Quantum Mechanics and Molecular Spectroscopy
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Lecture – 15
Absorption Probability

Welcome to lecture number 15 of the course quantum mechanics and molecular spectroscopy. As usual, we will have a quick recap of the previous lecture and continue with the present lecture.

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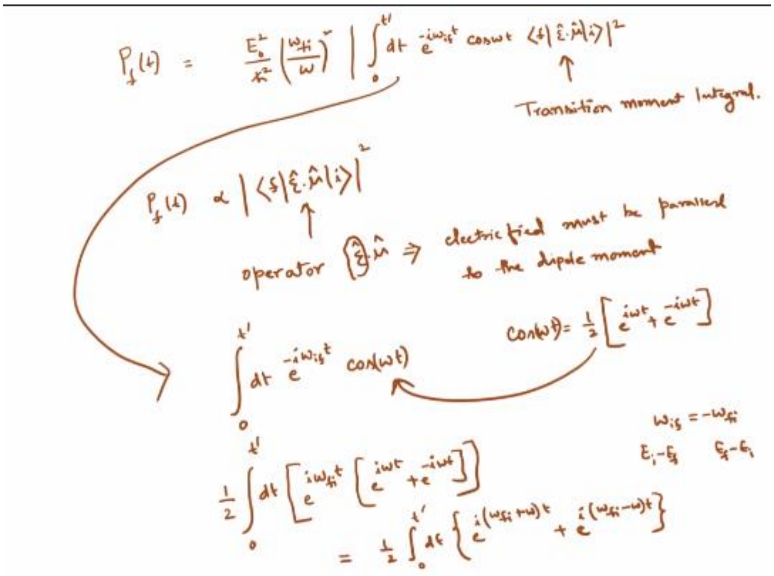

In the last lecture, we looked at the transition probability to state f and this was given by E0 square by h bar square omega fi by omega square modulus of integral 0 to t prime dt e to the power of –i omega if t Cos omega t f dot mu i square, yeah so this is the integral and this I told you is the transition moment integral. So, one can think of P of t to be proportional to the square of the transition moment integral okay.

And in the transition moment integral, the operator says, E dot mu says that the dipole moment of the molecule or the atom okay, by the way dipole moment is not same as the permanent dipole moment okay mu0, dipole moment of the molecule and epsilon, this is epsilon is nothing but your electric field. So electric field must be parallel to the dipole moment or at least should have some projection, it cannot be perpendicular okay.

Now, I take the other, so apart from that there is this integral in this okay. That integral is 0 to t prime dt e to the power of –i omega if t Cos omega t. I am going to manipulate this integral little bit. Now we know that Cos omega t = half of e to the power of i omega t + e to the power of –i omega t. So if I substitute that in here, then what I will get is 0 to t prim dt, I will write two, so I will take the half outside.

This is nothing but e to the power of, now omega if = – omega fi. This is nothing but Ei – Ef and this is nothing but Ef – Ei so that is just a reverse of sign, omega f and omega fi. So this can be written as into e to the power of i omega t + e to the power of –i omega t okay. So this will be nothing but half of 0 to t prime dt, then you will have 2 into e to the power of i omega fi + omega into t + e to the power of i omega fi –omega into t okay, so that is the integral.

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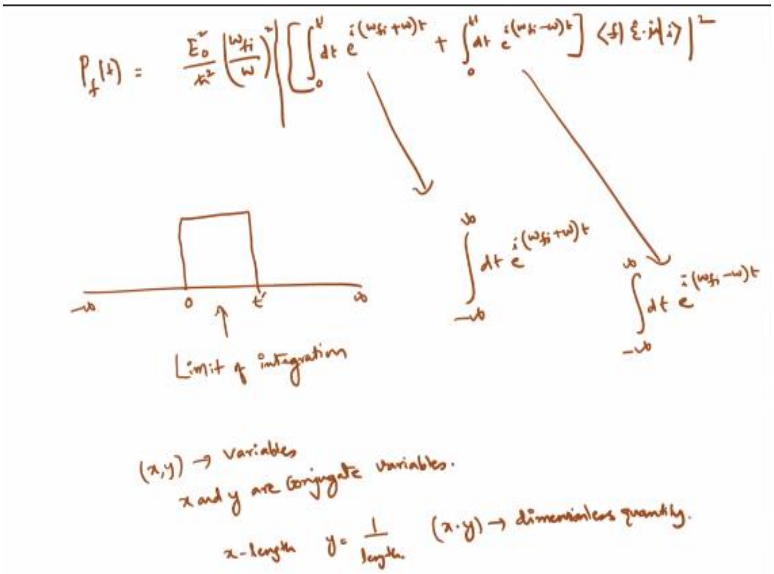

