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Abstract

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Academician of the Academy of Sciences of the BSSR B. I. STEPANOV and V. P. GRIBKOVSKII

ABSORPTION AND LUMINESCENCE OF A HARMONIC OSCILLATOR

The study of the optical properties of a quantum harmonic oscillator is of fundamental importance for clarifying the degree of correspondence between classical and quantum theories. In the literature there are only isolated attempts at comparing them. In some cases, conclusions of quantum theory concerning a system with two energy levels are compared with the conclusions of the classical theory of an electric dipole, which, of course, is not always justified. Sometimes the discrepancy between the results of the two theories is regarded as a shortcoming of classical theory, whereas in fact it is connected with the difference between the models of matter being investigated. L. I. Mandelstam repeatedly drew attention to this circumstance (^{1}).

In the present work a quantum-mechanical calculation is carried out of the power of absorption and luminescence of light by a linear harmonic oscillator. As a result of the calculation it is shown that all conclusions of classical theory concerning the integral absorption and luminescence of a harmonic oscillator coincide with the conclusions obtained within the framework of quantum theory. In calculating the absorption and luminescence power, the values of the probabilities of transitions between different energy levels given by quantum mechanics (^{2}) were used. The probability of a forced (induced) transition from the vibrational level v' to the level v is equal to $B_{v'v}s$, where s is the density of the exciting radiation, and $B_{v'v} = B'_0|D_{v'v}|^2$ is the Einstein coefficient, proportional to the square of the corresponding matrix element of the dipole moment, with

$$D_{v'v} = er_{v'v} = e\sqrt{\frac{h}{4\pi^2 m\nu_0}}\left(\sqrt{\frac{v}{2}}\,\delta_{v-1,v'} + \sqrt{\frac{v+1}{2}}\,\delta_{v+1,v'}\right). \qquad (1)$$

Here e is the electron charge. The coefficients $B_{v'v}$ can be expressed in terms of the level number and the constant B_0 by the formula

$$B_{v,v+1} = B_{v+1,v} = (v+1)B_0, \tag{2}$$

where

$$B_0 = \frac{\pi e^2}{3mh\nu} \tag{3}$$

is the Einstein coefficient for forced transitions between the zero and first levels. Using the Einstein relation between the probabilities of spontaneous and forced transitions, we obtain

$$A_{v,v-1} = vA_0, \tag{4}$$

where

$$A_0 = \frac{8\pi^2 e^2 \nu^2}{3mc^3} \tag{5}$$

is the probability of a spontaneous transition from the first level to the zero level.

Let us consider an ensemble of harmonic oscillators interacting with external radiation of density s. It should also be taken into account that the oscil-

oscillators are in a field of thermal radiation of density u. As shown in (^{3}), in some cases, especially in the infrared region of the spectrum, the background of thermal emission is of substantial importance and cannot be neglected. In the general case the distribution of oscillators over energy levels $n_v(t)$ changes with time and satisfies the following system of differential equations:

$$\frac{d}{dt}n_v(t) = -n_v(t)\left[A_{v,v-1} + B_{v,v-1}(u+s) + B_{v,v+1}(u+s)\right] + n_{v+1}(t)\left[A_{v+1,v} + B_{v+1,v}(u+s)\right] + n_{v-1}(t)B_{v-1,v}(u \tag{6}$$

Usually, in calculating the intensity of absorption and luminescence of light by a quantum system, the explicit form of the distribution function $n_v(t)$ is used. In the case of the harmonic oscillator, the power of absorption and luminescence can be determined without directly solving equations (6)*.

Following (^{5,6}), we shall regard forced emission as negative absorption. Then the absorption power of N oscillators is expressed by the sum

$$W_{\text{abs}} = \sum_{v=0}^{\infty} h\nu\left[n_v(t)B_{v,v+1}s - n_{v+1}(t)B_{v+1,v}s\right]. \tag{7}$$

Since, according to (2), $B_{v,v+1} - B_{v,v-1} = B_0$, summation over v gives

$$W_{\text{abs}} = NB_0 sh\nu. \tag{8}$$

Substituting into (8) the value of B_0 from (3), we obtain

$$W_{\text{abs}} = N\frac{\pi e^2}{3m}\,s. \tag{9}$$

As is seen from (9), the absorption power of the harmonic oscillator does not depend on the distribution function or on the background of thermal emission, and consequently does not depend on the temperature of the surrounding medium. The linear dependence of W_{abs} on the density s of the exciting light indicates exact fulfillment of Bouguer' s law. In addition, it is necessary to note that the formula for the absorption power contains neither Planck' s constant h nor the oscillator force constant k.

In the classical theory the absorption power of N harmonic oscillators is given by the same expression (9) (see formula (1.21) in (^{5})).

