Quantum Mechanics and Molecular Spectroscopy

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Lecture-04
Time-Dependent Perturbation Theory of Two States (Part-1)

Hello welcome to the lecture number 4 of the course quantum mechanics and molecular spectroscopy. Before we get on with the lecture number 4 we will have a quick recap of lecture number 3, in lecture number 3 we looked at 2 important points.

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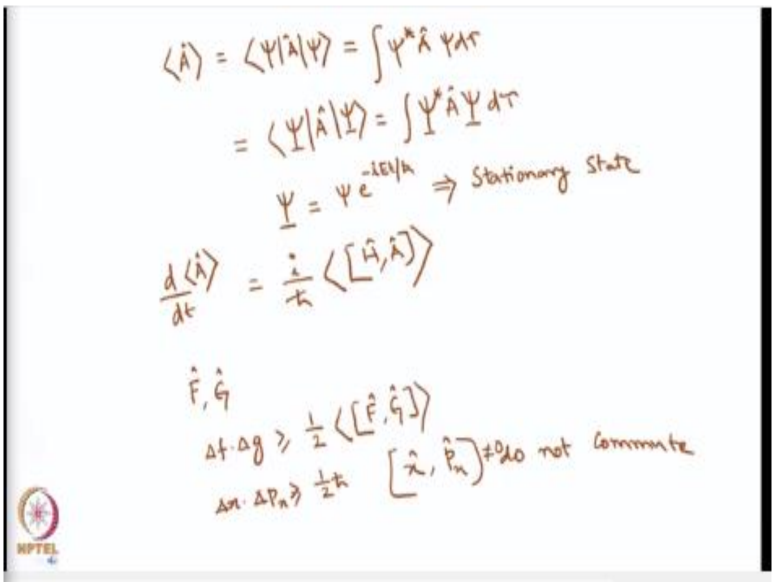

First is that an average value of A operator it is given by psi A psi this is nothing but integral psi star A operator ok. This is also equal to psi A psi this is equal to integral psi star A psi d tau where psi equals to small psi into e to the power of – i E t by h bar. And of course it is only valid if you know psi is a stationary state. Secondly we said that the time dependence of the average value of operator A is equal to i h bar average value of the commutator H, A ok.

It simply means that the average value of A or the expectation value of an operator A will have time dependence or not will depend on whether it will commute with the Hamiltonian or not. If it commutes with Hamiltonian then there will be no time dependence and if it does not commute with Hamilton it will show some time dependence. And I also told you that this is very useful in spectroscopy.

Because the operator A corresponding to the interaction of light with the matter or white with molecule or atom ok does not commute with the Hamiltonian of the molecule or the atom ok. Therefore 1 can make a transition from a one expectation value say 1s orbital or 1s energy level and hydrogen atom to some other energy level say 2s or 2p. There is another interesting thing that is if we have 2 operators F and G.

The uncertainity relation of the expectation value of operators F and G is equal to is always going to be greater than 1/2 of F and G commutators ok. For example we know that Heisenberg's uncertainty principle says delta x dot delta p x should be greater than or equal to 1/2 h bar which means the operator x and operator P x ok do not commute in fact this is not equal to 0 ok.

Now, so now we know the time dependence of an average value of A will just depend on that operator will commute with Hamiltonian or not ok. We will now go to the second part of our course that is the time dependent perturbation theory. To begin with I will show only time dependent perturbation theory of 2 states because it has some interesting consequences.

