Quantum Mechanics and Molecular Spectroscopy
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Lecture – 7
Time-Dependent Perturbation Theory of Many States (Part – 1)

Hello, welcome to lecture number 7 of the course quantum mechanics and molecular spectroscopy. Before we proceed with lecture number 7, in the previous two lectures, we looked at the perturbation theory of two states.

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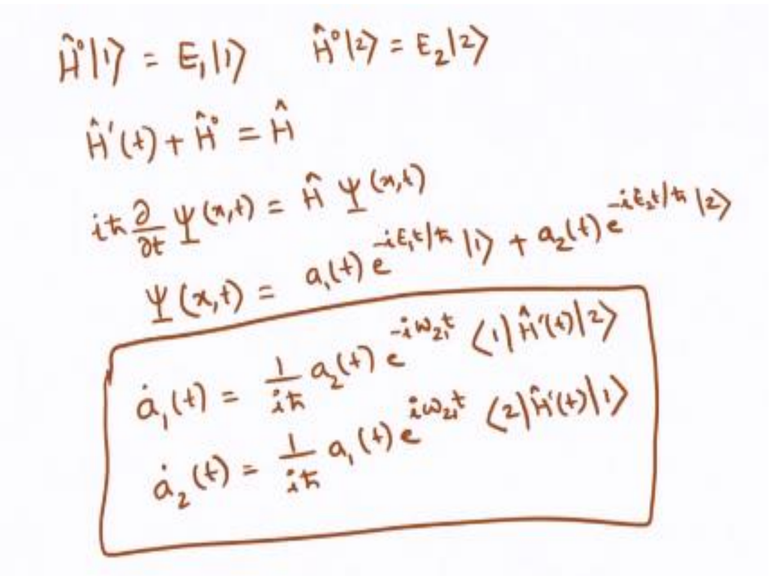

So, to begin with we had H0 acting on 1 will give you E1 1 and H0 acting on 2 will give you E2 2 okay. Then we had perturbation time dependent, which was H prime of t and this when added to H0 will give you the total Hamiltonian H and then we went about by solving the Schrodinger equation ih bar d by dt of psi of x, t = H into psi of x, t where psi of x, t is given as a1 of t e to the power of minus –i E1 t by h bar 1 + a2 of t e to the power of minus –i E2 t h bar 2 okay.

So, after doing all the required mathematics, we arrived at a1 dot of t = 1 over ih bar a2 of t e to the power of –i omega 21 t 1 H prime of t 2 and a2dot of t = 1 over ih prime a1 of t e to the power of i omega 21 t 2 two H prime of t 1 okay. So, these two are the coupled differential equations between a1 and a2 okay. Now, I told you since they are coupled differential equations, solution of a1 will depend on a2 and solution of a2 will depend on a1 okay.

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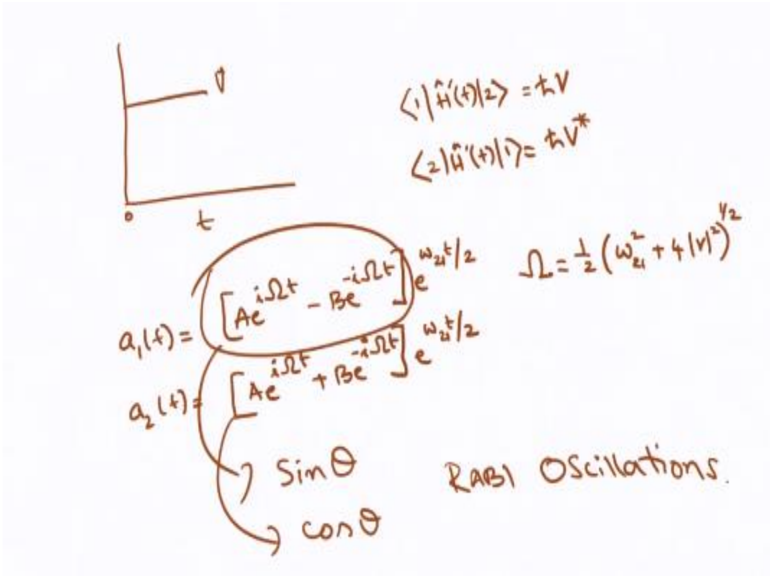

Now, we used a very simple approximation in which we said there is a perturbation, a constant perturbation that is switched on at time t = 0 okay. So, that perturbation is something like this t when t = 0 so some constant value. In such scenario, then it can be written as 1 H prime of t 2 = h bar V and 2 H prime of t 1 = h bar V star. Using these conditions and doing little bit more math, we converted the equations into second-order derivatives.

