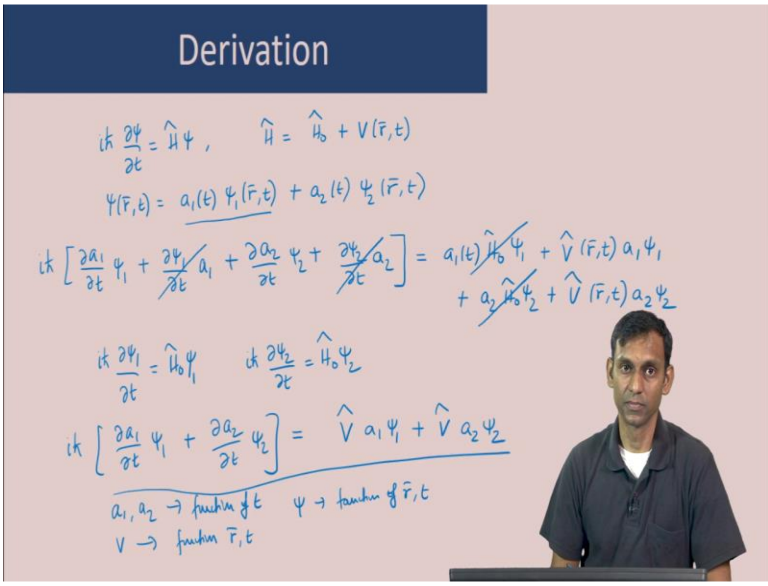
Fundamentals of Spectroscopy

Dr Sayan Bagchi
Physical and Material Chemistry Division, NCL Pune
Dr. Anirban Hazra
Department of Biotechnology
Indian Institute of Chemistry, IISER Pune

Lecture - 7
Intensity of a Transition Depends on the Transition Dipole Moment - II

(Refer Slide Time: 00:18)



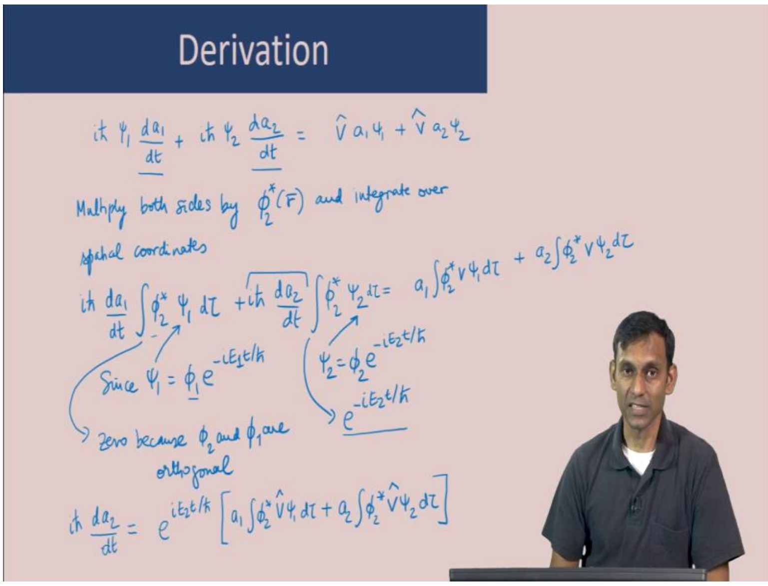
To obtain the expressions for a1 and a2 let us now substitute the form of Psi into the Schrodinger equation. So, the Schrodinger equation is ih bar del Psi by Del t is equal to H of Psi H is equal to H 0 + V of r, t and Psi is function of r and t which is a 1 of t Psi 1 r , t + a 2 of t Psi - of r , t now when we substitute in the Schrodinger equation we get the following expression i h bar del of a 1 by Del t Psi 1 + del of Psi 1 by Del t a 1 + del of a 2 by Del t Psi 2 + del of Psi 2 by Del t a 2 on the left hand side.

And on the right hand side we get H 0 operating on the first term gives a 1 t H 0 Psi 1 of r, t I am not going to write the variables because it is implicit here and we get + V of rt operating on a 1 Psi 1 + a 2 H 0 of Psi 2 + v of r, t operating on a 2 Psi 2 since Psi 1 and Psi 2 are solutions of the Schrodinger equation i h bar del Psi 1 by Del t is equal to H 0 of Psi 1 and using that we can cancel these two terms on both sides.

