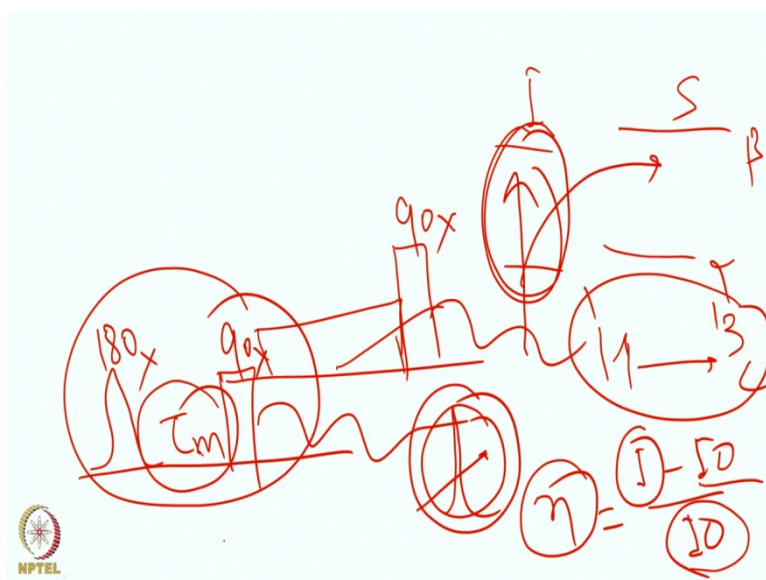


NMR Spectroscopy for Chemists and Biologists
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Lecture No. 21
The Nuclear Overhauser Effect

So welcome to today's lecture and we will continue with polarization transfer and will again go little more detail in nuclear will overhauser effect. So if you recollect in the last class, we looked at what is actually nuclear overhauser effect and how experiments are done and what we can get from nuclear overhauser effect related spectroscopy?

So to summarise, we looked at the population difference of two states for a particular nuclei give rise to an intensity and if we compare NMR with other electronic spectroscopy. The difference between the, in NMR the difference between two states is very small. Therefore, it is one of the least sensitive technique. But, among all the nuclei that are available for NMR, proton is the high sensitive because its magnetic moment higher and the population difference between two states it quite a large.

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We also looked at to enhance this polarization that we had, for enhancing the polarization between these two states, say α states and β states. If there is another spin which is coupled to this, we perturb these by radiofrequency pulse and if these two spins, say I spin or S spin, if they are two coupled, if you perturb I spin the effect of that will be seen on S spin. Now, then this can have a homonuclear effect or heteronuclear effect.

Homonuclear effect is generally used for measuring the distance between two coupled spin and this coupled spin what I mean by? Coupled through a space, they are close in space, close approximately in space. In heteronuclear case, this is used for transferring polarization from the highest sensitive nuclei to the lower sensitive nuclei. Like from proton to carbon 13 and this kind of concept is very much used in heteronuclear experiments that will be seen in the next class.

Now then we moved ahead and define two class of NOE, one was called continuous wave like irradiation NOE which is called steady-state. So we had seen that we irradiated with the continuous wave pulse and then we excited all the spins by 90° and we detected it. So we need to do two experiments, one experiment, where we irradiate, the next experiment where we do not irradiate and then we take the difference between these two states and then if you take the difference this signal intensity will increase or decrease and this is called NOE effect.

So we looked at the NOE will be given by $\frac{I - I_0}{I}$. So this (I) is of the saturated spectrum, this (I_0) is non-saturated spectrum and then this, you with the non-saturated spectrum gives the enhancement factor which is the NOE. So we looked at the another way to do it is by irradiating with a soft pulse and then here is time for mixing this spins. Then we apply a 90° pulse, this was 180° pulse and then measuring the FID.

So here if we vary the mixing time, we can actually quantify the distance between two spins in this transient NOE. Because this gives you the estimate how much your perturbation effect is moving? So we looked at this all qualitative and then we went ahead and try to understand what is the origin of this NOE effect? And I left you with the question that by doing those treatment of the population difference, where the NOE effect is coming from? So will continue from that states.

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Let these population differences be equal to d

The total intensities of the A transitions as well as of the X transitions are each equal to $2d$

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Where is the signal enhancement? c)

As the irradiation saturate the **A transitions**,

The relaxation processes tend to drive the system towards equilibrium.