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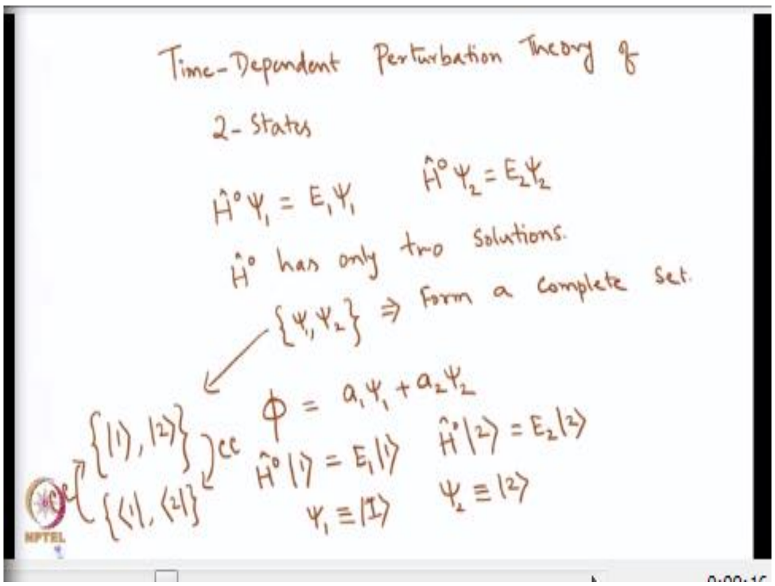

So, we will start with time dependent perturbation theory of 2 states ok, now what does this mean, means the following. For example if I had an Hamiltonian H 0 that means some Hamiltonian for which you know the solution and that acts on a wave function psi 1 that will give you E 1 psi 1. And this H 0 acts on psi 2 will give you E 2 psi 2 and H 0 has only 2 solutions ok that is.

So, therefore the psi 1 and psi 2 form complete set and what did they say about complete set any arbitrary function pi can now be written as a linear combination of a 1 psi 1 + a 2 ok. This is like a plane ok, if you have a plane you only need 2 coordinates sorry x and y. So, any point in the plane is a linear combination of x and y ok. So, we have a kind of a restricted environment where the Hamiltonian will be restricted to a plane that is consisting of psi 1 and psi 2 ok.

Now I am going to slightly rewrite this ok, so you have H 0 in terms of bracket notation 1 is equal to E 1 1 and H 0 2 is equal to E 2, 2 where psi 1 is identically equal to 1, psi 2 is identically equal to 2 ok. So, if psi 1 and psi 2 form a complete set then there is another complete set that is nothing but 1, 2. I also told you that there is also another complete set that is made up of complex conjugates of 1 and 2. So, that is nothing but set 1, 2, so these 2 are complex conjugates of each other ok.

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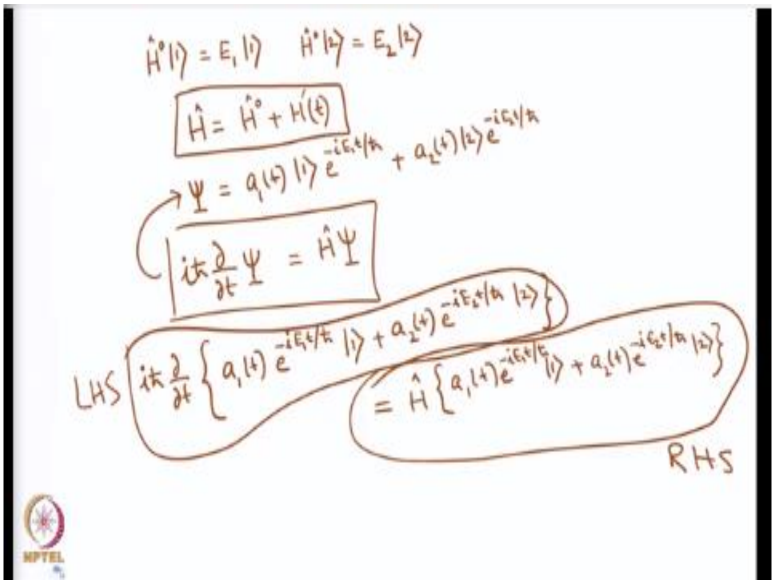

So, now we have this problem in which H 0 of 1 is equal to E 1 1 and H 0 of 2 is equal to E 2 of 2 ok. Now let there be a some kind of perturbation ok, so what will this perturbations to it will move the states. So, let me write the Hamiltonian corresponding to other when you have a perturbation the total Hamiltonian H will be nothing but H 0 less some perturbation H prime of t because we are looking at time dependent perturbation ok.

