Quantum Mechanics and Molecular Spectroscopy
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Lecture – 8
Time-Dependent Perturbation Theory of Many States (Part – 2)

Hello, welcome to lecture number 8 of the course quantum mechanics and molecular spectroscopy. As we usually do we will take a quick recap of lecture number 7.

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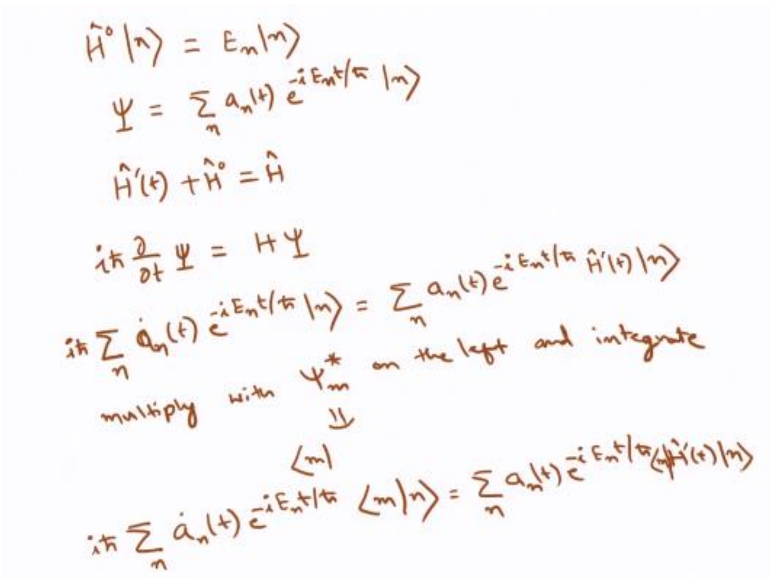

In the lecture number 7, I told you that we start with n state perturbation theory. It simply means that you start with the Hamiltonian H0 and for n state psi n you get value En n. This is something that you know and your total wave function psi can be written as sum over n an of t e to the power of –i En t by h bar n and then you have a time-dependent perturbation which is nothing but H prime of t so that the total Hamiltonian will be equal to this.

And then you propagate using time-dependent Schrodinger equation which is nothing but ih bar d by dt of psi = H of psi. Now we use this okay to get to equation after some rearrangement and algebra that sigma over n ih bar Cn dot t e to the power of –i En t by h bar n = sigma over n, sorry an, we have got an t not Cn t an t, an of t e to the power of –i En t by h bar H prime of t acting on n okay.

Now what we did is after that we multiplied with psi m star on the left, so that is nothing but multiply with m and integrate. When you do this what you get is ih bar sum over n an dot t e to the power of –i En t by h bar m n, this is equal to sum over n an of t e to the power of –i En t by h bar m H prime of t n, so that is what you get.

(Refer Slide Time: 03:54)

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

$$\{|n\rangle\} \Rightarrow \text{Complete Set}$$

$$\hat{H}^0 \psi_n = E_n \psi_n$$

$$\langle m|n\rangle = \delta_{m,n} \begin{cases} \nearrow 1 & m=n \\ \searrow 0 & m\neq n \end{cases}$$

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

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

So what we had is ih bar sigma over n an dot t e to the power of–i En t by h bar m n = sigma over n an of t e to the power of –i En t by h bar m H prime of t n and then we argued that since form complete set and these are solutions of H0 okay, they are orthogonal or orthonormal. That means m n = del m n that is nothing but is equal to 1 when m = n and is equal to 0 when m is not equal to n.

Similarly on the right hand side we said m H prime of t n = 0 if m = n and not 0 or may not be equal to 0 if m is not equal to n okay. This is 0 if m = n because we said that you cannot look at perturbation of the state onto itself or you cannot look at the transition from a state to itself okay. Therefore, these are known as self transitions okay, transitions of a state to itself which cannot be observed, so we take it to be 0.

So based on this, this equation will turn out to be ih bar, now we can drop summation because the left hand side of the equation will only survive when m = n or n = m. In that case we will get am dot of t e to the power of –i Em t by h bar okay and m and this integral will go to 1 and this equal to in the right hand side all the terms survive other than when m = n okay. So, that means sum over n not equal to m an of t e to the power of –i En t by h bar m H prime t n okay.

So we arrived at this equation towards the end of the last class. Now we will continue this equation.