And similarly using i h bar del Psi 2 by Del t is equal to H 0 Psi 2 we can cancel these two terms this on the left side and this term on the right side. So, now there are two terms on the left-hand side and two terms on the right-hand side so let us write those i h bar del a 1 by del t Psi 1 + del a 2 by Del t Psi 2 is equal to V a 1 Psi 1 + V a 2 Psi 2 we have to keep in mind that the functions a V and Psi depend on variables and they are implicit here and I am not writing them specifically but a 1 and a 2 are functions of t V is a function of r and t and similarly Psi is a function of r and t.

In the interest of making the notation compact I am not writing these when we have written this form here. I am going to copy this to the next page and then we will proceed with the derivation.

(Refer Slide Time: 04:23)

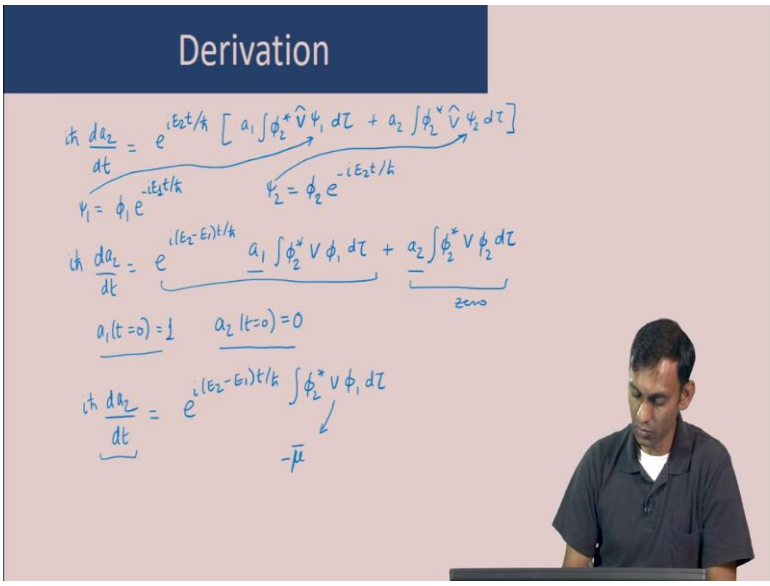


The equation here is very similar to what you had in the page before except that instead of the partial derivative with respect to time I have written this as a regular derivative because a does not really depend on any other variable besides time. So, here this is a regular derivative which is how it really should be. Now the next step is to multiply both sides of this equation from the left by Phi 2 star and integrate.

This gives i h-bar da1 by dt that goes outside the integral which depends on the spatial coordinates Psi 2 star Psi 1 T tau this is the spatial variable of integration and this integration is over all space and the other term is i h-bar da2 by dt Phi 2 star Psi 2 T tau is equal to integral a 1 does not depend on x so Phi 2 star V Phi 1 d tau + a 2 Phi 2 star V Psi 2 d tau since Psi 1 is equal to Phi 1 e to the power of minus i E 1 t by h bar when we substitute this here this first integral because of orthogonality of the Phi 2 and the Phi 1 becomes 0.

So this integral is 0 because Phi 2 and Phi 1 are orthogonal and similarly when we substitute for Psi 2 here which is Phi 2 e to the power of -i a 2 t by h bar when we substitute here then because these functions are normalized this simplifies and we get the net result of this integral to be simply e to the power of –i a 2 t by h bar. So, keeping only this part now on the left hand side and moving this e to the –i e - t on the right hand side we get i h-bar da 2 by dt is equal to e to the power of + i E 2 t by h bar multiplied by a 1 Phi 2 star d Psi 1 d tau + a 2 Phi 2 star V Psi 2 d tau. These are the interaction operator which we will see is just a multiplicative function.