And finally came up with a solution that is a1 of t = to Ae to the power of i omega t – Be to the power of –i omega t into e to the power of omega 21 t by 2 where omega is given as half of omega 21 square + four times modulus of V square to the power of half and a2 of t = Ae to the power of i omega t + Be to the power of –i omega t e to the power of omega 21 t by 2. Now, we said a1 t and a2 t are phase shifted with respect to each other by pi by 2.

Because this is like a Sin theta function and this is like Cos theta function. So, which means whenever a1 t increases, a2 t decreases, they are out of phase with respect to each other. We know function Sin theta and Cos theta are out of phase by pi by 2. So, whenever Sin theta goes up, Cos theta comes down and other way around. So, based on this, we came up of what is known as Rabi oscillations okay.

So, Rabi oscillations are between two states a1 and a2 where the population of states 1 and 2 will go up and down out of phase with respect to each other and this is the perturbation theory of the two states. Now, let us start with the perturbation theory of n states okay, generalized perturbation theory. Generalized time-dependent perturbation theory is what we are going to start now okay.

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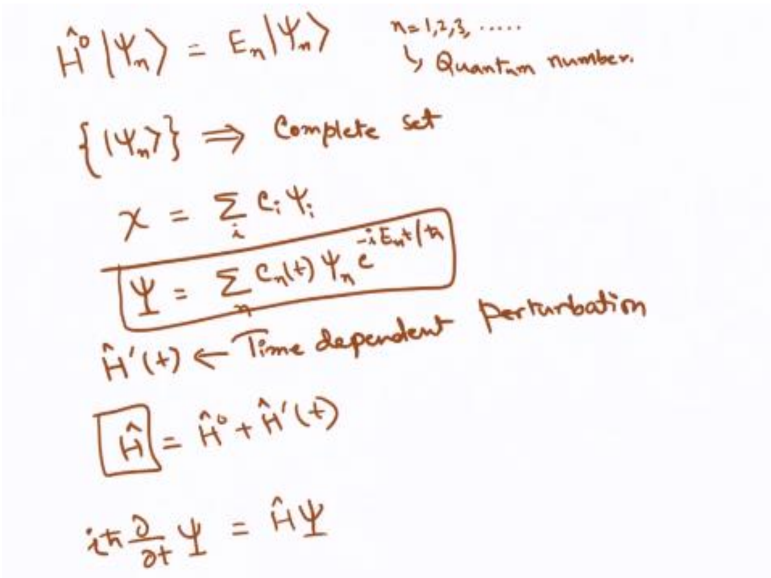

In such scenario, we will again start with an assumption that we know an Hamiltonian H0 for which there are n solutions okay such that this give you En psi n and n will go from for example 1, 2, 3, etc okay, so where this represents the quantum number. Now we know that if psi n forms a complete set okay, so any arbitrary function chi in the same variable can be written as sum over i Ci psi okay. This is something we already know, okay.

So a wave function psi can always be written as sum over n Cn of t psi n e to the power of –i En t by h bar okay. So, a time-dependent wave function is a linear combination of all the wave function psi n and their phase factors and their time-dependent coefficients. Now, if we have the time-dependent perturbation, which I will call it as H prime of t, this is my time-dependent perturbation, then my whole Hamiltonian H will be nothing but H0 + H prime of t.

So, when I know the total wave function psi and H, I can solve or attempt to solve the time-dependent Schrodinger equation which is nothing but ih bar d by dt of psi = H psi. So, we will do the same treatment that we did for the two states but in a slightly different manner okay. Now, let us get to it.

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$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

$$\underbrace{i\hbar\frac{\partial}{\partial t}\left[\sum a_n(t)e^{-iE_nt/\hbar}|n\rangle\right]}_{\text{LHS}} = \underbrace{\{\hat{H}^0+\hat{H}'(t)\}\left[\sum a_n(t)e^{-iE_nt/\hbar}|n\rangle\right]}_{\text{RHS}}$$

$$\text{LHS} = i\hbar\frac{\partial}{\partial t}\left[\sum_n \underbrace{a_n(t)}_{f(t)}\underbrace{e^{-iE_nt/\hbar}}_{g(t)}|n\rangle\right]$$

$$= i\hbar\left\{\sum_n \dot{a}_n(t)e^{-iE_nt/\hbar}|n\rangle - \sum_n \frac{iE_n}{\hbar}a_n(t)e^{-iE_nt/\hbar}|n\rangle\right]$$

$$= \boxed{i\hbar\sum_n \dot{a}_n(t)e^{-iE_nt/\hbar}|n\rangle + \sum_n a_n(t)e^{-iE_nt/\hbar}E_n|n\rangle}$$

So, my time-dependent perturbation theory is ih bar d by dt of psi = H psi. Now, what is psi which is nothing but ih bar d by dt of my psi is sigma over an of t e to the power of –i En t by h bar n okay that is the function psi n, you can go and look it back. So my n is this, psi is this, so I have just used this form okay equals to H is is nothing but H0 + H prime of t this acting on sigma over an t e to the power of –i En t by h bar n okay.

