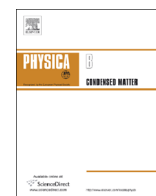




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Exactly soluble model of the time-resolved fluorescence return to thermal equilibrium in many-particle systems after excitation

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ABSTRACT

In this paper we consider the assembly of weakly interacting identical particles, where the occupation of single-particle energy-levels at thermal equilibrium is governed by statistics. The analytic form of the inter-energy-level jump matrix is derived and analytic solution of the related eigen-problem is given. It allows one to demonstrate the nature of decline in time of the energy emission (fluorescence, recombination) of such many-level system after excitation in a relatively simple and unifying way – as a multi-exponential de-excitation. For the system of L energy levels the number of the de-excitation lifetimes is $L - 1$. The lifetimes depend on the energy level spectrum as a whole. Two- and three-level systems are considered in detail. The impact of the energy level degeneracy on the lifetimes is discussed.

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1. Introduction

Fluorescence process is the emission of light from a substance after exciting it to higher energy states. Nowadays the field has a great history and an abundance of experimental results and methods, see e.g. the monograph [1] of Lakowicz and references given there. Typically the characteristic time of the emission decay is of the order of several ns. In the case when the excited state is the triplet one having spin orientation such as that of the ground state, the decay is much slower – its values are in the time-range $(1 \cdot 10^3) s$ – this phenomenon is called phosphorescence [2]. If one applies this way of thinking to excited semiconductors one deals with the recombination of the electron–hole pairs [3]. In case of the excitation constant in time we have the so called steady-state emission.

Important examples of such effects are the atomic spectra, like the commonly known Balmer spectra for hydrogen, in laboratory or on the cosmic scale, see e.g. [4]. Also, a system can be the gas of molecules executing their internal vibrations or rotations. Another example might be a semiconductor with a number of impurities or defects characterized by energy levels in the forbidden gap.

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The fluorescence phenomena have a rich experimental evidence, especially for the steady-state phenomena, where the experimental procedure is relatively simple. The time-dependent-emission decline is more complex. The time-resolved fluorescence vs. temperature data are rarely published. As an illustration of the temperature dependence we have taken the fluorescence exponential declines in corrole and corrole– fullerene-based dyad, Fig. 1 (although the quantum yield of them does not exceed 10%). It is worthy to note that the time-decline in the second case is characterized by two lifetimes [5]. Other examples can be found in the literature [1].

To investigate the fluorescence phenomenon, one can excite the system with some external agent, e.g. by an illumination or a voltage pulse, which causes the particles jump from lower energy levels to the higher ones. In principle the particles could stay in the excited states for ever, unless there is a mechanism of interaction between them, triggering an exchange of energy. If the system returns to the equilibrium state by emitting photons, we have the light emission process. The energy-level populations decline in time t , to finally return to the equilibrium population numbers n_i^0 .

It should be emphasized, that this process of de-excitation usually occurs in matter via several mechanisms, including the non-radiative ones, like internal conversion, intersystem crossing, intramolecular electron transfer, phonons, and magnons. In this

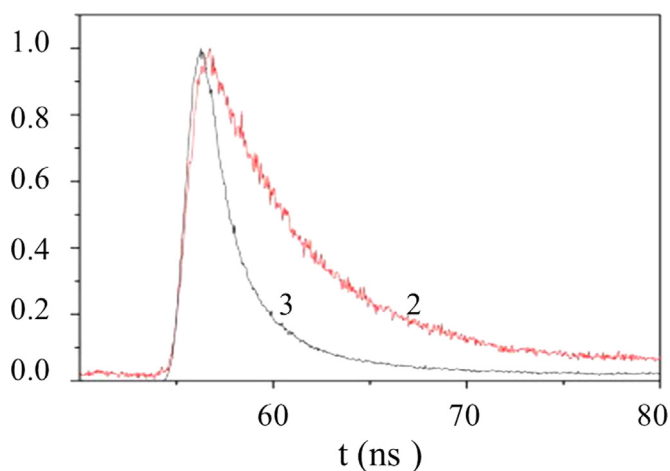


Fig. 1. Room temperature fluorescence decays of the corrole (lifetime 3.80 ns, label 2) and the corrole-based-fullerene (lifetimes 6.54 ns and 1.00 ns, label 3) dyad vs. time; excitation 405 nm; concentration 10^{-4} M. Based on paper [5].

paper we consider the idealized model of purely radiative de-excitation. Therefore, the model is not universal – it is of partial practical application. On the other hand, being analytically soluble and internally consistent in its mathematical aspect, it offers the advantage of full understanding of the radiative multi-exponential aspect of fluorescence decline. Hopefully the model will show in future a potential to include other energy decline mechanisms along a similar logical scheme.

