Quantum Mechanics and Molecular Spectroscopy
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Lecture – 6
Time-Dependent Perturbation Theory of Two States (Part – 3)

Hello, welcome to the lecture number 6 of the course quantum mechanics and molecular spectroscopy. We will have a quick recap of contents of lecture number 5.

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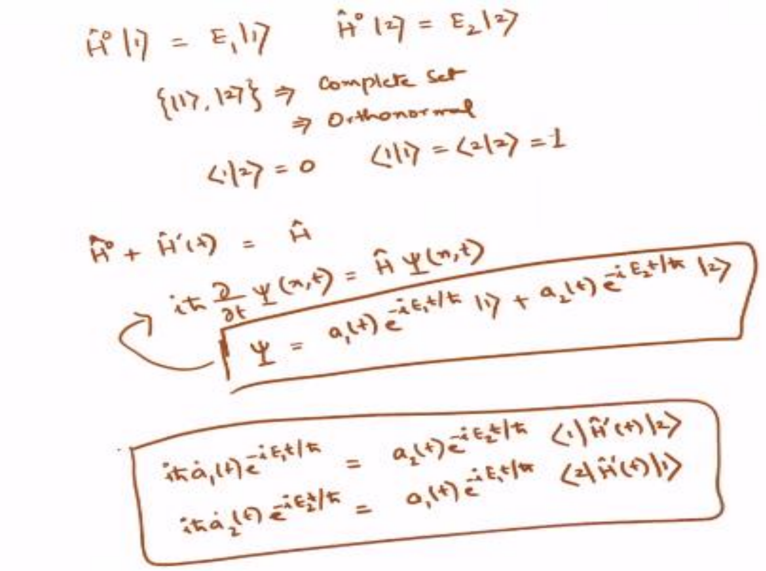

In the lecture number 5, we looked at the perturbation theory of two states in which if you had Hamiltonian H0 such that it acted on state 1 and produced E1 1 and H0 acting on state 2 gives you E2 2 and the states 1 and 2 form complete set and they are orthonormal. Orthonormal simply means integral of 1 over 2 = 0 and the integral of 1 over 1 should be equal to 2 over 2 which is equal to 1 okay.

Now, we said that there is a time-dependent perturbation that acts on states 1 and 2 of the system which is nothing but H prime of t and this when added to H0 will give you the total Hamiltonian H and it will follow the time-dependent Schrodinger equation okay. In this case, the psi is a superposition state, one can think of psi = 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 okay. So this is the wave function psi.

Now, by plugging the psi in the Schrodinger equation, we ended up with the following equation after doing some amount of algebra that is nothing but ih bar a1 dot t e to the power of –i E1 t by h bar should be equal to a2 of t e to the power of –i E2 t by h bar integral over 1 H prime of t 2. Similarly, we had ih bar a2 dot t e to the power of –i E2 t by h bar = a1 of t e to the power of –i E1 t by h bar 2 H prime of t 1 okay. So, these are the equations that we ended up in the last lecture.

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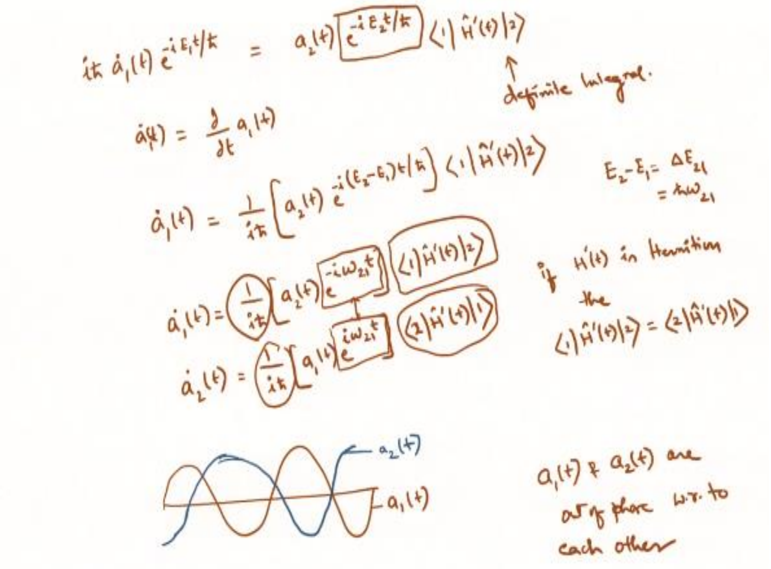

