NMR Spectroscopy for Chemists and Biologists

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Lecture No. 27

Density matrix description of NMR-I

Good morning, we are now entering into the most fundamental and rigorous description of NMR. Previously, we had used the vector notations for the magnetizations, magnetic moments, the fields, their interactions and so on. Although it is extremely useful, it becomes difficult to deal with those descriptions when we have to handle complex experiments involving multiple pulses and their response is difficult to describe.

There will be many situations of equilibrium and non-equilibrium states. Various kinds of equilibria and non-equilibria can be present, there can be non-equilibria in the populations of the individual energy levels, there can be non-equilibria of the phase coherences between the spins, the phase coherence as you know results in transverse magnetizations and the transverse magnetization evolve with different time, time constants then they longitudinal magnetizations and all of this has to be described in a more inclusive manner and in an exhaustive manner and also more rigorous manner, which obviously cannot be done by the vector descriptions.

So, the recourse is to go into the more basic description of the spin systems using quantum mechanics. So, certain amount of quantum mechanical knowledge is required here and I believe that the graduate students who are going to qualify in Chemistry and some aspects of structural biology or things like that or even Physics and they would have gone through such courses in quantum mechanics and the description what we are talking about here is known as the 'Density matrix description of NMR'.

Density matrix is not just a concept which is for NMR but it is a very general concept and therefore it deals with the description of any system in a very generalized manner. Let us begin by looking at the wave function of a spin system. In quantum mechanics you describe a you describe a system by a wave function, which is of course a vector and if you want to represent it as a vector, you represent it as a vector with an amplitude and phase and all of almost invariably the wave functions are described in quantum mechanics as in some kind of a super position of various Eigen states of a particular system.

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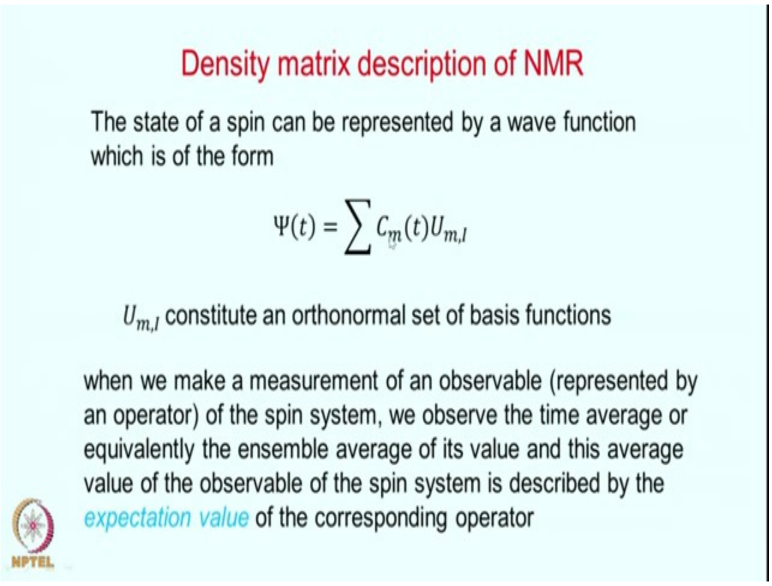

Density matrix description of NMR

The state of a spin can be represented by a wave function which is of the form

$$\Psi(t) = \sum C_m(t) U_{m,I}$$

$U_{m,I}$ constitute an orthonormal set of basis functions

when we make a measurement of an observable (represented by an operator) of the spin system, we observe the time average or equivalently the ensemble average of its value and this average value of the observable of the spin system is described by the *expectation value* of the corresponding operator

For example, here the wave function $\psi(t)$ is described with the superposition of various individual Eigen states of the spin system. Here, these are the individual Eigen states and for the spin states, if you have nucleus with the spin I and it azimuthal quantum number is m and we have already seen that it has $2I+1$ Eigen states. So, let us look at that in somewhat more detail.

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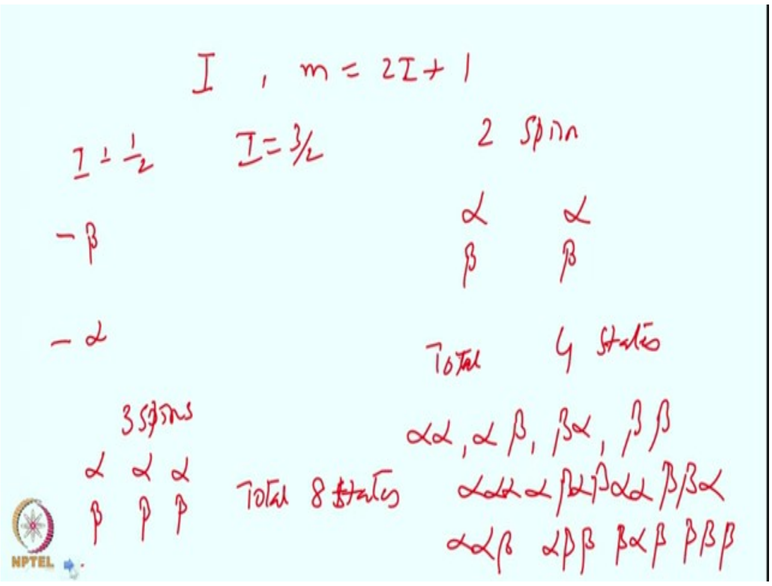

$I \; , \; m = 2I + 1$

$I = \frac{1}{2}$ $\quad I = 3/2$ $\quad$ 2 Spin

$- \beta$ $\qquad \alpha \quad \alpha$

$\qquad \beta \quad \beta$

$- \alpha$

Total 4 States

$\alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta$

3 Spins

$\alpha \quad \alpha \quad \alpha$

$\beta \quad \beta \quad \beta$ $\quad$ Total 8 States

$\alpha\alpha\alpha \;\; \alpha\beta\alpha \;\; \beta\alpha\alpha \;\; \beta\beta\alpha$

$\alpha\alpha\beta \;\; \alpha\beta\beta \;\; \beta\alpha\beta \;\; \beta\beta\beta$

So, if I have nucleus with a spin value of i, then I know that m takes $2I+1$ values. For example, if $I=\frac{1}{2}$ then we say, it has the α state and the β state, represented like this. There are two states, $2I+1=2$. If $I=\frac{3}{2}$then I have $2I+1$ states are 4, then I will have different 4 number of states. If I have 2 spins for example, this is for one spin, this is for a single spin.

If I have 2 spins, then each one of them can have α and the beta state, so this can have the α, β states and this other spin can also have the α, β states and therefore, I will have a total of 4 states, total 4 states, which we represent as $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ and$\beta\beta$.

This we have seen before when you were actually discussing analysis of spectra as discussed by Professor Ashutosh Kumar. Suppose I had 3 spins, all of these are spin half systems (I = 1/2). If I have 3 spins, then how many states I will have? I will have α, β for one, α, β for the second, α, β for the third, so I will total of 8 states.

So therefore, we write it as $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ and$\beta\beta$ and then here I multiply this by α here, alpha here, α here and α here, then in the same manner α and β here, then I have here $\beta\beta\alpha$, $\beta\alpha\beta$ and $\beta\beta\beta$.

So, total of 8 states. So, like that we will have different wave functions. We represent the generalized wave function as the superposition of this individual eigen states. These eigen states are not time dependent this are stationary states. But the wave function itself evolves with time.

