Quantum Mechanics and Molecular Spectroscopy
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Lecture – 5
Time-Dependent Perturbation Theory of Two States (Part – 2)

Welcome to lecture number 5 of the course quantum mechanics and molecular spectroscopy. In the previous lecture, we were looking at the time-dependent perturbation theory of 2 states.

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$H^0|1\rangle = E_1|1\rangle$ and $H^0|2\rangle = E_2|2\rangle$

$\{|1\rangle, |2\rangle\} \Rightarrow$ Orthonormal complete set

$\langle 1|2\rangle = 0 \quad \langle 1|1\rangle = \langle 2|2\rangle = 1$

$$\text{LHS} = i\hbar\left\{\dot{a}_1(t)\, e^{-iE_1t/\hbar}|1\rangle + \dot{a}_2(t)\, e^{-iE_2t/\hbar}|2\rangle\right\}$$

$$= \hat{H}'(t)\, e^{-iE_1t/\hbar} a_1(t)|1\rangle + \hat{H}'(t)\, e^{-iE_2t/\hbar} a_2(t)|2\rangle = \text{RHS}$$

multiply with ψ_1^* on left and integrate $\langle 1|$

$$i\hbar\left\{\langle 1|\dot{a}_1(t)\, e^{-iE_1t/\hbar}|1\rangle + \langle 1|\dot{a}_2(t)\, e^{-iE_2t/\hbar}|2\rangle\right\}$$

$$= \langle 1|\hat{H}'(t)\, e^{-iE_1t/\hbar} a_1(t)|1\rangle + \langle 1|\hat{H}'(t)\, e^{-iE_2t/\hbar} a_2(t)|2\rangle$$

If we had the time-independent Hamiltonian H0 and had 2 solutions E2 2 such that 1 and 2 form a complete set and so it also means form an orthonormal complete set. That means integral 1 overlap integral of 1 over 2 will be equal to 0 and overlap integral 1 over 1 = 2 over 2 = 1, okay. Now, in the last class, we had ended up with this equation ih bar a1 dot t e to the power of –i E1 t by h bar 1 + a2 dot t e to the power of –i E2 t by h bar 2.

Equals to H prime of t e to the power of –i E1 t by h bar a1 of t1 + H prime of t e to the power of –i E2 t by h bar a2 of t. So, this is where we stopped in the last lecture okay, and this we came from LHS and this came from the RHS. Now, we have to equate this and try to get going to what happens. Now, I am going to do one simple trick, that is I am going to multiply with psi 1 star on left and integrate, so which simply means that I will carry out the operation 1.

So, when you look at the LHS, then it will become ih bar okay 1 a1 dot t e to the power of –i

E1 t by h bar 1 + 1 a2 dot t e to the power of –i E2 t by h bar 2 that will be your left hand side and the right hand side will be 1 H prime of t e to the power of –i E1 t by h bar a1 of t 1 + 1 H prime of t e to power of minus –i E2 t by h bar a2 of t. So, these are the 4 terms that we have.

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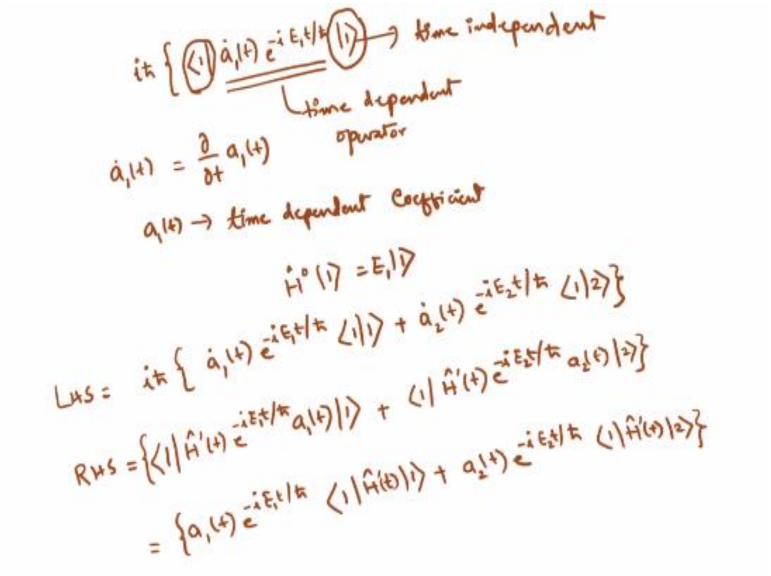

Now, if we look at the left hand side, then what we have is ih bar fun a1 dot t e to the power of minus –i E1 t by h bar 1 okay, I will come to second time a little bit later. First, let us just look at this term. What is a1 dot t, a1 dot t is nothing but d by dt of a1 of t. What is a1 of t? It is time dependent, okay. Nonetheless, even if it is time dependent, it is a constant, it is called change, but it is still a constant okay.