So expanding or continuing what we have P of f of t = E0 square by h bar square omega fi by omega whole square to modulus of integral dt 0 to t prime e to the power of i omega fi + omega t + 0 to t prime dt e to the power of i omega fi – omega t integral f E dot mu i whole square. Now the question is what does it say? It says that the omega or the electromagnetic field acts from time 0 to time t prime okay.

So think of it like this, so there is some perturbation, time-dependent perturbation that starts at 0 okay and ends at t prime, so 0 to t prime. So this is your limit of integration, so this will is nothing but your limit of integration okay, but if you consider the entire time of minus infinity to plus infinity okay, then what happens is from minus infinity to 0, there is no light, so there is no perturbation okay and similarly after t prime there is no perturbation.

So the effect of perturbation before t = 0 and after t = t prime is going to be non-existent. If that is non-existent, then without losing any physical concept, this integral can now be written as minus infinity to plus infinity dt e to the power of i omega fi + omega t and this integral can be written as integral dt minus infinity to plus infinity e to the power of i omega fi – omega t. Now, this is a case of adding zeros.

For example you want to know how much money you have in your bank within say some period of time okay, say first of a month to 15th of a month, but before that you neither you open the account on say first of the month and you have closed the account on 15th of the month and you want to know what is, but if I want to look at the entire time period before the first of the month, the previous month, and after 15th of that month okay you have the account is opened and closed.

So before the opening previous month and after 15th of month the money that account will have will have zeros, will add to zeros. So essentially, the entire transaction will try only between the first of the month to 15th of the month and transactions before that and transactions after that will not lead to any usefulness, so they are all zeros. So this is the similar scenario where you know the limit of integration is only between 0 and t prime.

But any extending the integration limits to minus infinity to plus infinity is like adding zeros and has no physical consequence except the fact that it turns out to be a standard integral okay. Now, one can write a standard integral between 2 variables let us say x and y okay such that x and y are conjugate. Now, what are conjugate variables? Variables that have inverse unit, so for example if x is length, then y will be 1 over length okay.

Such that product of x and y will give to dimensionless quantity okay, such variables are called conjugate variables. In quantum mechanics, x and momentum or position and momentum are conjugate variable, energy and time are conjugate variable and they are also related by the Schrodinger equation

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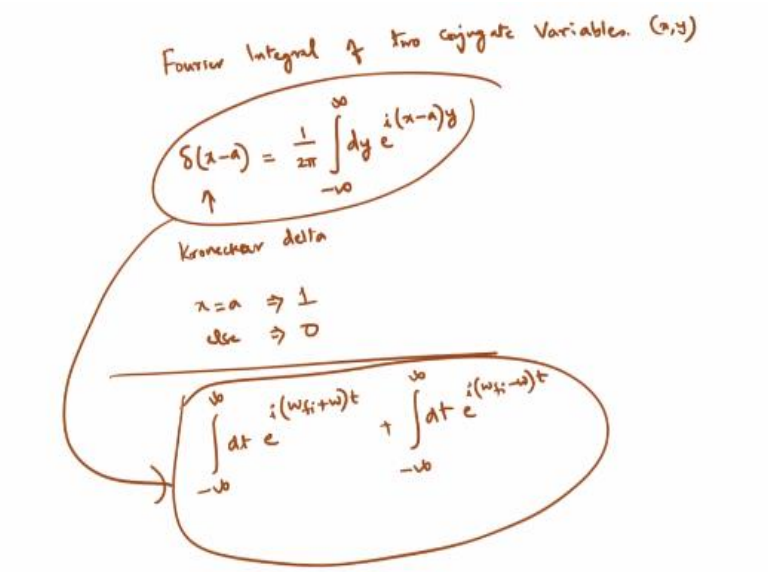

Now, one can write a Fourier integral of 2 conjugate variables, okay let us say x, y in such a way that x–a = 1 over 2 pi integral – infinity to + infinity dy e to the power of i to x–a y okay. Now, what is d? This is nothing but your Kronecker delta participant that means when x = a this will go to 1, else will go to 0 okay. Now let us look at the integrals that we had. What are the 2 integrals that we had in the previous case?