(Refer Slide Time: 08:06)

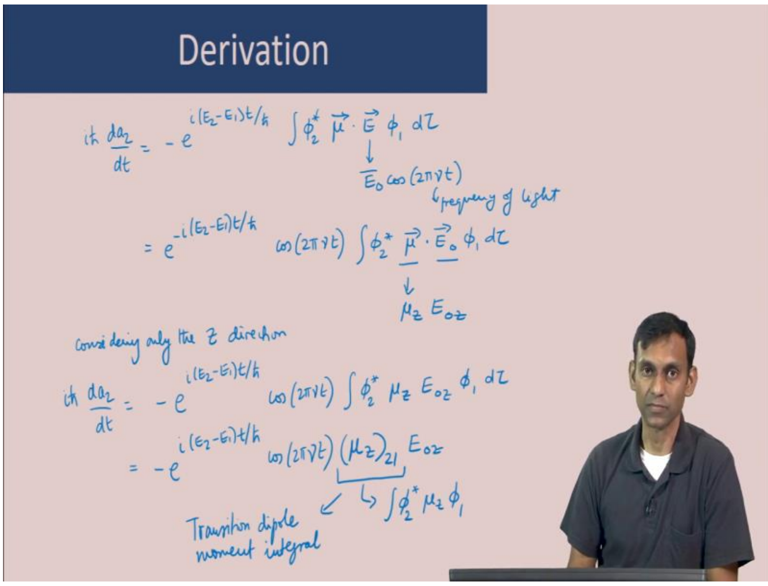


Let us copy this last line to a new page and continue with the derivation here is the expression from the previous page and using Psi 1 is equal to Phi 1 e to the power of -i a 1 t by h bar here and Psi 2 is equal to Phi 2 e to the power - i a 2 t by h bar here we can simplify this further this gives i h bar da 2 by dt is equal to e to the power of i E 2 – E 1 t by h bar a 1 Phi 2 star V Phi 1 d tau which is the first term in the above expression on the right hand side.

And the second term becomes a 2 Phi 2 star V Phi 2 d tau because the system is initially in the state Psi 1 a 1 of at time t is equal to 0 is equal to 1 and a 2 at time t is equal to 0 is equal to 0. Now since the perturbation due to the light can be considered to be small we can consider that these values of a 1 and a 2 here are very close to the initial values. So, we substitute these initial values into the above expression and get the following relation for da 2 by dt that is equal to e to the power of i E 2- E 1 t by h bar.

And the second term here is set to 0 this implies that the increase in a 2 which is da 2 by dt is primarily due to the first term here where a 1 is equal to 1 and that is because the system is initially in the state Psi 1. We will now substitute the expression for this interaction energy or perturbation which is minus mu dot e. And we will proceed with this derivation on the next page.

(Refer Slide Time: 10:52)

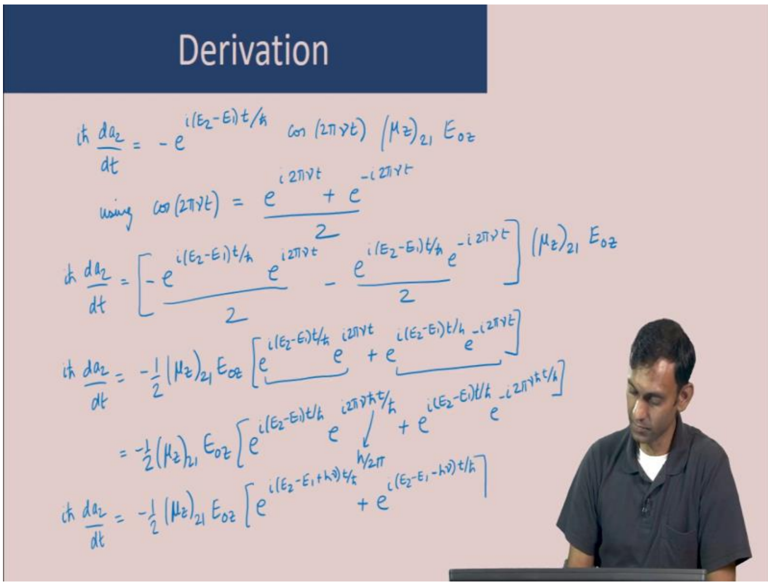


So, i h bar d a 2 by dt is equal to -e to the power of i E 2 - E 1 t by h bar and then the integral Psi 2 star the perturbation mu dot e and then Phi 1 d tau. Now the E as we have seen before is E 0 cosine of 2 pi nu t where nu is the frequency of the light. So, if we substitute this into the expression this further becomes e to the power of –i E 2 - E 1 t by h-bar the cosine comes out of the integral 2 pi nu t and integral Phi 2 star mu dot e Phi 1 d tau.