But you know this wave function 1 is a solution of the time independent Schrodinger equation. So, what was 1, 1 is nothing but H0 1 = E1 okay. So, the operator in here is time dependent and the wave function is time independent. Therefore, one can write, you can bring the operator outside because it is not going to affect the wave function. So, what we will have? Left hand side will have i h bar a1 dot t e to the power of–i E1 t by h bar 1 1.

And the second term which I have not written here, but you know by analogy one can write it as a1 dot t e to the power of –i E2 t by h bar 1, so that will be our left hand side. Now, let us look at the right hand side. So okay LHS is equal to, okay I will separate them and then equate it later. So RHS is equal to, what you had in RHS? RHS you had fun H prime of t e to the power of –i E1 t by h bar a1 of t 1, so that is what we have one of the terms okay.

Now you can see that e to the power of –i E1 t by h bar and a1 of t, these are just you know time dependent phase factor and coefficient which you can bring it on, but I cannot bring out H prime of t because it is a time-dependent perturbation. A perturbation always moves the states. So, it will affect your wave functions. A perturbation really affects the wave function and if you have time dependent perturbation, its effect will be different in different times.

Therefore, one can write this, the other time we had was 1 H prime of t e to the power of –i E2 t by h bar a2 of t 2 okay. So, that was your RHS. Okay, now this I can slightly rewrite because of the arguments that I use will be equal to a1 of t e to the power of –i E1 t by h bar 1 H prime of t 1+ a2 of t e to the power of –i E2 t by h bar 1 H prime of t. So, that is your RHS, okay. Now let us equate RHS and LHS and see what we get.

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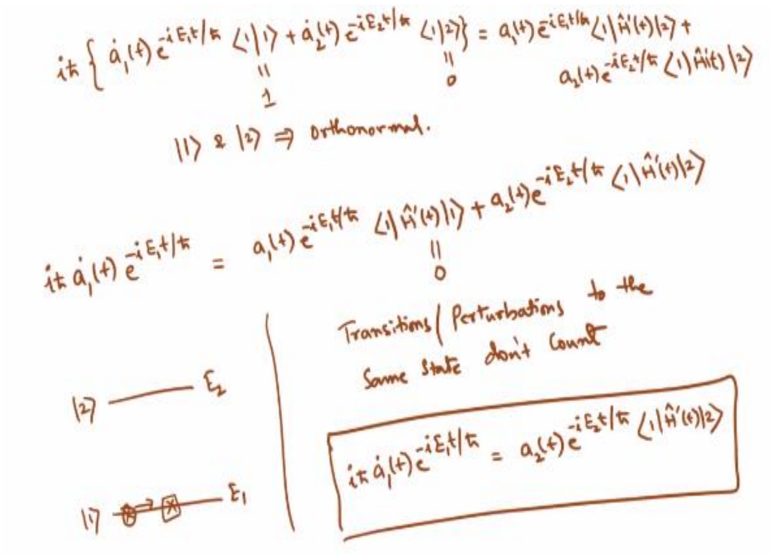

So ih bar into a1 dot t e to the power of –i E1 t by h bar 1 1+ a2 dot t e to the power of –i E2 t by h bar 1 2 should be equal to a1 of t e to power of –i E1 t by h bar 1 H prime t 2 + a2 t e to the power of –i E2 t by h bar 1 H prime t okay that is what you will get. Now, let us look at this. Now we know the wave functions 1 and 2 are orthonormal, which means 1 1 integral, overlap integral will go to 1 and 1 2 overlap integral will go to 0.

That means, on the left hand side only one term will survive. So, what you get is ih bar a1 dot t e to the power of –i E1 t by h bar, that 1 1 is just 1 should be equal to a1 of t e to the power of –i E1 t by h bar 1 H prime t 1 + a2 of t e to the power of –i E2 t by h bar 1 H prime t 2 okay. Now we have what? Now let us suppose you have 2 solutions, this is your 1 with E1 as energy and this is 2 with E2 as energy.