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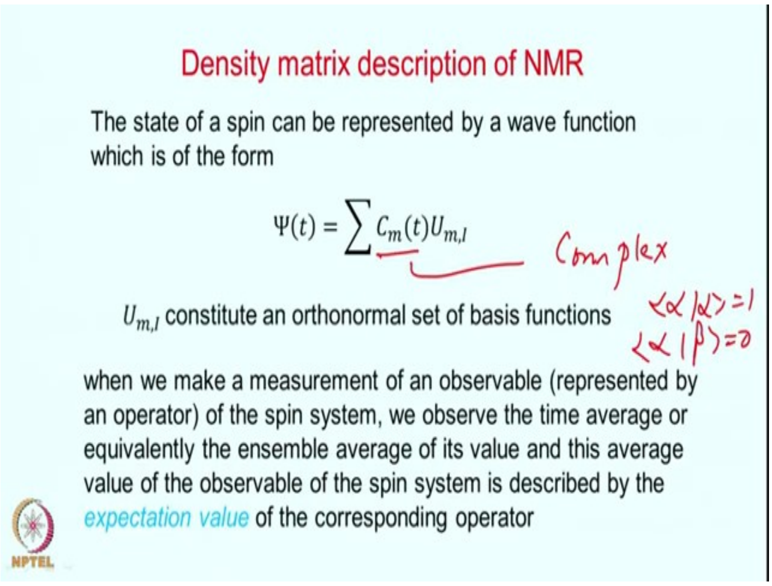

Density matrix description of NMR

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$$\Psi(t) = \sum \underline{C_m(t)}U_{m,I}$$

Complex

$U_{m,I}$ constitute an orthonormal set of basis functions

$\langle\alpha|\alpha\rangle=1$

$\langle\alpha|\beta\rangle=0$

when we make a measurement of an observable (represented by an operator) of the spin system, we observe the time average or equivalently the ensemble average of its value and this average value of the observable of the spin system is described by the *expectation value* of the corresponding operator

Therefore, what we do, we represent this as the superposition of the states where the coefficients, these coefficients are time dependent. *Cmt* this is the coefficient which is the wave function $\psi(t)$ is time dependent and these *Um* are stationary states and therefore to get this time dependence here, you write these coefficients as time dependent numbers. And since, the wave function is a complex wave function, because it is complex in nature, it has a vector, it has an amplitude and it has a phase, the coefficients themselves *Cmt*, these are also complex in nature. So, these are complex.

Complex numbers and the various eigen state, the states *UmI*, these constitute an orthonormal set. Orthonormal set, what does that mean? So, you have here for example, for the alpha alpha state, I have $¿\alpha \vee \alpha > ¿1$but $¿\alpha \vee \beta > ¿0$.

So, for the one spins case, when you have the 2 states here $¿\alpha \vee \alpha > ¿1$but $¿\alpha \vee \beta > ¿0$. Likewise, if we have the $¿\beta \vee \alpha > ¿0$ and $¿\beta \vee \beta > ¿0$. Similar thing applies to all other states in your spin system. For the two spin state, you will have 4 states and all of them are orthogonal to each other and they are also normalized because individual matrix elements of this are equal to 1.

Now, so this is a generalized description of your spin system. We represent it as a wave function as a superposition of a various eigen states of the spin system. Now, when we actually make a measurement of an observable, which is represented by an operator. For example, you may be measuring the X magnetization or the Y magnetization or something like that.

Then we observe the time average of an ensemble. So, here we have this is for individual spins. Individual spins are represented in that way, each spin evolves in a particular manner. For example, in the classical wave, it noted that the each spin is precessing around in in the cone, surface of a cone. Each spin precesses, when it precesses, it acquires a phase, it keep phase keeps changing.

That is what we say, its time constant is, I mean the *Cm*, the coefficient is changing, the phase is changing. When we the complex numbers, they have also an amplitude and phase. Therefore, their phase is changing. So, each spin has a particular value of *Cm(t)*.

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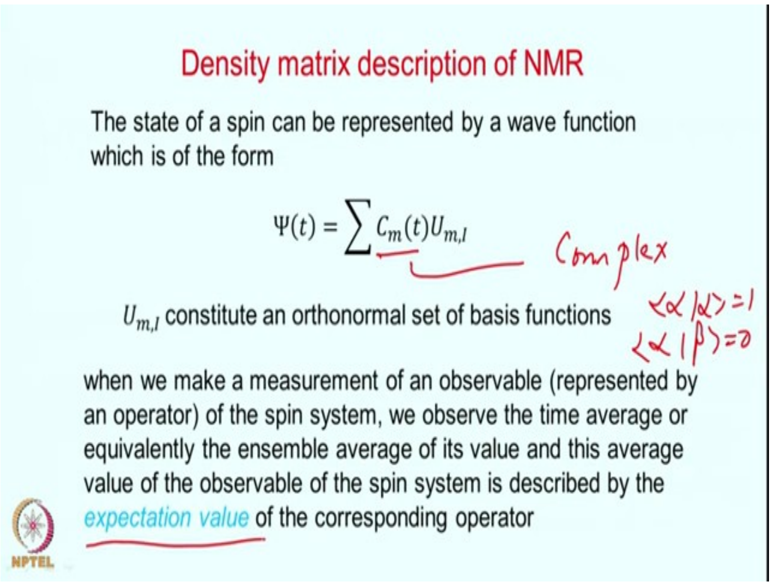

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when we make a measurement of an observable (represented by an operator) of the spin system, we observe the time average or equivalently the ensemble average of its value and this average value of the observable of the spin system is described by the *expectation value* of the corresponding operator

Now, when you are making a measurement on an ensemble, which consists trillions and trillions of of spins, so what we will measure is a ensemble average or the time average is something as called as time average of a particular spin over a long period of time. So, this is described by what is called as the expectation value of the operator.

Every physical observable is described by an operator and you measure the, when you make a measurement we say, we are getting the expectation value of this operator. This is basically representing a time average, a the ensemble average.

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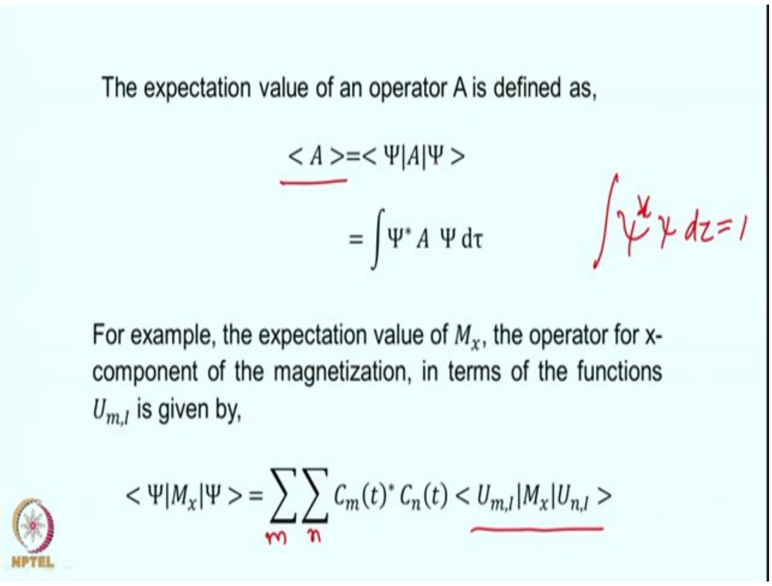

The expectation value of an operator A is defined as,

$$\underline{\langle A\rangle} = \langle \Psi|A|\Psi\rangle$$

$$= \int \Psi^* A\ \Psi\, d\tau$$

$\int \psi^* \psi\, dz = 1$

For example, the expectation value of M_x, the operator for x-component of the magnetization, in terms of the functions $U_{m,I}$ is given by,

$$\langle \Psi|M_x|\Psi\rangle = \sum_m \sum_n C_m(t)^* C_n(t) \underline{\langle U_{m,I}|M_x|U_{n,I}\rangle}$$

So, how does, how is that calculated? That is represented in this following manner. This is a standard notation for describing the expectation values. This is a standard notation, here we have a ket here and a bra here, generally we represent in this manner and if A is your observable on which you want make a measurement, you write this expectation value in this manner. This is the ψ wave function here and the ψ wave function here, this is the complex conjugate on this side and A is here.