On the other hand, the absorption coefficient of a system of particles with two levels (or of any other system with nonequidistant energy levels or a finite number of levels) depends both on the density of the exciting light and on the temperature. At this point an obvious divergence from the conclusions of classical electrodynamics is found. However, it is due only to the fact that a system with two energy levels is not the quantum analogue of the classical harmonic oscillator.

The luminescence power of N harmonic oscillators, taking into account the background of thermal emission, may be written in the form

$$W_{\text{lum}}(t) = \sum_{v=1}^{\infty}\left[n_v(t)\left(A_{v,v-1} + B_{v,v-1}u\right)h\nu - n_{v-1}(t)B_{v-1,v}uh\nu\right]. \tag{10}$$

The expression in square brackets gives the luminescence power for transitions between two neighboring levels (^{7}). We differentiate (10) with respect to time:

$$\frac{d}{dt}W_{\text{lum}}(t) = h\nu\sum_{v=1}^{\infty}A_{v,v-1}\frac{d}{dt}n_v(t). \tag{11}$$

* In (^{4}) the values of $n_v(t)$ are obtained in explicit form. Some additional information related to the topic of the present communication is also contained there.

Taking (6) into account, formula (11) is easily represented in the form of a differential equation for $W_{\text{lum}}(t)$:

$$\frac{d}{dt} W_{\mathrm{lum}}(t) + A_0 W_{\mathrm{lum}}(t) = A_0 N B_0 s h\nu. \tag{12}$$

The solution of (12), for constant s, has the form

$$W_{\mathrm{lum}}(t) = C e^{-A_0 t} + N B_0 s h\nu. \tag{13}$$

If at the initial moment of time $t = 0$ luminescence was absent, then $C = -N B_0 s h\nu$. In this case (13) gives the law for the rise of luminescence

$$W_{\mathrm{lum}}^{\mathrm{rise}}(t) = N B_0 s h\nu \left(1 - e^{-A_0 t}\right). \tag{14}$$

Putting $t \to \infty$ in (14), we find the value of the luminescence power in the stationary irradiation regime

$$W_{\mathrm{lum}}^{\mathrm{stat}} = N B_0 s h\nu = N \frac{\pi e^2}{3m} s. \tag{15}$$

As is seen from (9) and (15), the luminescence power in the stationary regime is equal to the absorption power and coincides exactly with the corresponding quantity of the classical theory $^{(5)}$.

If, as the initial conditions, one takes the value $W_{\mathrm{lum}}^{\mathrm{stat}}$ for the stationary regime and sets $s = 0$ in (13), it is not difficult to obtain the law of luminescence decay

$$W_{\mathrm{lum}}^{\mathrm{dec}}(t) = N B_0 s h\nu e^{-A_0 t} = N \frac{\pi e^2}{3m} s e^{-8\pi^2 e^2 \nu^2 t / 3mc^3}. \tag{16}$$

Expression (16) is identical to the classical law of damping of the emission of a harmonic oscillator, since the classical damping constant is $2\gamma = 8\pi^2 e^2 \nu^2 / 3mc^3$.

Thus, the final conclusions of the classical and quantum theories concerning the integral absorption and emission of a harmonic oscillator do not merely correspond, but completely coincide with one another.

It should be noted that, owing to its specific properties (equidistance of the energy levels, the selection rule, and the linear dependence of transition probabilities on the level number), the harmonic oscillator often behaves as a system of particles with two energy levels. This is manifested in the exponential character of the laws of decay and rise of fluorescence and in the similarity, and sometimes complete identity, of the expressions for the absorption power of the incident light. Indeed, formula (9), obtained as a result of taking account of negative absorption and transitions from all energy levels, coincides in essence with the expression that can be obtained for the absorption power of a system of particles with two levels, if it is conditionally assumed that all N particles are in the unexcited state.

At sufficiently low temperatures (for electronic levels, at room temperatures) and ordinary intensities of the incident flux, the overwhelming majority of oscillators are in the unexcited state, and therefore only the first pair of levels is significant. The population of the higher energy levels is negligibly small, and they have no influence on the processes of absorption and luminescence. In this case, the application of the two-level model for any calculations and the application of the harmonic-oscillator model lead to analogous results. If, however, the substance is at high temperatures and, consequently, there is a large number of excited particles, then the use of two-level models instead of the harmonic oscillator is inadmissible.

In the monograph (8), as well as in many other literary sources, formula (9) is obtained approximately. In its derivation it is tacitly assumed that,

that all particles are at the zero level and transitions only between two levels are considered. Such an assumption is valid only at absolute zero temperature and for the initial moments of excitation; therefore, the general conclusions drawn in those works about the coincidence of the results of the quantum and classical theories were not sufficiently substantiated.

Institute of Physics and Mathematics
Academy of Sciences of the BSSR

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