Time Dependent Quantum Chemistry
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Lecture 43
Nonradiative Transition Part 3

Welcome back to module 7, we are discussing non-Adiabatic Transition Nonradiative Transition, they are synonymous, but we have not discussed this non-Adiabatic coupling yet we will do that in a later stage we are using non-Adiabatic coupling, the concept of non-Adiabatic coupling which is involved in Nonradiative Transition, and we have said that it is constant it does not depend on time, that is why, but this is coupling two states which will undergo the Nonradiative Transition.

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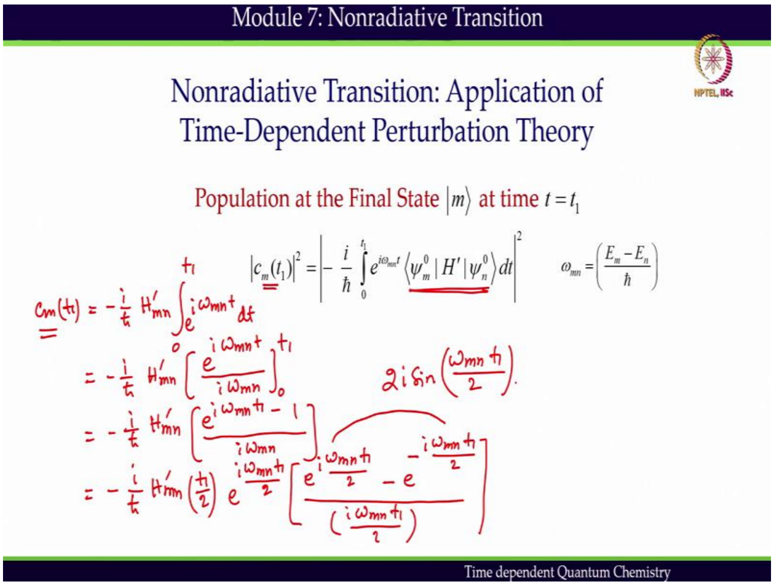

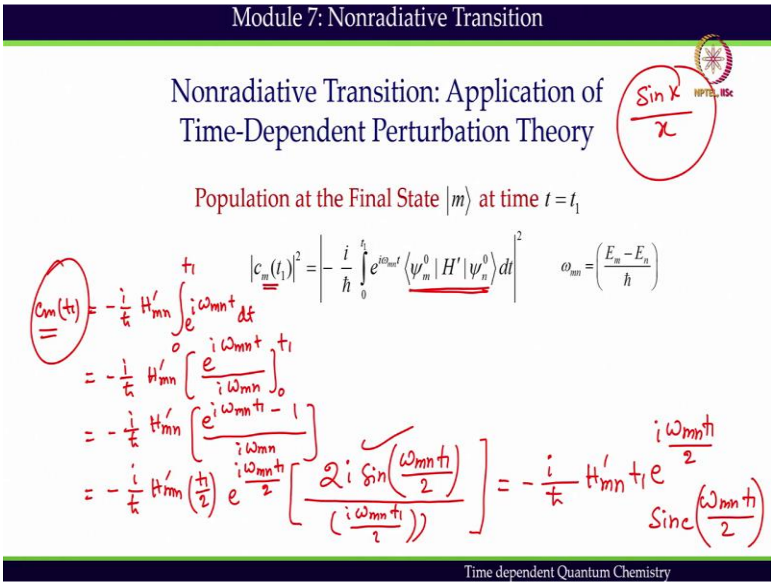

So, what we have seen so, far is that, this part is a Time Independent part and that is why it can be taken out of the integration. So, I can write it down directly like this way,

$$c_m(t_1) = -\frac{2\pi i}{h}\int_0^{t_1} e^{i\omega_{mn}t}\,dt$$

So, if we if we integrate this one, what I get is here

$$c_m(t_1) = -\frac{2\pi i}{h}H'_{mn}[\frac{e^{i\omega_{mn}t_1}}{i\omega_{mn}} - \frac{1}{i\omega_{mn}}]$$

0 to t_1 time is that t_1 time is the n time for the interaction immediately after the interaction we are trying to find out what is the c_m because from c_m I will be able to get the population at the m th state the final state.