Three transition probabilities (W_0, W_1, W_2)

W_1^A will be overridden by Irradiation

NPTEL

So we looked at the population between these states P_1, P_2, P_3 and P_4 has that term is called d and then we measure that in X there is enhancement of $2d$. So if you remember the previous lecture, here the enhancement was $2d$ between these two states. So we will continue from there and we try to look at the effect that is coming because of the irradiation of spin A . Okay.

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Where is the signal enhancement?

As the irradiation saturate the **A transitions**,

The relaxation processes tend to drive the system towards equilibrium.

Three transition probabilities (W_0, W_1, W_2)

~~SQ~~ W_1^A will be overridden by Irradiation

c)

So actually we should remember that there is another phenomena which is all the time active and this is called relaxation process. So in any of these phenomena very excite the nuclei, they always want to come back to equilibrium state and that phenomena is called relaxation and this relaxation actually drives the system towards equilibrium state.

Now, so in this case as we have discussed earlier, there are three kind of transition probability. Here **2 for** A spins, so this is call omega 1 single quantum transition, again omega 1 single quantum transition for 2A spin and 2 for X spin, single quantum transition and single quantum transition.

However, there are another two, which is this is called double quantum transition, here both spin flips, **like alpha**, alpha state, this goes to beta, beta states and here alpha, beta is states goes to beta, alpha state. So this is zero quantum transition. Now as we are irradiating this spin A. So single quantum transition which is because of omega 1 for A spin will be gone. Because we are irradiating it.

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Where is the signal enhancement?

As the irradiation saturate the **A transitions**,

The relaxation processes tend to drive the system towards equilibrium.

Three transition probabilities (W_0, W_1, W_2)

SQ W_1^A will be overridden by Irradiation

SQ: W_1^X cannot cause any population transfer

the population differences between states 1 and 3, and 2 and 4 are already equal to the equilibrium differences

Let us see:
Effect of W_2 alone

Steady-state populations are

Now what is happening to the X states? So single quantum transition for X spin cannot cause any population transfer, why? Because we have irradiated the single quantum transition, if you look at for X spin like here $\frac{d}{2}$ and $\frac{d}{2}$. That is differences in d here and here, so from each of them is d and that is why totally is $2d$. So that is not origin much population difference between states 1 and 3, and 2 and 4. So are actually already add equilibrium difference.

Now, so this is also not causing any enhancement. But let us look at this double quantum transition which is ω_2 . So ω_2 effect that is coming because of double quantum transition, actually causes something and that is here. This is basically at this, they introduces a

parameter call t . Now that is the steady-state population will happen because this double quantum relaxation is active. So it will change the population of state here P_1 and P_3 .

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W_2 changes the population faster than the saturating field and consequently there is a net gain by **state 1 and a net loss by state 4**

The population differences corresponding to the X transitions

$X_1 = P_1 - P_3 + t$; $X_2 = P_1 - P_3 + t$

This is the net increase

The diagram shows a four-level system. The top level is labeled $P_3 - \frac{d}{2} - t$ and the bottom level is $P_1 - \frac{d}{2} + t$, both circled in red. The middle level is $P_1 - \frac{d}{2}$. Transitions are labeled: A_2 (top to middle), A_1 (middle to bottom), W_0 (middle to middle), W_1 (top to bottom), W_2 (middle to middle), X_1 (middle to bottom), and X_2 (top to middle).

Now, so ω_2 changes the population and because of this relaxation is faster. So this happens faster than the saturating field and because of that, there is a net gain of the state 1 and 4. So if you look at here previously, this is $+t$ and this is $-t$. So that is the net gain we are talking because of fast relaxing, if double quantum transition that is the changes the population. Okay.

So now this that is what the transition changes. So

$$X_1 = P_1 - P_3 + t$$

and

$$X_2 = P_1 - P_3 + t$$

Because of that transition of double quantum.