The same thing is represented in different notation, if you want to use the integral because you want to take an average here, the summation.

$$< A >=< \Psi|A|\Psi >$$

$$\psi^{¿} \psi \, dz = 1$$

Otherwise you divide it by this integral here.

So, these are already normalized functions and therefore you can simply write it

$$= \int \Psi^{*} A \ \Psi \, \mathrm{d}\tau$$

Now, $d\tau$ is is a volume element, which is goes over all the variables in your spin system. For example, if you want to calculate the expectation value of M_x, the operator for X component of the magnetization, in terms of the functions UmI and then you write it in this manner Umx ψ is equal to summation.

Now, you see here, you have one summation for this psi another summation for this psi and therefore and there I will therefore have 2 indices here. One index for one wave function the other index for the other wave function. Therefore, I will have $\sum C_m(t)^{¿} C_n(t)$because this is as I said it is a complex conjugate here.

$$¿\psi|M_x|\psi \geq \sum_m \sum_n C_m(t)^{¿} C_n(t) < U_{m,I} \vee M_x \vee U_{n,I} > ¿$$

Since these are numbers, we can take this out and keep only this the eigen state and the operators here as in the vector notation, in this matrix element representation.

So, these are numbers, the numbers can be taken out, these are numbers which can be taken out and then we write this U_{mI}, this U_{mI} stays here, M_x stays here and U_{nI} stays here and we have double summation coming, goes in, going over the indices m and n.

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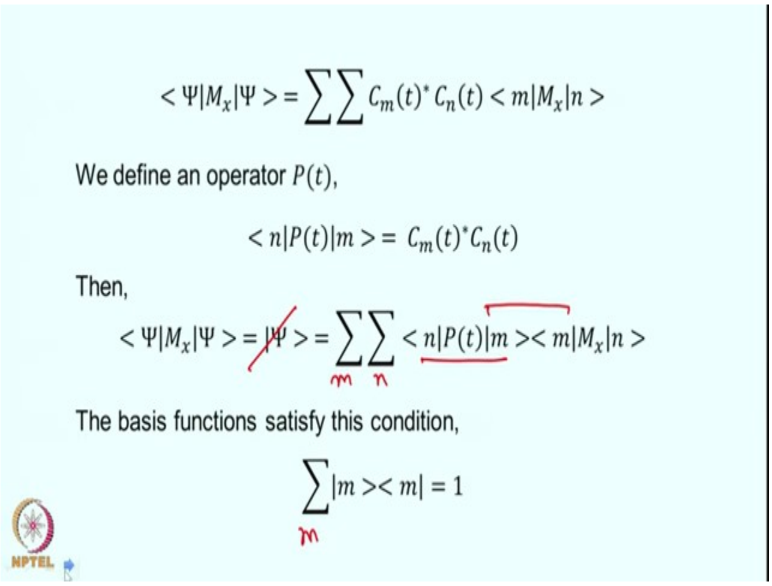

$$<\Psi|M_x|\Psi> = \sum\sum C_m(t)^* C_n(t) <m|M_x|n>$$

We define an operator $P(t)$,

$$<n|P(t)|m> = C_m(t)^* C_n(t)$$

Then,

$$<\Psi|M_x|\Psi> = \cancel{|\Psi}> = \sum_m \sum_n <\underline{n|P(t)|}\overbrace{m><m}|M_x|n>$$

The basis functions satisfy this condition,

$$\sum_m |m><m| = 1$$

Now, we simplify this notation slightly.

$$<\Psi|M_x|\Psi> = \sum\sum C_m(t)^* C_n(t) <m|M_x|n>$$

So, it is just to indicate that m is the actually the Eigen state for particular, one particular this one and this is the n here. This corresponds to this and this corresponds to this. So this is just the simplification of the notation.

Now, what we do now is, we define an operator, which is defined in this manner. This, we define this *P(t)* this an operator, now it is a time dependent. Remember, this is a time dependent part, this is time dependent therefore, the operator which we want to define is also time dependent and that is define in this manner

$$<n|P(t)|m> = C_m(t)^* C_n(t)$$

This term which is present here, we want to put it as a matrix of this form. The n and m varying. So, this, therefore, this will generate a matrix, each one of them this generate as a keep varying n from all the states and m also for all the states, you will generate that many matrix elements. How many matrix elements will generate for this?

So, if $n = 4$, m is equal to, I mean n runs from 1 to 4, m also runs from 1 to 4, you will get generate a 4 by 4 matrix. So like here, so this will be you will generate a 4 by 4 matrix when you vary all the m and the n. So therefore, now the expectation value

$\text{¿}\psi|M_x|\psi>\text{¿}\sum_m \sum_n \text{¿}n|P(t)|m>\text{¿}m|M_x|n>\text{¿¿}$

this one is put here, this is represented by this and this remains the same as that. This is not required here. So therefore, and now this goes over this terms m and n. Now, basis; now this is again a basic rule in quantum mechanics that when you have a complete orthonormal set this summation of this type over all the states *m*,

$$\sum |m><m| = 1$$

This is the ket here and this is the bra here. You take a some over all this states then this is equal to 1.

This is identity and we can simply use this identity for simplifying this equation. You notice here, this identity appears here in the middle. So, from here to here this identity appears. Therefore, if I take this sum, summation m and take this portion of this equation then this actually goes to 1. Therefore, this simplifies my equation.

