Quantum Mechanics and Molecular Spectroscopy
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Lecture – 14
Transition Moment Integral

Hello, welcome to lecture number 14 of the course quantum mechanics and molecular spectroscopy. As usual, we will have a quick recap of contents of lecture number 13 before we proceed with the lecture number 14.

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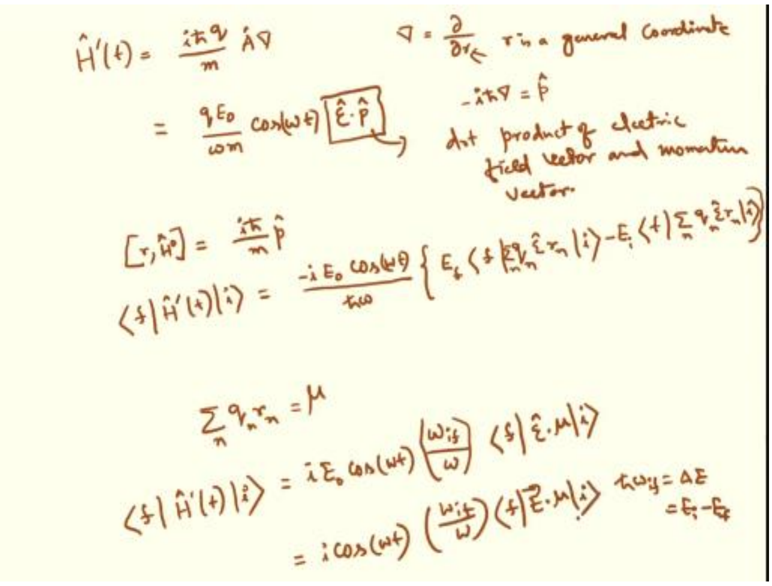

We started with the time-dependent perturbation and we showed that this was equal to ih bar q by m A del, where del is nothing but d by dr where r is general coordinate okay, it could be x, y, z or whatever okay. Now, this we could transform to q E0 by omega m Cos omega t E dot P okay because you should realize ih bar del – ih bar del is equal to operator P okay. So now what we are looking at is the dot product between the electric field vector and the momentum vector.

This is nothing but dot product electric field vector and momentum vector okay. That means for this to H prime t to be nonzero, the electric field and momentum should be in the same direction or should have you know projection onto each other okay. Now, we know that r, H0 commutator which I derived in the last class = ih bar by m P. So, one can replace this momentum operator by r, H0 okay.

Having all done, we come across this equation f H prime of t i, so all I am going to do is you know to do the relevant mathematics okay that I have done in the last lecture, you can look it up –i E0 R Cos omega t divided by h bar omega Ef f q sigma over n qn epsilon n rn i – Ei f sigma over n qn epsilon rn i, okay these are the integrals. Now, you could see that sigma over qn rn this is dipole moment of the molecule mu or the atom okay.

So this is just tells you how the charge is distributed okay. So, when we do that and do a little bit of rearrangement what you get is f H prime t i = E dot Cos omega t omega if by omega integral f mu i okay where h bar omega if = delta E = Ei – Ef okay. There is an Ef – Ei, but there is a negative sign, so I cannot cancel that okay, and there is an i here.

So, there is a ratio of omega if to omega and there is this integral okay and this slightly can be written as i Cos omega t omega if by omega, now E0 into E vector is going to give you electric field E, so f okay.

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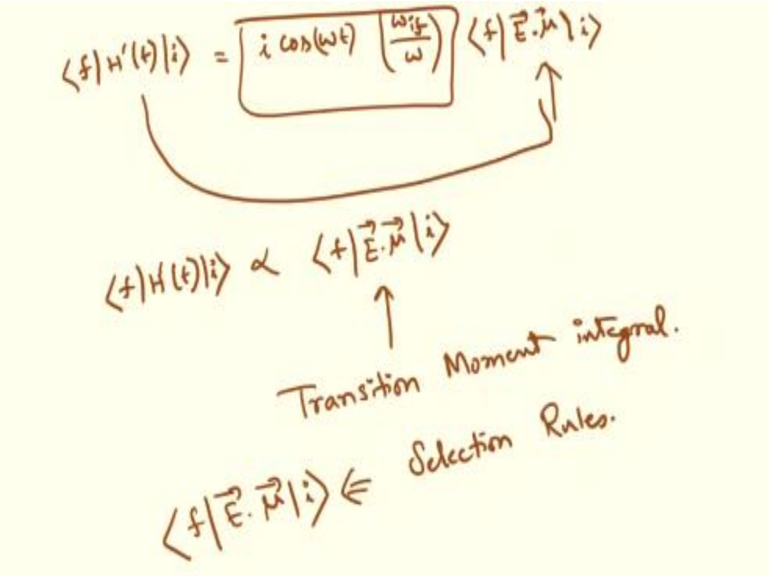