So, but this one I can write down as

$$c_m(t_1) = -\frac{2\pi i}{h}H'_{mn}[\frac{e^{i\omega_{mn}t_1} - 1}{i\omega_{mn}}]$$

If I use the limits and little bit trick will make here to get a convenient form of this expression,

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$$c_m(t_1) = -\frac{2\pi i}{h}H'_{mn}\frac{t_1}{2}e^{\frac{i\omega_{mn}t_1}{2}}[\frac{e^{\frac{i\omega_{mn}t_1}{2}} - e^{\frac{-i\omega_{mn}t_1}{2}}}{\frac{i\omega_{mn}t_1}{2}}]$$

So, what we see here is that this part $[e^{\frac{i\omega_{mn}t_1}{2}} - e^{\frac{-i\omega_{mn}t_1}{2}}]$ can be written as the $2i\sin\frac{\omega_{mn}t_1}{2}$. So, I will erase this part and we will just write down $2i\sin\frac{\omega_{mn}t_1}{2}$.

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So, as a result finally what I get here from here is that we can simplify it further and we can write down this is nothing but

$$c_m(t_1) = -\frac{2\pi i}{h}H'_{mn}\frac{t_1}{2}e^{\frac{i\omega_{mn}t_1}{2}}[\frac{2i\sin\frac{\omega_{mn}t_1}{2}}{\frac{i\omega_{mn}t_1}{2}}] == -\frac{2\pi i}{h}H'_{mn}t_1 e^{\frac{i\omega_{mn}t_1}{2}}sinc(\frac{\omega_{mn}t_1}{2})$$

that is the final form of $c_m(t_1)$ we get and once we get this, this Cardinal sin function is Cardinal sin function is nothing but it is a sin x/x. So, that is exactly what we have this is sin part here and then the another part this x part is here.

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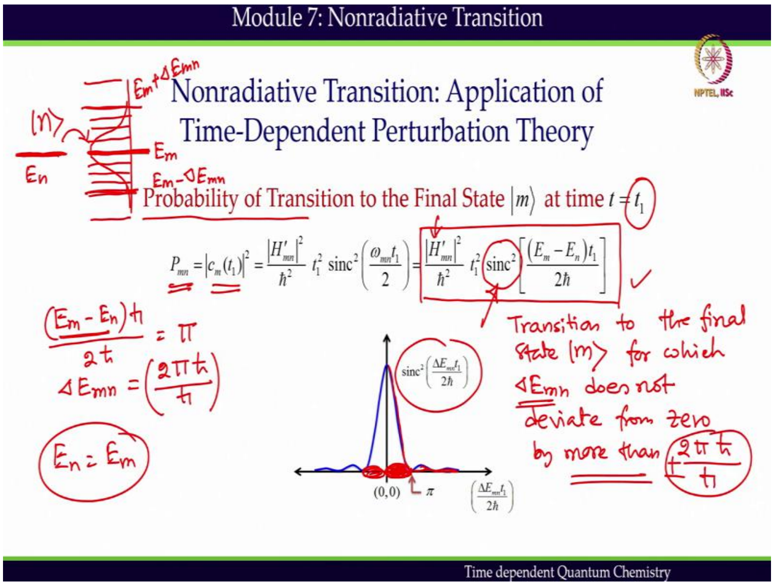

So, Cardinal sin function, we are using to express this population. So, finally we have to consider the square magnitude the square of the absolute value of the C_m and we take the square of it, and if we take the square of it finally, we get this expression for the population at the m th state. So, we started with |n> state discrete state and interaction was on for t1 time and we are trying to find out what is the population and the final state.

So, the population at the final state immediately after time t_1, when the process of interaction between two states switched off represents the probability of transition from initial state to the final state. So, probability of transition is nothing but how much population in the final state because the probability of being in state |m> is the probability of transition from state |n> to state |m> due to the constant perturbation. This part is not time dependent this is time independent.