(Refer Slide Time: 07:25)

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

$$\dot{a}_m(t) = \frac{1}{i\hbar}\sum_{n\neq m} a_n(t)\, e^{-iE_n t/\hbar} . e^{iE_m t/\hbar} \langle m|\hat{H}'(t)|n\rangle$$

$$= \frac{1}{i\hbar}\sum_{n\neq m} a_n(t)\, e^{-i[E_n - E_m]t/\hbar} \langle m|\hat{H}'(t)|n\rangle$$

$$E_n - E_m = \Delta E = \hbar\omega_{nm}$$

$$\dot{a}_m(t) = \frac{1}{i\hbar}\sum_{n\neq m} a_n(t)\, e^{-i\omega_{nm} t} \langle m|\hat{H}'(t)|n\rangle$$

$$\boxed{\frac{\partial}{\partial t} a_m(t) = \frac{1}{i\hbar}\sum_{n\neq m} a_n(t)\, e^{-i\omega_{nm} t} \langle m|\hat{H}'(t)|n\rangle}$$

So what do you have ih bar am dot of t e to the power of –i Em t by h bar = an sum over n not equal to m an of t e to the power of –i En t by h bar integral m H prime of t n okay. Now this is what is a given. Now we have one issue that we need to look at okay or we can just rearrange before we look into it. Let us do some rearrangement okay. So ih bar when if I want to take the other side, so this will become am dot t = 1 over ih bar okay.

And sigma over n not equal to m an of t e to the power of –i En t by h bar into e to the power of i Em t by h bar m H prime of t n. So this is equal to now if I write this 1 over ih bar sum over n not equal to m an of t e to the power of –i En – Em t by h bar m h okay m H prime of t n okay. Now I can write En – Em = delta E = h bar omega nm okay. So if I write that this is equal to 1 over ih bar sigma n not equal to m an of t e to the power of –i omega nm t.

Because this h bar here and this h bar will get cancelled and we will get m H prime of t n okay. Now this is going to be so the left-hand side is nothing but d by dt of am of t because I told you am dot is nothing but time derivative = 1 over ih bar sigma over n not equal to m an of t e to the power of minus –i omega nm t m H prime t n okay. So that is the integral that we get okay.

Now we will see that the time dependence of a coefficient m will depend on all the other coefficients an’s that n is not equal to m. That means if you have a3, let us take m = 3 and there are total number of wave function of 10, then time dependence of a3 will depend on a1, a2, a4, a5, a6, a7, a8, a9, a10 okay. So it will depend on the time dependence of all the rest of the coefficients.

(Refer Slide Time: 12:37)

$$\frac{\partial}{\partial t} a_m(t) = \frac{1}{i\hbar}\sum_n a_n(t)\, e^{-i\omega_{nm}t}\langle m|\hat{H}'(t)|n\rangle$$

$$\boxed{a_m(t) = \frac{1}{i\hbar}\int \sum_n a_n(t)\, e^{-i\omega_{nm}t}\langle m|\hat{H}'(t)|n\rangle\, dt}$$

$$\Downarrow$$

No approximation.

First-order approximation.

No perturbation $H^0|n\rangle = E_n|n\rangle$

$H^0|i\rangle = E_i|i\rangle$

$H^0|g\rangle = E_g|g\rangle$

So what we have is d by dt of am of t = ih bar 1 over sigma over n an of t e to the power of –i omega nm t m H prime of t n okay. Now, I just want to find out am of t. So am of t will be equal to 1 over ih bar integral of sum over n an of t e to the power of–i omega nm t integral m H prime t n dt okay. So that is the integrated form of this coefficient and this is the most important okay.

Now to get to this equation I have not made any approximations because all the; math that we did was completely rigorous. No approximation was made to get to this equation okay. Now unfortunately, this equation involves coupled differential equations of you know n coupled differential equations okay. So if there are total n coefficients, each mth coefficient will depend on rest of all the coefficients.

So you will get a series of coupled differential equations. Totally if you have 10 such coefficients or 10 such wave function, then you will get 10 coupled differential equations okay. If you have 20 of them, then you will get 20 different coupled differential equations which are going to be very difficult solve okay. So then at this point of time, let us make a small approximation and that approximation I will call it as first-order approximation.

What do I do in the first-order approximation? Okay to begin with when there was no perturbation, what did we have? When there was no perturbation, then we had H0 of n = En n okay. Now let us suppose there is an initial state i okay, so which means H0 of i = Ei i okay. What is this initial state i? Let us state this initial state as a ground state or we can say this is H0 of ground state g = E of ground state into ground state okay.

Now if we had a ground state, all the population would be in the ground state and all the excited states will not be having any population.

