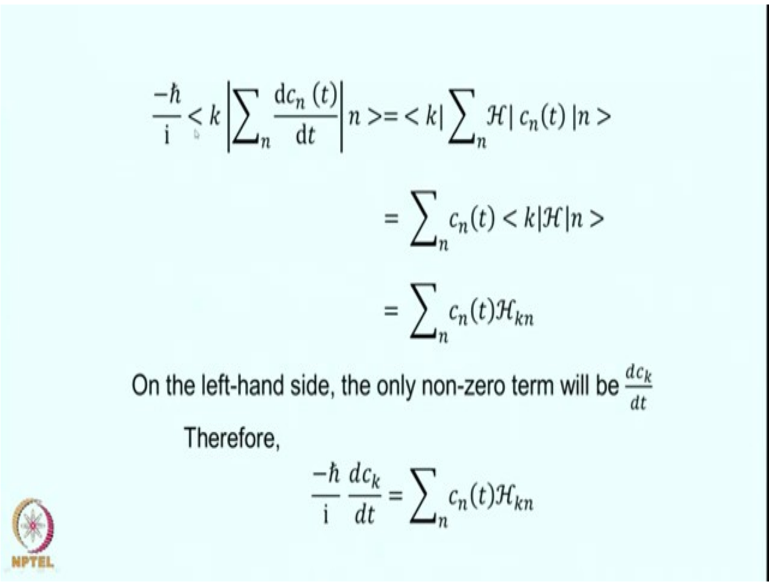

$$\frac{-\hbar}{i} < k \left| \sum\nolimits_n \frac{dc_n(t)}{dt} \right| n >= < k | \sum\nolimits_n \mathcal{H} |\, c_n(t)\, | n >$$

$$= \sum\nolimits_n c_n(t) < k|\mathcal{H}|n >$$

$$= \sum\nolimits_n c_n(t)\mathcal{H}_{kn}$$

On the left-hand side, the only non-zero term will be $\frac{dc_k}{dt}$

Therefore,

$$\frac{-\hbar}{i}\frac{dc_k}{dt} = \sum\nolimits_n c_n(t)\mathcal{H}_{kn}$$

So that means you multiply on the left you take this

$$\frac{-\hbar}{i} < k \left| \sum\nolimits_n \frac{dc_n(t)}{dt} \right| n >= < k | \sum\nolimits_n \mathcal{H} |\, c_n(t)\, | n >$$

Now, so therefore, this is equal to now

$$= \sum\nolimits_n c_n(t) < k|\mathcal{H}|n >$$

$C_n(t)$ is a constant and therefore we can take that out of this to the move it to the left and k will come inside so we will have $<k|\ \mathfrak{H}|\ n>$. So

$$= \sum\nolimits_n c_n(t)\mathcal{H}_{kn}$$

So therefore, this differential on the left hand side.

Now on the left hand side notice that there will be only one non-zero element the summation goes over all n, but this n and k are orthonormal therefore, this will survive only when $k=n$. Therefore, there only one element here $\frac{d c_k}{dt}$. Therefore, my summation will disappear

$$\frac{-\hbar}{\mathrm{i}}\frac{dc_k}{dt} = \sum_n c_n(t)\mathcal{H}_{kn}$$

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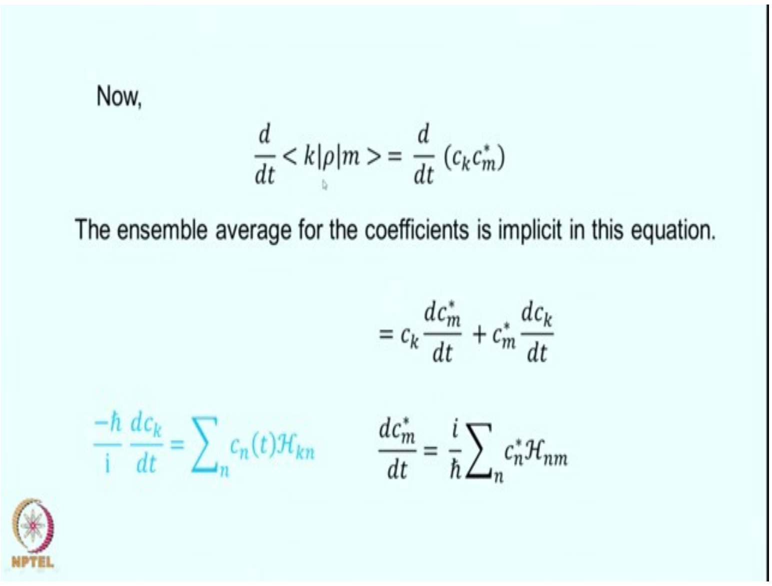