Therefore, the probability of transition from initial state to the final state is given by this and if we look at this Cardinal sin function, this function is actually is a very sharp function it says exhibits are very sharp peak with a width and here width when I say width, I will not use this full width half max generally we use this full width of maths, but I will say when the function becomes 0.

So, this is the width we are saying and this width would be when this $\frac{\pi(E_m - E_n)t_1}{h} = \pi$, then the function value becomes 0 and we are defining this is to be the width. So, if we have and then later there are some oscillation, but these are very low magnitude there is almost nothing so, you can say that this is a very sharp function sharp peak and then almost there is nothing.

So, that is why we are saying that this is the this particular region is the is defining the width of them have this this function cardinal sin function and if it is so, then I can write down this difference in the energy the energy difference between the initial and final state as

$$\Delta E_{mn} = \frac{\pi}{t_1}$$

So, what it suggest? It suggests that transition to the final state |m> it suggests that transition to the final state |m> for which ΔE_{mn} difference between these energy states this energy and this energy 2 state energy difference does not deviate from 0 by more than $\frac{\pi}{t_1}$ this value if it is deviating, then this value, then this function will become 0, this cardinal sin function becomes 0 and that is why population becomes 0.

So, what it suggests is suggest that I can have an population transfer from |n> state initial state to the final state only if this final state energy has to be within this width plus minus width. So, if this is the energy of E_m, then both side is possible this side and also this side is also possible this side. So, I have I will draw it like this way, let us say this is the allowed energy states. So, I cannot go beyond this energy spacing.

So, population transfer can only possible bit from initial state to the final state if the final state energy stays within this $E_m - \Delta E_{mn}$ or $E_m + \Delta E_{mn}$ within this state where we are assuming that E_n equals E_m. So, all these possible states can be populated with a varying population but it can be populated, but if the states are here or states or here it cannot be populated because it is going beyond the allowed energy spacing which will which will control which will be controlled by this cardinal sin function for this population in the final state.

So, bottom line what we have learned from this exercise that is that a transfer of population known as nonradiative transfer of population from initial state to the final state is possible only when if the final state energy a difference ΔE_{mn} does not deviate from 0 by more than this value this is going to be plus minus both values are possible. So, all those states are will be populated if they are within this energy bandwidth.

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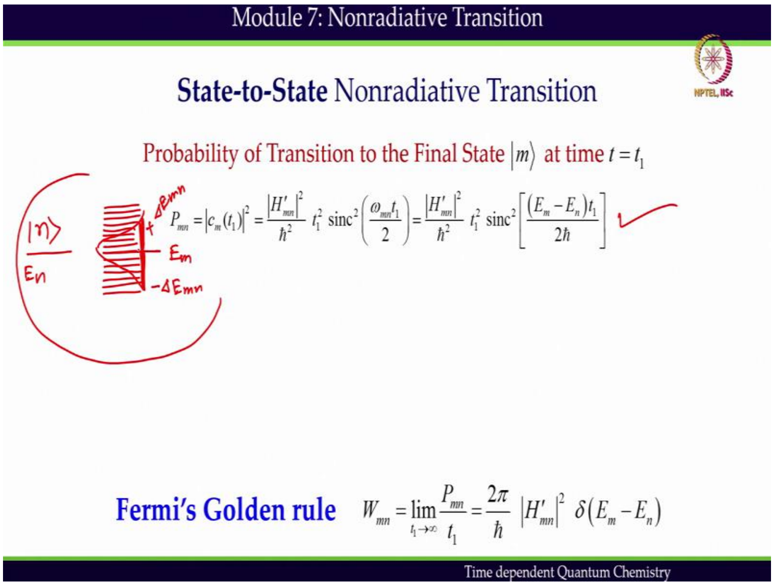