So let us suppose there is a molecule which is sitting here okay. I apply the perturbation and what happens is that the molecule after I apply perturbation still is in 1 okay. So, let us say after perturbation, I will get another molecule which is this, but it still is in the even state. That means whether you apply perturbation or not apply perturbation okay, you would not be able to differentiate.

So, if I start with state 1 and end up in state 1, you do not even know whether you have started and ended or not. Therefore, any perturbation which leads on to the same wave function E can be neglected okay. It is like transition to the same state. You start from ground state and you go back to the ground state, so you do not even know whether the transition has taken place or not taken place.

Therefore, one can equate this term to be 0 because the perturbation here acts on state 1 and overlaps with the state 1. That means you have started with state 1, ended with state 1, you do not even know whether the perturbation has taken place or not okay. So, effectively the first time will go to 0 okay. So this is nothing but transitions or perturbations to the same state do not count, okay.

Now, in such scenario, then your first term is gone, so what you get is ih bar a1 dot t e to the power of –i E1 t by h bar = a2 of t e to the power of –i E2 t by h bar 1 H prime t 2 okay. So that is one equation that we will get okay.

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$$i\hbar\left\{\dot{a}_1(t)e^{-iE_1t/\hbar}|1\rangle + \dot{a}_2(t)e^{-iE_2t/\hbar}|2\rangle\right\} = a_1(t)\hat{H}'(t)e^{-iE_1t/\hbar}|1\rangle + a_2(t)\hat{H}'(t)e^{-iE_2t/\hbar}|2\rangle$$

Multiply with ψ_2^* and integrate $\Rightarrow \langle 2|$

$$i\hbar\left\{\dot{a}_1(t)e^{-iE_1t/\hbar}\underbrace{\langle 2|1\rangle}_{=0} + \dot{a}_2(t)e^{-iE_2t/\hbar}\underbrace{\langle 2|2\rangle}_{=1}\right\} = a_1(t)e^{-iE_1t/\hbar}\langle 2|\hat{H}'(t)|1\rangle + a_2(t)e^{-iE_2t/\hbar}\underbrace{\langle 2|\hat{H}'(t)|2\rangle}_{=0}$$

$$\boxed{i\hbar\dot{a}_2(t)e^{-iE_2t/\hbar} = a_1(t)e^{-iE_1t/\hbar}\langle 2|\hat{H}'(t)|1\rangle}$$

Let us do this, let us go back to the first equation that I wrote in the beginning of the lecture that is nothing but ih bar a1 dot t e to the power of–i E1 t by h bar 1 + a2 dot t e to the power of–i E2 t by h bar 2 should be equal to a1 t H prime of t e to the power of –i E1 t by h bar 1 + a2 t H prime of t e to the power of –i E2 t by h bar. So, that was the equation that we started with. Multiply with psi 2 star and integrate okay.

This is equivalent of you know 2 okay. Now remember last time we multiplied with psi 1 star and integrated, now we are multiplying with psi 2 star and integrating. So, quickly I will write, skip couple of steps because you already know how we did with the psi 1 star. So, what we get is this ih bar a1 dot t e to the power of –i E1 t by h bar 2 1 + a2 dot t e to the power of –i E2 t by h bar 2 2.

Overlap integral should be equal to a1 of t e to the power of –i E1 t by h bar 2 H prime of t 1 + a2 t e to the power of –i E2 t by h bar 2 H prime t 2 okay. Now we use the same analogy as last time. So 2 1 overlap integral will go to 0, 2 2 integral will be 1, so this integral we do not know, we have to evaluate, but once again transitions from 2 2 will be equal to 0, so this will go to 0 okay.

So after this, we can rewrite this equation as ih bar a2 dot t e to power of –i to E2 t by h bar should be equal to a1 t e to the power of –i E1 t by h bar 2 H prime of t 1 okay, this is the second equation okay. Now what I will do is I will correct both the equations together.