Now, let us start looking at this equation little bit more carefully ih bar a1 dot t e to the power of –i E1 t by h bar = a2 t e to the power of –i E2 t by h bar 1 H prime of t 2 okay. Now, of course this is a definite integral. This definite integral will give you some number okay. It could be 0, but definitely it could be a number. If this is some number and a2 t is a coefficient and e to power of –i is the face factor.

So all this tells you that the time dependence of a, by the way a1 dot t is nothing but d by dt of a1 of t. So, the time dependence of a1 coefficient will depend on a2 coefficient okay. One can rewrite this little bit in a different way. So, a1 dot t is equal to, so one can take ih bar on the other side, ih bar into a2 of e to the power of, now you can take this exponential function on the other side, so what we will get is –i E2 – E1 into t by h bar and the integral 1 H prime of t 2 okay.

Now, of course we can write E2 – E1 is equal to delta E21, so this is equal to h bar omega 21. So, if I write that way, then I get a1 dot t = 1 over ih bar a2 of t e to the power of –i omega 21 t because this h bar and that h bar will get cancelled okay into 1 H prime t 2 okay. Now, you can also rewrite the same equation starting from the other equation for a2 dot. So that will come out to be a2 dot of t will be equal to 1 over ih bar a1 of t e to the power of i omega 21 t

2 H prime of t 1.

Now I will quickly realize if H prime of t is Hermitian, then the integrals 1 H prime t 2 should be equal to 2 H prime t 1, of course this is only true when H prime is Hermitian. Then you will see that this one and these two will be equal or if they are not even, if this H is not Hermitian, then this will be complex conjugates of each other. Now you will see that this is if you look at the constants, this ih bar is a constant, okay.

Now, these are some constants because they are definite integrals okay. We will have either complex conjugate of each other or they are equal to each other. Now, all you can see that a1 dot's dependence on a2 is with this function e to the power of –i omega 21 while as a2 dot's dependence will be on e to the power of i omega 2. So, these two functions are out of phase with respect to each other, simply something like this okay, so that will be our a2.

So, whenever a2 will go up a1 will come down and whenever a2 will come down a1 will go up okay. So that is the time dependence of the two, a1 and a2 which are out of phase, al of t and a2 of t are out of phase with respect to each other okay.

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$$\left.\begin{aligned} \frac{da_1(t)}{dt} &= \left[a_2(t)\, e^{-i\omega_{21}t} \langle 1|H'(t)|2\rangle\right]\frac{1}{i\hbar} \\ \frac{da_2(t)}{dt} &= \left[a_1(t)\, e^{i\omega_{21}t} \langle 2|H'(t)|1\rangle\right]\frac{1}{i\hbar} \end{aligned}\right\} \text{Coupled differential equations.}$$

$a(t)$ and $a_2(t)$ are out-of-phase with respect to each other.

Now, if such is the scenario, so we need to solve this coupled differential equations which are nothing but da1 of t by dt = a2 of t e to the power of –i omega 21 t 1 H prime t 2 and da2 t by dt = whole thing divided by 1 by ih bar, a1 of t e to the power of i omega 21 t 2 H prime of t 1 over ih bar okay. So these two are coupled differential equations okay and such that a1 of t and a2 of t are out of phase with respect to each other okay. Now of course it is kind of difficult to solve, but we will make an attempt.