Now,

$$\frac{d}{dt}< k|\rho|m > = \frac{d}{dt}(c_k c_m^*)$$

The ensemble average for the coefficients is implicit in this equation.

$$= c_k\frac{dc_m^*}{dt} + c_m^*\frac{dc_k}{dt}$$

$$\frac{-\hbar}{\mathrm{i}}\frac{dc_k}{dt} = \sum_n c_n(t)\mathcal{H}_{kn} \qquad \frac{dc_m^*}{dt} = \frac{i}{\hbar}\sum_n c_n^*\mathcal{H}_{nm}$$

So now, we also know the basic definition of the density matrix, so

$$\frac{d}{dt}< k|\rho|m > = \frac{d}{dt}(c_k c_m^*)$$

this was the basic definition of course the ensemble average is implicit here though ensemble average for the coefficient is implicit in this equation. Now on the right hand side you differentiate this explicitly, you get

$$= c_k\frac{dc_m^*}{dt} + c_m^*\frac{dc_k}{dt}$$

Now these are, remember coefficient these are time dependent of course and therefore, we can move them around.

Now looking at this, we can calculate what $\frac{dm^{\text{¿}}}{dt}$ is, we derive this equation for $d\,C_k/dt$. So therefore,

$$\frac{-\hbar}{\mathrm{i}}\,\frac{dc_k}{dt} = \sum\nolimits_n c_n(t)\mathcal{H}_{kn}$$

Now I want for the complex conjugate, so if I want to take the complex conjugate here at I take complex conjugate here at right hand side as well.

So when I do that it becomes

$$\frac{dc_m^*}{dt} = \frac{i}{\hbar}\sum\nolimits_n c_n^*\mathcal{H}_{nm}$$

And this element will be h you have to represent because you have to turn them around this way. So therefore, this will become $\mathfrak{H}_{nm}$ that is instead of k here, m here from the other side dm star will be m will come on this side, n will come on this side. Beacuse that is what happens when you take complex conjugate on this of the matrix element.

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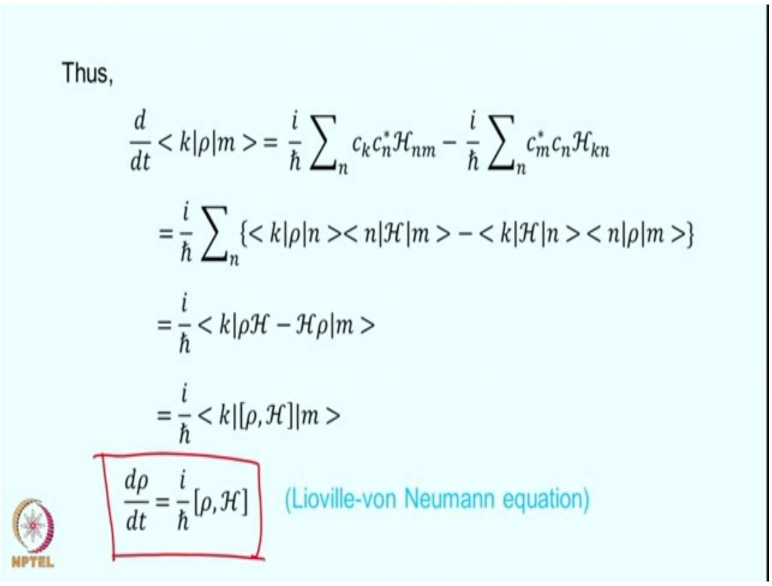