Those were minus infinity to plus infinity dt e to the power of i omega fi + omega t + – infinity to + infinity dt e to the power of i omega fi – omega t. Now you can look at these 2 integrals okay, you can compare this integral with these 2 integrals. They look very similar except the fact that the 2 pi is missing, but 2 pi can always be multiplied and divided.

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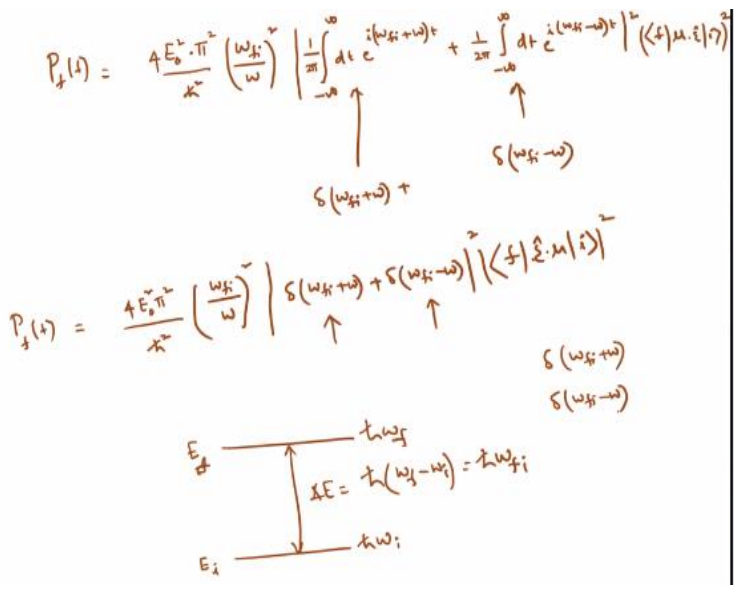

So if I do that, then Pf of t will become E0 square okay, so what I will do is I will multiply by pi square by h bar square omega fi by omega whole square modulus of integral dt 1 over 2 pi okay, sorry I will multiply it by 4 pi square okay, 1 over 2 pi dt – infinity to + infinity e to the power of i omega fi + omega t + 1 over 2 pi integral – infinity to + infinity dt e to the power of i omega fi –omega t square f mu dot epsilon i square okay.

Now if you have this, now look at this, this function can be written as del omega fi + omega and this function can be written as del omega fi – omega. So your P of t will now become four 4 E0 square pi square by h bar square omega fi by omega square modulus of del omega fi + omega + del omega fi – omega whole square f epsilon dot mu i whole square okay. So this is your probability of transition from state i to state f.

Now this involves 2 factors that are the Kronecker deltas, omega fi + omega and omega fi – omega. Now, let us consider a very simple scenario. The scenario is this okay, this is your Ei that will be nothing but h omega i and this is Ef this is the invert h bar omega f and this energy difference is delta E, this is equal to h bar into omega f – omega i, this is equal to h bar omega fi that is the energy separation.

So omega fi is nothing but the frequency of this energy separation okay. Now what is this, so which means in this case if you look at these, if you have del omega fi + omega and you have del omega fi – omega.

