Fundamental of Spectroscopy

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Lecture – 05
Spectroscopic Transitions

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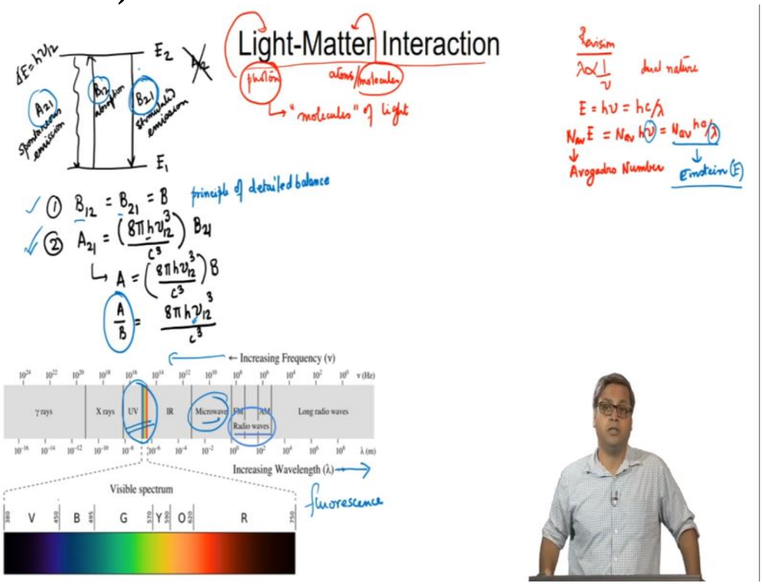

Light-Matter Interaction

Hello everyone, welcome to the lecture. In the last lecture, you have learned about the basic concepts of quantum mechanics. I hope these basic concepts, will help you to understand and appreciate spectroscopy or light matter interaction. Let us start with the revision of what you have learned about spectroscopy, from the very first lecture of this course. In the very first lecture, we started by describing light as an electromagnetic wave.

We learned what is wave length? That is lambda and its inverse relation to frequency that is wavelength is inversely proportional to frequency. From there on, we discussed about the dual nature of light. We have seen that according to the light quantum hypothesis of Einstein, light consists of photons. So, light consists of photons, and as we know, matter consists of atom and molecules. So, we can think, what is a molecule for matter, photon is for light. In other words, we can write photons as molecules of light.

So, we have seen that energy of one photon is given by E equals h mu equals hc / lambda. And from the problem that we solved in the first lecture, we saw the energy of one mole of photon is given by N av times E, where in av is Avogadro number and we can write N av times E as N av times h nu or N av times hc / lambda. This amount of energy is called 1, Einstein. Or in other words, one can express energy using Einstein or E as unit.

Note that this unit Einstein or E is dependent on the frequency or the wavelength of the light that is being used. We ended the lecture with a discussion on Einstein's coefficients; Einstein's A and B coefficients representing probability of our spectroscopic transition for example, absorption or emission are related. So, these Einstein's coefficients are related. And now let us consider 2 energy levels, the lower energy represented by E 1 and the higher energy represented by E 2. So, in this case, we have 3 Einstein's coefficients.

One is A 21 that is for spontaneous emission. Then B12 for absorption process and the B21 for stimulated emission. So, we should remember that there cannot be a process with coefficient A12. This is because, when the molecules are already at the ground state, we need some stimulation by light to take the molecules to the excited state. Or in other words, molecules in the ground state cannot reach the excited state spontaneously.

So, in the last class we saw, these 3 coefficients are related and we found 2 relations. Number 1 is B 12 = B21, and we can write this as B as Einstein B coefficient. The other relation is A 21, we can write this 8 pi h nu 1 2 cube by C cube times B 21. So here, h is the Planck's constant, nu 12 is a frequency for the transition, where delta E = h nu 12 and C is the speed of light. So we can write this as A that is Einstein’s A coefficient equals 8 pi h nu 12 cube by C cube times B.

Or in other words, we can again write A / B = 8 pi h mu 12 cube, C cube. The first relation states that, for the given 2 states, the probability of absorption and the probability of stimulated emission are the same. Note that the absorption and the stimulated emission occur via the same mechanism that is both a light induced phenomena. And this is known as principle of detailed balance.

The second relation indicates that the probabilities of the spontaneous emission that is A21 and that of the stimulated emission that is B21, they are not the same. The ratio A / B depends on the frequency or the wavelength of light for radiations, with lower frequencies the ratio A / B small. So, this figure shows the entire electromagnetic spectrum. We can see the frequencies of radio waves or microwaves are smaller than the frequencies of the UV visible region.