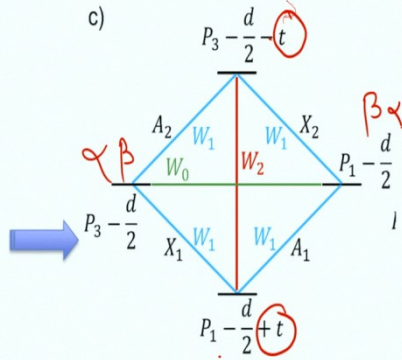
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SQ: W_1^x cannot cause any population transfer

the population differences between states 1 and 3, and 2 and 4 are already equal to the equilibrium differences

Let us see:
Effect of W_2 alone

Steady-state populations are



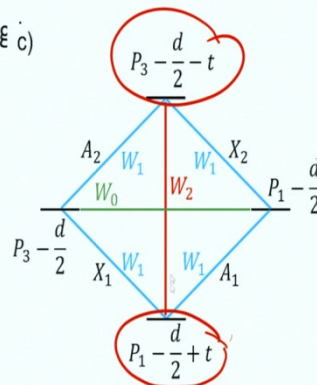
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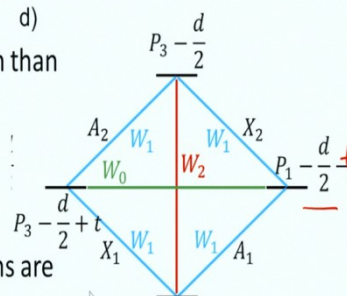
The population differences corresponding to the X transitions

$$X_1 = P_1 - P_3 + t; \quad X_2 = P_1 - P_3 + t$$

This is the net increase



ZQ transition causes population transfer between states 2 and 3
 The population transfer occurs from state 2 to state 3
 State 3 has actually a lower population than its equilibrium value.



Thus, the intensities of the X transitions are proportional to the populations



$$X_1 = P_1 - P_3 - t; \quad X_2 = P_1 - P_3 - t$$

Now similarly, there is another phenomena. So this is because of double quantum transition, another transition and relaxation. There is another phenomena that is called zero quantum transition. So zero quantum as we know that it is a spin flip-flop α, β going to β, α . So because of this zero quantum another state will happen and that happen between is state 2 and state 3.

So here should be minus. Okay, so now the population transfer occurs between state 2 and 3. State 3 has actually lower population than the equilibrium value and state 2 will be having higher population. Thus, there is a intensity of X transition is proportional to the population difference. As we know that what will be the distance? So

$$X_1 = P_1 - P_3 - t$$


$$X_2 = P_1 - P_3 - t$$

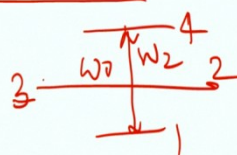
So if we looked at here what is happening? We are gaining some intensity by t because of this. And in this case we are losing some intensity because of the zero quantum transition. So there is a net gain in intensity and there is a net loss in intensity. So NOE is causing two effect, either intensity can increase or intensity can decrease. And, why this is happening? Not because of single quantum transition.

But there is a another phenomena which is active at that time because of relaxation property, double quantum and zero quantum. So this double quantum seems to be enhancing the intensity of these states and zero quantum is decreasing the intensity of the state.

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- Here, the X transitions have lost some intensity compared to the unperturbed state.
- Thus X transitions either gain intensity or lose intensity
Gain: positive NOE and
Loss: negative NOE
- The magnitude of the NOE is proportional to the difference in the two relaxation rates, which is referred to as the 'cross relaxation rate' σ .


$$\sigma = \omega_2 - \omega_0$$

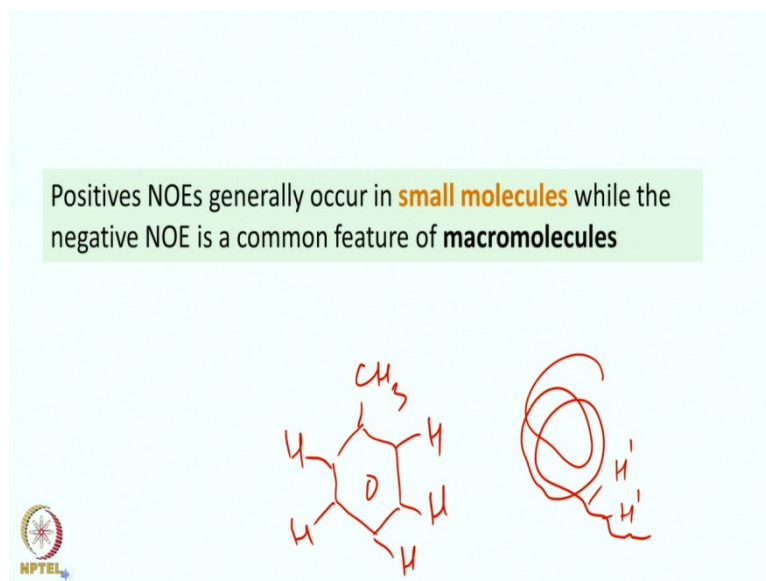


Now, X transition have lost some intensity compared to the unperturbed states in the previous case. So the X transition either gain density or loses intensity. The gain in intensity is called positive NOE and loss in intensity is called negative NOE. Now the magnitude of the NOE, as we know the proportional to the difference in the two relaxation rates. So, which is actually referred to cross relaxation rate.

