Approximate Methods in Quantum Chemistry
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Lecture-42
Topic-Einstein's Coefficients

Hello students! Welcome to this lecture. In the last lecture, we discussed about the effect of an oscillating perturbation in a quantum mechanical system. We derived in our last class the well-known Fermi's golden rule. In this lecture, we will continue our discussion along that line and discuss about the Einstein's coefficients.

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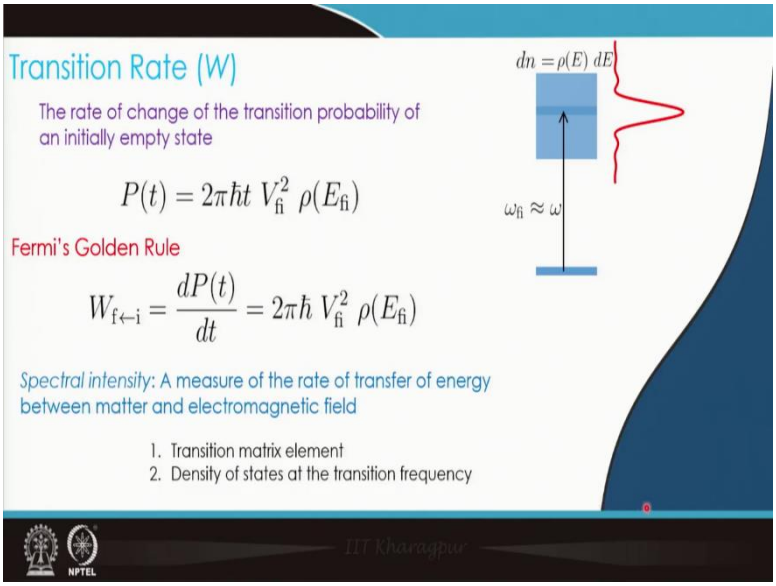

When a system initially prepared in state *i* is subjected to an electromagnetic radiation (example of oscillating perturbation), transition to the final state f is observed when the radiation frequency matches with the energy difference between the two states. When the final state is part of a continuum with energy density $\rho(E_{fi})$, the total transition probability is given by the

$$P(t) = 2\pi\hbar t\ V_{fi}^2\ \rho(E_{fi})$$

relation,

and the rate of change of transition probability (the so-called transition rate) is given by the Fermi's golden rule,

$$W_{f\leftarrow i} = \frac{dP(t)}{dt} = 2\pi\hbar\ V_{fi}^2\ \rho(E_{fi})$$

The transition rate, closely related to spectral intensity, depends on the transition matrix element (V_{fi}) and the density of states at that transition frequency.

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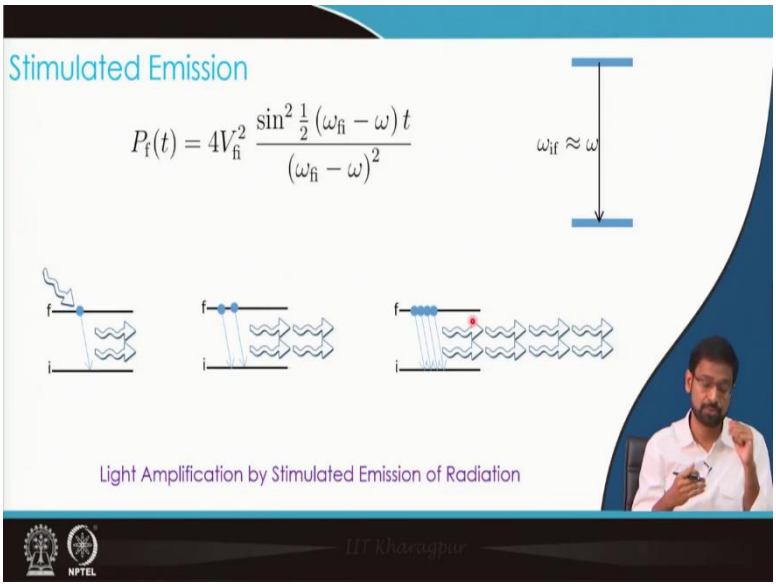