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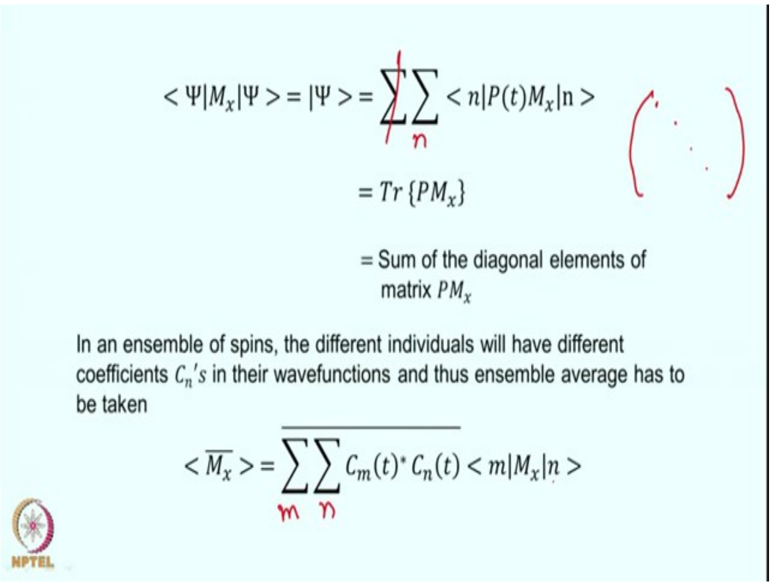

$$<\Psi|M_x|\Psi> = |\Psi> = \cancel{\sum}\sum_n <n|P(t)M_x|n>$$

$$= Tr\,\{PM_x\}$$

= Sum of the diagonal elements of matrix PM_x

In an ensemble of spins, the different individuals will have different coefficients C_n's in their wavefunctions and thus ensemble average has to be taken

$$<\overline{M_x}> = \sum_m \sum_n \overline{C_m(t)^* C_n(t)} <m|M_x|n>$$

Now, one more correction here. Once I removed this one of the summation,

$\text{¿}\psi|M|\psi \geq \text{¿}\psi \geq \sum_n \text{¿}n|P(t)M_x|n>\text{¿¿}$

I do not need this, so I will have only one summation and that is going over n. So, I will have $\left|P(t)M_x\right|n$. Now, therefore there is only one summation. Now, what does this tell me? This tells me that I have, if I have a matrix of $P(t)M_x$, this is one operator, this is another operator, the product of them is also an operator and I can have a matrix representation of this operator, if I want to write it like that.

So, this is a matrix representation of $P(t)M_x$ and all this *n, n, n, n* these are the diagonal elements of this matrix. Then I am taking a summation over all this matrix elements *n, n*. For *n* = 1, 2, 3, 4, 5 so like that. So, depending upon whatever number of states are there, so you will have the summation over all those states. So, that is called as the 'Trace'. So, this is the

$$= Tr\,\{PM_x\}$$

So, this is a sum of the diagonal elements of the $(P\,M_x)$.

Now, in an ensemble, the different individuals will have different coefficients as I said before, the different spins will have different coefficients and therefore we will have to take an ensemble average in order to represent the expectation value correctly. So, therefore when you take the ensemble average of this, of this operation, then we will have this, this same equation coming back

$¿\acute{M}_x>¿\sum\sum C_m'(t)^{¿}C_m(t)<m|M_x|n>¿$

The average will be taken over this, because this, this is not time dependent, if your M_x is not time dependent, this is not time dependent because m and n states are not evolving in time. What evolves in time are the coefficients and M_x is my operator. m and n states are not dependent on time, therefore when I take the ensemble average, I take the ensemble average over these time dependent quantities which are the *C's*.

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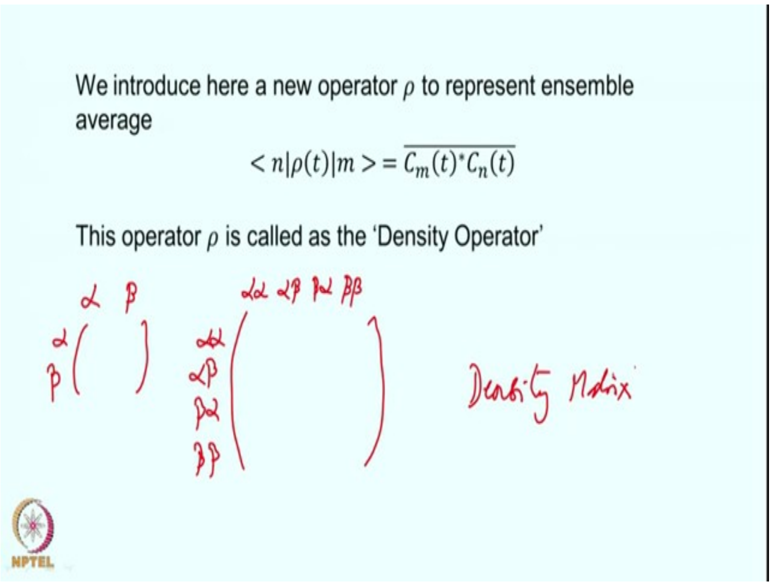

We introduce here a new operator ρ to represent ensemble average

$$< n|\rho(t)|m > = \overline{C_m(t)^* C_n(t)}$$

This operator ρ is called as the 'Density Operator'

So, now, this I represent by a new operator to represent the ensemble average, I called that as $\rho(t)$. This operator now instead of the *P(t)*, when I take the ensemble average, without the ensemble average this bar, I had called it as *P(t)*. Now, with the bar I simply call it as $\rho(t)$and this is called as the 'Density Operator' and density operator has the matrix representation depending upon the various states what we have.

For instants, if I have a single spin, I will have two states and therefore, I will have a 2 by 2 matrix and the two states are

$$\begin{array}{cc} & \alpha \\ \alpha & \left[\begin{array}{ccc} \beta & & \\ & & \end{array}\right] \\ \beta & \end{array}$$

Of course, in each of this side because n from alpha to beta, m also goes from alpha to beta therefore, I will have 2 by 2 matrix which is, so there were 4 elements.

So, if I have a 2 spin system, that will have 4 states. So 4 states, how will I write that here

$$\begin{array}{cl} & \alpha\alpha \quad \alpha\beta \\ \begin{array}{c} \alpha \\ \alpha \\ \alpha \end{array} & \left[\begin{array}{l} \beta\alpha \quad \beta\beta \qquad\qquad \\ \\ \\ \end{array}\right] \\ \beta & \\ \beta & \\ \alpha & \\ \beta & \\ \beta & \end{array}$$

So, this will be 4 by 4 matrix that is 16 elements. Therefore, the density matrix this is called as the density matrix. And so the operator which is it represents is the density operator.

So similarly, if I have 3 spins, then we will have 8 by 8 matrix and so on. So, when you go larger and larger spin systems, so the density matrix also becomes larger and larger.

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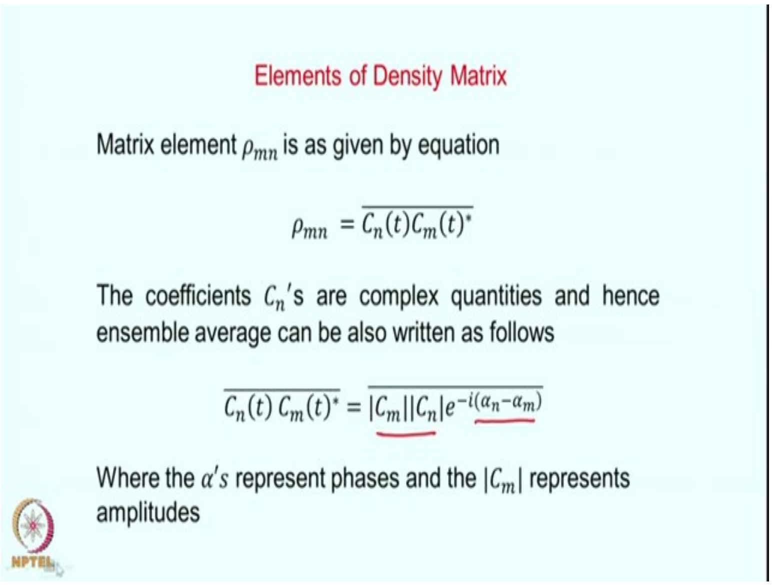

Elements of Density Matrix

Matrix element ρ_{mn} is as given by equation

$$\rho_{mn} = \overline{C_n(t)C_m(t)^*}$$

The coefficients C_n's are complex quantities and hence ensemble average can be also written as follows

$$\overline{C_n(t)\,C_m(t)^*} = \overline{\underline{|C_m||C_n|}e^{-i\underline{(\alpha_n-\alpha_m)}}}$$

Where the $\alpha's$ represent phases and the $|C_m|$ represents amplitudes

So now, what we have to do is, we have to understand the density matrix more clearly. So, let us try and calculate the elements of this density matrix. You put this definition once more, a particular element of the density matrix C is represent in this manner,

$$\rho_{mn} = \overline{C_n(t) C_m(t)^*}$$

This is one particular element of the density matrix. Now, the coefficients C_n's are as I said are complex quantity and hence ensemble average can also be written as follows.

