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SPECTROSCOPY OF ATOMS AND MOLECULES

Photon Distribution Functions of Fluorescence Photons from Single Nanoparticles: Three Different Photon Counting Methods

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Abstract—Mathematical expressions are derived for three photon distribution functions $w_N^M(T)$, $w_N^Z(T)$, and $w_N^O(T)$ corresponding to three different methods for counting fluorescence photons from a single nanoparticle excited by continuous laser radiation. Each of the three functions is expressed in terms of Poisson functions, which makes it possible to pass in the $w_N^M(T)$, $w_N^Z(T)$, and $w_N^O(T)$ functions from N multiple integrals to single or double integrals. This not only eases the numerical calculation of the photon distribution, but it also makes it possible to find that, for each exponential process in the dynamics of a nanoparticle, there is a Poisson function in the photon distribution function. All three photon counting methods yield the same photon distribution for continuous fluorescence and different photon distributions for blinking fluorescence.

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INTRODUCTION

Single semiconductor nanocrystals, quantum dots, and macromolecules excited by light from a cw laser emit a sequence of photons, which carries information on the quantum dynamics of a nanoparticle. The number of fluorescence photons of a nanoparticle counted within a time interval T fluctuates because photons are emitted at random time instants. The function $w_N(T)$ that describes the distribution of N photons counted in the interval T is termed the photon distribution function. Clearly, the form of this function depends on the method of counting of photons. This has been recently shown in the short communication by the author [1], where the theoretical expressions for three distribution functions $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$ corresponding to three different methods of counting of fluorescence photons of a single nanoparticle were presented. In [1], these methods were termed the method O, Z, and M, respectively. The essence of these methods is described in the next section of this study.

Experimentally, only one of these methods is commonly used, namely, the method M. Therefore, in earlier theoretical works, photon distributions were derived precisely for the method M of photon counting [2–10]. However, in practice, it was very difficult to calculate photon distributions by formulas of these theories for models of a nanoparticle of practical interest. For example, for a blinkingly or continuously fluorescing nanoparticle, the photon distribution was simply postulated to be Poissonian [9, 10].

Therefore, other approaches to the calculation of photon distributions of single nanoparticles were developed, which already did not correspond to the method M of photon counting [11–18]. For example, the method of the generating function, which was developed in [12–15] for counting distribution functions, corresponded to the method Z, and theoretical formulas of works [16–18] corresponded to the method O of photon counting.

In this study, a detailed derivation of the distribution functions $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$ is given. Then, transformations of these functions to forms that make it possible to perform numerical calculations are presented. Finally, all three types of distributions are compared with each other in the cases of continuous and blinking fluorescence photons.

DIFFERENT PHOTON COUNTING METHODS

Clearly, three different photon counting methods are possible. In the most widespread method, which we will term method M, the entire time axis is divided into intervals T and the number of intervals with a certain number of photons is counted. The beginning and the end of any time interval T are not related to the instant of detection of a photon. This method can be

applied to fluorescence of both single molecules and ensembles of molecules. It is the method M for which the well-known expressions for the photon distribution function and the Mandel parameter Q that defines the statistics of emitted photons were derived [4]. The photon distribution function that is derived below and that corresponds to this photon counting method will be denoted as $w_N^M(T)$.

However, the method M is not the only possible method of measuring the photon distribution function. In studies of fluorescence of single atoms and molecules, photons can also be counted by other methods. For example, Zoller et al. [11] suggested to count all intervals T of the same length each of which begins at the instant of emitting of a fluorescence photon and ends when the experimenter stops counting time. At different intervals, different numbers of photons will be counted; i.e., the photon distribution along the interval of the given length will be found. In this method, which we will term method Z, the field of events is the set of semiopen intervals $[0, T)$ of the same length.

This method of counting is more convenient for the theoretical consideration of the problem than method M, because the fluorescence photon detected at the beginning of the time interval determines the initial state of the quantum system; i.e., it indicates that, at the beginning of the interval, the nanoparticle is in the ground electron state with a probability of one. The photon distribution function that corresponds to this method of counting and that will be derived below will be denoted as $w_N^Z(T)$. It defines the probability of observation of N photons in the interval T without taking into account the photon that opens this interval.