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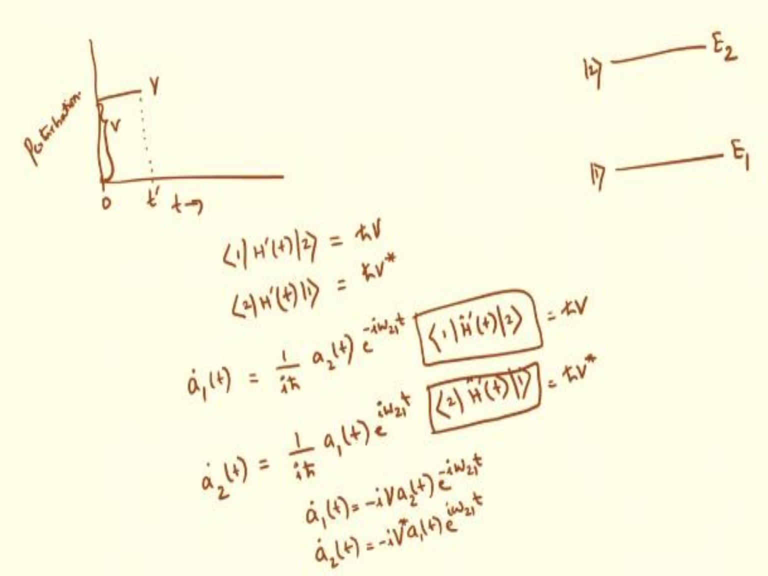

Now let us assume there are 2 two states, 1 and 2 with energies E1 and E2 okay. Now at time t = 0, I am going to switch on a constant perturbation okay and it is constant. So what happens is that a time and only if I think of perturbation, so I will switch on a time t = 0, this is time, it is equal to 0, I will switch on a constant perturbation for some time okay until this goes to say t prime okay and I will have some value, let us call it as V okay.

So this is V okay. Now in such a way that this 1 H prime of t 2 becomes h bar V and 2 h prime of t 1 becomes h bar V star okay, where V and V star are complex conjugates with respect to each other. In fact, if you look at these integrals, these integrals are complex conjugates of each other So if such is the scenario, then your a1 dot t will be equal to 1 over ih bar a2 of t e to the power of –i omega 21 t.

And you had this integral 1 H prime to H bar t 2 okay and other integral was a2 dot t = 1 by ih bar a1 of t e to the power of i omega 21 t 2 H prime t 1. Now, this integral of course is equal to h bar V and this integral equals to h bar V star okay. Then what happens? I can rewrite these equations as the following a1 dot t is equal to, this h bar and this h bar will cancel, i in the denominator will go to the numerator as –i.

So, –i V a2 of t e to the power of –i omega 21 t that will be a1 dot and your a2 dot t will be equal to minus –i V star a1 of t e to the power of i omega 21 t okay.

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$\dot{a}_1(t) = -iV a_2(t) e^{-i\omega_{21}t}$ $\qquad$ $\dot{a}_2(t) = -iV^* a_1(t) e^{i\omega_{21}t}$

$a_2(t) = -\frac{1}{iV}\dot{a}_1(t) e^{i\omega_{21}t}$ $\qquad$ $a_1(t) = -\frac{1}{iV^*}\dot{a}_2(t) e^{-i\omega_{21}t}$

Differentiate both the equations w.r.t 't'

$$\ddot{a}_1(t) = -iV\dot{a}_2(t)e^{-i\omega_{21}t} - \omega_{21}Va_2(t)e^{-i\omega_{21}t}$$
$$\ddot{a}_2(t) = -iV^*\dot{a}_1(t)e^{i\omega_{21}t} + \omega_{21}V^*a_1(t)e^{i\omega_{21}t}$$