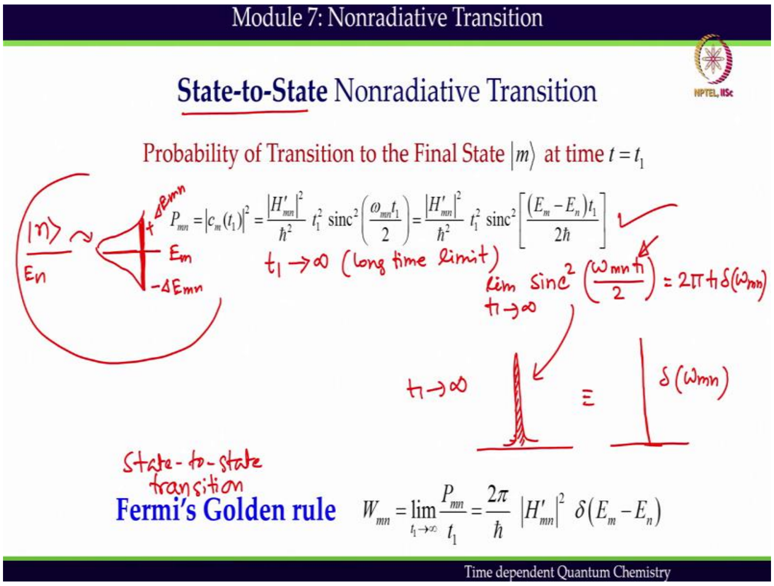

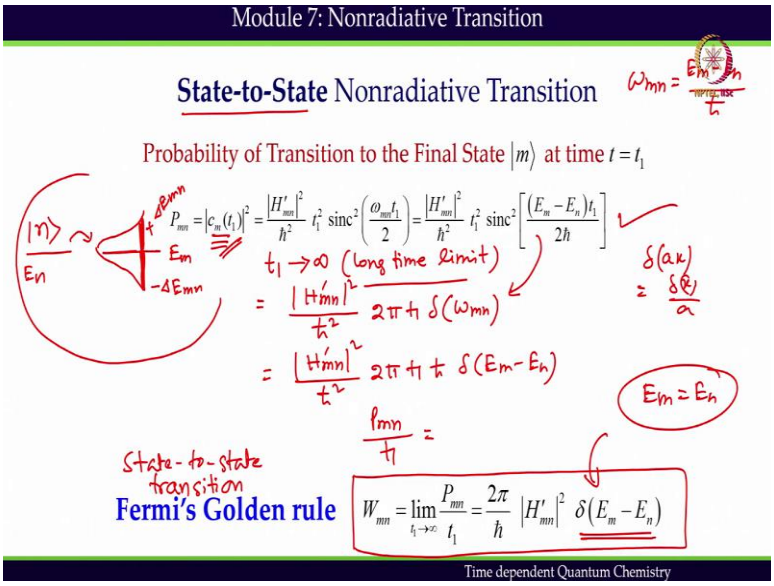

So, what we have noticed that the transition from initial state |n> may occur towards all possible final states whose energy E_m is located in the energy bandwidth of this. So, I have this |n state and then I may have many other states here as the final states, but only those states which are within this bandwidth. So, this is if it is E_n energy, then the same energy would be Em and then I will have this is - ΔE_{mn} and this is + ΔE_{mn} they have to be within this bandwidth.

But it may so happen I mean this is call allowed according to this equation all possible allowed transitions under this nonradiative process is this but if I have a situation where I really do not have these many states even within the bandwidth. So, I do not have all the states let us say I have only 1 state, if I have 1 state available within the allowed bandwidth, then what will happen it is called it is going to be then state to state transition.

So, I will have a state to state transition, because I do not have many final states and within this state to state transition if the straight state to state transition is going on, then one can say that I can take one particular limit this is a mathematical limit we are taking t_1 tends to let us say infinity, what does it mean it means that I am allowing the system to be to interact for a long time. So, it is it means that I am using the long-time limit t_1 is the interaction time 0 to t1 is the interaction time.