It is also possible to consider time intervals whose beginnings and ends coincide with the emission instants of fluorescence photons. The memory function of these intervals was considered in [19]; the photon distribution function in this type of interval has not been considered. In [16], these time intervals were considered as a field of events, as a method of photon counting. For this method, which we will term the method O, an expression for the photon distribution function was derived in [16]. In this study, this function is denoted as $w_N^O(T)$ to distinguish it from the functions $w_N^M(T)$ ($w_N^Z(T)$, which will also be discussed below. The function $w_N^O(T)$ defines the probability of emission of N photons in the time interval T without taking into account the photons that open and close this interval. For this reason, N photons that were emitted in the interval between these two photons were referred to in [16] as intermediate photons. Consequently, $w_N^O(T)$ describes the distribution of intermediate photons.

The main result of [16] was finding a method that made it possible to express N multiple integrals for photon distribution functions via single and double integrals of Poisson functions. This not only made the calculation of distribution functions significantly easier but also set up a one-to-one correspondence between each exponential process in the quantum dynamics of a nanoparticle and the corresponding Poisson function in the expression for the photon distribution function. In this study, this efficient method will also be applied to the functions $w_N^M(T)$ and $w_N^Z(T)$.

THREE PHOTON-DISTRIBUTION FUNCTIONS

We obtain information on the quantum state of a nanoparticle at a time instant when a fluorescence photon is emitted. Therefore, it is natural to begin with the consideration of the method O of photon counting, where there are two such time instants.

Method O of Photon Counting

Let

$$dS(t) = s(t)dt \tag{1}$$

be the probability of detecting a fluorescence photon in the interval $(t, t + dt)$ if a preceding photon was emitted at $t = 0$. Function $s(t)$ is the probability density and it is equivalent to function $w_2(t)$ considered in [20]. Function $s(t)$ determines the correlation between two successively emitted photons. Therefore, in [21, 22], this function was referred to as the start–stop correlator. Clearly, the function

$$S(T) = \int_0^T s(t)dt \tag{2}$$

defines the probability of detecting the second photon by the time instant T. The functions

$$\begin{aligned} s_1(T) &= \int_0^T s(T-t_1)s(t_1)dt_1, \\ s_2(T) &= \int_0^T s(T-t_2)s_1(t_2)dt_2, \ldots, \\ s_N(T) &= \int_0^T s(T-t_N)s_{N-1}(t_N)dt_N, \ldots \end{aligned} \tag{3}$$

define the probabilities to detect one, two, ..., N photons between the photon that opens the interval $[0, T]$ and the photon that closes this interval. The probabil-

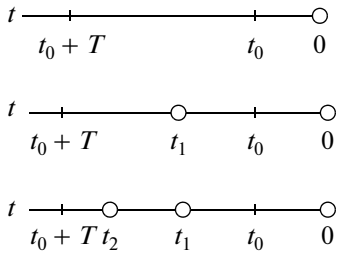

Fig. 1. Time intervals with fluorescence photons (circles).

ity density to detect N of these intermediate photons is expressed via the start–stop correlator $s(T)$ as follows:

$$s_N(T) = \int_0^T dt_N \int_0^{t_N} dt_{N-1} \ldots \int_0^{t_2} dt_1 s(T - t_N) \times s(t_N - t_{N-1}) \ldots s(t_2 - t_1) s(t_1). \quad (4)$$

Consider the infinite series

$$p(T) = s(T) + \sum_{N=1}^{\infty} s_N(T). \quad (5)$$

The function $p(T)$ determines the correlation between two photons that open and close the interval $[0, T]$ irrespective of how many intermediate photons were emitted in this interval. Therefore, the function $p(T)$ was referred to as the full two-photon correlator [21, 22]. The authors of [20] denoted this function as $g_2(T)$. The full two-photon correlator $p(T)$ is related to the fluorescence second-order autocorrelation function $g^{(2)}(T)$ by the simple relationship [21, 22]

$$g^{(2)}(T) = \lim_{t \to \infty} \frac{\langle I(t) I(t+T) \rangle}{\langle I(t) \rangle^2} = \frac{p(T)}{p(\infty)}. \quad (6)$$

Here, $p(\infty)$ is equal to the average fluorescence intensity $\langle I \rangle$ that appears in the formulas of the Mandel theory for the first two moments of the distribution function,

$$\langle N \rangle = \langle I \rangle T, \quad \langle N^{(2)} \rangle = 2 \langle I \rangle^2 \int_0^T dx \int_0^x dx_1 g^{(2)}(x - x_1). \quad (7)$$

The full correlator and the start–stop correlator are related to each other as follows:

$$p(T) = s(T) + \int_0^T s(T - t) p(t) dt. \quad (8)$$

This integral equation can be easily derived using formulas (4) and (5). Since the function $p(T)$ takes into account $[0, T]$ with any number of intermediate photons, the ratios

$$w_0^O(T) = \frac{s(T)}{p(T)}, \quad w_N^O(T) = \frac{s_N(T)}{p(T)} \quad (9)$$

can be considered to be the probabilities of detecting the interval $[0, T]$ without and with N intermediate photons, respectively. They are expressed solely via the start–stop correlator. The sum of all the probabilities is unity

$$\sum_{N=0}^{\infty} w_N^O(T) = 1. \quad (10)$$

Previously, Eqs. (9) were derived in [16].