So, here frequency is increasing on the left side and wavelength which is inversely proportional to frequencies increasing the right side. Hence, A by B ratio is small in the radio wave or the microwave range. This means spontaneous emission in this wavelength range is less likely to occur compared to stimulated emission. On the other hand, for larger frequencies or shorter wavelengths, that is in the UV visible region the A by B is large and the spontaneous emission is more likely to occur in this wavelength range.

You may have already heard about the process called fluorescence. So, fluorescence is a spontaneous emission process, occurring mainly in the UV visible range. Existence of these 2 relations, this 1 and 2 between the 3 parameters, A21, B12 and B21 indicates the determination of any one of them will give information of the other 2.

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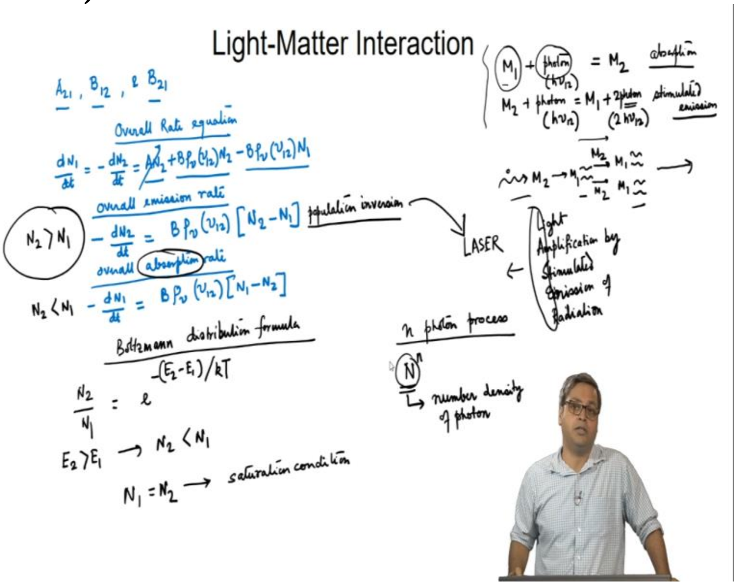

Light-Matter Interaction

$A_{21}, B_{12}, \& B_{21}$

Overall Rate equation

$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = AN_2 + B\rho_\nu(\nu_{12})N_2 - B\rho_\nu(\nu_{12})N_1$

overall emission rate

$N_2 > N_1$ $\quad -\frac{dN_2}{dt} = B\rho_\nu(\nu_{12})[N_2 - N_1]$ population inversion → LASER

overall absorption rate

$N_2 < N_1$ $\quad -\frac{dN_1}{dt} = B\rho_\nu(\nu_{12})[N_1 - N_2]$

Boltzmann distribution formula

$\frac{N_2}{N_1} = e^{-(E_2-E_1)/kT}$

$E_2 > E_1 \rightarrow N_2 < N_1$

$N_1 = N_2 \rightarrow$ saturation condition

$M_1 + \underset{(h\nu_{12})}{\text{photon}} = M_2$ absorption

$M_2 + \underset{(h\nu_{12})}{\text{photon}} = M_1 + \underset{(2h\nu_{12})}{2\text{photon}}$ stimulated emission

LASER ← Light Amplification by Stimulated Emission of Radiation

n photon process

N^n → number density of photon

When light falls on matter, all the processes represented by A 21, B 12 and B 21 that is spontaneous emission, absorption and stimulated emission can take place. The net result can be studied by considering the overall rate equation. So we can write and overall rate equation. There for the 2 level system, one can write the overall rate equation as d N 1 dt = - d N 2 dt = A N 2 + B Rho nu mu 12 N 2 - B rho nu nu 12 N 1.

So now, we can see this first term comes from spontaneous emission, the second term comes from stimulated division and the third term comes from exemption. So, if we consider that the probability of the spontaneous emission is very small or this A time is very small. We can write. So we can neglect this and we can write an overall emission rate. So the overall emission rate and innovation process molecules go from higher energy levels to lower energy levels. So, how the molecules at a higher energy level E 2 are changing over time.

So, we can write – d N 2 dt = B rho nu 12 N 2 – N 1. Similarly, we can write an overall absorption rate. So, overall absorption rate and because in the absorption process, the molecules go from lower energy level to higher energy level. So, in this case we are talking about the rate of change of the molecules from the lower energy level. In that case, the overall absorption rate is - d N1 dt and that is equals B rho nu nu 12 N 1 – N 2.