Thus,

$$\frac{d}{dt}<k|\rho|m> = \frac{i}{\hbar}\sum\nolimits_n c_k c_n^*\mathcal{H}_{nm} - \frac{i}{\hbar}\sum\nolimits_n c_m^* c_n\mathcal{H}_{kn}$$

$$= \frac{i}{\hbar}\sum\nolimits_n \{<k|\rho|n><n|\mathcal{H}|m> - <k|\mathcal{H}|n><n|\rho|m>\}$$

$$= \frac{i}{\hbar}<k|\rho\mathcal{H} - \mathcal{H}\rho|m>$$

$$= \frac{i}{\hbar}<k|[\rho,\mathcal{H}]|m>$$

$$\boxed{\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho,\mathcal{H}]}$$ (Lioville-von Neumann equation)

Substituting this then we get

$$\frac{d}{dt}<k|\rho|m> = \frac{i}{\hbar}\sum\nolimits_n c_k c_n^*\mathcal{H}_{nm} - \frac{i}{\hbar}\sum\nolimits_n c_m^* c_n\mathcal{H}_{kn}$$

That was the substitution of those equations here, so this will now be equal to

$$= \frac{i}{\hbar} \sum\nolimits_{n} \{< k|\rho|n >< n|\mathcal{H}|m > - < k|\mathcal{H}|n > < n|\rho|m >\}$$

So now the summation is taken out here, put it together for the entire equation you have put the whole thing in curly bracket here and you have a summation *n* here. Now we notice interesting that has happened here with the summation *n* we have got this element here, summation *n* this is ket and this is bra this runs over all the *n*.

Similarly, here also we got this ket n and bra n so this summation runs over all the *n*. And you remember from previous classes that summation *n* this sort of a operator this is projection of operators sum overall the projection operators is equal to 1. Therefore, this element vanishes. Similarly, this element vanishes and the summation also vanishes. Therefore,

$$= \frac{i}{\hbar} < k|\rho\mathcal{H} - \mathcal{H}\rho|m >$$

So therefore, I have here

$$= \frac{i}{\hbar} < k|[\rho, \mathcal{H}]|m >$$

now what is this here? This is called as the commutator between the two operators rho and h. It is typically written in this manner rho H m so therefore, if I combine this, if you compare this two equations, then I will have

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \mathcal{H}]$$

This is called as Lioville-von Neumann equation. This is most important equation for calculation of all the density matrix elements of any experiments. So this is the fundamental equation, where the time evolution of the system is described and you calculate elements of the density operator as you carry out various manipulations with your spin-system. And in the end when you actually are ready to measure you take the expectation value with regard to the I_x to the I_y operator and that gives you the measurement.

So therefore, this is crucial equation here and we have to see how this equation can be solved and this there are standard methods also, this we will not much go into the detail solution, how it will solve? But we will take the solutions of this as they appear and we can use this solution to calculate the evolution of the density operator as a function of time.

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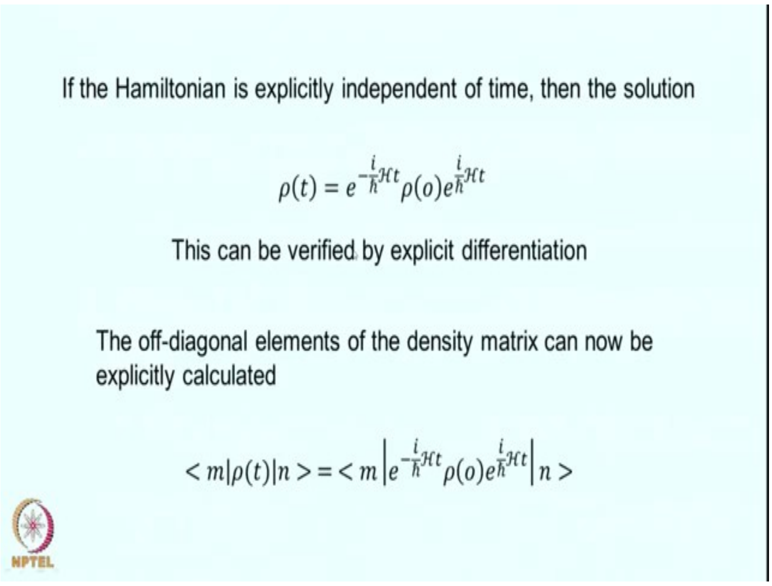

If the Hamiltonian is explicitly independent of time, then the solution

$$\rho(t) = e^{-\frac{i}{\hbar}\mathcal{H}t}\rho(o)e^{\frac{i}{\hbar}\mathcal{H}t}$$

