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Classical Derivation of Expressions for Einstein's Coefficients

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ABSTRACT: The paper is devoted to classical derivations for Einstein's coefficients for spontaneous emission, absorption and stimulated emission of light. The derivation is based on spectroscopic correspondence principle between quantum and classical physics and classical electrodynamics for interaction between charged harmonic oscillator with electromagnetic field.

Key words: Einstein's coefficients, correspondence principle, harmonic oscillator

1. SPECTROSCOPIC CORRESPONDENCE PRINCIPLE

Einstein's coefficients were introduced phenomenologically to describe the probability per unit time of three fundamental photo-processes: photo-absorption, spontaneous emission, and stimulated emission due to the interaction of thermal radiation with a two-level system [1]. The consistent derivation of the expressions for these coefficients is possible only within the framework of quantum electrodynamics, a complex physical discipline that considers radiation and matter on a quantum basis [2]. Nevertheless, if we use the principles of correspondence between quantum and classical physics [3] and the concept of oscillator strength, the corresponding formulas can be obtained in the classical way, which will be done below.

The principle of spectroscopic correspondence allows us to represent an atom in its interaction with radiation in the form of a set of charged harmonic oscillators corresponding to transitions between the energy levels of an atom $n \to j$ ($\mathrm{E}_j > \mathrm{E}_n$). These oscillators, which describe the response of the system to an electromagnetic disturbance, are called transition oscillators. Their coordinate satisfies the equation for forced oscillations, in the right side of which the force is substituted as a coefficient $f_{jn} \neq 0$ (dipole allowed transition):

$$\ddot{x}_{jn} + 2\delta_{jn}\dot{x}_{jn} + \omega_{jn}^2 x_{jn} = f_{jn}\frac{e}{m}E(t). \tag{1}$$

here $\omega_{jn} = \left(\mathrm{E}_j - \mathrm{E}_n\right)/\hbar$ – transition frequency, δ_{nj} – relaxation constant, e – oscillator charge, points above the coordinate symbol mean time differentiation, electric field strength $E(t)$.

In the absence of a radiation field, the transition oscillator is at rest: $x_{jn} = 0$ and $\dot{x}_{jn} = 0$. The external field begins to "swing" it, giving energy - there are forced oscillations of the transition oscillator, the time dependence of which $x_{jn}(t)$ can be found from equation (1).

Thus for forced oscillations of the transition oscillator, we can obtain the following expression:

$$x_{jn}(t) = f_{jn}\frac{e}{m}\int_{-\infty}^{\infty}\frac{E(\omega')\exp(-i\omega' t)}{\omega_{jn}^2 - \omega'^2 - 2i\omega'\delta_{jn}}\frac{d\omega'}{2\pi}, \tag{2}$$

here $E(\omega')$ – Fourier transform of electric field strength $E(t)$.

An oscillating charged oscillator emits electromagnetic waves in accordance with the formula for the power of dipole radiation (3). In the case of oscillations under the influence of an external field, this radiation is stimulated. If the pulse of the external field has ended, and the charged oscillator is still oscillating, then the corresponding radiation is spontaneous.

EINSTEIN COEFFICIENT FOR SPONTANEOUS EMISSION

The probability per unit time of spontaneous emission at the transition between atomic energy levels $j \to n$ is given by the Einstein coefficient A_{nj}. The explicit form of this coefficient can be obtained on the basis of classical consideration using the spectroscopic principle of correspondence. To do this, we proceed from the well-known formula of classical electrodynamics for the instantaneous radiation power of a dipole moment [4]:

$$Q = \frac{2e^2\,\ddot{x}^2}{3c^3}, \tag{3}$$

where $\ddot{x}$ is the charge acceleration. This formula is valid in the dipole approximation so Q is called the power of the dipole radiation.

