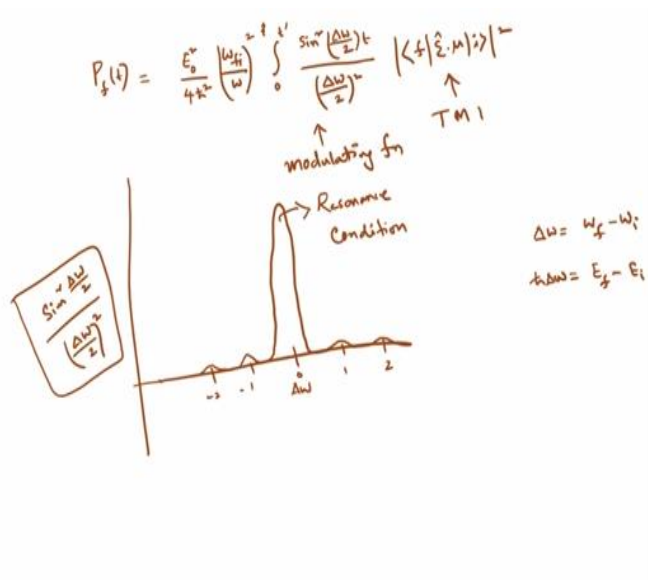


Quantum Mechanics and Molecular Spectroscopy
Prof. G Naresh Patwani
Department of Chemistry
Indian Institute of Technology, Bombay

Lecture No -17
Transition to Continuum States: Fermi's Golden Rule

Hello, welcome to lecture number 17 of quantum mechanics and molecular spectroscopy. In the previous class we were looking at the transition probability and we arrived at the equation

(Refer Slide Time: 00:29)

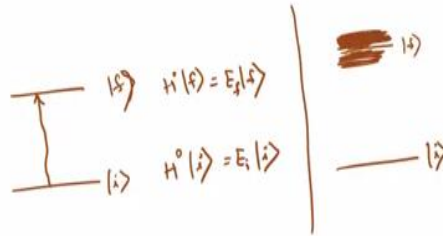


P_f of t equals to E_0 square by $4h$ bar square ω_f by ω square integral 0 to t prime sine square $\Delta\omega$ by 2 into t divided by $\Delta\omega$ by 2 whole square, integral f epsilon dot mu i whole square. And this I told you is the transition moment integral TMI and this is the modulating function. Now when you plot this modulating function as a function of $\Delta\omega$, where $\Delta\omega$ is nothing but $\omega_f - \omega_i$ and $h\Delta\omega$ is equal to $E_f - E_i$, in that scenario this will look like this, something like that.

This is the function sine square $\Delta\omega$ by 2 divided by $\Delta\omega$ by 2 square, now if this function looks like this, means the maximum absorption will happen $\Delta\omega$ by 1 is equal to 0 that is what at the resonance condition. But you should always see there will be very tiny absorptions even in the wings, and that wings are governed by this, where in the wings it will get absorbed will govern by this equation and will depend exactly on $\Delta\omega$.

(Refer Slide Time: 03:24)

$$P_{f,i}(t) = \frac{E_0^2}{4\hbar^2} \left(\frac{\omega_{if}}{\omega}\right)^2 \frac{\sin^2\left(\frac{\Delta\omega t}{2}\right)}{\left(\frac{\Delta\omega}{2}\right)^2} |\langle f | \hat{H} | i \rangle|^2$$



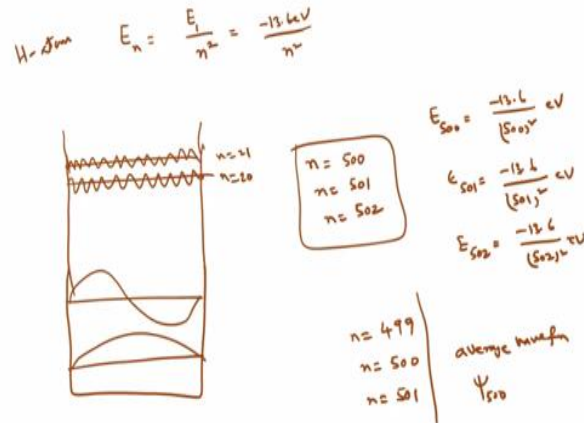
Continuing with the present lecture, now let us go back and look at this equation little bit more carefully, where $P_{f,i}(t)$ is equal to E_0^2 square by $4\hbar^2$ square ω_{if} by ω square sine square $\Delta\omega t$ by 2 by $\Delta\omega$ by 2 square $f \epsilon \mu i$ whole square. I made a small mistake in the last slide, this integral does not exist because sin square came over only it was like a standard integral, now this is what we get.