This can be verified by explicit differentiation

The off-diagonal elements of the density matrix can now be explicitly calculated

$$< m|\rho(t)|n > = < m\left|e^{-\frac{i}{\hbar}\mathcal{H}t}\rho(o)e^{\frac{i}{\hbar}\mathcal{H}t}\right|n >$$

Now, if the Hamiltonian is explicitly independent of time in that Lioville equation then the solution of this is easily written in this manner, we are not deriving this explicitly from that point. But this equation can be verified by explicit differentiation

$$\rho(t) = e^{-\frac{i}{\hbar}\mathcal{H}t}\rho(o)e^{\frac{i}{\hbar}\mathcal{H}t}$$

So $\rho(0)$means this is time $t=0$. And these two operators on the left and the right this describe the evolution of density operator as a function of time.

So this can be easily verified by explicit differentiation of this this is independent of time and these are the two three which actually dependent on the time. Therefore, we can differentiate it and reorganize the element and then we will find that it satisfies that Lioville Neumann equation.

Now using this definition let us try and calculate the off diagonal elements of the density matrix so what we do, we take the matrix element here rho in the middle and then *m* here and *m* here. This is basically

$$< m|\rho(t)|n > = < m\left|e^{-\frac{i}{\hbar}\mathcal{H}t}\rho(o)e^{\frac{i}{\hbar}\mathcal{H}t}\right|n >$$

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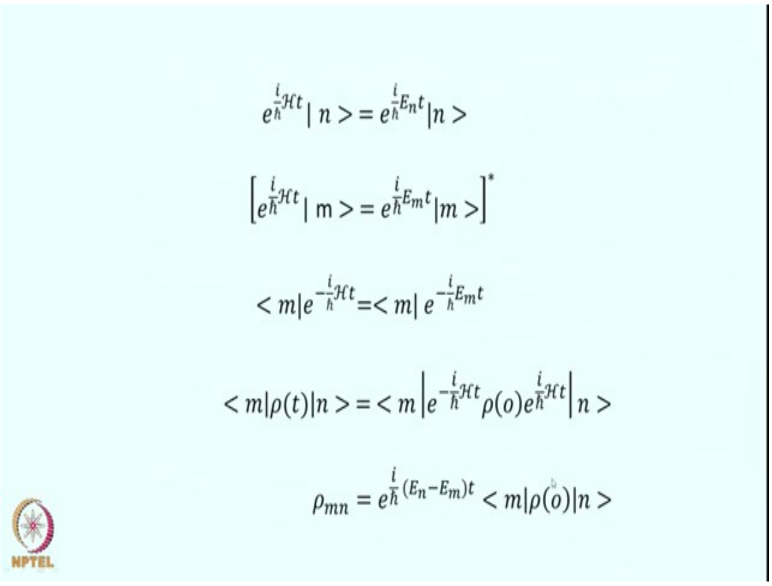

$$e^{\frac{i}{\hbar}\mathcal{H}t}| n > = e^{\frac{i}{\hbar}E_n t}|n >$$

$$\left[e^{\frac{i}{\hbar}\mathcal{H}t}| \mathrm{m} > = e^{\frac{i}{\hbar}E_m t}|m >\right]^*$$

$$< m|e^{-\frac{i}{\hbar}\mathcal{H}t} = < m| e^{-\frac{i}{\hbar}E_m t}$$

$$< m|\rho(t)|n > = < m\left|e^{-\frac{i}{\hbar}\mathcal{H}t}\rho(o)e^{\frac{i}{\hbar}\mathcal{H}t}\right|n >$$

$$\rho_{mn} = e^{\frac{i}{\hbar}(E_n - E_m)t} < m|\rho(o)|n >$$

Now, how do we calculate these elements? Now you noticed earlier we defined with exponential operators, what is the result when you operate on particular state, if you have eigen value equation then

$$e^{\frac{i}{\hbar}\mathcal{H}t}| n > = e^{\frac{i}{\hbar}E_n t}|n >$$

where E_n is eigen value of the state n. So for the Hamiltonian $\mathfrak{H}$, for the operator h then you get this eigen value E_n for the state n. Therefore,

$$\left[e^{\frac{i}{\hbar}\mathcal{H}t}| \mathrm{m} > = e^{\frac{i}{\hbar}E_m t}|m >\right]^*$$