For practical purposes, the average radiation power over a period T of oscillation $\langle Q\rangle_T \equiv \langle Q\rangle$ is of interest. In the case of a harmonic oscillator under consideration, this power can be expressed in terms of the total energy of the oscillator E, if we use the equation of motion, according to which $\ddot{x} = -\omega_0^2\,x$. From here we find: $\ddot{x}^2 = \omega_0^4\,x^2$. On the other hand $\omega_0^2\,x^2 = 2U/m$, where U is the potential energy of the harmonic oscillator, so $\ddot{x}^2 = 2\omega_0^2\,U/m$ and $Q = 4e^2\,\omega_0^2\,U/3mc^3$. Averaging the last equality over the period and considering that $2\langle U\rangle_T = \mathrm{E}$, we obtain the desired representation:

$$\langle Q\rangle = A_{sp}\,\mathrm{E}, \tag{4}$$

here

$$A_{sp} = \frac{2e^2\omega_0^2}{3mc^3} \tag{5}$$

is the coefficient of the dimension of the reciprocal time, which describes the probability of spontaneous emission, i.e., radiation arising in the process of free oscillations of a charged particle. According spectroscopic correspondence principle (5) must be multiplied by the force the oscillator. Then instead of (5) we have:

$$A_{nj} = \frac{2\,f_{jn}\,e^2\omega_{jn}^2}{3mc^3}. \tag{6}$$

Formula (6) gives an expression for the Einstein coefficient for spontaneous emission through the oscillator strength of the corresponding transition. Note that the oscillator strength can be calculated theoretically or determined experimentally.

If we now substitute the expression for the oscillator strength [2]

$$f_{nj} = \frac{2\,m_e\,\omega_{nj}\left|\langle n|\mathbf{d}|\,j\rangle\right|^2}{3e^2\,\hbar\,g_j}, \tag{7}$$

in the right-hand side of equality (6), then we arrive at the following formula for the Einstein coefficient for spontaneous emission

$$A_{nj} = \frac{4\,\omega_{jn}^{3} \left|\mathbf{d}_{nj}\right|^{2}}{3\,g_{j}\,\hbar c^{3}}\,, \tag{8}$$

where $\mathbf{d}_{nj}$ is the matrix element of the electric dipole moment, g_j is statistical weight of j state.

EINSTEIN COEFFICIENT FOR ABSORPTION OF RADIATION

To derive the formula for the Einstein coefficient for absorption B_{jn}, while remaining within the framework of classical physics, we proceed from equality (1), from which we can obtain expressions for the transition oscillator velocity

$$\dot{x}_{jn}(t) = -i\, f_{jn} \frac{e}{m} \int_{-\infty}^{\infty} \frac{\omega' E(\omega') \exp(-i\,\omega' t)}{\omega_{jn}^{2} - \omega'^{2} - 2i\omega'\delta_{jn}} \frac{d\omega'}{2\pi}\,. \tag{9}$$

Next, we use the expression for the instantaneous power of interaction between the electric field $\mathbf{E}(t)$ and the charge e moving along the axis x, referring to the one-dimensional oscillator:

$$P(t) = e\,\dot{x}(t) E_{x}(t). \tag{10}$$

Substituting expression (9) and representing the field $E_x(t)$ through the Fourier transform into equality (10), averaging over the states of the field using formula

$$\langle \mathbf{E}(\omega)\mathbf{E}(-\omega')\rangle = (2\pi)^{3}\, \rho(\omega)\delta(\omega - \omega'). \tag{11}$$

and moving on to integration over positive frequencies, we find for average power:

$$P \equiv \langle P\rangle = \frac{2\pi e^{2}}{3m} \int_{0}^{\infty} \frac{4\,\omega'^{2}\, \delta_{0}\, \rho(\omega')d\omega'}{\left(\omega_{0}^{2} - \omega'^{2}\right)^{2} + \left(2\omega'\delta_{0}\right)^{2}} \approx \frac{2\pi^{2} e^{2}}{3m} \int_{0}^{\infty} G^{(h)}(\omega')\rho(\omega')d\omega'\,, \tag{12}$$

here

$$G^{(h)}(\omega') = \frac{(\delta_{0}/\pi)}{(\omega_{0} - \omega')^{2} + (\delta_{0})^{2}} \tag{13}$$