This is the probability of transition from an initial state i to a final state f , of course as you look at this is a t dependent. That means as long as the perturbation is there, the transition will take place, so longer the perturbation longer will be the transition probability because that time comes here, so you see the perturbation can actually be prolonged and you can increase the transition probability. Now there is one issue that we will look at in this lecture is the; what if state f is not isolated?

So in this case what is happening? You are going from initial state i which is precisely defined to a final state f which is precisely defined, so we know that $H^0|i\rangle$ is equal to $E_i|i\rangle$ and $H^0|f\rangle$ is equal to $E_f|f\rangle$. But this is when f is separated out, that means f is a clean state that does not have anything in its vicinity, but that may not be possible all the time. So what if f lies in the midst of some states?

Let us look at the possibility that there is an initial state i which is a ground state which is well separated but there is a final state f which is in between many many such states. A state f is embedded in a density, it is not a cleanly separated state but state f is embedded and where you can think of hydrogen atom.

(Refer Slide Time: 07:03)



Now hydrogen atom, let us say E_n for H atom is given by let us say, E_1 by n square, just proportional to square of the principal quantum number and E_1 is the principal quantum number 1 state. This is generally equal to if energy is -13.6 eV divided by n square. Now if you go and look at that state and look at large values of n , let us say the value of n is equal to 500, n is equal to 501, n is equal to 502.

If you go to such states, E_{500} is equal to -13.6 divided by 500 square in eV, E_{501} is equal to minus 13.6 divided by 501 square into eV and E_{502} is equal to -13.6 by 502 square in eV. If we plot these energies, they will be very close to each other, in fact the difference will be less than milli electron volts, in fact it will be micro electron volts. So, essentially the energy levels 500, 501 and 502 are lying on top of each other, so such will be the scenario.

And the other thing is what happens to the wave function? Now let us look at, I will give an example very simply as a particle in a box. Now the particle in a box wave function will look like this, for n is equal to 1 it looks like this, n is equal to 2 it will look like this. Now going to

very high values of n is equal to let us say 20 and 21, so for 20 it will have 19 nodes, I do not know many nodes are there and for 21 there will be just one extra.

What happens is that the wave function does not really change much between n is equal to 20 and n is equal to 21. So when you go very high in energy where the energy levels are densely packed, the wave function changes are also very small. So in this case let us say if I have any n, let us redefine that n is equal to 499, n is equal to 500, n is equal to 501, if you take three states one can describe the state by wave function on the average by average wave function will look like psi 500 approximately.

It will not change too much with respect to 500, if you go down by 1 to 499 or 1 up by 501 and energy also will remain more or less constant. In such a scenario, if there are a lot of states.

(Refer Slide Time: 10:36)

$$P(t) = \int_{\pm} P_f(t) \rho_f(E) dE$$

density of states
Number of energy levels in unit energy.

$$P(t) = \frac{E_0}{4t^2} \left(\frac{\omega_{fi}}{\omega} \right)^2 \int_{\pm} \frac{\sin^2\left(\frac{\Delta\omega}{2}t\right)}{\left(\frac{\Delta\omega}{2}\right)^2} \rho_f(E) dE \left| \langle f | \hat{z} | i \rangle \right|^2$$

For a very narrow range of energy close in
the function is minimal and can be ignored.

$$P(t) = \frac{E_0}{4t^2} \left(\frac{\omega_{fi}}{\omega} \right)^2 \left| \langle f | \hat{z} | i \rangle \right|^2 \int_{\pm} \frac{\sin^2\left(\frac{\Delta\omega}{2}t\right)}{\left(\frac{\Delta\omega}{2}\right)^2} \rho_f(E) dE$$

Constant



Now what I want to get is the transition probability P of t of a state f but not really of a state f, but states around f, total probability will be nothing but integral over f, P f of t density of states E dE. What is this density of state? That means, for a unit energy how many energy levels are packed? That is the rho E, so rho E is nothing but density of states, density of state simply means number of energy levels in unit energy.