Similarly,

$$< m|e^{-\frac{i}{\hbar}\mathcal{H}t} = < m| e^{-\frac{i}{\hbar}E_m t}$$

Now, if I take the complex conjugate of this, what is the complex conjugate then what I get on the left hand side? I get here instead of the ket I get the bra this here and this one will now get the minus sign, $e^{\frac{-i}{\hbar}Ht}$. Essentially this will be operating on the left. And that is equal to m and you take complex conjugate here so this state will come here so this is $e^{\frac{-i}{\hbar}E_m t}$.

$$< m|\rho(t)|n > = < m\left|e^{-\frac{i}{\hbar}\mathcal{H}t}\rho(o)e^{\frac{i}{\hbar}\mathcal{H}t}\right|n >$$

So you put that definition here, because now you want to operate this one on this side and this one on this side. So this operating on this side gives me $e^{\frac{-i}{\hbar}E_n t}$for this now is number this one operating on this side gives me this number

$$\rho_{mn} = e^{\frac{i}{\hbar}(E_n - E_m)t} < m|\rho(o)|n >$$

m $e^{\frac{-i}{\hbar}E_m t}$. So therefore, I take out these two numbers out then, I get $e^{\frac{i}{\hbar}(E_n - E¿¿m)t¿}$, E_n comes from here and -E_m comes from here the and the state m and $\rho(0)$ stays here and n stays here. So therefore, the off diagonal element of the density matrix. Now, we noticed this is energy difference between the two states between the states n and m.

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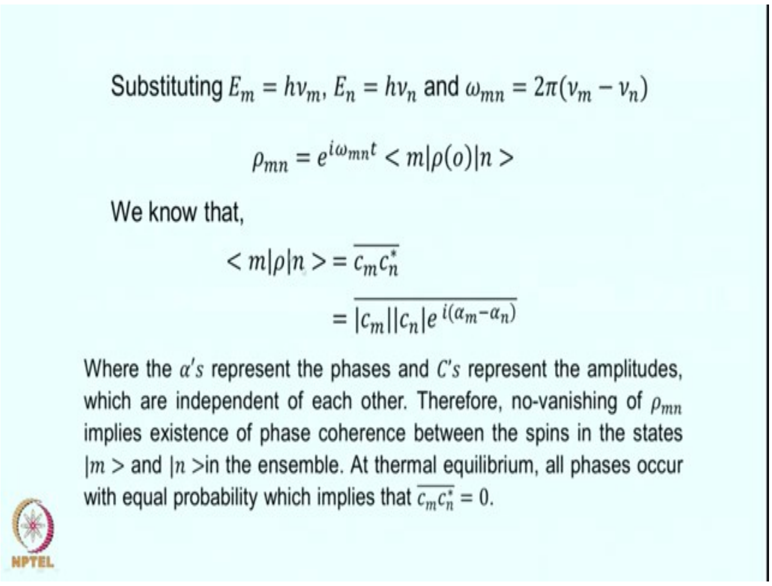

Substituting $E_m = h\nu_m$, $E_n = h\nu_n$ and $\omega_{mn} = 2\pi(\nu_m - \nu_n)$

$$\rho_{mn} = e^{i\omega_{mn}t} < m|\rho(o)|n >$$

We know that,

$$< m|\rho|n > = \overline{c_m c_n^*}$$
$$= \overline{|c_m||c_n|e^{\,i(\alpha_m - \alpha_n)}}$$

Where the $\alpha's$ represent the phases and $C's$ represent the amplitudes, which are independent of each other. Therefore, no-vanishing of ρ_{mn} implies existence of phase coherence between the spins in the states $|m>$ and $|n>$in the ensemble. At thermal equilibrium, all phases occur with equal probability which implies that $\overline{c_m c_n^*} = 0$.

So now, if I write

Substituting $E_m = h\nu_m$, $E_n = h\nu_n$ and $\omega_{mn} = 2\pi(\nu_m - \nu_n)$

So now this is in variance, these are in hertz frequencies. So therefore, if I put that in here

$$\rho_{mn} = e^{i\omega_{mn}t} < m|\rho(o)|n >$$

Now we also know that it

$$< m|\rho|n > = \overline{c_m c_n^*}$$

and ensemble average.