Now, your integral f H prime of t i will be equal to i Cos omega t omega if by omega integral f E dot mu, mu also is a vector by the way, the dipole moment is a vector i okay. So essentially you know if we leave out this okay, it depends on this integral. So, this integral has been transformed with some prefactor into this integral okay. So, you can think of it like this f H prime of t i is proportional to f E dot mu i okay and this moment integral is called transition moment integral okay.

So f E dot mu i okay is one of the most important integrals in spectroscopy, it is a transition moment integral and that will determine whether the transition will take place or not, if transition moment integral goes to 0, the selection rule is decided by this okay. Now let us give a simple example okay.

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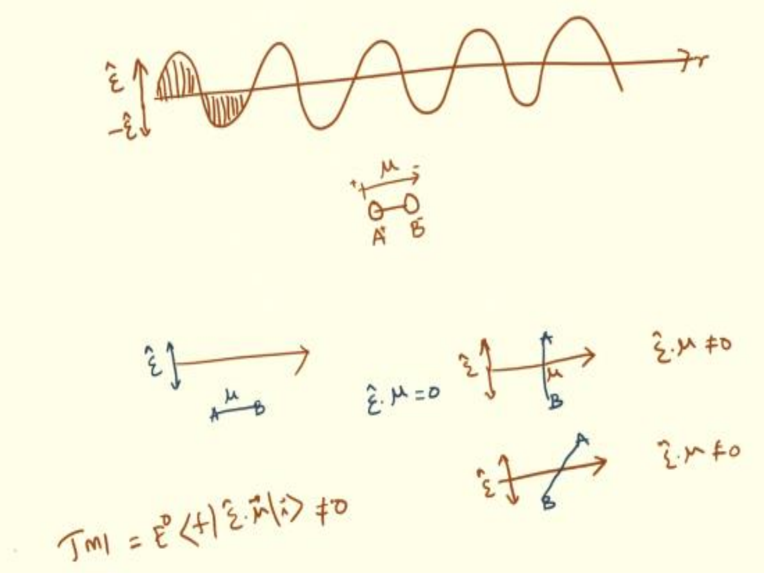

Let us suppose that there is an electromagnetic radiation which is going like that okay. So this is the direction of propagation r okay and your electric field vector E is along this okay. Of course, when it goes down, it becomes –E. So the electric field vector is going up and down okay in this direction E and E, so it changes sign. Now if you take a diatomic molecule, let us consider a single diatomic molecule AB okay.

Since the diatomic molecule is linear, the dipole moment is in this direction mu okay. So if you consider A as positive and B as negative that negative directions, so it is positive negative okay. So now, you can see that if the propagation direction is r and the dipole moment is along the r, so now think of it like this. So if your light is propagating like that, and your molecule AB is like that okay.

Now, what is the E? E is perpendicular. So, your epsilon dot, so this is your mu and this is director and your epsilon vector is like this okay, epsilon dot mu = 0 because the dipole moment of the molecule AB and your vector epsilon are perpendicular to each other. That means under the circumstances, the molecule will not absorb light or there will be no transition.

On the other hand if AB is like this, if you have AB like this and your propagation direction is like this okay and your electric field vector is like this okay. Now epsilon and mu are parallel to each other. So the dot product will be maximum, so this will be epsilon dot mu will be not equal to 0 or any direction that is has a projection, that means okay. So this will have some projection onto epsilon, even that case epsilon dot mu will not be equal to 0 okay.

That means the transient moment integral that is f okay E0, transient moment integral = E0 dot mu, this will become nonzero. So, which means if the dipole moment and epsilon the electric field should have projection onto each other, only then the transient moment integral will not go to 0. So, that tells you the direction in which the electric field vector and the dipole moment have to be aligned with respect to each other okay.