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$$\boxed{\begin{aligned} i\hbar\, \dot{a}_1(t)\, e^{-iE_1t/\hbar} &= a_2(t)\, e^{-iE_2t/\hbar} \langle 1|\hat{H}'(t)|2\rangle \\ i\hbar\, \dot{a}_2(t)\, e^{-iE_2t/\hbar} &= a_1(t)\, e^{-iE_1t/\hbar} \langle 2|\hat{H}'(t)|1\rangle \end{aligned}}$$

$$\Downarrow$$

$$\begin{aligned} \dot{a}_1(t) &= \frac{1}{i\hbar} e^{-i(E_2-E_1)t/\hbar} \langle 1|\hat{H}'(t)|2\rangle \\ \dot{a}_2(t) &= \frac{1}{i\hbar} e^{i(E_2-E_1)t/\hbar} \langle 2|\hat{H}'(t)|1\rangle \end{aligned}$$

$E_2 - E_1 = \Delta E = \hbar\omega_{21}$

So, first equation was ih bar a1 dot t e to the power of –i E1 t by h bar should equal to a2 of t e to the power of –i E2 t by h bar 1 H prime of t 2 and ih bar a2 dot t e to the power of –i E2 t by h bar, this is equal to a1 of t e to the power of –i E1 t by h bar 2 H prime t okay. Now, there is something else that I can do is I will take the ih bar, slightly rearrange these two equations okay.

So, a1 dot t equals to, the ih bar I can take onto that side, so i becomes 1 over ih bar okay, e to the power of E1 t, iE1 t by h bar I will take to the other side. So that will become e to the power of –i E2 – E1 t by h bar 1 H prime of t 2 and other equation will become a2 dot t = 1 over ih bar e to the power of okay, now this is E2 so that will become i E2 - E1 into t by h bar 2 H prime t 1.

Now, let us say E2 - E1 = delta E, this is equal to h bar omega 21, omega 21 will be the angular frequency that corresponds the energy difference between the E2 and E2 one states. So therefore, now you can see when I replace E2 - E1 as h bar omega 21, this h bar in the numerator and this h bar in the denominator will get cancelled.

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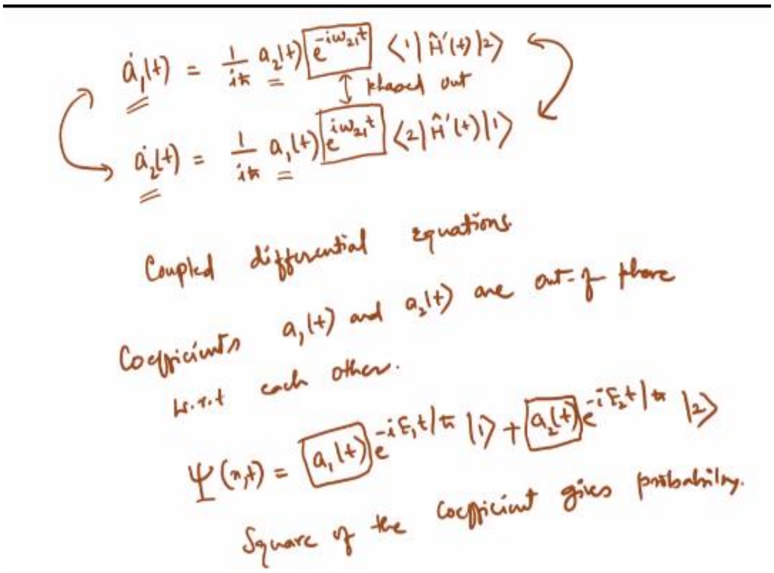

So, what you finally end up with the following equations, a1 dot t = 1 over ih bar a2 t e to the power of –i omega 21 t 1 H prime of t 2 and a2 dot t = 1 over ih bar a1 of t e to the power of i omega 21 t 2 H prime of t 1 okay, so these are. So which means the time dependence of a1 will depend on a2 and time dependence of a2 will depend on a1. That means these 2 equations are coupled differential equations okay.

Now more importantly one thing that you can look at is the following, a1 changes okay with respect to a2 and a2 changes with respect to a1 okay. Now, there is one thing that is very interesting you see is this here. This is e to the power of –i omega t and this is e to the power of +i omega t. So which means these two are phased out. What it means? It means when a1 goes up a2 comes down and a2 goes up a1 comes down.

So, these are phased out are out of phase with respect to each other. So, coefficients a1 t and a2 t are out of phase with respect to each other okay. So, what is a1 and t, psi of x, t = a1 of t e to the power of –i E1 t by h bar 1 + a2 of t e to the power of –i E2 t by h bar 2. So, this was our total wave function okay and these are the coefficients, time-dependent coefficients of the a1 and a2 and we know the square of the coefficients gives you the probability.

Therefore so when you see that a1 and a2 are out of phase with respect to each other that means the probability of finding a1 state if it goes up, the probability of finding a2 state will go down. Similarly, the probability of a2 state will go up and the probability of a1 state will go down. So they are going to be with respect to each other phased out or you know out of phase. We will stop here and continue in the next lecture. Thank you.