Now going back to the earlier definition of these coefficients that they have an amplitude and the phase so we write in this manner esemble average is written in this way

$$= \overline{|c_m||c_n|e^{\,i(\alpha_m-\alpha_n)}}$$

these are the some phases, some numbers which represent the phases. Now, if these are random by the hypothesis of random phases so these elements this average will go to 0 in the case of equilibrium state.

However, if this is non-zero then non-vanishing of ρ_{mn} implies existence of phase coherence between the spins in the states m and n in the ensemble. And thermal equilibrium all phases occur with equal probability which implies that $C_{m}^{¿}=0$. So therefore, at equilibrium this off diagonal elements density matrix are 0 and at if there is deviation from equilibrium then you will have off diagonal elements non- zero. And we showed in the very beginning that if there is off diagonal element of the density matrix which is non-zero. That amounts to transfer magnetization I_x or I_y.

The appearance of I_x or I_y therefore implies a phase coherence here between the spins in the states m and n. So therefore, transverse magnetization therefore gets connected to the phase coherence between the spins. So anytime you have a transverse magnetization we say there is phase coherence between the spins. And decay of the phase coherence amounts to decay transverse magnetization

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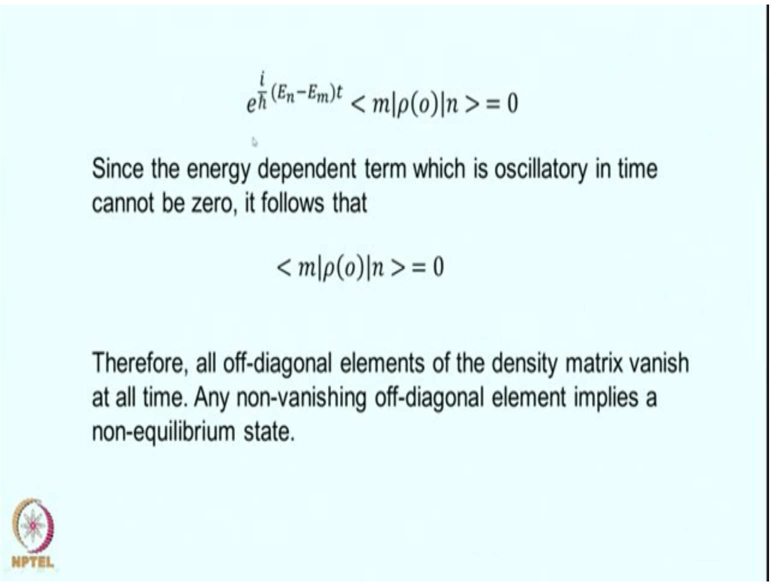

$$e^{\frac{i}{\hbar}(E_n-E_m)t} < m|\rho(o)|n > = 0$$

Since the energy dependent term which is oscillatory in time cannot be zero, it follows that

$$< m|\rho(o)|n > = 0$$

Therefore, all off-diagonal elements of the density matrix vanish at all time. Any non-vanishing off-diagonal element implies a non-equilibrium state.

So, now putting that thing here at equilibrium this equation has to go to 0 and now this is never 0 sorry this one is never 0, this is an oscillatory function, so if this function has to be 0 then it is this one which has to go 0. So that means this element is 0 at equilibrium this element is 0. So if we create a non-equilibrium state where in this element is non-zero. Then we have created off diagonal element which is non-zero so any non-vanishing off diagonal element implies a non-equilibrium state.