The previous exercise was carried out for a situation when the initial state i is lower in energy than the final state f, hence the process is absorption. We can redo the entire exercise, where the system is prepared in state f while the state i is initially empty, reflecting an emission process. The end result for the transition probability would be similar to that of absorprtion, except for some changes in the indices, e.g.,

$$P_f(t) = 4V_{fi}^2 \frac{\sin^2 \frac{1}{2}(\omega_{fi} - \omega)t}{(\omega_{fi} - \omega)^2}$$

This process is called as the stimulated emission, which is the exact opposite of the absorption. In case of absorption, upon irradiation of electromagnetic radiation on an initial state i and the system absorbs the energy of the radiation and goes on to an excited state f. In the opposite of stimulated emission, the system in a higher energy state f absorbs the energy from a photon of the electromagnetic radiation and comes down to the lower energy state i. Since the perturbation Hamiltonian is Hermitian, V_{fi}=V_{if}. Hence, the rate of transfer is going to be the same, for both absorption and the stimulated emission.

In case of absorption, there is a conservation of energy at play, i.e., the energy of the initial state added to the radiation energy equals the energy of the final state. In case of stimulated emission, the system in the final state absorbs a photon and comes down to the lower energy state by losing two photons of the same frequency, thereby conserving the total energy. The absorption of one photon by the excited state leads to the emission of two photons of the same

frequency. Now, if these two emitted photons can interact with two other molecules in their excited states, they would result in emission of four photons of same frequency. If we have a steady supply of molecules in their excited state, this effect will cascade and we will get a large number of photons of same frequency. This causes light amplification. Since this light amplification arises due to stimulated emission, the process is called light amplification by stimulated emission of radiation (LASER). The preparation of a large number of atoms/molecules in their excited state, also known as population inversion, is an important technical challenge to be met for laser action.

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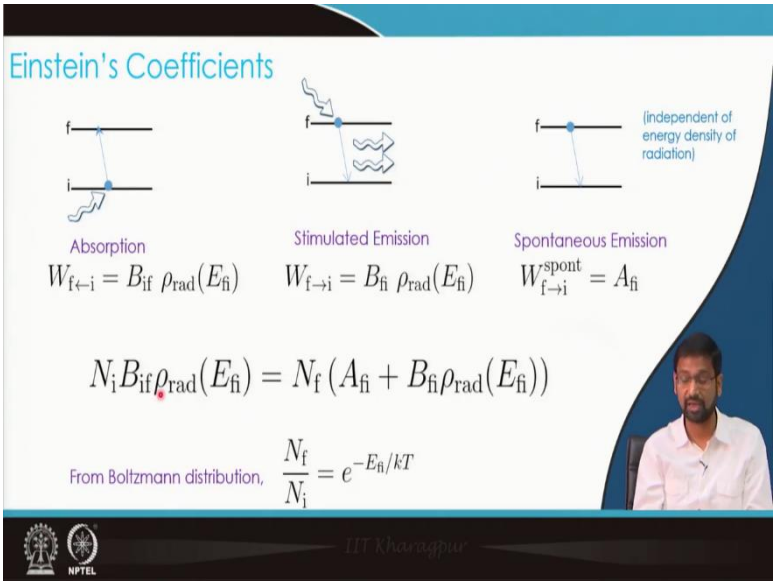

So far, we have discussed the following two processes: absorption and stimulated emission. It turned out that there exists another route of emission, called spontaneous emission. This process, unlike the previous two, is independent of the energy density of radiation. When the system is in the excited state, it decays to the lower energy state spontaneously. In reality, this "spontaneous" emission is triggered by the zero-point fluctuation present in the electromagnetic radiation, without explicit absorption of any photon. A similar spontaneous absorption (by interacting with zero-point fluctuation of the electromagnetic radiation) is not possible without explicit absorption of a photon. Hence, when the system is in the excited state, it relaxes back to the lower energy state. This gives rise to a finite lifetime of the excited state. The system in the ground state does not find a lower energy stationary state, and hence remains there forever.