So, we can see, if N 2 < N 1, that is the lower energy level is more populated than the upper level, we will get a net absorption. Only in the event, when N 2 is > N1, we would observe an net emission. Normally, for systems at thermodynamic equilibrium, the ratio N 2 by N 1 is given by the Boltzmann distribution formula. So, this Boltzmann distribution formula tells us N 2 by N 1 = e to the power – E 2 – E 1 / kT.

So, as we know that E 2 corresponds to the energy of the higher energy level. So, E 2 is better than E 1. So, under this condition we get N 2 < N 1. That is, the lower level is always more populated than the upper limit. Thus under ordinary condition of thermodynamic equilibrium, one would always get that the absorption of light. For an overall induced emission to occur, one requires a situation where N 2 > N 1 that is population of the upper state is greater than the population of lower state.

And this is known as the condition of population inversion. For that, if we have N 1 = N 2, there will be no net absorption or emission of radiation and this is known as the saturation condition. We can see that the absorption process can be written as M 1 + photon that with energy h nu 12 that gives a new state of the matter that is M 2. So, M 1 was the initial state of the matter with energy E 1.

Now, when photon comes in with frequency nu 12, we get the matter in the new energy state that is M 2 and this is for absorption process. Similarly, for stimulated emission, we can write

M 2 + photon that is h nu 12 gives M 1 + 2 photon, that is 2 h nu 12. In chemical parlance this process written can be thought of as an autocatalytic reaction. Because the photon that is being created or in terms of chemical reactions is photon is a product, this photon is catalysing the reaction. So, this is an example of auto catalysis.

Again this process indicates that the number of photons get increased as the process continues. For example, we can write this a photon and M 2 this gives M 1 and 2 photons. Then each of these photons will interact with M 2 and will create 2 more photons. So, we have 4 photons and this process will go on. So, we can see one can multiply the number of photons in this manner.

Increase in the number of photons of a given frequency means, an increase in the intensity of light of the frequency or in other words, because there is an increase in the intensity of light we have light amplification. Thus, we can have light amplification by stimulated emission of radiation. So, if I take the first alphabets, what I get is laser. But one has to keep in mind that the condition of population inversion is the necessary condition for LASER.

And other important thing to note in this context is that the representation of a spectroscopic transition by a process, like M 1 + photon gives M 2, implies that one molecule interacts with only one photon at a given time. Thus the B coefficient determines the probability of absorption or emission of a single photon. Multi photon processes that are processes involving more than 1 photon interacting with 1 molecule cannot be treated by this procedure.

Individually, the probability of such a process is very, very small. And in normal cases, the rate of this process can be neglected. But, let us say for an n photon process, the probability or the rate is proportional to N to the power n, where N is the number density of photons. Or in other words, this is a number of photons per unit volume. So, for ordinary light source, this capital N is small enough, making the rate negligible.

But if one uses a light source with high photon density, for example, if one uses a laser source, multi photonic processes can take place.

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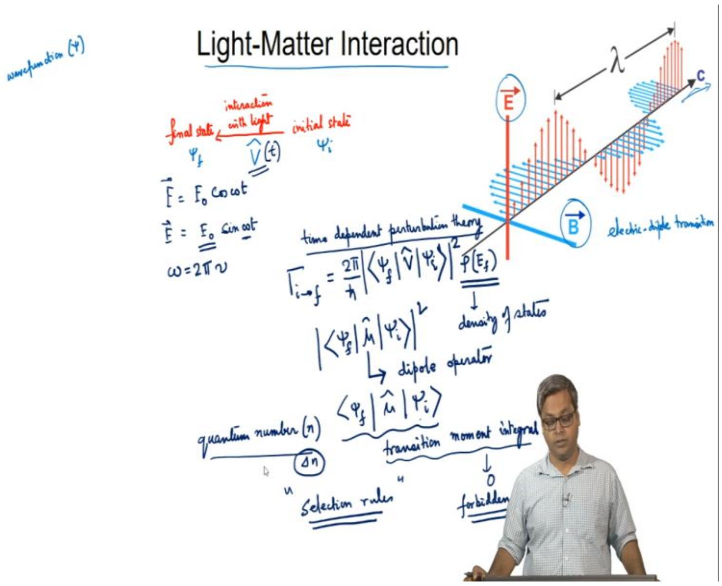

Light-Matter Interaction

wavefunction (ψ)

final state $\xleftarrow[\hat{V}(t)]{\text{interaction with light}}$ initial state