Now let us suppose ok if there is a point or a ball kept on the surface of a floor. And then one can think of playing a football, so constantly someone is kicking it ok because then the balls will keep moving all over the floor. Or if you go to a football match ok then there is this floor or the ground in which there is a football is kept and the players are kicking the ball in different directions and that is your time dependent perturbation.

So, what will it happen, it will keep moving it is position but let us assume that it is always restricted to the ground ok, so but it is position is going to change. So, every time you have a new position it can be written as a linear combination of some nu x and y. So, it has to be a linear combination of nu 1 and 2 and this position is going to be time dependent. Therefore the wave function psi can be now written as a 1 of t to 1 e to the power of - i E 1 t by h bar + a 2 of t 2 e to the power of - i a to t by h bar.

So, that is my wave function, that wave function works with this entire Hamiltonian. Of course if H prime t goes to 0 then a 1 and a 2 will collapse to some value ok either a 1 will go to 0 or a 2 will be go to 0 ok. So, now we will go back to our Schrodinger equation which is nothing but i h bar d by dt of psi equals to H psi. So, finally what we want to do is, we want to solve this Schrodinger equation with this wave function ok, so let us do it.

So, this will be i h bar d by dt of a 1 of t e to the power of - i E 1 t by h bar 1 + a 2 of t e to power of - i E 2 t by h bar to 2 ok. This should equal to h r sorry h into a 1 t e to the power of - i e 1 t h bar 1 + a 2 of t e to the power of - i E 2 t h bar 2 ok. Now this is a long equation, so what I am going to do is I am going to call this as LHS that is left hand side then I am going to call this as RHS. I will evaluate the left hand side and right hand side independently and then equate them later.

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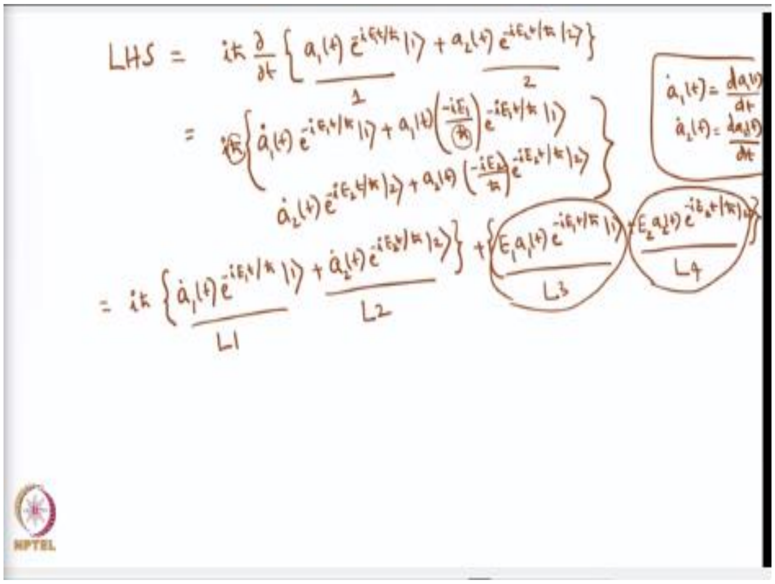

So, let us start with LHS, LHS equals to i h bar d by dt of a 1 of t a 2 the power of - i E 1 t by h bar 1 + a 2 of t e to the power of - i E 2 t by h bar 2 ok. Now let us take the derivative, now you will see that in each of these terms ok term 1 and term 2. There are 2 time dependent parts a 1 t and e to the power of - i E 1 t h bar similarly a 2 t e to the power of - e 2 t by h bar. So, you have to use a product rule of differentiation what you get is i h bar a 1 t. ok where a 1 t. is equal to d a 1 t by dt.