Now, what I do is, I simply represent this as complex quantities, so it has an amplitude and a phase. So, for the $C_n(t)$, I write it as

$$\overline{C_n(t)\, C_m(t)^*} = \overline{|C_m||C_n| e^{-i(\alpha_n - \alpha_m)}}$$

If it is $-i$ this then complex conjugate will be the $+i$.

Now, this is the phase and this is the total amplitude. Where the α's represent the phases and the C_m represent the amplitudes. This particular matrix element therefore, has an amplitude and a phase.

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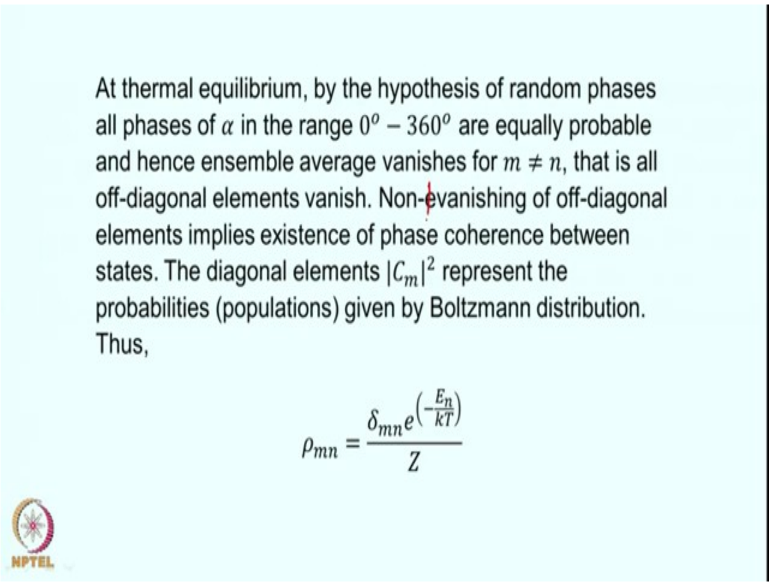

At thermal equilibrium, by the hypothesis of random phases all phases of α in the range $0^o - 360^o$ are equally probable and hence ensemble average vanishes for $m \neq n$, that is all off-diagonal elements vanish. Non-vanishing of off-diagonal elements implies existence of phase coherence between states. The diagonal elements $|C_m|^2$ represent the probabilities (populations) given by Boltzmann distribution. Thus,

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

Now, let us see what is a consequence of this, as you look at the individual elements. Here is, we have to understand this very clearly. Every sentence is quite important, we can go slow and to try and understand this very clearly. At thermal equilibrium say by the hypothesis of random phases, all phases of α, all phases α in the range 0 to 360 are equally probable and hence ensemble average vanishes for $m \neq n$.

When you take an average over this $\alpha - \alpha_n$, all possible orientations in the, in the space are possible because every phase is possible, when I say phase, it is an angle in the transverse plan. So therefore, all possible orientations are possible, that means all the off-diagonal elements vanish. Whenever $m \neq n.$ when you take an ensemble average the all the elements will vanish, m is not equal to n we call it as off-diagonal element, when $m = n.$ we call it as a diagonal element.

Now, so all off-diagonal elements vanish. Non-vanishing of off-diagonal elements means there is a kind of a phase coherence between the individual spins in the ensemble. That is why there is no cancellation, complete cancellation does not happen, so some amount of false phase coherence is present among the spins and that leads to non-vanishing of the off-diagonal elements.

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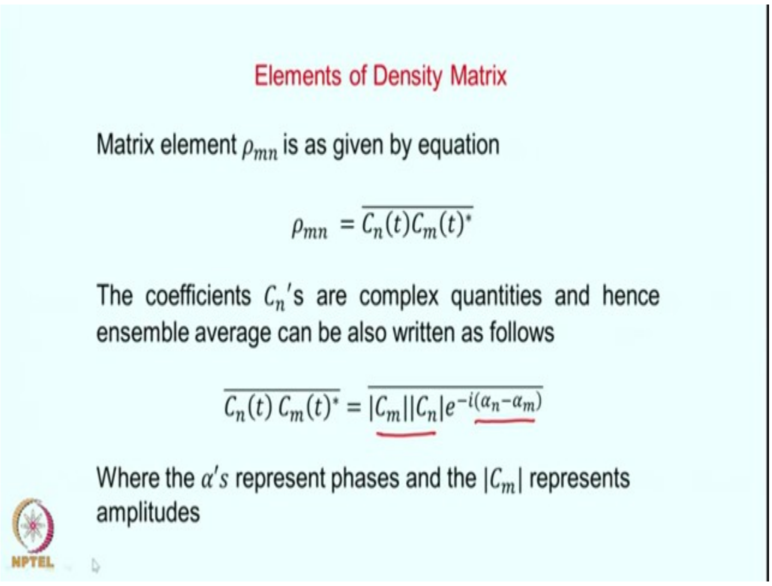

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$$\overline{C_n(t)\,C_m(t)^*} = \overline{\underline{|C_m|}|C_n|e^{\underline{-i(\alpha_n-\alpha_m)}}}$$

Where the $\alpha's$ represent phases and the $|C_m|$ represents amplitudes

What do the diagonal elements represent? The diagonal elements when $\alpha_m = \alpha_n$ that means, I mean $m = n$then numerator part actually goes to 0. Here, $m = n$, this one goes to 0, then I have $¿C_n \vee ¿^2 ¿$ or $¿C_m \vee ¿^2 ¿$. Now, what does this $¿C_m \vee ¿^2 ¿$ represent?

It represents the probability, when you took the summation, when you wrote the wave function as summation $C_m(t)$ U_{mI} then the coefficient actually square of that coefficient represents the probability that the particular spin is in that Eigen state and therefore we are taking the superposition of the individual Eigen states to represent the wave function. Therefore, this $¿C_n \vee ¿^2 ¿$ essentially represents the probability that the spin system is in that Eigen state.