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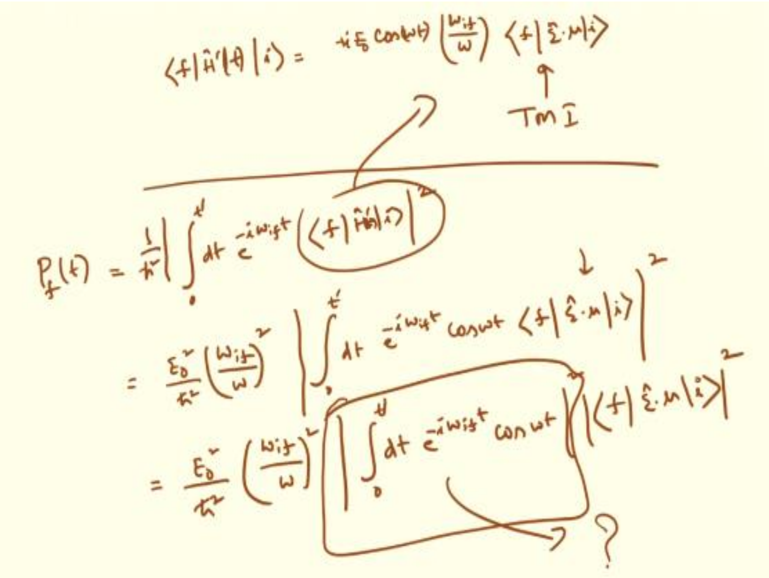

Now, so what we have is basically your f H prime t i = +i E0 Cos omega t omega if by omega integral f dot mu dot i. So, as I told you this is nothing but your transient moment integral okay and I also told you that the dipole moment and the electric field should have projection onto each other. They must be aligned. If they are perpendicular to each other, there will be no, the transient moment integral will go to 0 okay.

Now, there is another thing that you can do is that if you know, this is just a transition, but your transition probability Pf of t is given by 1 by h bar square integral of 0 to t prime dt e to the power of –i omega if t integral f H prime of t i whole square, but now we have evaluated this integral as this okay. So, this will be equal to E0 square by h bar square omega if by omega whole square 0 to t prime dt e to the power of minus –i omega if t Cos omega t integral f epsilon dot mu i whole square.

Now, this is the integral that does not involve time and this is the integral does involve, So, I can separate it out as 2 integrals. So, this is nothing but E0 square by h bar square omega if i omega square integral 0 to t prime dt e to the power of –i omega if t Cos omega t square into f epsilon dot mu i whole square okay. So, we will know how to evaluate this integral if you know e dot mu i operator and if you know the states f and i okay and these are just the pre factors.

So, now it comes to evaluating this integral, we do not know that okay. Now, let us look at that integral.

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$$\int_0^{t'} dt\, e^{-i\omega_{if}t}\cos\omega t$$

$$= \int_0^{t'} dt\, e^{-i\omega_{if}t}\frac{\left[e^{i\omega t}+e^{-i\omega t}\right]}{2} \qquad \omega_{if} = -\omega_{fi}$$

$$= \frac{1}{2}\int_0^{t'} dt\left[e^{i(\omega-\omega_{if})t} + e^{-i(\omega+\omega_{if})t}\right]$$

$$= \frac{1}{2}\int_0^{t'}\left[e^{i(\omega_{fi}+\omega)t} + e^{i(\omega_{fi}-\omega)t}\right]dt$$

$$= \frac{1}{2}\int_0^{t'} e^{i(\omega_{fi}+\omega)t}\,dt + \frac{1}{2}\int_0^{t'} e^{i(\omega_{fi}-\omega)t}\,dt$$

So, the integral 0 to t dt e to the power of –i omega if t Cos omega t is something that I need to evaluate okay. Now, this integral this is equal to 0 to t prime dt e to the power of –i omega if t Cos omega t, Cos omega t can always be written as e to the power of i omega t + e to the power of –i omega t by 2, is not it, Cos theta definition is that okay e to the power of i theta + to the power of –i theta by 2.

Now, if I slightly rearrange, this equation will become 0 to t prime dt e to the power of, if I take i common then I get omega – omega if t okay + e to the power –i, if I take minus common, then I will get omega + omega if t and there is a half outside, I will get 2 integrals. Now, I am going to slightly rearrange this. So, this is called half integrals 0 to t prime, so omega if so this will become e to the power of i omega fi + omega t to + e to the power of okay.

