Lesson 4 - Electromagnetic Transitions
Unit 4.1 Selection rules and Einstein equations

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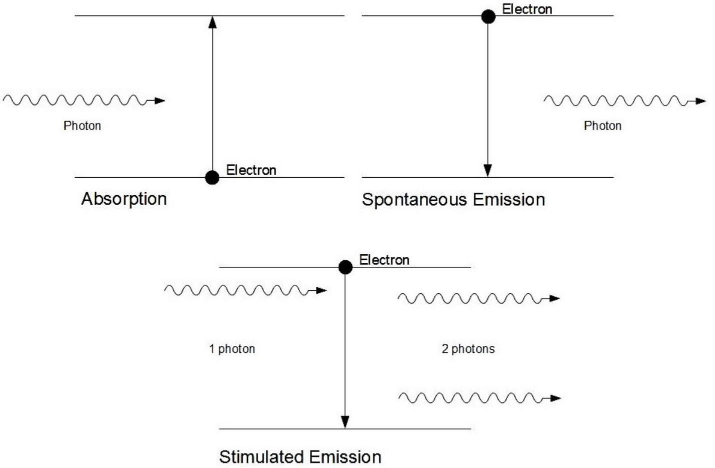
Electromagnetic transitions and selection rules (I)

We have seen that there are 3 main mechanisms of electromagnetic transition: absorption, spontaneous emission, and stimulated emission.



Electromagnetic transitions and selection rules (II)

Within the dipolar approximation, no electromagnetic transition will occur between the atomic states $|a\rangle$ and $|b\rangle$ unless at least one component of the dipole transition matrix element

$$\langle b|\mathbf{d}|a\rangle = -e \int d^3\mathbf{r}\ \psi_b^*(\mathbf{r})\ \mathbf{r}\ \psi_a(\mathbf{r}) \tag{1}$$

is nonzero.
Explicitly, in the dipole approximation, given the quantum state

$$\psi_{n,l,m}(\mathbf{r}) = R_n(r) Y_{l,m}(\theta, \phi) \tag{2}$$

with n the principal quantum number, l the orbital quantum number, and and its third component $m = -l, -l+1, ..., l-1, l$ its third component, one finds the selection rules

$$\Delta l = \pm 1 \qquad \Delta m = 0, \pm 1 \tag{3}$$

where $\Delta l = l - l'$ and $\Delta m = m - m'$. This means that in the electric dipole transitions the photon carries off (or brings in) one unit of angular momentum.
Remark: the above selection rules can be violated by rare electromagnetic transitions involving higher multipolarities.

Two-level system and Einstein coefficients (I)

In the previous lectures we have deduced the transition probabilities in the electromagnetic transitions adopting the formalism of second quantization of light which dates back to 1927.
Historically, in 1919 Albert Einstein was the first to observe that, given an ensemble of N atoms in two possible atomic states $|a\rangle$ and $|b\rangle$, with $N_a(t)$ the number of atoms in the state $|a\rangle$ at time t and $N_b(t)$ the number of atoms in the state $|b\rangle$ at time t, it must be

$$N = N_a(t) + N_b(t) \tag{4}$$

and consequently

$$\frac{dN_a}{dt} = -\frac{dN_b}{dt} \ . \tag{5}$$

Einstein suggested that, if the atoms are exposed to an electromagnetic radiation of energy density per unit of frequency $\rho(\omega)$, the rate of change of atoms in the state $|a\rangle$ must be

$$\frac{dN_a}{dt} = A_{ba}\, N_b + B_{ba}\, \rho(\omega_{ba})\, N_b - B_{ab}\, \rho(\omega_{ba})\, N_a \ . \tag{6}$$

where the parameters A_{ba}, B_{ba}, and B_{ab} are known as Einstein coefficients.

Two-level system and Einstein coefficients (II)

Einstein was able to determine the relationship among the coefficients A_{ba}, B_{ba} and B_{ab} by supposing that the two rates in Eqs. (5) and (6) must be equal to zero at thermal equilibrium, i.e.

$$\frac{dN_a}{dt} = -\frac{dN_b}{dt} = 0 \,, \tag{7}$$

In this way Einstein found

$$A_{ba}\frac{N_b}{N_a} = \rho(\omega_{ba})\left(B_{ab} - B_{ba}\frac{N_b}{N_a}\right) \,. \tag{8}$$

Because the relative population of the atomic states $|a\rangle$ and $|b\rangle$ is given by a Boltzmann factor

$$\frac{N_b}{N_a} = \frac{e^{-\beta E_b}}{e^{-\beta E_a}} = e^{-\beta(E_b - E_a)} = e^{-\beta\hbar\omega_{ba}} \,, \tag{9}$$

Einstein got

$$\rho(\omega_{ba}) = \frac{A_{ba}}{B_{ab}e^{\beta\hbar\omega_{ba}} - B_{ba}} \,. \tag{10}$$

Two-level system and Einstein coefficients (III)

At thermal equilibrium we know that

$$\rho(\omega_{ba}) = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega_{ba}} - 1} \ . \tag{11}$$

It follows that

$$A_{ba} = B_{ba} \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} \ , \qquad B_{ab} = B_{ba} \ . \tag{12}$$

In this way Einstein obtained the coefficient A_{ba} of spontaneous decay by simply calculating the coefficient of stimulated decay B_{ba}.
This was a remarkable result because Einstein derived the formula for A_{ba} without knowing the formulism of second quantization of light with the creation of photons from the vacuum.

Two-level system and Einstein coefficients (IV)

By using the results we have obtained in the previous lectures, it is clear that

$$
\begin{aligned}
A_{ba} &= W_{ba}^{spont} = \frac{\omega_{ba}^3}{3\pi\epsilon_0\hbar c^3} \, |\langle a|\mathbf{d}|b\rangle|^2 \ , && (13) \\
B_{ba} &= \frac{\tilde{W}_{ba}^{stimul}}{\rho(\omega_{ba})} = \frac{\pi^2 c^3}{\hbar\omega_{ba}^3} A_{ba} \ , && (14) \\
B_{ab} &= \frac{W_{ab}^{absorp}}{\rho(\omega_{ba})} = \frac{\pi^2 c^3}{\hbar\omega_{ba}^3} A_{ba} \ . && (15)
\end{aligned}
$$

It is important to stress that the laser device, invented in 1957 by Charles Townes and Arthur Schawlow at Bell Labs, is based on a generalization of equations (5) and (6) of Einstein for ma two-level system.
In the laser (light amplification by stimulated emission of radiation) one has population inversion, which is achieved with an out-of-equilibrium pumping mechanism strongly dependent on the specific characteristics of the device.