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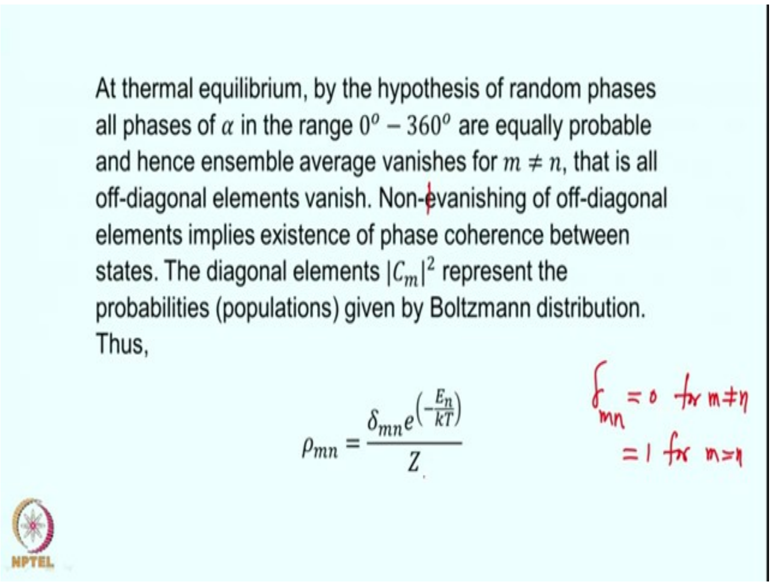

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$$\rho_{mn} = \frac{\delta_{mn} e^{\left(-\frac{E_n}{kT}\right)}}{Z}$$

$\delta_{mn} = 0$ for $m \neq n$
$= 1$ for $m = n$

So therefore, we write that in this manner, that and what is the probability? Probability tells me the population of the individual state. We have discussed this before, what is the probability, that the spin is in the particular Eigen state and that essentially asking what is a population and the population is given by the Boltzmann distribution this also we have considered before.

So therefore,

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

it is off-diagonal element, then it is 0. So, that is why we put this as δ_{mn}, δ_{mn} is a Kronecker delta, so if $m = n$, δ_{mn}means is a Kronecker delta, $\delta = 0\, for\, m \neq n$ and $\delta = 1\, for\, m = n$.

So therefore, if $m = n$, this is the diagonal element and the diagonal element is simply $\frac{e^{\left(\frac{-E_n}{kT}\right)}}{Z}$ where Z is the partition function. This is what we have seen, this is the result of the Boltzmann statistics.

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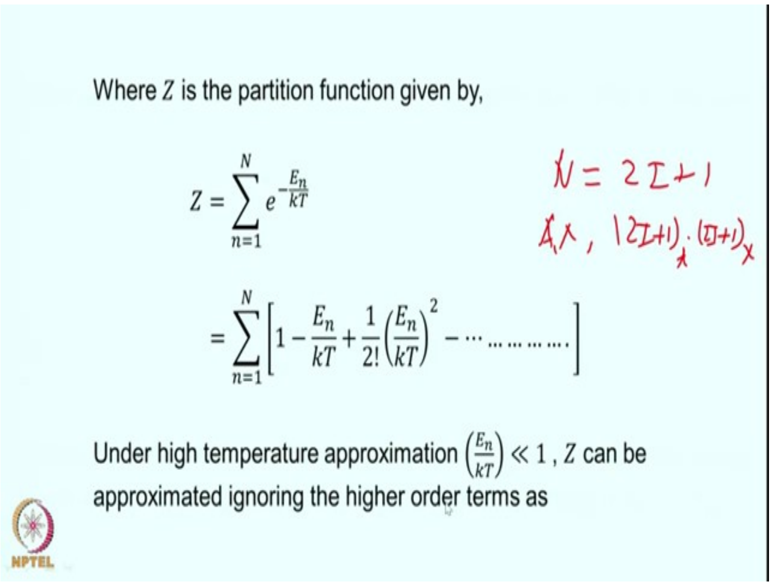

Where Z is the partition function given by,

$$Z = \sum_{n=1}^{N} e^{-\frac{E_n}{kT}}$$

$N = 2I+1$

$AX, \; (2I+1)_A \cdot (2I+1)_X$

$$= \sum_{n=1}^{N} \left[1 - \frac{E_n}{kT} + \frac{1}{2!}\left(\frac{E_n}{kT}\right)^2 - \cdots \ldots \ldots \ldots \ldots \right]$$

Under high temperature approximation $\left(\frac{E_n}{kT}\right) \ll 1$, Z can be approximated ignoring the higher order terms as

What happens next? Boltzmann statistics is given by the partition function definition we had given earlier here and this is the summation over all the energy values. All the probabilities for the individual states, where *N* is the total number of states. So, *N* what we have here, is the total number of states on your spin system, that depends upon the value of *I*.

For any I you have the number of states is $2I+1$. So, let me write that here, $N=2I+1$. $N=2I+1$ for particular, if there is a single spin or if it is multiple spins then this is a product of the two spins. If I has things like *A* and *X*, then I will have $2I+1(A)*2I+1(X)$.

So, therefore for two spins, two spin have systems, I will have 2 here and 2 here I get 4, 4 by 4 matrix. So, that *N* depends upon the number of spins and the *I* values. So, this 1's $e^{\left(\frac{-E_n}{kT}\right)}$ runs over all the individual states.

Now, we expand this as we did before as 1 to *N*,

$$= \sum_{n=1}^{N} \left[1 - \frac{E_n}{kT} + \frac{1}{2!}\left(\frac{E_n}{kT}\right)^2 - \cdots \ldots \ldots \ldots \ldots \right]$$

Under high temperature approximation, we have seen that $\frac{E_n}{kT} \ll 1$ and then Z can be approximated ignoring the higher order terms in this equation.

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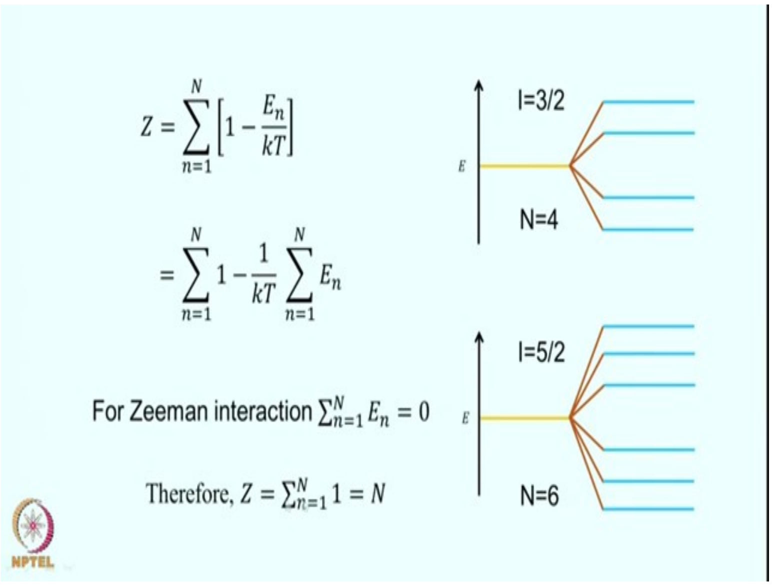

$$Z = \sum_{n=1}^{N}\left[1-\frac{E_n}{kT}\right]$$

$$= \sum_{n=1}^{N} 1 - \frac{1}{kT}\sum_{n=1}^{N} E_n$$

For Zeeman interaction $\sum_{n=1}^{N} E_n = 0$

Therefore, $Z = \sum_{n=1}^{N} 1 = N$

So, when we do that, we see all the higher order terms are gone, I keep only the first one here,

$$Z = \sum_{n=1}^{N}\left[1-\frac{E_n}{kT}\right]$$

This automatically leads to a further simplification. Now, I separate these two, I write

$$= \sum_{n=1}^{N} 1 - \frac{1}{kT}\sum_{n=1}^{N} E_n$$

Now, what is the summation En? In order to understand this, let us look at this energy level diagram once more here. Let us take $I=\frac{3}{2}$ for a single spin. The same thing is apply to other spins as well. So, in the absence of any magnetic field, you have the degenerate states, all the 4 states are degenerate here, $I=\frac{3}{2}, 2I+1=4$.