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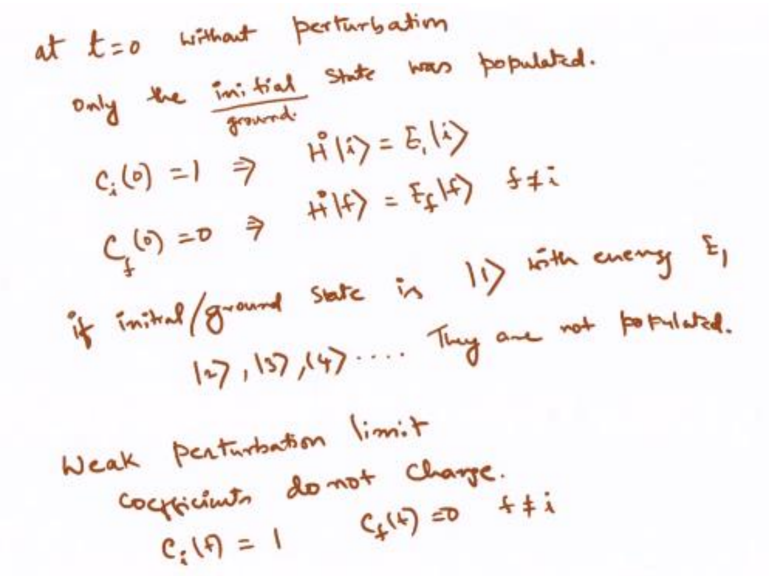

That means at t = 0 without perturbation, only the initial state was populated. That means Ci of 0 = 1 and this will correspond state H0 i = Ei i and C of any other state, let us say f okay of 0 = 0 and this will corresponds to H0 of f = Ef of f where f is not equal to i okay is 0 that is the reason. So only the ground state is populated or only the initial state is populated. I could say initial a ground okay. So Ci of 0 =1 and Cf of 0 = 0, okay.

Of course f here means all the other states other than the initial state. So if let us say quantum number 1 is i initial state is quantum number 1, then H1 or C1 is 1 and C2, C3, C4, C5, etc are zeroes okay. If with energy E1 as in the case of you know harmonic oscillator, sorry in the case of harmonic oscillator 0 state is populated, as in the case of particle in a box only n = 1 state is populated okay.

Now anything other than 1, that means states 2, 3, 4, etc they are not populated okay. So that is the scenario when you switch on when you do not have the perturbation or without the perturbation. Now what you want to do is that let us consider a weak perturbation limit. Now what does weak perturbation limit says if you have a weak perturbation limit, we will assume that under such limit thus even when you switch on the perturbation, the coefficients do not change too much okay.

So weak perturbations what happens is that coefficients do not change okay. This is the approximation that I am using. So we have using a weak perturbation limit and then we are saying that the coefficients do not change. That means Ci of t will still be equal to 1 and Cf of t will be equal to 0 for f not equal to i okay.

(Refer Slide Time: 20:36)

$$a_m(t) = \frac{1}{i\hbar}\int \sum_{n\neq m} a_n(t)\, e^{-i\omega_{nm}t} \langle m|\hat{H}'(t)|n\rangle\, dt$$

$$a_i(t) = 1 \qquad a_n(t) = 0 \quad n \neq i$$

$$a_f(t) = \frac{1}{i\hbar}\int \underset{\substack{\| \\ 1}}{a_i(t)}\, e^{-i\omega_{fi}t} \langle \underset{f}{m}|\hat{H}'(t)|\underset{i}{n}\rangle\, dt$$

$$a_f(t) = \frac{1}{i\hbar}\int_0^{t'} e^{-i\omega_{fi}t} \langle f|\hat{H}'(t)|i\rangle\, dt$$

$$\boxed{P_f(t) = |a_f(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^{t} e^{-i\omega_{fi}t} \langle f|\hat{H}'(t)|i\rangle\, dt\right|^2}$$

Now let us go back to our initial equation. What was that? I said Cm of t = 1 over ih bar integral sum over n, sorry an, not C, an of t e to the power of –i omega nm of t m h bar okay. Now what I am going to say, so ai of t = 1 and = an of t = 0 if n is not equal to i. In such scenario, then I can write af of t that is what you wrote earlier = 1 over ih bar integral of, all of them will go to 0 because the coefficients will be 0.

Only one coefficient will survive that will be ai of t e to the power of –i omega fi t m H prime of t n dt, a of t this is equal to 1, so one has no meaning in multiplying. So we will get af of t = 1 over ih bar integral, of course we have to integrate over some time t, t prime e to the power of –i omega fi t and this will become f H prime okay, this will become f and this will become i of t i dt okay.

So that is my coefficient of f state and if I want to consider the probability of f state P of f of t, then I will take modulus of af of t whole square. So this will become 1 over h bar square integral 0 to t e to the power of –i omega fi t f H prime of t i dt whole square okay. So this is the probability of finding the fth wave function. So that allows the transition from i state to f state and the probability of fth transition. So we will stop it here.