Now once again here we have two psi, this is equal to LHS, this is equal to RHS. So, what we will do is we will evaluate LHS and RHS separately and then equate them at a later stage okay. So let us start LHS. LHS = ih bar d by dt of psi. This is nothing but sigma over n t e to the power of minus –i En t by h bar n. So this is nothing but ih bar okay. Now, each term we will have 2 things that is an of t and e to the power of.

So this is function f of t and this is function g of t, and of course the wave function n is itself time independent, so it will not be able to take a time derivative of it, it is just a constant. So, each term, so this is summation over n. So, you will have as many terms in this as the number of wave functions in your complete set. So, if there are 20 wave functions in the complete set, so this expansion will be for 20 terms.

If there are 100 wave functions on complete set, then this expansion will be of 100 terms. If there are infinite numbers of wave function, then this expansion will be of infinite number of terms okay. Now, in such a scenario, each term of course will be of two functions. So when you take a derivative use the product rule and so what you get is ih bar okay, now I will take the derivative with respect to sum over n an dot of t e to the power of –i En t by h bar n sigma over n i En by h bar an of t e to the power of –i En t by h bar acting on n, right.

Something like that. So, I am just going to rewrite it in a way is equal to ih bar sigma over n an dot t e to the power of –i En t by h bar n and here this i and this i will become minus one and there is already minus sign, it will become plus, so + and this h bar and this h bar will cancel. So, what we will get is an of t e to the power of, sigma over n, –i En t by h bar En n. So, we will get 2 terms okay.

But of course each of these terms is summation of many, many terms depending on the value of n. So, you remember this, my LHS is this okay. Now, let us look at the RHS.

(Refer Slide Time: 15:14)

$$RHS = \left\{\hat{H}^0 + \hat{H}'(t)\right\}\left[\sum_n a_n(t)\, e^{-iE_nt/\hbar}|n\rangle\right]$$

$$= \sum_n a_n(t)\, e^{-iE_nt/\hbar} E_n|n\rangle + \sum_n a_n(t)\, e^{-iE_nt/\hbar}\hat{H}'(t)|n\rangle$$

$$LHS = RHS$$

$$i\hbar\sum_n \dot{a}_n(t)\, e^{-iE_nt/\hbar}|n\rangle + \boxed{\cancel{\sum_n a_n(t)\, e^{-iE_nt/\hbar} E_n|n\rangle}} = \boxed{\cancel{\sum_n a_n(t)\, e^{-iE_nt/\hbar} E_n|n\rangle}} + \sum_n a_n(t)\, e^{-iE_nt/\hbar}\hat{H}'(t)|n\rangle$$

$$\boxed{i\hbar\sum_n \dot{a}_n(t)\, e^{-iE_nt/\hbar}|n\rangle = \sum_n a_n(t)\, e^{-iE_nt/\hbar}\hat{H}'(t)|n\rangle}$$

$n=1,2$

What is the RHS? RHS = H0 + H prime of t acting on sigma over n an of t e to the power of –i En t by h bar n. So, this is nothing but when H0 acts, H0 is time independent. This is just a kinetic energy and potential energy operators of the original Hamiltonian and we know in chemistry we said that the original Hamiltonian that is independent of time okay? So H0 when acts on this, so this will not act on an or e to the power of –i En t.

It just acts on n and gives you sigma over n an of t e to the power of –i En t by h bar, when H0acts on n, we will get En n that is the first and the second term will be + an of t e to the power of –i En t by h bar and H prime of t will act on n okay, so that is the two values, of course there is sum over n. Now let us equate the LHS and RHS. Now my LHS was, so we have to now make LHS = RHS.

So, LHS was sigma over n an dot t ih bar e to the power of –i En t by h bar n that is my LHS okay + sigma over n an of t e to the power of minus –i En t h bar En n that should be equal to my RHS which is nothing but sigma over n an of t e to power of –i En t by h bar En n + sigma over n an of t e to the power of –i En t by h bar H prime of t acting on n okay. Now we will see that the second term of the LHS = the first term of the RHS okay, so we can cancel these two okay.