We shall consider here a system of N identical particles, each represented by the same ladder of energy levels E_i . It means that it is also the energy spectrum of the whole many-particle system, the number of particles adding itself to the degeneracy of the energy levels. As the example one can consider a gas of atoms or molecules, interacting “weakly” so that the energy levels are such as the ones for individual free atom. This “weak” interaction between particles (collisions or interaction with electromagnetic field) is understood to be present, to allow the system to attain the thermal equilibrium at some temperature T . It is assumed that after a short excitation the system returns to the energy level populations n_i^0 corresponding to the thermal equilibrium.

Einstein's theory of atomic emission and absorption [6,7] deals with the model atom of two energy levels $E_2 > E_1$ bathed in the electromagnetic field. One considers in this model three phenomena: spontaneous one-photon emission characterized by the coefficient A_{21} , stimulated emission – B_{21} , stimulated absorption – B_{12} . The symmetry alone suggests that perhaps something like an intrinsic absorption with the coefficient A_{12} could appear too. In this paper we show, that indeed such “intrinsic” absorption enters in a natural way, as a condition for the system's return to thermal equilibrium. It is worthy to emphasize, that if one tries to impose this two-level model upon a real multi-level atom, one eliminates a priori a possibility of the impact of the remaining energy levels on the emission process. This effect shows openly in the model proposed in this paper.

The present model can be treated as the mathematical background of the idea of Jablonski diagrams [1], but perhaps not in case of the phosphorescence. As mentioned above, many transitions between energy levels in real atoms/molecules are forbidden by the parity argument. To first order in long-wave perturbation it is the electron dipole mechanism, which rules some inter-level transitions [2,7]. It means that only such transitions are allowed, which do not violate the spin and the symmetry selection rules. (Practically such transitions do occur, but at relatively slow pace.) However here we consider the multi-level systems where such parity forbidden transition are absent or can be ignored, and only

the statistical energy factor, which is responsible for population of the energy levels and the intensity of the inter-level transitions, enters the theory.

We shall consider what happens after applying the igniting pulse disturbing the thermodynamic equilibrium, whatever is the mechanism of return to the equilibrium. The essence of this mechanism is assumed to be already contained in the energy-level population statistics at equilibrium. It allows us to avoid considering e.g. a direct impact of the electromagnetic field onto the excitation and de-excitation processes, as it occurs in the above Einstein model. Due to such assumption the number of considered energy levels is not limited and the contribution of all inter-level jumps to the emission lifetimes is systematically accounted for.

In Section 2 we shall examine the relaxation (decay) processes after excitation in rather general terms, using the master equation idea. We show that one can express them in terms of the eigenvectors (eigenmodes) and eigenvalues (eigenrates or eigenlifetimes) of the decay (relaxation) matrix – the jump probability matrix W_{ij} . In Section 3 we show that once the energy level population at equilibrium is known, one can determine the mathematical form of the jump matrix. Moreover, the analytical form of the eigenvalues and eigenvectors has been derived whatever the number of energy levels is.

The jump matrix is real, but not symmetric, so in general the eigenvectors are not orthogonal. The time-decay of population fluctuations after an initial excitation can be expressed as linear combination of its eigenvectors multiplied by the exponential-decline factors given by the corresponding eigenvalues (decay eigenlifetimes or decay eigenrates), see Section 4. We believe that such general formulation of the problem is presented here for the first time.

As an example the eigenproblem of such jump-matrix has been presented in Sections 5 and 6, and solved for systems of particles characterized by two and three energy-levels. The corresponding eigenvectors and eigenvalues (decay rates, lifetimes) have been analytically found and shown as a function of temperature. The basic impact of different degenerations N_i is demonstrated for $L=2$: the two-level case. Extension of this procedure to higher number L of energy levels is straightforward.

In Section 7 we demonstrate the many-level nature of the fluorescence decay in time which in general involves many intrinsic excitations and de-excitations at the same time. Analysis of the experimental data [5] in Section 8 shows the impact of different degeneracies of energy levels on the decay lifetimes. Some conclusions are summarized in Section 9.

2. Relaxation kinetic equations

Let n be the number of particles in the system, N_l be the number of states at the energy level E_l , where $l=1,2 \dots L$, and $p(E_l)=p_l$ be the particle population probability for this energy level. Therefore, the average number of particles at this energy level is $n_l=N_l p_l$ and the total number of particles is $n = \sum_{l=1}^L n_l$, whereas the total number of available energy states is $N = \sum_{l=1}^L N_l$. The general convention is that the energy level values grow with the growing index l : $E_{l+1} \geq E_l$.

The particle jump from one of its energy levels to the lower may be accompanied with the emission of an energy quantum due to the electron jump from E_l to E_i . The change in time of the number of particles at the energy level E_i can be expressed via the master equation for $dn_i(t)/dt = N_i dp_i(t)/dt$

$$N_i \frac{dp_i}{dt} = \sum_{l \neq i} e_l N_l p_l W_{li}^0 c_l - N_i p_i e_i \sum_{l \neq i} W_{il}^0 c_l \quad (2.1)$$

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