So, what are those two relaxation rate? This ω_2 , which is between state 1 and 4 and then here ω_0 , which is between state 3 and 2. Now, so therefore, this cross relaxation rate depends upon difference between ω_2 and ω_0 . And that actually gives rise to different kind of NOE positive or negative. Okay. So where is positive NOE and where is negative NOE?

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Positives NOEs generally occur in **small molecules** while the negative NOE is a common feature of **macromolecules**



So positive NOE are generally occurs in a small molecules, small organic molecules. While negative NOE is a common feature of macromolecule. Now this is very interesting and I will leave you with this thought that why small molecule shows positive NOE and macromolecules shows negative NOE. So let us on basis of this, let us try to thing little bit what is happening in macromolecule and what is happening in small molecule?

So macromolecule generally what we mean is like a protein, so this is suppose a protein. Now a protein has thousands of proton atoms, so this is active nuclei. There are thousands, 10 thousands of proton atom. Whereas let us take a small molecules something like this sphere we have different protons here. Now if you look at macromolecules what is happening?

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For macromolecules:

Very efficient redistribution of magnetizations by zero quantum transition processes among various nuclei within the molecule.

For small molecules:

The population changes and hence the magnetization changes, by dissipative processes to the lattice by double quantum transitions.



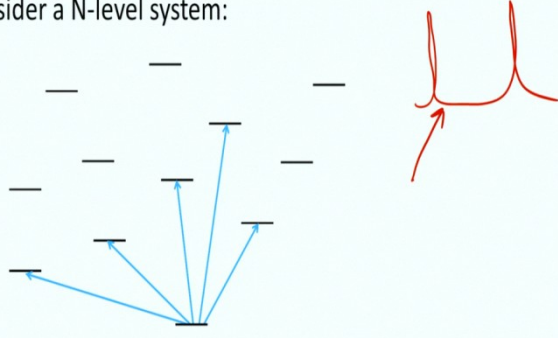
Because of this abundant active nuclei. The redistribution of magnetizations happens very fast or very efficiently by this zero quantum phenomena and actually that happens within the, like distribution of the magnetization. So because of this zero quantum phenomena distribution of magnetization leads to negative NOE. However, for small molecule redistribution of population happens. But here it is mostly dominated by double quantum transition.

So if zero quantum is there, there is a negative NOE. If double quantum transition is dominating factor of redistribution of magnetization, then it is positive NOE. So for macromolecules like we have in proteins, we have negative NOE. For the small molecules, like small organic molecule, we have positive NOE.

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Origin of NOE: A more rigorous treatment

- NOE arises due to interplay between relaxation and population distribution upon perturbation
- The time evolution of these populations is the crucial process
- Let us consider a N-level system:



The diagram illustrates an N-level system with energy levels represented by horizontal lines. Blue arrows indicate transitions between these levels. To the right, a red NMR spectrum shows a multiplet with a central peak and two side peaks, with a red arrow pointing to the central peak. The NPTEL logo is visible in the bottom left corner of the slide.

So let us move ahead. That was a qualitative description of NOE. How NOE can arise and how they are coming and what kind of NOE we have and we look at the two kinds of NOE steady-state experiment or transient NOE experiments? And the outcome in one case was positive and negative. So let us little bit rigorously, let us try to understand what is the origin of this NOE?

So as we understood that NOE arises due to interplay between relaxation and population distribution upon perturbation. Perturbation we are perturbing one spin, like that we had seen earlier, so if you have two coupled spins say I spin and S spin, we are perturbing one spin either by continuous wave radio irradiation or by pulse radio irradiation and then there is a redistribution of population happens and there are already existing relaxation mechanisms that actually causes the NOE. That is what we have looked in the last class.