So and these states now split when you apply the magnetic field and two of them go up and two of them come down by similar amounts, to the extends this goes up, this comes down, this goes up, this comes down to the same amounts, therefore you have a negative energy here and a positive energy there and the total of this is 0.

So similarly, if you take $I = \frac{5}{2}$, I will have 6 states here, 3 states up here and 3 states down here and the sum of all of this is 0. In general therefore, the summation En over all the states is actually 0. Therefore, this portion becomes 0. So, what happens? Therefore, Z is simply equal to the number of states.

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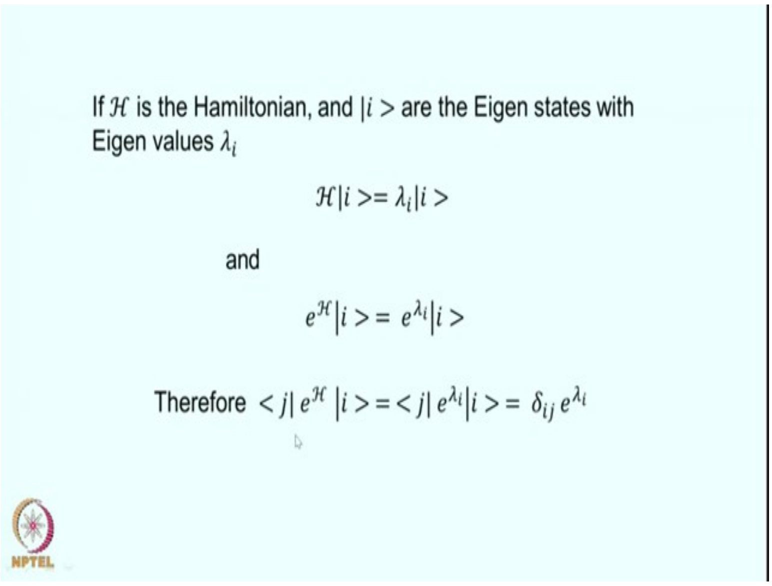

If $\mathcal{H}$ is the Hamiltonian, and $|i>$ are the Eigen states with Eigen values λ_i

$$\mathcal{H}|i>= \lambda_i|i>$$

and

$$e^{\mathcal{H}}|i> = e^{\lambda_i}|i>$$

Therefore $<j|\, e^{\mathcal{H}}\, |i> = <j|\, e^{\lambda_i}|i> = \delta_{ij}\, e^{\lambda_i}$

Now, here is a little bit of digression to be able to follow the mathematics little bit better afterward. Suppose, we have the Hamiltonian represented as H and if it has Eigen values λ_i and we often write this as

$$\mathcal{H}|i>= \lambda_i|i>$$

So, this is the usual Eigen value equation and if this is the case then it follows that e to the power H this is an operator, exponential operator of the same Hamiltonian and this if this is operating on the same state i, it gives me

$$e^{\mathcal{H}}|i> = e^{\lambda_i}|i>$$

So, here λ_i is the Eigen value and here $e^H$is the operator if I take, then I will have e^{λ_i}.

Therefore $<j|\, e^{\mathcal{H}}\, |i> = <j|\, e^{\lambda_i}|i> = \delta_{ij}\, e^{\lambda_i}$

that means if $i=j$, then this is equal to 1 or if it is not equal to, $i\neq j$ then this is 0, this is a Kronecker delta. Therefore, I write it as e^{λ_i}, I take it, this out since this is a number and then I represent this j i as δ_{ij}. $\delta_{ij} e^{\lambda_i}$.

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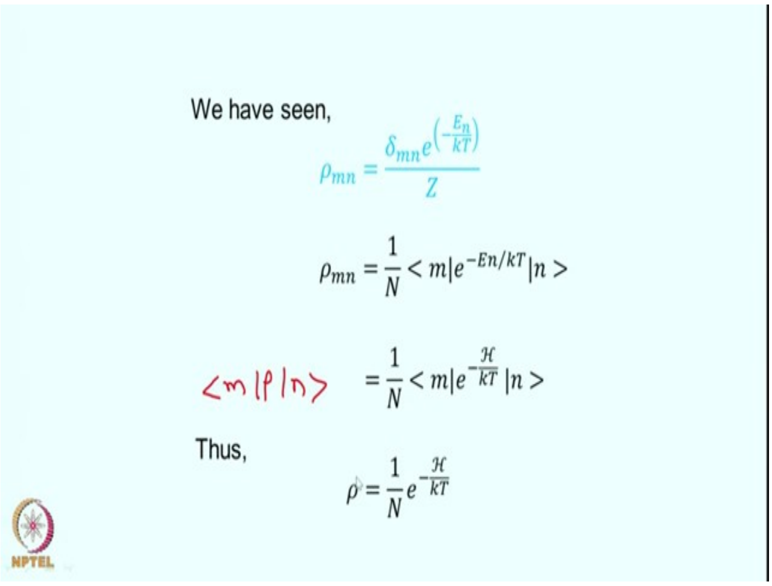

We have seen,

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

$$\rho_{mn} = \frac{1}{N} < m|e^{-En/kT}|n >$$

$$<m|\rho|n> \quad = \frac{1}{N} < m|e^{-\frac{\mathcal{H}}{kT}}|n >$$

Thus,

$$\rho = \frac{1}{N} e^{-\frac{\mathcal{H}}{kT}}$$

And we are going to use that here. So, therefore we wrote

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

So and now, I recall again that $\rho_{mn} = 1\, if\ m \neq n, then\, \delta_{mn} \rightarrow 0$ and if $m = n,$, then I have simply $\frac{e^{\left(\frac{-E_n}{kT}\right)}}{Z}$. This is a partition function, this is a partition function and this is the probability and this represents the populations.

So, together I write this as

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

Then let us write this in the matrix form like this,

$$\rho_{mn} = \frac{1}{N} < m|e^{-En/kT}|n >$$

So therefore, essentially this if I were to take this out, this m and n here and that is δ_{mn}.

So, $\delta_{mn} e^{\left(\frac{-E_n}{kT}\right)}$. So, this is the same thing written in this manner. Now, what I do for the En, now I know that the En is the Eigen value of the operator H or when Hamiltonian operates on the state n it gives me the Eigen value E_n. Therefore, here I will put this as the result of the exponential operator operating on the state N.

So, instead of $\frac{E_n}{kT}$ of multiplying on the state N, I write this as now the coming out is result of the operation of the exponential operator operating on N. So therefore, now you have an operated term introduced here. So, the $\rho_{mn}$is now a matrix element here between the states m and N with the operator in the middle as $e^{\left(\frac{H}{kT}\right)}$

$$= \frac{1}{N} < m|e^{-\frac{\mathcal{H}}{kT}}|n >$$

So, therefore if I write this also as in the operator form, so this also I write it as ρ_{mn} and this is equal then what happens? I can take this *mn* out, ignoring this *m* and *n* I will have

$$\rho = \frac{1}{N} e^{-\frac{\mathcal{H}}{kT}}$$

So, this gives me an different representation of the density operator. This is the density matrix and this is the density operator.

