Lecture – 9
First-Order Correction to Time-Dependent Perturbation Theory

Hello, welcome to lecture number 9 of quantum mechanics and molecular spectroscopy course. Before we proceed with this lecture, let us have quick recap of the previous lecture. In the previous lecture, we started with the time-dependent perturbation theory of many states.

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So we had this time-independent Hamiltonian H0 solutions of which were H psi n = En psi n where n = for example 1, 2, 3, etc., okay. It is like a particle in a box or something like that okay for which we already know the solutions and we know in such a scenario, the function psi n form a complete set okay. Now if they form a complete set, then I told you any arbitrary function phi can be written as a linear combination of these functions.

Furthermore, since these are stationary states because the Hamiltonian itself is time independent, we can always write psi of n = psi n e to the power of –i En t by h bar. Apart from that, the total wave function can always be written as psi as a sum over n an e to the power of –i En t by h bar multiplied by psi n. Of course if you have time-dependent coefficients that means the wave function itself is moving in time, then you can always write psi as sigma over n an of t e to the power of–i En t by h bar to psi n.

And I also told you this psi n can be written also as n, this is an equivalent description of it. Then under this condition, we solve the time-dependent Schrodinger equation with acting of a perturbation. So ih bar d by dt of psi = H psi and in this case H = is equal to H0 + H prime of t okay.

Now if you have that, then you can expand your LHS will be equal to ih bar d by dt of psi which is equal to ih bar d by dt of sigma over n an of t e to the power of –i En t by h bar n okay and your RHS = H0 + H prime of t psi, this is equal to acting on psi, so this is equal to H0 + H prime of t acting on sigma over n an of t e to the power of –i En t by h okay.

So after expanding this that we looked at in the last class, we come up with the expression an dot t ih bar e to the power of –i En t by h bar n = an of t sigma over n H prime of t acting on e to the power of –i En t by h bar okay. What you can do is multiply with psi m star on the left and integrate. In such scenario what you get is im h bar sigma over n m an dot t e to the power of –i En t by h bar n = sigma over n an of t m H prime t e to the power of –i En t by h bar n okay.

So this we can rewrite as ih bar sigma over n an dot t e to the power of –i En t by h bar m n, this is equal to n time sigma over n an dot t m H prime of t n e to the power of –i En t by h bar. We know m n = delta m, n and m H of t of n = 0 for m = n and not equal to 0 perhaps for m not equal to n. In this case, this is equal to 0 if m not equal to n and is equal to 1 if m = n.

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

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

$$E_n - E_m = \Delta_{nm}$$
$$= \hbar \omega_{nm}$$

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

FIRST-ORDER PERTURBATION THEORY

$$a_i(0) = 1 \qquad a_{n \neq i}(0) = 0 \qquad a_{f \neq i}(0) = 0$$

Under weak perturbation limit
Coefficients do not deviate from original values.

So on the left hand side, only one term will survive where m = n. So what you will get is ih bar am dot t e to the power of –i Em t by h r, this is equal to sigma over n not equal to m an of t e to the power of minus –i En t by h bar m H prime t n okay. So this is the important difference, so there is only one term on the left hand side and there are all the terms n terms on the right hand side except n = m okay.

Now, I can slightly rewrite it as am dot t equals to if I take i on the other side it will become – i, so –i by h bar and e to the power of -Em t by h bar will become other side it will become plus i Em t by h bar. So this will become sigma over n not equal to m an of t e to the power of –i En – Em of t by h bar m H prime of t n okay. Now you can say En – Em = delta nm, this is nothing but h bar omega nm.

So this will come out to be –i by h bar sigma n not equal to m an of t e to the power of –i omega nm t m H prime t by n okay, this is am dot t. So for each mth coefficient, the time dependence will depend on the time dependence on the rest of the coefficients okay. So in this case, we will have n coupled differential equations okay. These have to be solved and you know it is going to be very difficult to solve n coupled differential equations.

Therefore, we play one and we use something called first-order perturbation theory okay. Let us suppose a system or a molecule, atom or whatever is it in ground state okay and that I will call it as an i of initial state. So let us say a of i at time t = 0 = 1 and a of n not equal to i at 0 = 0 or say a of f not equal to i of 0 will be equal to 0 okay. That means only population in the ground state and others are not populated at all okay.