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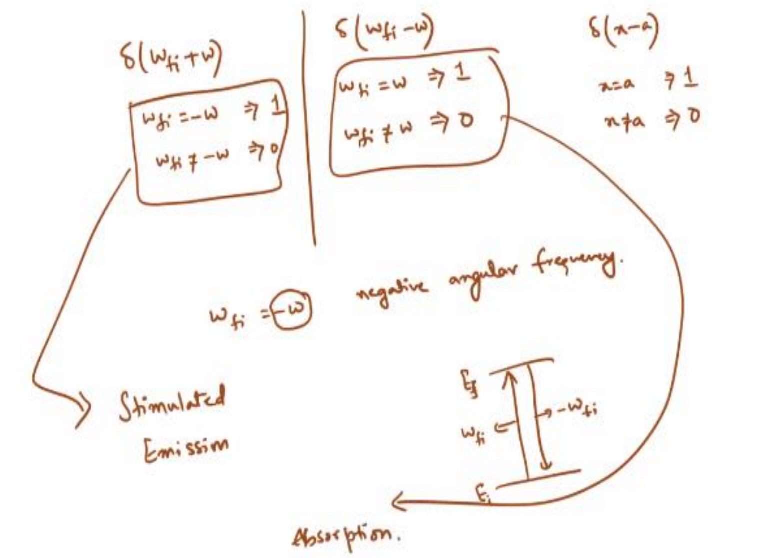

Del omega fi + omega, now remember we showed when you have del x–a okay. So this implies if x = a, then this function will go to 1 and x is not equal to a, this function will go to

0. If I apply the same principle omega fi + omega, this means when omega fi = – omega, this function will go to 1. When omega fi is not equal to– omega, this function will go to 0. Similarly if you have del omega fi – omega, then omega fi = omega, this function will go to 1.

And omega fi is not equal to omega this function will go to 0. Now there is one issue is that what is this condition? Omega is angular frequency, how can angular frequency be negative? Okay, so here I am looking at a condition omega fi = – omega okay, which means this has to be negative and negative angular frequency does not exist okay. One way to look at the negative angular frequency is emission of light when positive.

So which means when you go from top to bottom that is Ei to Ef one can think of the frequency to be positive and when you go down the frequency, so this will correspond to omega fi and this will correspond to – omega fi okay. So when the frequency negative simply means it is a case of stimulated emission. So this corresponds to stimulated and this will correspond to absorption okay.

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$$P_f(t) = \frac{4\pi^2 E_0^2}{\hbar^2}\left(\frac{\omega_{fi}}{\omega}\right)^2 \left|\underset{\text{Stimulated Emission}}{\delta(\omega_{fi}+\omega)} + \underset{\text{Absorption.}}{\delta(\omega_{fi}-\omega)}\right|^2 \left|\langle f|\hat{\varepsilon}\cdot\mu|i\rangle\right|^2$$

$$=$$

$$\boxed{\omega_{fi} = -\omega \qquad \omega_{fi} = \omega}$$

not simultaneously possible.

For absorption from initial state $|i\rangle$ to a final state $|f\rangle$

$$\boxed{P_f(t) = \frac{4\pi^2 E_0^2}{\hbar^2}\left(\frac{\omega_{fi}}{\omega}\right)^2 \left|\underset{\text{Kronecker delta}}{\delta(\omega_{fi}-\omega)}\right|^2 \underset{\text{TM1}}{\left|\langle f|\hat{\varepsilon}\cdot\mu|i\rangle\right|^2}}$$

Now, let us go back to our probability that is nothing but Pf of t = 4 pi square E0 square by h bar square omega fi by omega square modulus of, now there are 2 terms. So there are 2 terms, let me write down omega fi + omega + delta omega fi – omega square integral f epsilon dot mu i whole square okay. Now you look at there are 2 terms, this one and this. So I told you this is nothing but stimulated emission and this is nothing but absorption.

Now it turns out that it is not possible for omega fi to be positive of omega and omega fi to be negative of omega simultaneously okay. So omega fi can be equal to – omega and omega fi = omega is not simultaneous. That means stimulated emission and absorption cannot happen simultaneously, they have to happen one after the other okay. So in that case since they cannot happen simultaneously, you cannot have both the conditions.

You can have only one condition and if you are dealing with absorption, then this condition will happen and when you are dealing with stimulated emission this condition will be valid. So for absorption from initial state i to a final state f, the probability of this transition is equal to 4 pi square epsilon 0 square by h bar square omega fi by omega whole square del omega fi – omega whole square integral f epsilon dot mu i whole square okay.

So, this is the probability of transition for the absorption from an initial state i to a final state f okay. Now, there are several factors here, one is the transient moment integral TMI and then there is this Kronecker delta and then there is a ratio of omega fi to omega okay and many other factors are dependent, but this is the probability of transition and then we will look at this particular equation in the next lecture more carefully. I am going to stop it here and thank you very much.