

**Quantum Optics and Laser 2021/22**  
**ESSAY - COEFFICIENTS  $\mathbb{A}$  AND  $\mathbb{B}$  OF EINSTEIN**  
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## 1 INTRODUCTION

In 1916, Albert Einstein [1] [2] published a paper on a beautifully simple analysis of the interaction of radiation with an atomic system and in particular of the processes occurring in the formation of an atomic spectral line. In the article, he considers the simple case of two discrete energy levels: the first of energy  $\mathcal{E}_1$  with statistical weight (also referred to as degeneracy or multiplicity)  $g_1$ , the second of energy  $\mathcal{E}_2 = \mathcal{E}_1 + h\nu_0$  ( $h$  being Planck's constant), with statistical weight  $g_2$ . In a nutshell, the system makes a transition from  $1 \rightarrow 2$  by absorption of a photon of frequency  $\nu \approx \nu_0$  and energy  $h\nu$ ; similarly, a transition from  $2 \rightarrow 1$  occurs when a photon with the same characteristics is emitted.

Einstein identifies three processes: spontaneous emission, stimulated emission, and absorption. With each phenomenon is associated an Einstein coefficient (EC), which is a measure of the probability of that particular process occurring.

In this essay we will first review the various formulations for derivations for the ECs compared in [3], describing the different phenomena involved and explained in [4]. We will then see the detailed balancing condition and the relations that binds the ECs together; finally, we will define the oscillator strength and express the ECs as their function.

A final disclaimer: for his derivation, Einstein considered the case of isotropic radiation of frequency  $\nu$  and spectral energy density  $\rho(\nu)$ , under conditions of thermal equilibrium.

### 1.1 SPONTANEOUS EMISSION

Spontaneous emission is the process by which an atom decays from a upper energy level to a lower one and release its energy in the form of a photon. The process is called spontaneous because the transition happens without any outside influence and is independent of the number of photons that may already be in the electromagnetic mode.

The process is described by the Einstein coefficient  $\mathbb{A}_{21}$  (with dimensions  $\text{s}^{-1}$ ) which gives the probability per unit time that an electron makes the jump. Due to the energy-time uncertainty principle, the transition actually produces photons within a narrow range of frequencies: in particular, in a cavity of volume  $V$  that can sustain a number of electromagnetic modes, the rate for this spontaneous transition depends on  $\nu$  in a way that characterises that atomic transition through

$$\mathbb{A}_{12} = \frac{c}{V} \sigma(\nu). \quad (1)$$

The quantity  $\sigma(\nu)$  is called transition cross section, a function of  $\nu$  centred around the atomic resonance frequency  $\nu_0$ .

If  $n_i$  is the number density of atoms in state  $i$ , then the change in the number density of atoms in

state 2 per unit time due to spontaneous emission will be

$$\left(\frac{dn_2}{dt}\right)_{\text{sp}} = -\mathbb{A}_{21}n_2; \quad (2)$$

the number of atoms  $n_2(t) = n_2(0) \cdot \exp(-\mathbb{A}_{21}t)$  decays exponentially with time constant  $1/\mathbb{A}_{21}$ . The same process produces the increase of the population of state 1,

$$\left(\frac{dn_1}{dt}\right)_{\text{sp}} = \mathbb{A}_{21}n_2. \quad (3)$$

## 1.2 PHOTON ABSORPTION

If the atom is initially in the lower energy level and the radiation mode contains a photon, the latter may be annihilated, causing an electron to jump from a lower energy level to a higher one. The process is described by the Einstein coefficient  $\mathbb{B}_{12}$  (in units of  $\text{m}^3\text{J}^{-1}\text{s}^{-2}$ ), which gives the probability per unit time per unit spectral radiance of the radiation field that an electron will jump to the higher energy state. Similarly to what has been seen before, the change in the number density of atoms in state 1 per unit time due to absorption will be

$$\left(\frac{dn_1}{dt}\right)_{+\text{abs}} = -\mathbb{B}_{12}n_1\rho(\nu), \quad (4)$$

where  $\rho(\nu)$  denotes the radiance in a 1 Hz bandwidth of the isotropic radiation field at the frequency of the transition.