Among the three processes, the absorption and stimulated emission are dependent on the radiation density, while the spontaneous emission is not. Einstein expressed the transition rates for absorption (f←i) and emission (f→i) with the proportionality constants B_{if} and B_{fi} as following,

$$W_{f\leftarrow i} = B_{if}\ \rho_{rad}(E_{fi}) \qquad W_{f\rightarrow i} = B_{fi}\ \rho_{rad}(E_{fi})$$

while the transition rate for the spontaneous emission (independent of radiation) is expressed as the proportionality constant A_{fi},

$$W^{spont}_{f\rightarrow i} = A_{fi}$$

The three coefficients A_{fi}, B_{if} and B_{fi} are called the Einstein's coefficients.

If N_i and N_f are the number of molecules in the initial and final states, respectively, the total absorption is given by,

$$N_i B_{if} \rho_{rad}(E_{fi})$$

and the total emission (both spontaneous and stimulated) is given by,

$$N_f\left(A_{fi} + B_{fi}\rho_{rad}(E_{fi})\right)$$

At equilibrium,

$$N_i B_{if} \rho_{rad}(E_{fi}) = N_f\left(A_{fi} + B_{fi}\rho_{rad}(E_{fi})\right)$$

However, from Boltzmann distribution,

$$\frac{N_f}{N_i} = e^{-E_{fi}/kT}$$

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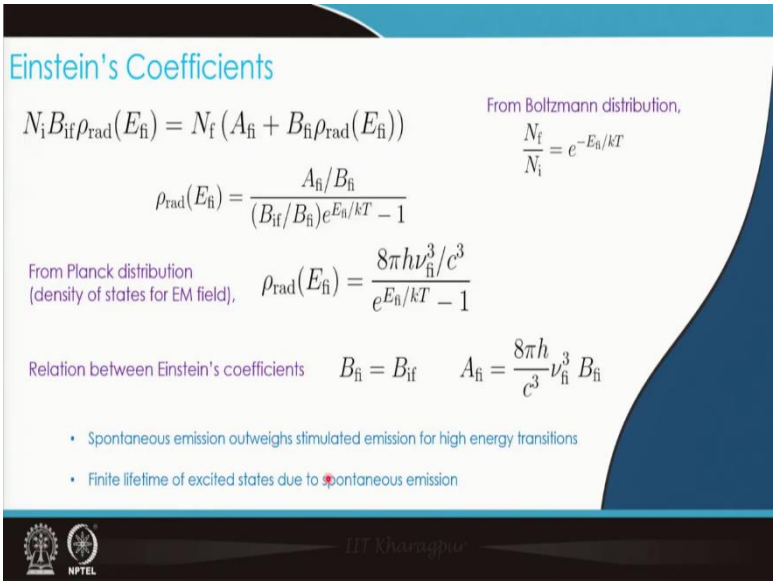

Now, using the above two relations, we can obtain

$$\rho_{\mathrm{rad}}(E_{\mathrm{fi}}) = \frac{A_{\mathrm{fi}}/B_{\mathrm{fi}}}{(B_{\mathrm{if}}/B_{\mathrm{fi}})e^{E_{\mathrm{fi}}/kT} - 1}$$

However, from Planck distribution of density of states for electromagnetic field, we have

$$\rho_{\mathrm{rad}}(E_{\mathrm{fi}}) = \frac{8\pi h\nu_{\mathrm{fi}}^3/c^3}{e^{E_{\mathrm{fi}}/kT} - 1}$$

Comparing the above two definitions of density of states, we can assign the following relations between the Einstein's coefficients:

$$B_{\mathrm{fi}} = B_{\mathrm{if}} \qquad A_{\mathrm{fi}} = \frac{8\pi h}{c^3}\nu_{\mathrm{fi}}^3 \; B_{\mathrm{fi}}$$

The second equation gives an important relation between the spontaneous and stimulated emission coefficients. Apart from the constants (speed of light, Planck's constant), the relation shows that spontaneous emission is far stronger than the stimulated emission when the frequency of the transition is high (depends on the cubic power of the radiation frequency). The system will decay spontaneously, instead of being available for the laser action, when the radiation frequency is large, for example, the X-ray radiation. On the other hand, stimulate resonance is more likely with microwave radiation.

From the last few lectures we learnt how we can discuss spectroscopy with the help of time-dependent version of quantum mechanics.

Thank you for your attention.