Now, we also looked at time evolution of this populations is a crucial process and that actually further leads to redistribution and readjustment of the population. So let us look at generalise phenomena, where we have to consider a system, which is actually N-level system. So, say here is the ground state and then there are N-level system of these different levels and then transitions are happening here. So what will be the population and let us look at what happens upon perturbation so that we can understand what is the origin of NOE phenomena.



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Upon perturbation of the spin system, the recovery of the population of a state i will be governed by the equation,

$$\frac{dP_i}{dt} = \sum_j W_{ij}(P_j - P_j^0) - (P_i - P_i^0) \sum_j W_{ij}$$

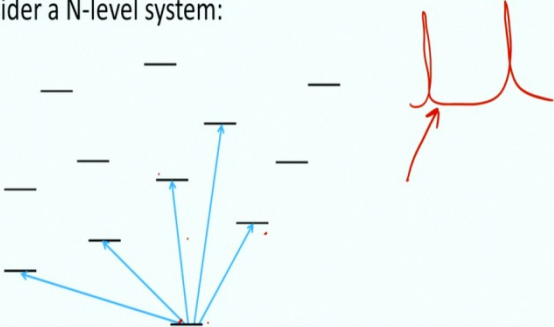

➤ Here W_{ij} is the transition probability from state i to state j ,
 ➤ P 's are the populations at any time t and
 ➤ P^0 's are the equilibrium populations of the different states.

"Master Equation"

Origin of NOE: A more rigorous treatment

➤ NOE arises due to interplay between relaxation and population distribution upon perturbation
 ➤ The time evolution of these populations is the crucial process
 ➤ Let us consider a N-level system:

So, if we start with this and we start perturbing the system because per NOE perturbation is very important. If recovery population of say any state i will be governed by the following equation. I will take a time little bit to explain what actually this equation means? So here rate of change of population of i th spin with time. So this is governed by few of the parameter, like here, this is the transition probability.

So transition probability between i and j . So what I mean? Again I will draw this little diagram, so this is transition probability between say i^{th} state and j^{th} state. And what is the population of P_j at any time and what was the equilibrium population minus the population of i state at any time and that will be subtracted with P_i^0 , that is the equilibrium population. So

this together is subtracted from here and then you actually. So here you sum over transition probability of all j^{th} state and here some over all, here again j^{th} state. So the population difference between j state and i state to sum over that multiply with the transition probability. That gives you a rate of change of population with time. Okay.

So as we discussed P_0 's are the equilibrium population and P_j is a population at any time t . So if you calculate this equation, we can find it out rate of change of population with time and this is called master equation. So basis of actually on the basis of this, we can find it out what is the decay or what is the change in the population of any state that we showed in generalize equation between any two states, like this state and this state or this state and this state. We only need to know what is the population at the anytime t what is the equilibrium population of these 2 states and what is the transition probability and one need to sum over all the j^{th} and if we do that, then we can calculate that dP_i with time.

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For weakly coupled AX spin system :

Suppose M_A and M_X are the z-magnetizations of the spins A and X respectively,

Related to populations P_1 to P_4 as follows:

$$M_A = \frac{1}{2} [P_1 + P_2 - P_3 - P_4]$$

$$M_X = \frac{1}{2} [P_1 + P_3 - P_2 - P_4]$$

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So, let us take an simple example like to weakly coupled spin that the AX spin. So if we see the energy level that we have discussed earlier. So this is α, α state with the population P_1 . Then we have α, β state population P_3 and here β, α state with population P_2 and β, β state with P_4 . These are different transition probability. So here is a single quantum, so this from here to here, this is a single quantum transition. From α, α state to β, α state, again single quantum transition.

So we have a here two for A spin and two X spin single quantum transition. Then we have a double quantum transition, like α, α state going to β, β state or P_1 going to P_4 . That is a

double quantum transition and here it is zero quantum transition α, β state going to β, α state. So these are all transition probability and the population of various state. Now suppose, we have a M_A magnetization associated with A spin and M_X is the z magnetization associated with X spin.

So the related population of P_1 and P_4 can be given by something like this. So M_A that is z magnetization of A state will be

$$M_A = \frac{1}{2} [P_1 + P_2 - P_3 - P_4]$$

So that will be for A spin. Similarly, because why A spin here? If you look at this transition and here we are changing from α to β , and here it is going again, α to β okay. So similarly, for X spin one can write

$$M_X = \frac{1}{2} [P_1 + P_3 - P_2 - P_4]$$

So we have the magnetization coming from A and X of for two spin system.