Unit energy is kind of you can define one joule or one calorie or one kilojoule or one kilocalorie or centimeter inverse or eV or milli eV, it is up to you what will be the interval that you want to define. If I use that then my P of t will be equal to E_0^2 square by $4\hbar^2$ square omega f i by omega whole square integral f, rho E of f, sine square delta omega by 2 to t by delta omega by 2 whole square rho f of E dE, that is my density of states.

If I define for very narrow range, change in wave function is minimal and can be ignored, in that case then your f epsilon dot mu i, so what I am saying is that this f, even though I am looking at transitions to many of these states, I will take an average value and that change is not going to be very much different, there is a modulus square here. I am going to slightly rewrite this. This P of t is equal to E_0^2 square by $4\hbar^2$ square omega f i by omega square modulus of f epsilon dot mu i whole square integral over f sine square delta omega by 2 t by delta omega by 2 whole square rho f of E dE.

So that is the integral I need to evaluate and this I told you is a constant because the wave function f in average sense is already defined. When you have that so let us slightly look at delta omega, now what is delta omega?

(Refer Slide Time: 14:54)

Handwritten derivations showing the relationship between energy levels and transition probability:

$$\Delta\omega = \omega_n - \omega = \frac{E}{\hbar} - \omega \quad E = \hbar\omega_n$$

$$x = \frac{1}{2} \left(\frac{E}{\hbar} - \omega \right) t \quad dE = \left(\frac{\hbar}{t} \right) dx \quad \text{Variable transformation}$$

$$P(t) = \frac{E_0^2}{4\hbar^2} \left(\frac{\hbar^2}{\omega} \right) \left| \langle 1 | \hat{E} | 0 \rangle \right|^2 \int_{-\omega}^{\omega} \frac{\sin^2 \left(\frac{\Delta\omega}{2} \right) t}{\left(\frac{\Delta\omega}{2} \right)^2} \rho(E) dE$$

Change in the integration limit

$$P(t) = \frac{E_0^2}{2\hbar} \left(\frac{\hbar^2}{\omega} \right) \left| \langle 1 | \hat{E} | 0 \rangle \right|^2 t \int_{-\omega}^{\omega} \frac{\sin^2 x}{x^2} dx$$

$$\int_{-\omega}^{\omega} \frac{\sin^2 x}{x^2} dx = \pi$$



Delta omega is nothing but omega f i minus omega, this is nothing but E by h bar minus omega, where E is equal to h bar omega f i, so this E is the energy states that we have. This is your i that

is E_i but this is like E , the states around which you are looking at the energy. Now if I define x as half of E by $\hbar \omega$ into t , then your dE will be nothing but $2\hbar \omega dt$. My initial equation was, I am just choosing something called variable transformation I am just trying to change from dE or E to x and I define x in terms of E .

What we had is $P(t)$ is equal to E_0^2 by $4\hbar^2 \omega^2 f^2$ by ω^2 modulus of $f(\epsilon)$ dot μ_i whole square integral sine $\frac{\Delta \omega}{2}$ sine square into t by $\frac{\Delta \omega}{2}$ whole square $\rho f(E) dE$. After this transformation I can write $P(t)$ is equal to E_0^2 square by $2\hbar \omega f^2$ by ω^2 integral $f(\epsilon)$ dot μ_i square into t $\rho f(E)$ integral $-\infty$ to $+\infty$ sine square x by $x^2 dx$.

Now there is one thing that I want to do is the range, here I have defined over some range f , but here I have defined over $-\infty$ to $+\infty$, so there is a change in the integration limit. This change in the integration limit comes because you have redefined your range in E , so essentially I will tell you what it means. It means that if you have some energy that around E you are looking at, so essentially you are looking at this small range defined by some average wave function f .

But if you move away from this or above this, the average wave function is no longer the same, so your wave function has changed. The wave functions corresponding to the energy have changed, this integral will not matter anymore, therefore you can extend the range from minus infinity to plus infinity because it is similar to extension of adding 0s, because the wave functions are going to be different.

Because of this energy range and you are fixing your energy to a small energy range, this integration can be extended to minus infinity. Now it turns out that integral minus infinity to plus infinity sine square x by $x^2 dx$ is nothing but π .