Now both the quantities mu and II not are vector quantities so they have three components x y and z. So, the dot product of these two terms will give us 3 terms corresponding to the x y and z terms. For simplicity we will consider only the term corresponding to z and the other terms will be just similar so we can write them down if necessary the term corresponding to z will simply be mu z here multiplied by E 0 z. So, considering only the z direction the expression becomes i h bar da 2 by dt is equal to -e to the power of i E 2 - E 1 t by h bar cosine of 2 pi nu t multiplied by Phi 2 star mu z E 0 z Phi 1 d tau.

And this we can write as minus e to the power of i E 2 – E 1 t by h bar cosine 2 pi nu t multiplied by mu z of 2 , 1 E 0 z where we define this as the integral Phi 2 star mu z Phi 1 and this is the transition dipole moment integral, in particular this is the transition dipole moment integral in the z direction.

(Refer Slide Time: 14:22)

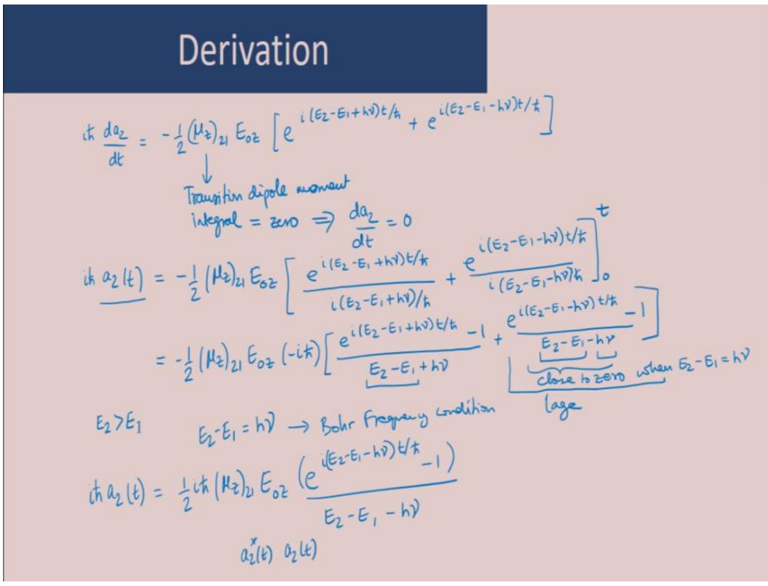


This is the expression we had on the previous page and using cosine of 2 pi nu t is equal to e to the power of i 2 pi nu t + e to the power of -i 2 pi nu t by 2 we can simplify this further so i h bar da 2 by dt is equal to minus e i E 2 - E 1 t by h bar multiplied by e to the power of i 2 pi nu t by 2 - e to the power of i E 2 - E 1 t by h bar e to the power of -i 2 pi nu t by 2 and this whole thing multiplied by the mu z transition dipole moment integral and the E0 z.

Therefore i h-bar be a 2 by dt is equal to minus half mu z 2 1 E of 0 z multiplied by e to the power of i E 2 - E 1 t by h bar e to the power of i 2 pi nu t + e to the power of i E 2 - E 1 t by h bar and e to the power of -i 2 pi nu t and this we can simplify further by adding the powers in these two terms. So, for that we do this is minus half mu z 2 1 E 0 z and we write this as E 2 - E 1 t by h bar and write this as e to the power of i 2 pi nu h bar t by h bar and similarly we do that for the other other term.

Using h bar is equal to h over 2 pi we can simplify this further and so i h bar da 2 by dt is equal to minus half mu z 2 1 E of 0 z and exponential i E 2 - E 1 + h nu t by h bar + e to the power of i E 2 - E 1 - h nu t by h-bar.

(Refer Slide Time: 17:43)



We have copied here the expression for d a2 by dt from the previous page and the important thing to note is that if this transition dipole moment is equal to 0 this is the transition dipole moment integral if this is equal to 0 it implies that da 2 by dt is equal to 0 in other words if the transition dipole moment integral is 0 then there are no transitions from the state 1 to the state 2 that is what this implies that transitions can occur from state 1 to state 2 only when this transition dipole moment is non zero.