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Upon perturbation of the spin system, the recovery of the population of a state i will be governed by the equation,

$$\frac{dP_i}{dt} = \sum_j W_{ij} (P_j - P_j^0) - (P_i - P_i^0) \sum_j W_{ij}$$

➤ Here W_{ij} is the transition probability from state i to state j ,
 ➤ P 's are the populations at any time t and
 ➤ P^0 's are the equilibrium populations of the different states.

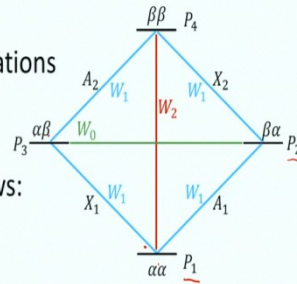
"Master Equation"



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Suppose M_A and M_X are the z-magnetizations of the spins A and X respectively,

Related to populations P_1 to P_4 as follows:



$$M_A = \frac{1}{2} [P_1 + P_2 - P_3 - P_4]$$

$$M_X = \frac{1}{2} [P_1 + P_3 - P_2 - P_4]$$



Populations changes as follows:

$$\frac{dP_1}{dt} = -(W_1^A + W_1^X + W_2)(P_1 - P_1^0) + W_2(P_4 - P_4^0) + W_1^X(P_2 - P_2^0) + W_1^A(P_3 - P_3^0)$$

$$\frac{dP_2}{dt} = -(W_1^A + W_1^X + W_0)(P_2 - P_2^0) + W_1^A(P_4 - P_4^0) + W_1^X(P_1 - P_1^0) + W_0(P_3 - P_3^0)$$

$$\frac{dP_3}{dt} = -(W_1^A + W_1^X + W_0)(P_3 - P_3^0) + W_1^A(P_1 - P_1^0) + W_1^X(P_4 - P_4^0) + W_0(P_2 - P_2^0)$$

$$\frac{dP_4}{dt} = -(W_1^A + W_1^X + W_2)(P_4 - P_4^0) + W_1^A(P_2 - P_2^0) + W_1^X(P_3 - P_3^0) + W_2(P_1 - P_1^0)$$



Now, so population change, then we can put that in master equation that we have described here and as we discussed we need only three things, first the transition probability, second population at any time t and the equilibrium population. If we put that in the master equation for this two spin system, one can write it, dP_1 . That is change of population of state one will be given by the transition probability of A spin. The single quantum transition plus single quantum transition of X spin plus double quantum transition and this is the population difference at any time t with P_1^0 . That it will be population.

So we have to sum this and actually for ω_2 , that is P_4 and equilibrium population of P_4 . Then again single quantum transition for X, for P_2 states and single quantum constant for A of P_3 states. So if you sum all those we can get what is the change of the population with time for like P_1^0 . Similarly, one can find it out by putting all those and some over the all states, for P_2 .

So again here it will be single quantum transition for this, zero quantum transition and that will be multiply with the population of P_2 . I will just go and explain you.

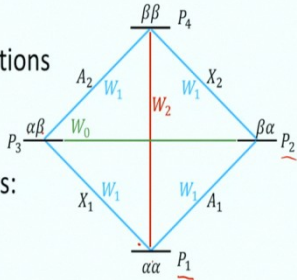
This is the P_2 , so here, zero quantum transition means transition happening from $\alpha\beta$ state to $\beta\alpha$ state. So if you take all this and again here single quantum transition, here single quantum transition for X , here single quantum transition for A . And zero quantum transition for this spin third. So if you take this, you can get the rate of change of population of state two P_2 . Similarly, for P_3 and one can get P_4 . So now, we got the population change time for all these states.