HOME WORK

$$\ddot{a}_1(t) = -a_1(t)VV^* - i\omega_{21}\dot{a}_1(t)$$
$$\ddot{a}_2(t) = -a_2(t)VV^* + i\omega_{21}\dot{a}_2(t)$$

So I am going to rewrite them again. So what you had is a1 dot t = –iV a2 of t e to the power of –i omega 21 t okay and a2 dot t = –iV star a1 of t e to the power of i omega 21 t. So what I am going to do is I am going to rewrite this equation a slightly different way. So what I will do is this I will write in terms of a1 and a2. So, one can rewrite this equation as this will become a2 of t = -1 by iV a1 dot t e to the power of i omega 21 t because if this I take on the other side –i omega 21 becomes plus.

And this will become a1 of t will become -1 by iV star a2 dot t e to the power of –i omega 21 t okay. Now what I will do is I will differentiate once more. Differentiate bot the equations with respect to time okay. So what I will get is if I differentiate once more and rearrange okay, what I will get is the following a1 double dot t = –iV a2 dot t e to the power of –i omega 21 t – omega 21 two one V a2 of t e to the power of –i omega 21 t okay.

Similarly, I can get a2 dot t = –iV star a1 dot t e to the power of i omega 21 t + omega 21 to V star a1 of t e to the power of i omega 21 t okay. Then what I can do is instead of a1 and a2, I can plug these here and finally what I can get is the following. After rearrangement what I get is a1 double dot t = –a1 of t V V star – i omega 21 a1 dot t. Similarly a2 dot t = –a2 of t V V star + i omega 21 a2 dot t.

So, one can do you know you can all use these 4 equation equations and rearrange okay because wherever there is an a1 you can plug it in a2 dot and then you can do amount of rearrangement. It is not very easy, one can do it as a homework. So this is conversion of these to this okay, you can try it as a homework. It is not very easy, it takes a little more than 10 or

15 minutes or this is just simple math, so one can be able to do it. So what we have is these 2 equations okay.

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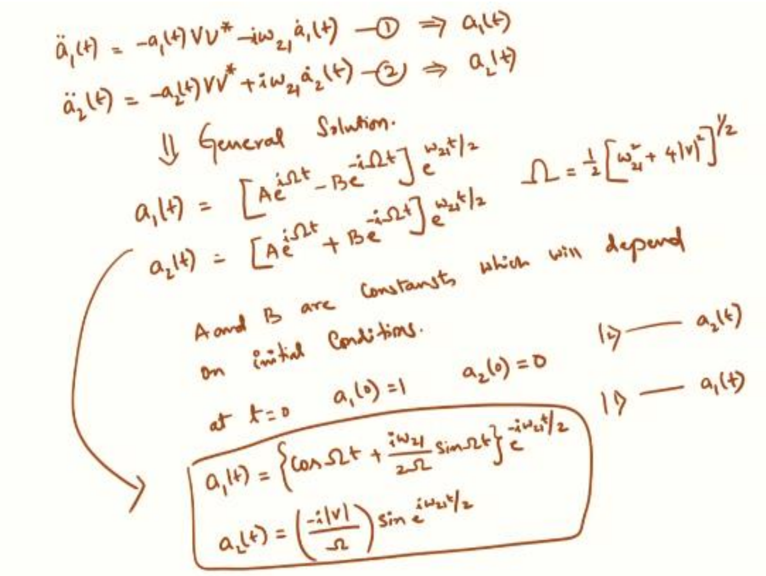

So the 2 equations that we have is very simply that a1 double dot t = –a1 of t V V star – i omega 21 a1 dot of t, a2 double dot of t = –a2 of t V V star + i omega 21 of a2 dot t. Now, by writing this we have done one thing very simple. Now, the equation 1 will only consist of a1 of t, a1 of t, its first derivative and its second derivate and this equation 2 will have only a2 of t. So, a2, its first derivative and its second derivatives with respect to.