So, we are allowing the system to interact for a long time and if it is long time, then one can write down this

$$\lim_{t_1 \to \infty} sinc^2\left(\frac{\omega_{mn} t_1}{2}\right) = 2\pi t_1 \delta(\omega_{mn})$$

So, this is a definition of a delta function I had a very sharp.

So, basic idea is that this this function is a very sharp function this Cardinal sin function and at that infinite t limit which means very very long t_1 is very very long, then what happens this sharply peak function Cardinal sin function adopts the Dirrac delta function in the limit that the peak height of the sharply peaked function becomes infinite.

So, this becomes like this with 0 width is a delta function in the limit of this t tends to infinity which means the area under the carve will go 0 because it is now for the long time and it becoming the height would be infinite and it be it behaves like a delta function $\delta(\omega_{mn})$. So, within this limit within this long-time limit, this entire population in the |m> th state can be written as follows, one can write down as follows, this is going to be then.

$$P_{mn} = \frac{4\pi^2 {H'_{mn}}^2}{h^2} 2\pi t_1 \delta(\omega_{mn})$$

So, this function is becoming a delta function for a long-time limit and this is a property of delta function which is $\delta(ax) = \frac{\delta(x)}{a}$. So, because

$$\omega_{mn} = 2\pi \frac{E_m - E_n}{h}$$

We Will be able to write down this as follows. This is going to be then

$$P_{mn} = \frac{4\pi^2 {H'_{mn}}^2}{h^2} h t_1 \delta(E_m - E_n)$$

what I get here.

So, rate of transition, so this is the population at the |m> th state. This is the population at the |m> th state and the rate of transition if we try to find out the rate of transition that is going to be

$$\frac{P_{mn}}{t_1} = W_{mn} = \frac{4\pi^2 {H'_{mn}}^2}{h} \delta(E_m - E_n)$$

So, what we get here is that presence of a delta function in this equation, this delta function in this equation it means that this function will have a finite value finite positive value whenever you have E_m equals E_n. If they are not equal then this entire value becomes 0.

So, presence of a delta function in this equation mandates the fact that in the limit t tends to infinity which is the long-time limit only transition which will be allowed is the one for which the initial and final state must be equal. So, this must be equal otherwise the transition will not be allowed because delta function will be 0 for every other state, this requirement is serendipitously fulfilled by certain electronically excited states of helium and neon in He-Ne laser.

So, in He-Ne laser we have seen that this helium excited state and neon excited state they are coinciding with each other they should have the same energy and then only this helium can transfer energy it can it can deexcite and the entire energy can be given to excite a helium sorry neon ground state system to the excited state system. This equation is called Fermi's

Golden rule of State to State Nonradiative Transition, where we have this involvement of the delta function.

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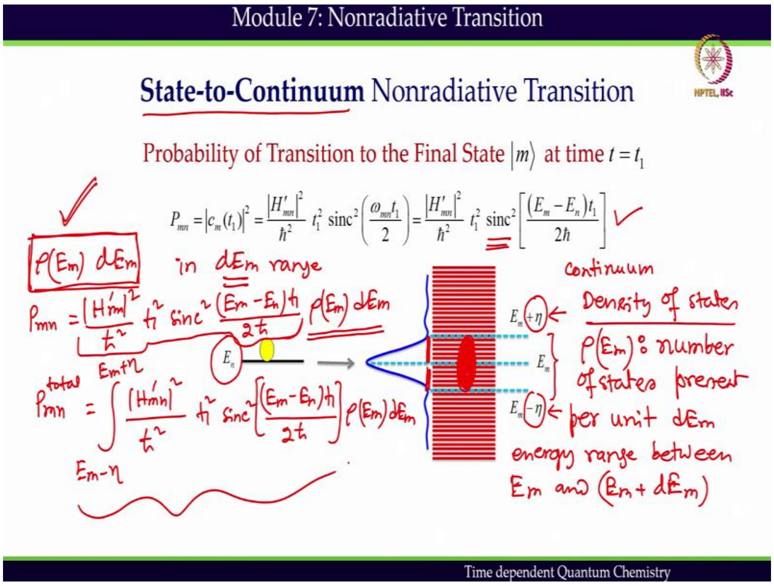

We will now move forward to the State to Continuum Nonradiative Transition, in the State to Continuum Nonradiative Transition our starting point again this population in the |m> th state which is defined by this cardinal sin function square function, this is a very sharp function and the concept again has been depicted here as you can see that this state can transfer population to the to a number of states possibly number of states if they are available, but within the band within the energy bandwidth.