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For weakly coupled AX spin system :

Suppose M_A and M_X are the z-magnetizations of the spins A and X respectively,

Related to populations P_1 to P_4 as follows:



$$M_A = \frac{1}{2} [P_1 + P_2 - P_3 - P_4]$$

$$M_X = \frac{1}{2} [P_1 + P_3 - P_2 - P_4]$$

We define equilibrium magnetizations M_A^0 and M_X^0 as,

$$M_A^0 = P_1^0 + P_2^0 - P_3^0 - P_4^0$$

$$M_X^0 = P_1^0 - P_2^0 + P_3^0 - P_4^0$$

Then the rate of change of magnetizations M_A and M_X of A and X spins

$$\frac{dM_A}{dt} = -(2W_1^A + W_0 + W_2)(M_A - M_A^0) + (W_2 - W_0)(M_X - M_X^0)$$

$$\frac{dM_X}{dt} = -(2W_1^X + W_0 + W_2)(M_X - M_X^0) + (W_2 - W_0)(M_A - M_A^0)$$

So now, we can define the equilibrium magnetization that is actually M_A^0 and M_X^0 . So this is equilibrium magnetization for A spin and this is for X spin, so as we said the magnetization depends upon what is the population in different state in the equilibrium state. So that will give us the equilibrium magnetization of A spin. So here, if you look at what actually it is in a simple term. It has a population

$$M_A^0 = P_1^0 + P_2^0 - P_3^0 - P_4^0$$

So two of these states minus two of these state will give you equilibrium magnetization for A spin. Similarly, one can write for X spin. So A transition are this and this, X transition for this

and this. So we just need to take the difference appropriately. So that we can get so for P_I this is the case, so here and here that is the transition happening and if we go back one can see

$$M_X^0 = P_1^0 - P_2^0 + P_3^0 - P_4^0$$

So then rate of change of magnetization, one can write it with time. So for A spin M_A and for X spin M_X , one can find it out by putting all these equilibrium magnetization, so here $2\omega_1^A$. That is transition probability for A spin plus zero quantum transition probability plus double quantum transition probability and that is difference of magnetization for A spin at any time t minus equilibrium population and that is added with the double quantum transition minus the quantum transition and the difference in the magnetization of X spin.

So similarly, one can write it for X spin, one can find it out, this will be the like with transition probability this is the magnetization. So now here, one can find the rate of change of magnetization for both spin A spin and X spin. So then let us simplify this complex equation.

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We define equilibrium magnetizations M_A^0 and M_X^0 as,

$$M_A^0 = P_1^0 + P_2^0 - P_3^0 - P_4^0$$

$$M_X^0 = P_1^0 - P_2^0 + P_3^0 - P_4^0$$

Then the rate of change of magnetizations M_A and M_X of A and X spins

$$\frac{dM_A}{dt} = -(2W_1^A + W_0 + W_2)(M_A - M_A^0) + (W_2 - W_0)(M_X - M_X^0)$$

$$\frac{dM_X}{dt} = -(2W_1^X + W_0 + W_2)(M_X - M_X^0) + (W_2 - W_0)(M_A - M_A^0)$$


Let us define further,

$$\rho_A = (2W_1^A + W_0 + W_2)$$

$$\rho_X = (2W_1^X + W_0 + W_2)$$

$$\sigma_{AX} = W_2 - W_0$$

Then we obtain

$$\frac{dM_A}{dt} = -\rho_A(M_A - M_A^0) - \sigma_{AX}(M_X - M_X^0)$$

$$\frac{dM_X}{dt} = -\rho_X(M_X - M_X^0) - \sigma_{AX}(M_A - M_A^0)$$

The entities ρ_A and ρ_X are called **auto-relaxation rates** of the spins A and X

σ_{AX} is called the **cross-relaxation rate** between the two spins

We can write a generalized equation in matrix form

$$\frac{dm}{dt} = -\underline{R}m$$

Here m is a column vector representing the deviations in the Magnetisations from equilibrium values and

R is a matrix of relaxation rates called the **relaxation matrix**

For two spins like AX

$$m = \begin{pmatrix} (M_A - M_A^0) \\ (M_X - M_X^0) \end{pmatrix}$$

$$R = \begin{pmatrix} \rho_A - \sigma_{AX} \\ \sigma_{AX} - \rho_X \end{pmatrix}$$

And for that lets define that here, sigma A one can write it this term, whole this term, one can write it, σ_A and σ_X we can write it whole these terms. So we can simplify and then define this σ , $\sigma_{AX} = \omega_2 - \omega_0$, that is double quantum transition minus zero quantum transition. So if we define this, then the previous equation that we had simply going little bit of algebraic representation.