So what we end up in this case is ih bar sigma over n an dot t e to the power of –i En t by h bar n = sigma over n an of t e to the power of –i En t by h bar H prime of t n okay. So, this is what you get, you can go back and quickly look at the two state perturbation theory. This equation looks very similar when n is equal to just two state. When n is equal to 1, 2, then this equation is exactly equal to what we got for the two state perturbation theory.

However, in this case since we are starting for n states or many states, a generalized form can be written like this okay.

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$$i\hbar \sum_n \dot{a}_n(t)\, e^{-iE_nt/\hbar} |n\rangle = \sum_n a_n(t)\, e^{-iE_nt/\hbar} \hat{H}'(t)|n\rangle$$

multiply with ψ_m^* on the left and integrate. $\psi_m^* = \langle m|$

$$i\hbar \sum_n \dot{a}_n(t)\, e^{-iE_nt/\hbar} \langle m|n\rangle = \sum_n a_n(t)\, e^{-iE_nt/\hbar} \langle m|H'(t)|n\rangle$$

$$\{\psi_n\} = \{|n\rangle\} \Rightarrow \text{Complete set}$$

$$\hat{H}^0|n\rangle = E_n|n\rangle$$

$$\langle m|n\rangle = \delta_{m,n}$$

LHS $n = m$ LHS will survive else it will go to zero.

Now, what I am going to do is that I start with the equation ih bar sigma over n an dot of t e to the power of –i En t by h bar to n = sigma over n an of t e to the power of –i En t by h bar H prime t acting on n okay. Now let us quickly multiply with psi m star on the left and integrate. So if I do that I will get ih bar sigma over n an dot t e to the power of –i En t by h bar m n. Of course, phi m star = m.

This is equal to over n an of t e to the power of i En t by h bar m H prime of t n okay. Now, we know that the wave functions psi n which is nothing but n they form complete set and they are the solutions of the Hamiltonian H0. Therefore, the integral mn = delta m, n. That means when m = n, this integral, the overlap integral will go to 1, otherwise it will go to 0 okay. Now if you plug in that, so which means for anything other than value of n = m.

So if you take the left hand side for anything for n = m okay, this term will survive. For n = m, LHS lectures will survive, else it will go to 0 okay.

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$$LHS = i\hbar \sum_n \dot{a}_n(t)\, e^{-iE_n t/\hbar} \langle m|n\rangle$$

$$= i\hbar\, \dot{a}_m(t)\, e^{-iE_m t/\hbar} \qquad n=m \Rightarrow \langle m|n\rangle = 1, \quad m\neq n \Rightarrow \langle m|n\rangle = 0$$

$$RHS = \sum_n a_n(t)\, e^{-iE_n t/\hbar} \langle m|\hat{H}'(t)|n\rangle$$

$\langle m|\hat{H}'(t)|n\rangle = 0$ if $m=n$

$\langle m|\hat{H}'(t)|n\rangle$ will Survive if $m\neq n$

$$i\hbar\, \dot{a}_m(t)\, e^{-iE_m t/\hbar} = \sum_{n\neq m} a_n(t)\, e^{-iE_n t/\hbar} \langle m|\hat{H}'(t)|n\rangle$$

So, which means that LHS will now be equal to sigma over n ih of an dot t e to the power of –i En t by h bar m n. So, only when m = n or n = m, this will survive. That means, you can drop the summation, this will become ih bar okay am dot t e to the power of –i Em t by h bar because for n = m, this will go to, m n will go to 1 and m is not equal to n, this integral m n will go to 0. That means only one term will survive, all the rest of the terms will go to 0 okay.

Now, if we look at the RHS, this will be equal to sigma over n an of t e to the power of –i En t by h bar m H prime t n. Now, if you take the integral m H prime t n okay, this integral will be 0 if m = n okay. Now you can see that this is going to it because what you are looking at is you are looking at the transition onto itself okay. You are looking at the transitions of itself when m = n, you know that we cannot look at transition from a given state to itself okay.

That means only the terms m H prime t n okay will survive if m is not equal to n okay. Now, which means I can rewrite this equation as ih bar am dot t e to the power of –i Em t by h bar should be equal to sum over n not equal to m. So, now we can take all these terms except that when m is not equal to n. So, when m = n of course I told you this will not survive okay, m not equal to n an of t e to the power of –i Em t by h bar m okay.

So this is the equation that we need to deal with. Okay, we will stop here for this lecture and continue in the next lecture. Thank you.