So, this is the definition of the bandwidth we have given this bandwidth is ΔE within this bandwidth plus minus, So, this is $+\Delta E$ and this part is $-\Delta E$ that is given by E this η plus minus η. So, several final states are available if they are available, then the allowed bandwidth the bandwidth of this transition which is controlled by this cardinal sin function will allow the transition to happen from initial discrete initial state to the number of final states.

And if the final states are so closely spaced in energy, they can form the Continuum they may look like a Continuum and if it is Continuum, if you are dealing with Continuum then we have to make use of a quantity called Density of States, because we do not have one state we have multiple states and when you have many states together very closely spaced together then often we use this quantity called Density of states.

Density of states $\rho(E_m)$ at a particular energy level it is defined by number of states number of states present per unit energy range between E_m and E_m+dEm. So, within this range within this interval per unit range how many states I have that is called Density of states. So, in that case this $\rho(E_m)dE_m$ will represent the number of states present in the dE_m range.

And we have already realized that, so, this is the number of states present in this range dE_m range and for each state the probability of transition is given by.

$$P_{mn} = \frac{4\pi^2 {H'_{mn}}^2}{h^2} 2\pi t_1 sinc^2 \frac{\pi(E_m - E_n)t_1}{h}$$

This is the probability of transition to each state. And we have this many states that is why total transition probability would be for transferring the population to this many states will have $\rho(E_m)$multiplied by $\rho(E_m)dE_m$.

$$P_{mn} = \frac{4\pi^2 {H'_{mn}}^2}{h^2} 2\pi t_1 sinc^2 \frac{\pi(E_m - E_n)t_1}{h} \rho(E_m)dE_m$$

So, this is the total probability of transition from to these many states. And if we say that the Raditionalist Transition occurs from an initial state to a group of final states, whose energy E_m lies within an energy interval from $E_m+\eta$ to E_m $-\eta$, in that case, the total probability total probability will be given by this integration,

$$P_{mn}{}^{total} = \int_{E_m-\eta}^{E_m+\eta} \frac{4\pi^2 {H'_{mn}}^2}{h^2} 2\pi t_1 sinc^2 \frac{\pi(E_m - E_n)t_1}{h} \rho(E_m)dE_m$$

So, we are integrating the contribution coming entirely from this region, this energy space, all the contributions were calculating. So, each one each state probability of transition is given by this part, only this part. Then we are multiplying by this because this is the number of states I have within this energy range. And in the end, I am just integrating the total contribution.

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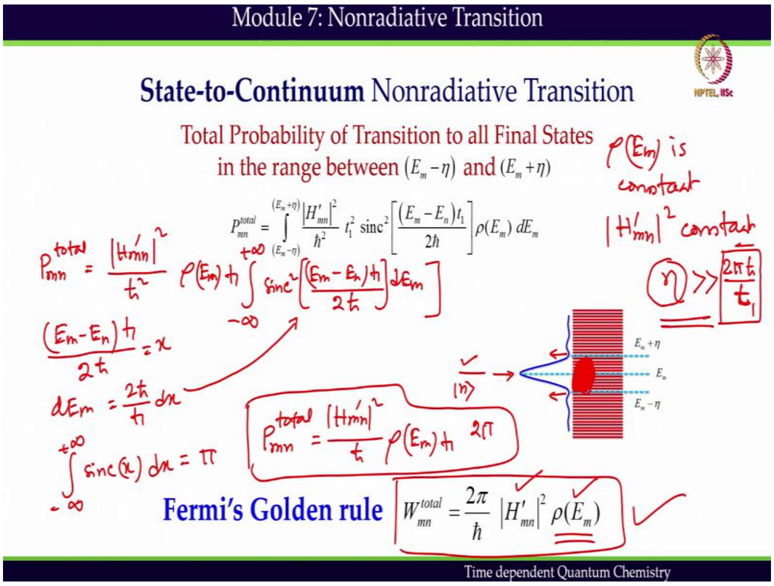

So, if we if we do that, then then what will happen? Here we can assume that for each state, so, I had an |n> state here, and it is transferring the population within this entire interval.