So, what we have done by doing this, we have separated out the coupled differential equations in a1 and a2 as second order differential equations in a1 and a2 respectively. So, they are no longer coupled okay, but while going from first order equations we went to second order differential equations to uncouple them. Now, if you have such a case one can find a general solution.

The a1 of t will be equal to 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 and a2 of t = Ae to the power of i omega t + Be to the power of For –i omega t e to the power of omega 21 t by 2 where omega equal to half of omega 21 square + four times modulus of V square whole to the power of half and A and B are constants which will depend on initial conditions okay.

Now, one can solve this with the condition that at t = 0 a1 of 0 = 1 and a2 of 0 = 0. Why are we doing that? Because if we had two states 1 and 2 and their coefficients being a1 of t and a2 of t at time t = 0, we are assuming that the population is only in the state 1 and state 2 has no population and when you do that, these equations will run on to a1 of t will be equal to Cos omega t + i omega 21 by 2 omega Sin omega t whole e to the power of –i omega 21 t by 2.

And a2 of t will be equal to –i modulus of V by omega Sin e to the power of i omega 21 t by 2. So, these are the 2 equations that end up and one can then equate to get the probability.

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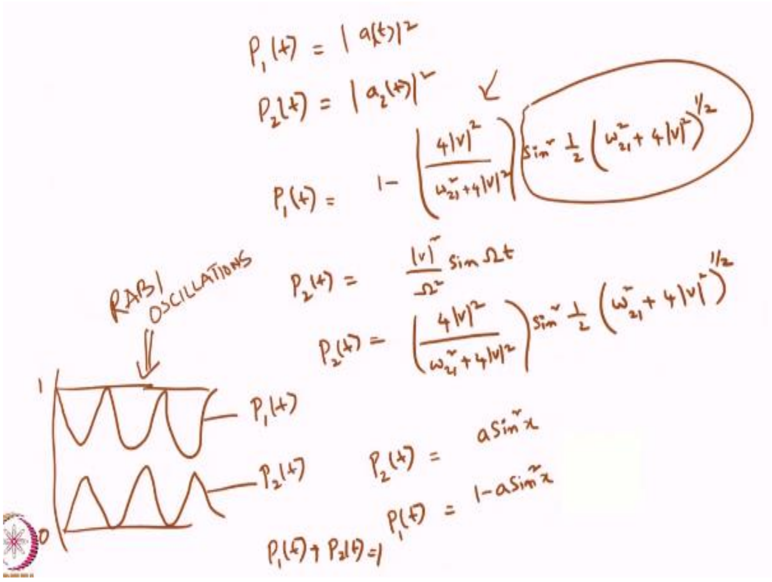

So, P1 of t will be nothing but modulus of a1 of t whole square and P2 of t that is probability of finding the system in state 2 is a2 of t modulus squared okay. In such scenario, what we will get is the following okay. P1 of t after doing some math, what we will get is 1 – 4 modulus of V square divided by omega 21 square + four times modulus of V square into Sin square half of omega 21 square + four times modulus of V whole square to the power of half.

And P2 of t will be equal to modulus of V by omega square Sin omega t which will be nothing but for time modulus of V square divided by omega 21 square + four times modulus of V whole square Sin square half of omega 21 square + four times modulus of V square to the power of half. Now, one can think of this is P2 of t, but think of it like this. So, there is some function that is Sin square x and some multiplier.

Now, let us look at P2, P2 of t, now this is Sin square of some function okay multiplied by something. So, let us call it as a Sin square x okay. So P1 of t is nothing but 1 – a Sin square of x. So, at time t = 0, let us this is 0 and this is 1 that is the population, if I take population, then my a1 will go up or go down like that. So, this is P1 of t and a2 will whenever will go like this, so this is P2 of t such that P1 of t + P2 of t = 1.

These oscillations of states 1 and 2 are called Rabi oscillations okay. So we will stop here and continue in the next lecture. Thank you.