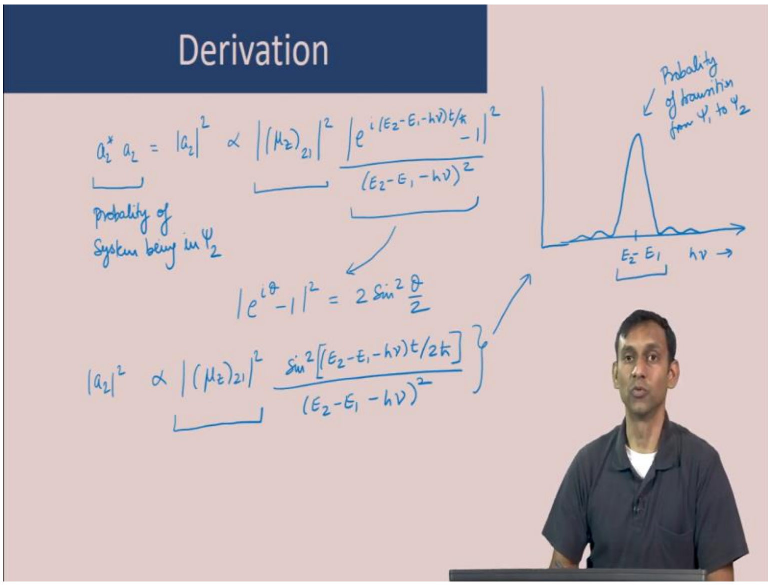
Now integrating this differential equation from time 0 to t we get the following so i h bar a 2 of t becomes minus half mu z E of 0 z and the integral here is e to the power of i E 2 – E 1 + h nu t by h bar and it is an integral with respect to the time variable and we get i 2 - E 1 + h nu divided by h bar here + e to the power of i E 2 – E 1 - h nu t by h bar divided by i E 2 – E1 - h nu by h bar and this integral is in the limits 0 to t. And substituting the limits of integration and simplifying this a little further we get minus half u z 2 1 E 0 Z and we move the i to the numerator so we get -i and we move the h bar to the numerator so we get h bar there.

And substituting for time t is equal to t we get e to the power of i E 2 - E 1 + h nu t by h bar and substituting for t time is equal to 0 we get e to the power of 0 which is 1 divided by E 2 - E 1 + h nu for this term and similarly e to the power of i E 2 - E 1 - h nu t by h bar -1 divided by E 2 - E 1 - h nu. Now supposing that E 2 is greater than E 1 we notice that this term E 2 - E 1 is a positive number and when this E 2 - E 1 becomes equal to H nu then this term becomes close to 0 and in this case when the difference in energy between the two states is equal to the energy associated with the light this is called the Bohr frequency condition.

And at this time it should be clear that the second term here is the dominant term is this becomes this second term becomes very large because the denominator becomes very small. And then under those conditions the contribution to the a 2 is greatest for the second term. So, when E 2 - E 1 is equal to h nu it is only the second term on the right hand side which contributes and we can write i h bar a 2 is equal to half i h bar nu z of 2 1 0 z and only the second term which is e to the power of i E 2 - E 1 -h nu t by h bar - 1 divided by E 2 - E 1 - h nu.

The probability of transition to the state 2 or the intensity of absorption from the state 1 to 2 depends on a 2 star a 2 function of t and let us write the expression for this now because we already have the expression for a 2.

(Refer Slide Time: 23:00)



Using the expression for E 2 derived on the previous page we can write the expression for a 2 star a 2 which is the probability of the system being in a 2 system being in Psi 2 and this is proportional to the transition dipole moment integral Square and the term that you see here. Now the numerator of this term can be simplified further by using the identity e the power of i theta - 1 mod squared is equal to 2 sine squared theta by 2. So, this a 2 mod squared becomes proportional to mu z 2 1 squared sine squared E 2 - E 1 - h nu t by 2 h bar divided by E2 – E1 - h nu whole square.

If we plot this function versus h nu then the function looks something like this where the peak of this function is at h nu is equal to E 2 – E 1 this represents the probability of the transition from state 1 to 2 and shows that this probability is the largest when h nu is equal to the difference between the energies of the two states. So, we have seen that the probability of transition or the intensity of absorption from one state to another depends on two critical things one is the transition dipole moment integral and the second is the light having a frequency which is equal to the difference in energy of the two states.

This will be a very important concept in spectroscopy and will be applicable to all types of spectroscopy you.