Similarly a 2.t is equal to da 2 t by dt, it just a notation ok just keep in mind when I say put a dot over something, it means it is a time derivative ok, e to the power of - i e 1 t by h bar 1 + a 1 t. Now a 1 t, now I will take the time derivative of the other one this will be - i e 1 by h bar e to the power of - i E 1 t by h bar to 1. Similarly you get a 2.t e to power of - i E 2 t h bar 2 + a 2 t - i E to t by h bar into e to the power of - i E 2 t by h bar to 2.

So, this I can rewrite as is equal to h bar a 1.t e to the power of - i E 1 t by h bar 1 + a 2.t e to the power of - i E 2 t by h bar 2 ok. Now you can see there is an i here and there is an i here, i square that will be - 1 and there is a - sign as well. So, that will become + 1, there is the h bar in the numerator and there is an h bar in the denominator, so these 2 get cancelled. So, essentially what you get is that + E 1 into a 1 t e to the power of - i e 1 t by h bar 1 + E 2 to a 2 t e to the power of - i to t by h bar 2.

So, there are 4 terms, I will call this us L 1 that is LHS 1, L 2 that is LHS 2, L 3 LHS 3, L4 LHS 4 ok.

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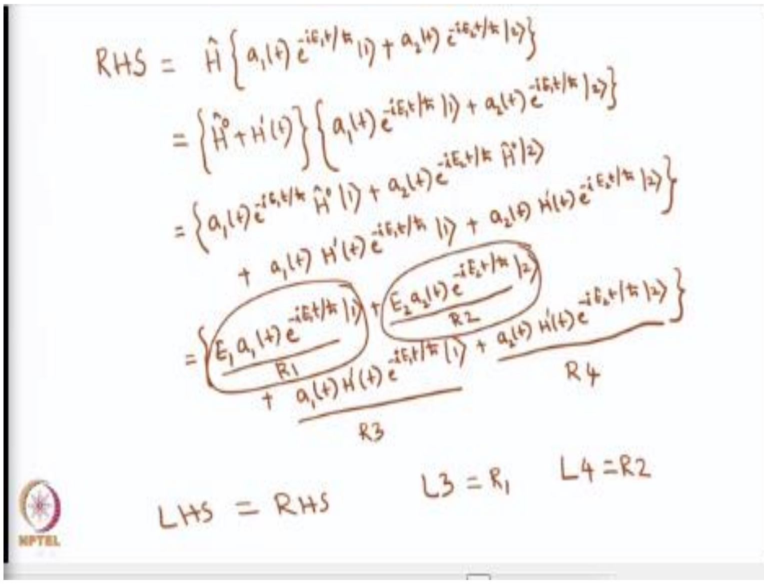

Now let us look at the RHS, this is nothing but your h ok acting on your wave function that is nothing but a 1 of t E to power of - i E 1 t by h bar 1 + a 2 t e to the power of - i a 2 t by h bar 2 ok. Now I want to quickly go back and see that you know there are 4 terms ok, the first 2 terms of the time derivatives with respect to a 1 and a 2 and the second 2 terms are have this energy values E 1 and E 2, so something that you must remember ok.

Now this is equal to this is nothing but is equal to your H is nothing but H 0 + H prime t ok. Now this must act on a 1 of t e to the power of - i E 1 t by h bar 1 + a 2 t e to the power of - i E 1 t by h bar 2 ok. So this will be not nothing but a 1 of t E to the power of - i e 1 t by h bar, H 0 will only act on 1. So, H 0 acting on 1 + a 2 times t e to the power of – i E 2 t by h bar H 0 acting on 2.