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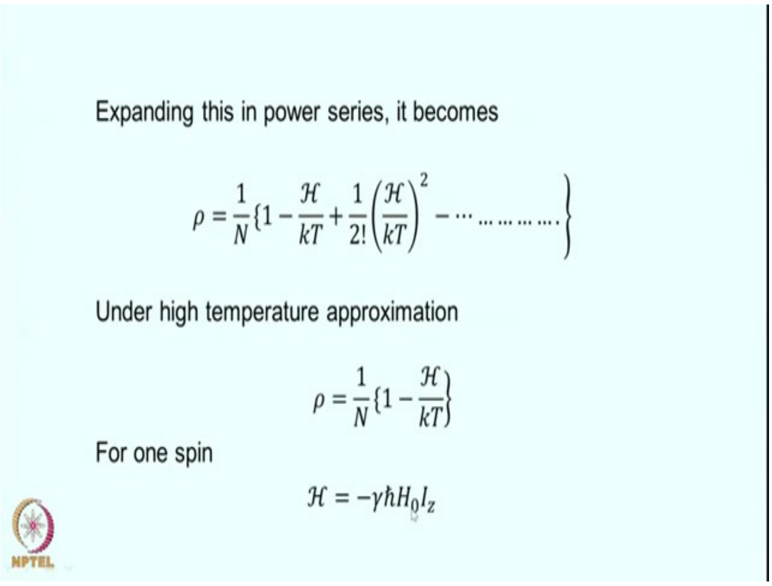

Expanding this in power series, it becomes

$$\rho = \frac{1}{N}\{1 - \frac{\mathcal{H}}{kT} + \frac{1}{2!}\left(\frac{\mathcal{H}}{kT}\right)^2 - \cdots \ldots\ldots\ldots\ldots\}$$

Under high temperature approximation

$$\rho = \frac{1}{N}\{1 - \frac{\mathcal{H}}{kT}\}$$

For one spin

$$\mathcal{H} = -\gamma\hbar H_0 I_z$$

So, once again I will do the same trick expand this density operator as a power series.

$$\rho = \frac{1}{N}\{1 - \frac{\mathcal{H}}{kT} + \frac{1}{2!}\left(\frac{\mathcal{H}}{kT}\right)^2 - \cdots \ldots\ldots\ldots\ldots\}$$

Once again under high temperature approximation, the higher order terms can be neglected and I will have simply

$$\rho = \frac{1}{N}\left\{1 - \frac{\mathcal{H}}{kT}\right\}$$

So, H is now we know what is a Hamiltonian $\mathfrak{H}$ for a single spin, I can simply write it as

$$\mathcal{H} = -\gamma\hbar H_0 I_z$$

This is a Zeeman interaction, Zeeman interaction between the single spin with the field H_0 and that gives you $-\gamma\hbar H_0 I_z$. Remember this is $\mu . H_0$ and the $\mu . H_0$ give me $\mu Z H_0$and $\mu Z H_0$=$-\gamma\hbar H_0$. So, this is the if you simply recall the previous lectures in the previous classes, what is a Hamiltonian and you will simply see that this is for single spin $-\gamma\hbar H_0 I_z$.

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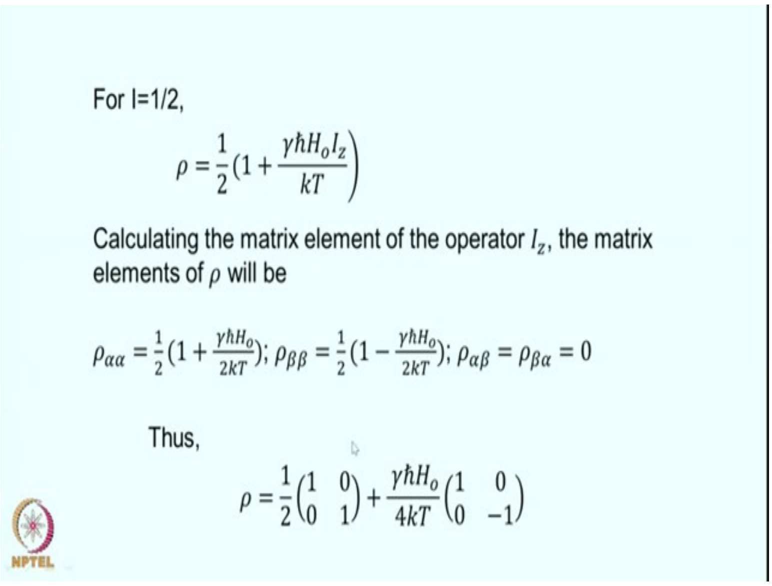

For I=1/2,

$$\rho = \frac{1}{2}(1 + \frac{\gamma\hbar H_o I_z}{kT})$$

Calculating the matrix element of the operator I_z, the matrix elements of ρ will be

$$\rho_{\alpha\alpha} = \frac{1}{2}(1 + \frac{\gamma\hbar H_o}{2kT});\ \rho_{\beta\beta} = \frac{1}{2}(1 - \frac{\gamma\hbar H_o}{2kT});\ \rho_{\alpha\beta} = \rho_{\beta\alpha} = 0$$

Thus,

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

For the spin half, so this will be number of states is 2, therefore

$$\rho = \frac{1}{2}(1 + \frac{\gamma\hbar H_o I_z}{kT})$$

Now, if you calculate the matrix elements of this operator, the matrix elements of rho will be rho alpha alpha, you can calculate this explicitly here,

$$\rho_{\alpha\alpha} = \frac{1}{2}(1 + \frac{\gamma\hbar H_o}{2kT});\ \rho_{\beta\beta} = \frac{1}{2}(1 - \frac{\gamma\hbar H_o}{2kT});\ \rho_{\alpha\beta} = \rho_{\beta\alpha} = 0$$

But I will show you the explicit calculations and when you do this, this the first element of the density operator matrix is is equal to half this much and the this the fourth element for the two spin system, no this is a single spin, for the single spin there are, this is a 2 by 2 matrix and there are 4 elements, $\alpha\alpha$is one element, $\beta\beta$is one element, $\alpha\beta$ is one element and $\beta\alpha$ is one element and it terms so that when I actually calculate putting this Iz operator here they calculate the matrix elements $\alpha\alpha$, then this $\alpha\beta$ and $\beta\alpha$ go to 0 and $\alpha\alpha$ gives you

$$\rho_{\alpha\alpha} = \frac{1}{2}(1 + \frac{\gamma\hbar H_o}{2kT});\ \rho_{\beta\beta} = \frac{1}{2}(1 - \frac{\gamma\hbar H_o}{2kT});\ \rho_{\alpha\beta} = \rho_{\beta\alpha} = 0$$

And now if I put this all together, I will have

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

So, this one is 1 plus, if you put it together of course, this the same thing is put in this manner. This 1 is here, this 1 is here and these 1's have entered into this term, where this 1 and these 0's are coming, these 0's are coming because $\alpha\beta$ and $\beta\alpha$ are 0. Because this you remember, this is α and this is β here and α here and β here, so this $\alpha\beta$ the cross terms are 0 and it is only the diagonal terms which are non-zero.

So, I think this is a good point to stop and we will continue with this discussion of the elements of the density operator in further detail in the next classes.