ψ_f ψ_i

$\vec{E} = E_0 \cos\omega t$

$\vec{E} = E_0 \sin\omega t$

$\omega = 2\pi\nu$

time dependent perturbation theory

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \rho(E_f)$$

$\downarrow$ density of states

$$\left| \langle \psi_f | \hat{\mu} | \psi_i \rangle \right|^2$$

$\hookrightarrow$ dipole operator

$$\underbrace{\langle \psi_f | \hat{\mu} | \psi_i \rangle}_{\text{transition moment integral}}$$

$\downarrow$ 0 forbidden

quantum number (n) Δn

"Selection rules"

As spectroscopy process can be represented, as there is an initial state and the initial state interacts with light. So, we have interaction with light and there is a final state. According to quantum mechanics, the states can be represented via wave function psi. Let psi i and psi f, be the wave functions of the initial and the final steps respectively. Interaction in quantum mechanics is represented by term V in the Hamiltonian operator of the system. Light matter interaction is treated in quantum mechanics by considering matter having quantum states.

Light is however, treated classically as a source of field, electric or magnetic field described by wave theory. Based on Maxwell's electromagnetic theory, electromagnetic waves are changing electric and magnetic fields. The electric field as you can see is perpendicular to the magnetic field. And both fields are directed at right angles to the direction of propagation of light. For a light matter interaction, the involved interaction is between the charge or charge distribution in atoms and molecules and the electric field or the magnetic field of light.

Since the interaction with magnetic field is very small, compared to that with the electric field, we will confine our discussion on the interaction with the electric field only. Spectroscopy transition involved in such a case is called electric dipole transition. Now, the electric field of light depends on time. Given by E = E 0 cos omega t or we can also write E = E 0 sin omega t where omega is the angular frequency of light, which is related to the frequency that we know nu.

So, omega is related to nu by omega = 2 pi nu and E 0 is a constant. Thus the interaction term V in the Hamiltonian of a light matter system depends on time and we can write V as a function of time. For small magnitude of V, one can use the time dependent perturbation theory in quantum mechanics to give expression for the probability of transitions, enabling the B coefficient to be evaluated. According to the time dependent perturbation theory, the transition probability per unit time, from the initial to the final state is given by the Fermi-golden rule.

So the transition probability from the initial to the final state for unit time is 2 pi / h cross. And then we have this final state the interaction term initials state, this whole modulus is squared and rho of E f, where this rho E f is the density of states. So, because the interaction is between the electric field of light and the charge or the charge distribution, that is the dipole of the matter. So, it comes out that the probability is proportional to psi f mu psi i whole square, where this is, is the mu is the dipole operator.

Thus the integral psi f mu psi i is often called the transition moment integral. And this transition moment integral plays a central role in determining the probability of a transition. In the event that this transition moment integral is 0, the probability of the transition is also 0. Such transitions are said to be forbidden. One can calculate the conditions under which this transition moment integral is 0, and one gets to something known as selection rules for this transitions to occur.

Intuitively, the wave functions in the transition moment integral in general depends on quantum numbers, say n. And such selection rules are often stated in terms of change in quantum numbers or delta n. This will be discussed further in specific cases, when we go into different forms of spectroscopy. So, this brings us to the end of this lecture. Again, we will solve a couple of problems, and then we will come to the end.

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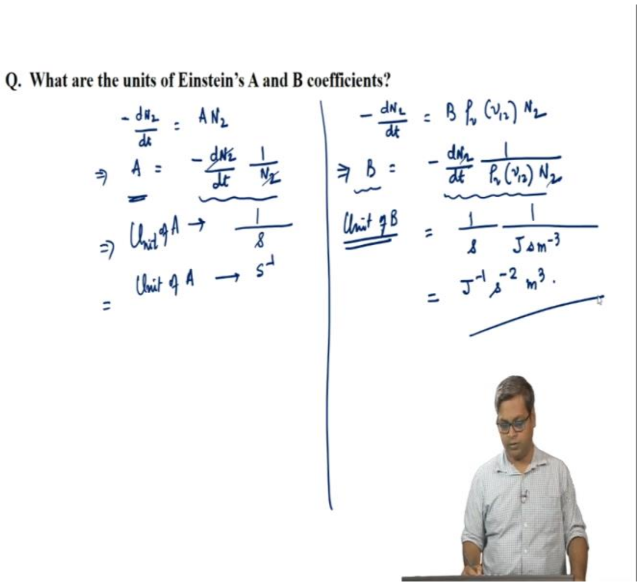