Now in the first-order perturbation theory, we will assume that at later time t when the perturbation has acted and the perturbation is so small that the coefficients do not deviate much. So what we say is that under weak perturbation limit, coefficients do not deviate from original values okay.

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

$$a_i(t) = 1 \qquad a_{n=1}^{(t)} = 0$$

$$\dot{a}_f(t) = \frac{-i}{\hbar} a_i^{(0)} e^{-i\omega_{if}t} \langle f | \hat{H}'(t) | i \rangle$$

$$\frac{d}{dt} a_f(t) = \frac{-i}{\hbar} a_i(t) e^{-i\omega_{if}t} \langle f | \hat{H}'(t) | i \rangle$$

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

If such is the case, then am dot t = i by h bar – sigma over n not equal to m an of t e to the power of –i omega nm t m H bar t n okay. Now I said that for all other coefficients are going to be 0 except the coefficient of i. So that means ai of t = 1 an not equal to i = 0 of t. So in such scenario so if I start from a value of i and go to f of t will be equal to –i h bar because only one will survive that is ai, ai i e to the power of minus –i omega if t f H prime t i okay.

So that is what it is. So this is nothing but d by d t of af of t = –i h bar ai of t rather e to the power of –i omega f t f h bar t i. So if I integrate this af of t = –i h bar integral ai of t e to the power of –i omega ift f h t i dt acting for some time 0 to t prime okay. So this is the coefficient that we need to evaluate okay.

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Now in this equation, so af of t = –i by h bar integral 0 to t prime ai of t okay e to the power of –i omega if t f H prime of t i okay, something that I kind of missed out but this is equal to 1, this will become –i h bar integral 0 to t prime e to the power of –i omega if t, but this also an integral okay, integral psi f star H prime of t psi i d tau dt. So it is there is a two integral, there is one integral over this d tau and other is over dt okay.

Now very importantly, for this af of t to not to vanish or become 0, this integral should not be 0, that is one condition. If this integral becomes 0 or f H prime of t i if this should not be equal to 0, this integral. If this integral becomes 0, of course the whole af of t will become 0 okay. Now if this does not have to become 0, which means if you start with some initial state, i is the ground state or initial state okay and f is your final state.

Then your H prime t operator that is the time-dependent operator or time-dependent perturbation operator must be able to project your initial state onto a final state okay. So what does it mean? Now if you look at this integral okay, this is nothing but integral psi f star H prime of t psi i d tau. Now when H prime acts on psi f, it will result in some other function okay, let us call it as integral psi f star if H prime t acts on psi get the function phi and d tau.

Now this is nothing but psi f phi that is nothing but an overlap integral. So what does it mean? It means when H prime t or the perturbation acts on your ground state, it should create a new function which will have overlap with your final function. So overlap is nothing but the projection, so that overlap is nothing but whether when one function is projected on to other they have some commonality okay.

So in this case when H prime t acts on a ground state, the resulting function must be able to project onto your final state, only then this integral will become non-zero okay. So that is the most important point of spectroscopy, that the perturbation operator should be able to take your initial function and project onto the final function. Otherwise if let us suppose if this is just an operator 1, operator 1 or identity operator, then what you get is that f will project on to i.

Because we know f and I are the solutions of the time-independent Schrodinger equation, they will be orthogonal and they will go to 0. So that means an identity operator will never be able to cause transitions from initial state i to final state f, instead of that you will need something more than that, some time-dependent operator that will allow that projection of your initial state onto the final state okay.

Now that is only the coefficient, but in quantum mechanics probability is equal to square of the coefficient okay.

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

must not be zero

Selection Rules.

So P of t f = 1 over h bar square modulus of integral e to the power of –i 0 to t prime omega if t into f H prime of t i dt modulus square, so that is going to be the probability and this probability must be not equal to 0 and more importantly this integral must not be 0. If this integral goes to 0, then P of t will go to 0 that will be no probability of having a transition. So you can now quickly realize the fact that this integral governs the selection rules okay.

Because whether it is going to be 0 or non zero in spectroscopy means the selection rules okay and H prime t will have some form which we have not discussed, but we will come to that in the next lecture or the lectures following that. Whatever is the form of H prime t, it should make sure that this integral will not go to 0 and thus will correspond to the selection rules okay. We will stop here for this lecture and continue in the next lecture.