You see because H 0 is your initial Hamiltonian which is nothing but your time independent Hamiltonian. So, it will not act on anything that is time dependent ok. So, either a 1 t or a to the power of –i E 1 t by h bar, it will only act on the state a 1 and give you E 1 1 ok. Similarly the second part of the equation ok + a 1 t H prime t now acting on e to the power of - i E 1 t by h bar acting on 1 + a 2 times t H prime t acting on a to the power of - i E 2 t by h bar 2 ok.

So, these are the 4 terms that you will get, now when H 0 acts on 1 will give me E 1 1. So this will become E 1 a 1 of t e to the power of - i E 1 t by h bar 1 + second one h 0 acting on 2 will give you E 2 t. So, E 2 a 2 of t e to the power of - i E 2 t by h bar 2 + the 2 terms that is a 0 a 1 t H prime of t acting on e to the power of - i E 1 t by h bar 1 + a 2 of t H prime of t acting on e to the power of - i E 2 t by h bar 2.

So, here also we get 4 terms, this I will call it as right hand side 1 R1, right hand side term 2, R2, right hand side term 3, R3, right hand side term 4, R4. So, but you know LHS and RHS must be equal, so LHS must be equal to RHS. Now you will quickly see that L3 term is equal to R1 term and L4 term is equal to R2 term. So, this one here and this one here R 1, R2 will be equal to L3, L3 and L4. So, since L3 and L4 are equal to R1 + R2, so which means you can cancel out each.

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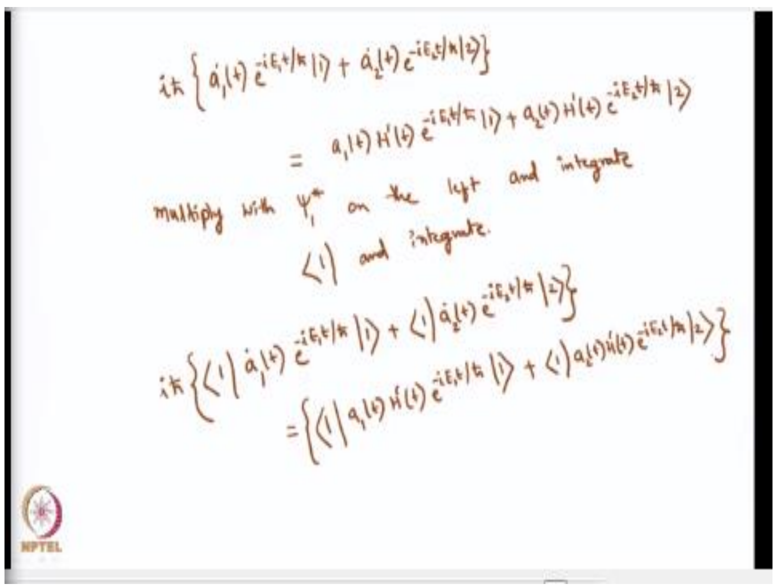

So, what you will be left out with is i h bar a 1.t e to the power of - i E 1 t by h bar 1 + a 2.t e to the power of – i a 2 t by h bar 2 is equal to a 1 t H prime t acting on e to the power of – i E 1 t by h bar 1 + a 2 t H prime t acting on e to the power of - i E 2 t e by h bar t, so this is what you get from that equation ok. Now let us do some little bit of math ok, now what I am going to do is the following.

I am going to multiply with psi 1 star on the left and integrate, this simply means that I will put a function like that and multiply and integrate. Now if I do that you will get i h bar 1 a1.t e to the power of - i E 1 t by h bar 1 + 1 a 2.t e to the power of - i E 2 t by h bar 2, this is equal to 1 a 1 t H prime t e to the power of - i E 1 t by h bar 1 + 1 a 2 t H prime t e to the power of - i E 2 t by h bar 2 ok, I will have 4 integrals that I have to evaluate.

If I can evaluate these 4 integrals then I will know the time dependence of this perturbation. We will carry on the remaining part in the next lecture, I am going to stop now, thank you.