For the thermodynamic of the process and for the application of Kirchhoff's law, it is necessary for the total absorption to be expressed as the algebraic sum of two components, namely the direct photon absorption and what is commonly called stimulated (or induced) emission. The two are often referred as positive and negative absorption and are described by the coefficients  $\mathbb{B}_{12}$  (hence the notation in the derivative above) and  $\mathbb{B}_{21}$  respectively. We will see this latter case in the following section.

## 1.3 STIMULATED EMISSION

If the atom is in the upper energy level and the mode contains a photon, the atom may be induced to emit another photon in the same mode. This process, also known as induced emission, is the inverse of absorption. The presence of a photon in a mode of specified frequency, propagation direction and polarisation, stimulates the emission of a duplicate photon with precisely the same characteristics as the original. This process is the phenomenon that underlies the operation of laser amplifiers and laser. Still, laser radiation is very far from the present case of isotropic radiation. From the thermodynamic viewpoint, this process must be regarded as negative absorption, as mentioned before. The process is described by the Einstein coefficient  $\mathbb{B}_{21}$  (in units of  $\text{m}^3\text{J}^{-1}\text{s}^{-2}$ ), which gives the probability per unit time per unit spectral radiance of the radiation field that an electron in state 2 with energy  $\mathcal{E}_2$  will decay to state 1 with energy  $\mathcal{E}_1$ , emitting a photon with an energy  $\mathcal{E}_2 - \mathcal{E}_1 = h\nu$ . The change in the number density of atoms in state 1 per unit time due to induced emission will thus be given by

$$\left(\frac{dn_1}{dt}\right)_{-\text{abs}} = \mathbb{B}_{21}n_2\rho(\nu). \quad (5)$$

## 2 DETAILED BALANCING

The ECs are fixed probabilities per time associated with each atom: as such, they do not depend on the state of the gas of which the atoms are part. Therefore, any relationship that we can derive between the coefficients will be valid universally. This holds in particular at thermodynamic equilibrium, a condition for which simple balancing holds: the net change in the number of any excited atoms is zero, being balanced by loss and gain due to all processes. Not only that: we will also have detailed balancing, which connects any microscopic process and its inverse process, here absorption and emission. This property, which is only valid at equilibrium, assures that the net exchange between any two levels will be balanced.

Let again be  $n_1, n_2$  the number densities of atoms in levels 1 and 2 respectively; putting together Eq. (3), Eq. (4), Eq. (5), detailed balance requires that [5]

$$\mathbb{A}_{21}n_2 + \mathbb{B}_{21}n_2\rho(\nu) - \mathbb{B}_{12}n_1\rho(\nu) = 0. \quad (6)$$

Now, in order to derive universal relationships between the ECs, we can exploit our knowledge of the equilibrium energy distribution of the atoms at temperature  $T$  (Maxwell–Boltzmann distribution) and the equilibrium distribution of the photons (Planck’s law of black body radiation). From the Maxwell–Boltzmann distribution we know that for the number of excited atomic species  $i$  holds that:

$$\frac{n_i}{N} = \frac{g_i \exp\left(-\frac{\mathcal{E}_i}{k_B T}\right)}{Z}, \quad (7)$$

where  $N$  is the total number density of the atomic species, excited and unexcited,  $k_B$  is Boltzmann’s constant,  $T$  is the temperature,  $g_i$  is the degeneracy of state  $i$ , and  $Z$  the partition function. From Planck’s law we have that for the energy per unit time per unit solid angle per unit projected area (i.e. the spectral radiance), when integrated over an appropriate spectral interval at frequency  $\nu$ , holds that

$$\rho_\nu(\nu, T) = F(\nu) \cdot \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}, \quad (8)$$

where

$$F(\nu) = \frac{2h\nu^3}{c^2}. \quad (9)$$

Substituting these expressions in Eq. (6) leads to - remembering  $\mathcal{E}_2 - \mathcal{E}_1 = h\nu$  and setting  $\mathcal{X}_\mp \equiv \exp\left(\mp \frac{h\nu}{k_B T}\right)$

$$\mathbb{A}_{21}g_2\mathcal{X}_- + \mathbb{B}_{21}g_2\mathcal{X}_- \cdot \frac{F(\nu)}{\mathcal{X}_+ - 1} = \mathbb{B}_{12}g_1 \frac{F(\nu)}{\mathcal{X}_+ - 1} = \quad (10)$$

$$\mathbb{A}_{21}g_2(\mathcal{X}_+ - 1) + \mathbb{B}_{21}g_2F(\nu) = \mathbb{B}_{12}g_1\mathcal{X}_+F(\nu). \quad (11)$$