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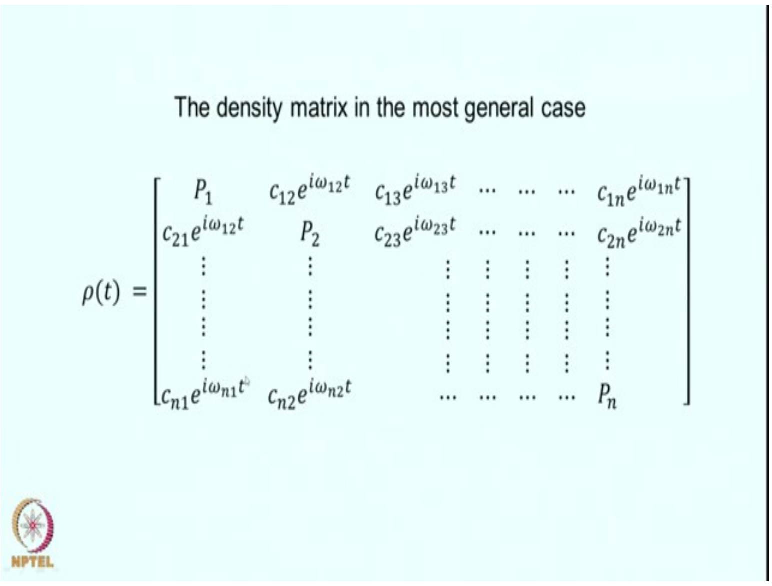

The density matrix in the most general case

$$\rho(t) = \begin{bmatrix} P_1 & c_{12}e^{i\omega_{12}t} & c_{13}e^{i\omega_{13}t} & \cdots & \cdots & \cdots & c_{1n}e^{i\omega_{1n}t} \\ c_{21}e^{i\omega_{12}t} & P_2 & c_{23}e^{i\omega_{23}t} & \cdots & \cdots & \cdots & c_{2n}e^{i\omega_{2n}t} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ c_{n1}e^{i\omega_{n1}t} & c_{n2}e^{i\omega_{n2}t} & \cdots & \cdots & \cdots & \cdots & P_n \end{bmatrix}$$

So therefore, extending to multiple spin-systems and a variety of situations a very generalized density Metrix can be written in this manner. In the most general case you have rho of t which is written as we have the populations on of the n state here suppose you have total of n states here. You have the populations along the diagonal P_1 P_2 P_3 P_4 so on and so forth. And on the off diagonal elements you have these elements coefficients.

$$\rho(t) = \begin{bmatrix} P_1 & c_{12}e^{i\omega_{12}t} & c_{13}e^{i\omega_{13}t} & \cdots & \cdots & \cdots & c_{1n}e^{i\omega_{1n}t} \\ c_{21}e^{i\omega_{12}t} & P_2 & c_{23}e^{i\omega_{23}t} & \cdots & \cdots & \cdots & c_{2n}e^{i\omega_{2n}t} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ c_{n1}e^{i\omega_{n1}t} & c_{n2}e^{i\omega_{n2}t} & \cdots & \cdots & \cdots & \cdots & P_n \end{bmatrix}$$

This and then we have oscillatory function $i\omega_{12}t$ between this represents energy difference between the states 1 and 2. And this is that coefficient which we saw in the previous slide and likewise this coefficient keeps varying from element to element here and this oscillation frequency also is changing with element to element.

Because energy levels are changing so if you have so many energy levels there will be oscillations of different types. And one can create all these kinds of phase coherences which means if I have the element which is non-zero here it would mean that I have created the phase coherence between the states 1 and 3. Here there is face coherence created between the states 1 and 2. That is by C_{12} term, C_{13} term.

And this is by the 1n element, this is the but the first state and the n state and this is the oscillation. This time evolution is given by this and this actually depends the non-equilibrium situations where you have created a phase coherence between the sates 1 and n.

So, this will be the complex conjugates here, so we have C_{21} P_2, so and it will be written in the same manner C_{23} and so on so forth, C_{2n} and here we get we have written as omega n1, if you notice here. So therefore, if I want to write it as ω_{1n} to represent this then I will put a minus sign here and then it will become consistent what we said before.

So, when I said n_1 n_2 n_3 this remains the same then they have populations here. Therefore, the density matrix has complete information about the spin-system. It carries all the information through the pulse sequence, if you generate pulse sequence spin echo for example if we consider or just a Fourier transform experiment with a single pulse what all happen, how many if there are many frequencies how they all become magnetization which is observed in the FID. All of this can be calculated. You have to take the trace of observable with this density operator and it will tell you what is all the information present in the spin- system and which can be used for measurement and interpretation of your results.

So I think this is the crucial stage and we can stop here and evolution of the density operator calculation will be required for interpretation of any experimental sequence we may design. So we will stop here and we continue with this density operator, density matrix calculations in the future classes, we may also think of some simplifications in the calculations, how to arrive at these results in a much simpler form. Those things will come in due course.