Now this omega fi it will become – omega fi and I can take –ei from outside, so it will become i into omega fi – omega t dt okay. So, I have these 2 equations now, so which means I have this is equal to there are 2 integrals, integrals 0 to t prime e to the power of i omega fi + omega t dt + half integral 0 to t prime e to the power of i omega fi – omega t dt okay.

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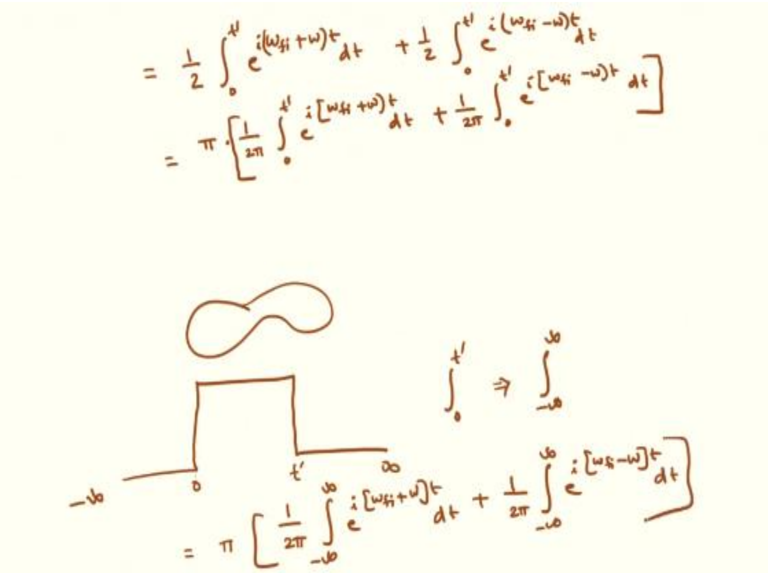

So, this is our next step, half of integrals 0 to t prime e to the power of i omega fi + omega t dt + half integrals 0 to t prime e to the power of i omega fi – omega t dt okay. Now what I will do is I will multiply pi and divide by pi for both of them. So, this is equal to pi into 1 by 2 pi integral 0 to t prime e to the power of i omega fi + omega t dt + 1 over 2 pi 0 to t prime e to the power of i omega fi – omega t dt okay.

Now, I will make a small mathematical trick. Let us suppose you have some atom or a molecule, some system okay. So let us say some atom or a molecule and at time t = 0 you switch on the light okay and at time t = t prime you switch off the light. So, what you do is that you start switching on the light and then at time t = t prime, so this is 0 and this is t prime.

So, you switch on the perturbation at time t = 0 and switch off the perturbation at time t = is equal to t prime and you will see now this will be minus infinity and this will be plus infinity okay. Once the perturbation is switched off or not switched on okay, the perturbation does not really add, that means instead of integrating over from 0 to t because then what happens here it is all zeros, no perturbation.

So which means if you have no perturbation, it does not add the integral. So which means instead of 0 to t prime as your definite integral ends okay, you can write it as minus infinity to plus infinity. Even though it is from minus infinity to plus infinity, the actual region in which the light adds or the light acts on the molecule is only 0 to t prime, rest of the time you are just adding zeros okay, so it does not really matter okay.

So, I want to make this transformation. It will not change any physical principle, however, it will reduce these equation to some standard integrals. So when I have done that, then I can write it as pi to 1 over 2 pi minus infinity to plus infinity e to the power of i omega fi + omega into t dt + 1 over 2 pi integral minus infinity to plus infinity e to the power of i omega fi – omega t dt okay.

So what I have done is I have just change the limits of your integral instead of going from 0 to P prime, I have taken from minus infinity plus infinity okay. Minus infinity to 0, there is no light acting on it okay, so the contribution to that integral is essentially 0, but after t prime to infinity again there is no light, so the contribution to the integral from t prime to infinity will also be 0.

So, essentially what you are doing you are adding lot more zeros and the number is not going to change by adding zeros, but this transformation or this simple mathematical trick allows you to get to a standard integral okay. So this is our integral that we need to evaluate okay. So, I will stop here and continue in the next lecture. Thank you.