We can simplify this equation. So rate of change of magnetization of A spin can be written like ρ_A . So if you look at the previously, here we have define this as a

$$\frac{dM_A}{dt} = -\rho_A(M_A - M_A^0) - \sigma_{AX}(M_X - M_X^0)$$

Similarly, for rate of change of magnetization of X spin one can write like this. So here we have

$$\frac{dM_X}{dt} = -\rho_X(M_X - M_X^0) - \sigma_{AX}(M_A - M_A^0)$$

So now, if you look at here what is happening? This is autocorrelation function because they are correlating with self. So A is correlating with A, so one can define entity this ρ_A and ρ_X are auto relaxation rate for spin A and spin X and this is called cross relaxation rate. Self-correlation means like it is correlating with itself, what was the magnetization or what was the population at time t with time $t + \Delta t$. But cross relaxation correlating with other spins. So that is what here is σ_X

So σ_X is called cross relaxation rate between two spins A spin and X spin. Then one can write actually a generalised equation for rate of change of magnetization, like this, we can write the dm with respect to the change of magnetization m with time, one can write for

$$\frac{dm}{dt} = -Rm$$

So R one can define R and m are basically here m is a column vector. So here like we can write here column vector and then vector representing deviation from the magnetization from the equilibrium values.

So like previously here, this is the M_A and one can write the R is a matrix of relaxation rates. So we call it either auto relaxation or cross relaxation rate. So we can write the magnetization product with the relaxation rate, like for two spin, one can write this

$$m = \begin{pmatrix} M_A - M_A^0 \\ M_X - M_X^0 \end{pmatrix}$$

$$R = \begin{pmatrix} \rho_A - \sigma_{AX} \\ \sigma_{AX} - \rho_X \end{pmatrix}$$

So that means the change of magnetization of any spin now, you can define in two terms, one is relaxation matrix term and then actually magnetization deviation in the magnetization from its equilibrium state. Okay, so if we can define that then we will generalize the equation what happens upon perturbation? How the population gets redistributed or in other term how magnetization value changes?

So if we can see that there, one can find it out what will be the case for steady-state NOE. So here in steady-state NOE what we were doing? We had two spin, one spin was A , other spin was X , one spin was saturated and we are looking at the effect of that saturation on the other spin.

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Steady state NOE

For steady state NOE, on spin X due to irradiation of spin A , we can set

$$\frac{dM_X}{dt} = 0; M_A = 0$$

We can write a generalized equation in matrix form

$$\frac{dm}{dt} = -\underline{R}m$$

Here m is a column vector representing the deviations in the Magnetisations from equilibrium values and R is a matrix of relaxation rates called the relaxation matrix

For two spins like AX

$$m = \begin{pmatrix} M_A - M_A^0 \\ M_X - M_X^0 \end{pmatrix}; \quad R = \begin{pmatrix} \rho_A - \sigma_{AX} \\ \sigma_{AX} - \rho_X \end{pmatrix}$$

Let us define further,

$$\rho_A = (2W_1^A + W_0 + W_2)$$

$$\rho_X = (2W_1^X + W_0 + W_2)$$

$$\sigma_{AX} = W_2 - W_0$$

Then we obtain

$$\frac{dM_A}{dt} = -\rho_A(M_A - M_A^0) - \sigma_{AX}(M_X - M_X^0)$$

$$\frac{dM_X}{dt} = -\rho_X(M_X - M_X^0) - \sigma_{AX}(M_A - M_A^0)$$

The entities ρ_A and ρ_X are called **auto-relaxation rates** of the spins A and X



σ_{AX} is called the **cross-relaxation rate** between the two spins

So now if we perturb one spin in the steady-state NOE, just to remind you we were doing experiments like this, we are saturating this, we are applying a pulse and looking at the response of that perturbation. So this is saturation pulse. So if we do that what is going to happen of magnetization of the spin? If you irradiates so for a steady-state NOE, if you spin X what is happening? Because of irradiation of spin A. That we are going to look at in detail using this generalised magnetization form that we had in few lectures.

So and how this gives rise to enhancement in the magnetization or reduction in the magnetization that actually results in the value of the positive NOE or negative NOE. So that is going to be topic for our next class. So I hope that you understood this and if you have a question, please come back this is little bit mathematical. So will go slowly and will try to develop the concept of origin of NOE in a more rigorous manner, more mathematical manner and will continue with steady-state NOE and transient NOE. How the enhancement comes because of perturbation of couple nuclei with X. Thank you very much.