Within this entire interval I am transferring the population when I am transferring the population will assume that for each state transition, I will consider that the density of states this $\rho(E_m)$ is constant, to make the mathematical derivation simple. Density of states will be constant and will say that H'_{mn} this coupling term is also constant.

So, for each state final state density of states is constant and coupling constant and that… So, if it is constant, then we can take them out of the integration and if we do that, then finally this integration becomes

$$P_{mn}{}^{total} = \frac{4\pi^2 {H'_{mn}}^2}{h^2} 2\pi t_1^2 \int_{E_m-\eta}^{E_m+\eta} sinc^2 \frac{\pi(E_m - E_n)t_1}{h} \rho(E_m) dE_m$$

So, just an integration between these two and we have already understood that non-radiative transition may occur from an initial state ׀n to those final states whose energy E_m is located within this energy bandwidth, that is exactly what we have already understood. So, one way to further reduce this equation is to assume that $\eta \gg \frac{h}{t_1}$, what does it mean? It means that the number of available states it showing that number of available states. So, η is controlling how many states I am going to integrate and this part is controlling how many states I have available.

So, this condition suggests that the available number of states are significantly greater than the required final states within this energy bandwidth. So, this bandwidth which is plus minus this value this ΔE_{mn} value this is given by h/t_1. So, what we are saying is that number of states here as depicted here number of states are much larger than the required bandwidth for this transition and if this is so, then one can assume that this integration can be considered to be from minus infinity to plus infinity within this limit.

So, if I have states which are available, available states is much larger than the states where I can transfer the population. If it is so, then I can transform this integration within the limit of minus infinity to plus infinity, because if we do that, then very easily we can calculate this this integration it is because I can assume that

$$\frac{\pi(E_m - E_n)t_1}{h} = x$$

And in that case, I can write down

$$dE_m = \frac{h}{t_1} dx$$

I can plug that in here.

And I will be able to reduce it in a following way, I can use the standard integral, a standard integral for the cardinal sin function is follows

$$\int_{-\infty}^{+\infty} sinc(x)dx = \pi$$

So, we will use the standard integral. And if we do that, then total probability

$$P_{mn}{}^{total} = \frac{4\pi^2 {H'_{mn}}^2}{h^2} 2\pi t_1^2 \, \rho(E_m)\frac{h}{t_1}$$

So, we get this t_1 will be cancelling each other. So, I get these h will be cancelling each other. So, I get finally, this is what we get

$$P_{mn}{}^{total} = \frac{4\pi^2 {H'_{mn}}^2}{h} 2\pi t_1 \, \rho(E_m)$$

And as a result, the rate of transition will be given by this equation.

$$W_{mn}^{total} = \frac{4\pi^2 {H'_{mn}}^2}{h} 2\pi \, \rho(E_m)$$

So, what we see here is that this equation is quite similar to State-to-State transition except for the fact that here I have density of states. And their I have for the State-to-State transition I had this for delta function.

But we remind here is that this this rule Fermi's Golden rule for the state to Continuum transition, the derivation has been gone under the assumption that I have available states much larger than where I can transport the population. So, within this limit, I will be able to get this. So, there are two rules we have found already. And these two rules are suggesting that the transition rate will depend on density of states and the coupling strength.

If the coupling strength is strong, then transition rates would be high and if the coupling strength is weak, then transition will be transition rates will be low, how fast the energy population can be transferred from the initial state to the final state. We will stop here and we will continue the session in the in the next class.