Since this latter equation must hold  $\forall T$ ,

$$\mathbb{B}_{21}g_2 = \mathbb{B}_{12}g_1 \wedge -\mathbb{A}_{21}g_2 + \mathbb{B}_{21}g_2F(\nu) = 0. \quad (12)$$

Through Eq. (12) one finds the interrelations between all three ECs coefficients, namely

$$\begin{aligned} \frac{\mathbb{A}_{21}}{\mathbb{B}_{21}} &= F(\nu) \\ \frac{\mathbb{B}_{21}}{\mathbb{B}_{12}} &= \frac{g_1}{g_2}. \end{aligned} \quad (13)$$

Note that these last relations have no reference to the temperature  $T$ : as were the premises, Eq. (13) must hold whether or not the atoms are in thermodynamic equilibrium.

### 3 OSCILLATOR STRENGTH

Oscillator strengths (also called  $f$  values) may be defined by comparing the emission rate or absorption rate of the atom with the emission or absorption rate of a classical, single-electron oscillator with given oscillation frequency  $\omega_{21}$ . We define an emission oscillator strength  $f_{21}$  by the relation

$$f_{21} = -\frac{1}{3} \frac{\mathbb{A}_{21}}{\gamma_{cl}} \quad \gamma_{cl} = \frac{e^2 \omega_{21}^2}{6\pi\epsilon_0 m_e c^3}, \quad (14)$$

where  $e$  and  $m_e$  are the electron charge and mass respectively. The classical radiative decay rate of the single-electron oscillator at frequency  $\omega_{21}$  is given by  $\gamma_{cl}$ . An absorption oscillator strength  $f_{12}$  is then defined by

$$g_1 f_{12} = -g_2 f_{21} \equiv g f. \quad (15)$$

The latter can be expressed as a function of  $\phi_\omega$ , the normalised distribution function in angular frequency and  $\sigma$ , the cross section for absorption, as

$$f_{12} = \frac{\sigma}{\phi_\omega} \cdot \frac{2\epsilon_0 m_e c}{\pi e^2}. \quad (16)$$

We may now relate the absorption oscillator strength to the  $\mathbb{A}$  value:

$$f_{12} = \frac{g_2}{g_1} \cdot \frac{2\pi\epsilon_0 m_e c^3 \mathbb{A}_{21}}{\omega_{21}^2 e^2}. \quad (17)$$

Rearranging and remembering  $\omega_{21} = 2\pi\nu$ ,

$$\mathbb{A}_{21} = f_{12} \frac{g_1}{g_2} \cdot \frac{2\pi e^2}{\epsilon_0 m_e c^3} \nu^2 \propto f_{12} \frac{g_1}{g_2} \nu^2. \quad (18)$$

This allows the ECs to be expressed in terms of the single oscillator strength associated with the particular atomic spectral line. A similar reasoning can be carried out for  $\mathbb{B}_{12}$  and  $\mathbb{B}_{21}$ , obtaining

$$\mathbb{B}_{12} = f_{12} \cdot \frac{e^2}{4\epsilon_0 m_e h \nu}, \quad (19)$$

$$\mathbb{B}_{21} = f_{12} \frac{g_1}{g_2} \cdot \frac{e^2}{4\epsilon_0 m_e h \nu}. \quad (20)$$

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- [1] A. Einstein, Deutsche Physikalische Gesellschaft **18**, 318 (1916).
  - [2] A. Einstein, Physikalische Zeitschrift **18**, 121 (1917).
  - [3] R. C. Hilborn, “Einstein coefficients, cross sections, f values, dipole moments, and all that,” (2002), [arXiv:physics/0202029](https://arxiv.org/abs/physics/0202029) [[physics.atom-ph](https://arxiv.org/abs/physics/0202029)].
  - [4] B. E. A. Saleh and M. C. Teich, *Fundamentals of photonics; 2nd ed.*, Wiley series in pure and applied optics (Wiley, New York, NY, 2007).
  - [5] G. B. Rybicki and A. P. Lightman, *Radiative Processes in Astrophysics* (Wiley, New York, NY, 1985).