- homogeneous line shape. In the derivation of (12), it was also taken into account that in a random electromagnetic field all polarizations are equally probable, so $\langle E_x^2\rangle = \langle \mathbf{E}^2\rangle/3$. The approximate equality in formula (12) corresponds to the assumption of a weak relaxation of a harmonic oscillator $\delta_0 << \omega_0$. In the limit of zero relaxation $\delta_0 \to 0$, the line shape (13) is approximated by the delta function:

$$G^{(h)}(\omega') \to \delta(\omega' - \omega_{0}). \tag{14}$$

Expression (12) describes the energy that is absorbed by a harmonic oscillator per unit time when exposed to radiation with a spectral density $\rho(\omega')$. In the case of an electromagnetic field with a wide spectrum far exceeding the line width of the harmonic oscillator $\Delta\omega >> \delta_0$, the substitution (14) can be made on the right-hand side of equality (12). As a result, we get:

$$P = \frac{2\pi^2 e^2}{3m} \rho(\omega_0) \ . \tag{15}$$

Relation (15) describes, in particular, the interaction of thermal radiation with a harmonic oscillator when the condition is satisfied. It can be seen that the absorbed power is determined by the spectral density of the radiation energy at the natural frequency of the oscillator.

Further, using correspondence principle, we find for the period averaged power absorbed at the transition under consideration under the action of radiation with a spectral energy density :

$$P_{jn} = f_{jn} \frac{2\pi^2 e^2}{3m} \rho(\omega_{jn}) \ . \tag{16}$$

Recall that in obtaining this relation it was assumed that the width of the radiation spectrum is much larger than the width of the transition spectrum in the atom. That is the case, for example, for thermal radiation.

By definition, the Einstein coefficient for absorption (upon transition of an atom from state $|n\rangle$ to state $|j\rangle$) is

$$B_{jn} = \frac{w_{jn}}{\rho(\omega_{jn})} . \tag{17}$$

In accordance with the physical picture of the process, the probability per unit time of photo-absorption w_{jn} is equal to the ratio of the absorbed power to the transition energy:

$$w_{nj} = \frac{P_{nj}}{\hbar \omega_{nj}} . \tag{18}$$

Collecting formulas (16) - (18), we obtain:

$$B_{jn} = \frac{2\pi^2 e^2 f_{jn}}{m \hbar \omega_{jn}} . \tag{19}$$

Given the explicit form of the oscillator strength (7), we find from here the expressions for the Einstein coefficient through the matrix element of the transition dipole moment:

$$B_{jn} = \frac{4\pi^2 |\mathbf{d}_{jn}|^2}{3 g_n \hbar^2} . \tag{20}$$

EINSTEIN COEFFICIENT FOR STIMULATED EMISSION OF RADIATION

The formula for the Einstein coefficient describing stimulated emission follows from (20) if we use equality $g_m B_{mn} = g_n B_{nm}$:

$$B_{nj} = \frac{4\pi^2 |\mathbf{d}_{nj}|^2}{3 g_j \hbar^2} . \tag{21}$$

Note that the matrix element of the dipole moment can be considered symmetric in its indices: $\mathbf{d}_{nj} = \mathbf{d}_{jn}$.

The approach described is valid if the external field is not too strong, when the amplitude of the transition oscillator is linear in the electric field in the electromagnetic wave. Otherwise, nonlinear effects need to be considered and a more complex consideration is required.

We note that the Einstein coefficient for spontaneous emission can be represented as

$$A_{nj} = B_{nj}\, \rho_{vac}\left(\omega_{nj}\right) \tag{22}$$

here

$$\rho_{vac}\left(\omega\right) = \frac{\hbar \omega^3}{\pi^2 c^3} \tag{23}$$

is the value that can be interpreted as the spectral energy density of vacuum fluctuations of the electromagnetic field. The notation (22) - (23) corresponds to the interpretation of spontaneous emission as induced by vacuum vibrations of electromagnetic field.

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