Q. What are the units of Einstein's A and B coefficients?

$$-\frac{dN_2}{dt} = AN_2$$

$$\Rightarrow A = \underbrace{-\frac{dN_2}{dt}\frac{1}{N_2}}$$

$$\Rightarrow \text{Unit of } A \rightarrow \frac{1}{s}$$

$$= \text{Unit of } A \longrightarrow s^{-1}$$

$$-\frac{dN_2}{dt} = B\rho_\nu(\nu_{12})N_2$$

$$\Rightarrow B = \underbrace{-\frac{dN_2}{dt}\frac{1}{\rho_\nu(\nu_{12})N_2}}$$

$$\text{Unit of } B = \frac{1}{s}\frac{1}{J\,s\,m^{-3}}$$

$$= J^{-1}s^{-2}m^{3}.$$

So, the first question we have is what are the units of Einstein's A and B coefficients? So, we will start with Einstein's A coefficient, we can write minus d N 2 dt = A N 2 for spontaneous emission. So, from this you can write A = - d N 2 dt and 1 / N 2. So N 2 or d N 2 these are numbers are change in numbers. So, we can, if you look into the units of A, in that case, the unit on the left hand side should be equal to the unit on the right hand side. In other words, this number and number will cancel.

So the unit we have is one by unit of time that is 1 / second. So the unit of A is second inverse. So now let us go to Einstein's B coefficient. For B coefficient, we can write – d N2 dt = B Rho nu mu 12 N2. So, we can write now, B = - d N2 dt 1 by rho nu nu 12 and N 2. Again the units of N 2 and d N 2, they can cancel out. So, the unit of B, because again, the unit in the left hand side will be same as the unit in the right hand side, the unit here will be 1 over second it is 1 by dt.

And then, the unit of rho nu nu 12, as I discussed in the first lecture, it is Joule second metre to the power -3. In other words, the unit of B becomes joule inverse second to the power -2 meter cube.

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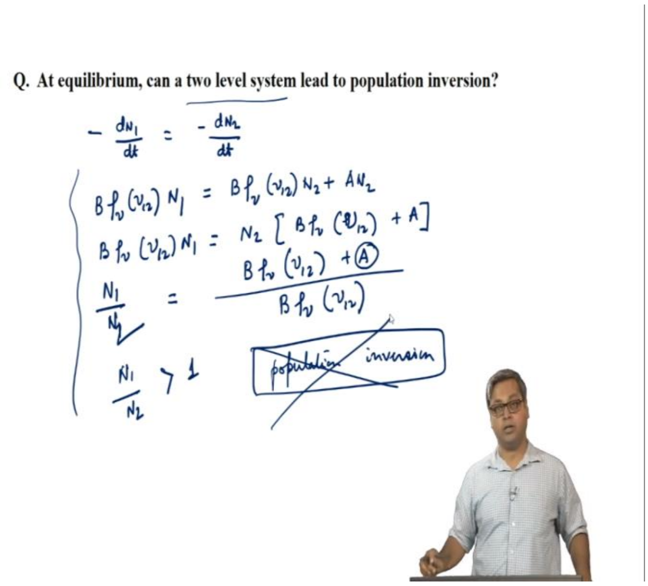

Q. At equilibrium, can a two level system lead to population inversion?

$$-\frac{dN_1}{dt} = -\frac{dN_2}{dt}$$

$$B\rho_\nu(\nu_{12})N_1 = B\rho_\nu(\nu_{12})N_2 + AN_2$$

$$B\rho_\nu(\nu_{12})N_1 = N_2\left[B\rho_\nu(\nu_{12}) + A\right]$$

$$\frac{N_1}{N_2} = \frac{B\rho_\nu(\nu_{12}) + \textcircled{A}}{B\rho_\nu(\nu_{12})}$$

$$\frac{N_1}{N_2} > 1 \qquad \boxed{\cancel{\text{population inversion}}}$$

So, the second question we have is that equilibrium can a 2 level system lead to population inversion. So, at equilibrium, the rate of absorption will be equal to the rate of emission, so, we have 2 emission processes. So, in other words I can write – d N 1 dt will be equal to - d N 2 dt. So, - d1 N 1 dt is B, rho nu nu 12 N1. This will be equal to B rho nu nu 12 N 2 + A N 2. So we can write, B rho nu nu 12 N 1, this will be if I take N 2 common is B rho nu, nu 12 + A.

So now if I compute N 1 by N 2, what I get is B Rho nu, nu 12 + A by B rho nu nu 12. So now we see this A is not 0, and because A is not 0, so N 1 by N 2 is always greater than 1. In other words, it will always has more molecules in the lower level than at the high level. So, this is true for the 2 levels system and thus, we can see, we can never reach a case of population inversion in a 2 level system. However, if you are interested you can see that for more than 2 levels system, population inversion can be reached.