(Refer Slide Time: 19:36)



$$P(t) = \frac{\pi E_0^2}{2\hbar} \left(\frac{\omega_f}{\omega}\right)^2 |\langle f | \hat{e} \cdot \mu | i \rangle|^2 \rho_f(\epsilon) \cdot t$$

$$W_{fi} = \frac{P(t)}{t} = \frac{\pi E_0^2}{2\hbar} \left(\frac{\omega_f}{\omega}\right)^2 |\langle f | \hat{e} \cdot \mu | i \rangle|^2 \rho_f(\epsilon)$$

↑
rate of absorption

$$W_{fi} = 2\pi\hbar |\mu|^2 \rho_f(\epsilon)$$

$$|\mu|^2 = \frac{E_0^2}{4\hbar^2} |\langle f | \mu | i \rangle|^2 \left(\frac{\omega_f}{\omega}\right)^2$$

↑
Transition Dipole

$$W_{fi} = K \rho_f(\epsilon) \quad W_{fi} = \rho_f(\epsilon)$$

$W_{fi} \propto \rho_f(\epsilon) \Rightarrow$ Fermi's Golden Rule.

If I do that then P of t will be equal to pi E0 square by 2 h bar omega f i by omega square integral f epsilon dot mu i square rho E at f into t, so that is my final equation. If I define something called Wf i, this is nothing but the rate of absorption, that is nothing but this has probability by time, so that is nothing but P of t by t, that is nothing but pi epsilon0 by 2 h r omega f i by omega square modulus epsilon naught i square root.

Now I can define some quantity such as Wf i equals to 2 pi h bar modulus of mu square into rho of f, where now you can look at this equation and then decide modulus of mu square is equal to E0 square by 4 h bar square f epsilon dot mu i square omega phi by omega square. There are two values, this is called the dipole transition, by the way this is TMI, that is transition moment integral, so this is called transition dipole and transition dipole is defined like this and Wf i, that rate for absorption will depend on these values.

For a given f, this is a constant and omega fi is constant and if you know what wavelength of light you are shining, this is constant. So all these are constants, everything that inside is a constant, which means for a given transition mu square is a constant and you know Wf i, that is rate, 2 pi h bar also is a constant, mu square is constant. So 2 pi h bar is some constant K into rho f of E, which means your rate W f i is given by rho f E, which means that from initial state i to a density of states around f, this rate of transition will depend on the density of states.

So the rate of transition ϕ is proportional to density of states around f and this is called Fermi's golden rule.

(Refer Slide Time: 24:09)

The slide contains handwritten notes in brown ink. On the left, there is a diagram of energy levels: a single level labeled $|i\rangle$ at the bottom and a cluster of levels labeled $|f\rangle$ at the top. A vertical line connects them, labeled "Rate of transition". To the right, the following equations are written:

$$W_{fi} = \frac{\pi E_0^2}{2\pi} \left(\frac{\mu_{fi}}{\hbar}\right)^2 \rho_f(E_f)$$

$$W_{fi} = 2\pi\hbar |\mu|^2 \rho_f(E)$$

$$|\mu|^2 = \frac{E_0^2}{4\hbar^2} \left(\frac{\mu_{fi}}{\hbar}\right)^2 |\langle f|E|i\rangle|^2$$

An arrow points from the last equation to the text "Transition dipole". Below these, a bracket groups the following two proportionalities:

$$W_{fi} \propto |\mu|^2$$

$$W_{fi} \propto \rho_f(E)$$

These are collectively labeled "Fermi's Golden Rule." At the bottom left of the slide is the NPTEL logo.

So essentially the transition between a state i to a densely packed states around f , this rate of transition W_{fi} is equal to πE_0^2 square by $2\hbar$ bar ω_{fi} by ω_{fi} square f epsilon dot μ_i modulus square into ρ_f . This can be written as W_{fi} is equal to $2\pi\hbar$ bar modulus of μ square ρ_f of E and modulus of μ square is equal to E_0^2 square by $4\hbar$ bar square ω_{fi} by ω_{fi} square modulus of f epsilon dot μ_i square.

So this is the transition dipole which of course for given transition is constant, you can think of it like this your rate constant W_{fi} is proportional to modulus of μ square and W_{fi} is proportional to ρ_f of E . The rate for the transition between i and the dense states f is given by the transition dipole and density of state and these constitute Fermi's Golden Rule. I will stop here and continue in the next lecture thank you.