Method Z of Photon Counting

The time interval $[0, T)$ of the length T is opened by the first photon and no photon is emitted at the end of the interval. The probability of detecting an interval of this length that does not contain intermediate photons is given by

$$w_0^Z(T) = 1 - \int_0^T s(t) dt = 1 - S(T). \quad (11)$$

The probability of detecting the interval $[0, T)$ with one and N photons is given by the expressions

$$w_1^Z(T) = \int_0^T dt_1 w_0^Z(T - t_1) s(t_1),$$
$$w_N^Z(T) = \int_0^T dt_N \int_0^{t_N} dt_{N-1} \ldots \int_0^{t_2} dt_1 w_0^Z(T - t_N) \times s(t_N - t_{N-1}) \ldots s(t_2 - t_1) s(t_1). \quad (12)$$

These probabilities are also expressed solely via the start–stop correlator. The sum of all these probabilities is unity,

$$\sum_{N=0}^{\infty} w_N^Z(T) = 1. \quad (13)$$

Method M of Photon Counting

We consider initially an auxiliary case where, unlike the method Z, we are interested in the probability of detecting a photon in the $(t_0, T + t_0)$ whose beginning is separated by the time t_0 from the instant $t = 0$ when a fluorescence photon was emitted. This situation is shown in Fig. 1. The probability of detecting a photon in the interval $(t_0, T + t_0)$ under the addi-

tional condition that the preceding photon was emitted at $t = 0$ is given by the following expression:

$$\rho_1(T + t_0, t_0, 0) = \int_{t_0}^{T+t_0} dt_1 w_0^Z(T + t_0 - t_1)s(t_1) = \int_0^T dx_1 w_0^Z(T - x_1)s(x_1 + t_0). \quad (14)$$

In a similar way, we can write the expression for the probability of detecting two photons in the interval $(t_0, T + t_0)$ under the additional condition that the preceding photon was emitted at $t = 0$,

$$\rho_2(T + t_0, t_0, 0) = \int_0^T dx_2 w_0^Z(T - x_2) \times \int_0^{x_2} dx_1 s(x_2 - x_1)s(x_1 + t_0). \quad (15)$$

The probability of detecting N photons ($N \geq 2$) in the interval $(t_0, T + t_0)$ under the additional condition that the preceding photon was emitted at $t = 0$ is given by

$$\rho_N(T + t_0, t_0, 0) = \int_0^T dx_N \int_0^{x_N} dx_{N-1} \ldots \int_0^{x_2} dx_1 w_0^Z(T - x_N) \times s(x_N - x_{N-1}) \ldots s(x_2 - x_1)s(x_1 + t_0). \quad (16)$$

The probability $\rho_N(T + t_0, t_0, 0)$ is the conditional probability, since it determines the probability to observe N photons in the interval $(t_0, T + t_0)$ under the condition that no photons were emitted in the interval $(t_0, 0)$. This can be expressed via the unconditional probability as

$$\rho_N(T + t_0, t_0, 0) = w_N(T + t_0, t_0)w_0^Z(t_0), \quad N \geq 1. \quad (17)$$

Here, $w_N(T + t_0, t_0)$ is the unconditional probability of detecting N photons in the interval $(t_0, T + t_0)$ irrespective of whether or not photons were emitted at time instants preceding the instant t_0. Reasoning in a similar way, we can write the following expression for the probability of detecting the interval $(t_0, T + t_0)$ without photons:

$$\rho_0(T + t_0, t_0, 0) = w_0(T + t_0, t_0)w_0^Z(t_0). \quad (18)$$

Here, $\rho_0(T + t_0, t_0, 0) = w_0^Z(T + t_0)$ is the probability of not detecting a photon in the interval $(0, T + t_0)$, and $w_0(T + t_0, t_0)$ is the probability not to detect a photon in the smaller interval $(t_0, T + t_0)$. Consequently, the unconditional probability $w_0(T + t_0, t_0)$ is defined by the following expression:

$$w_0(T + t_0, t_0) = \frac{w_0^Z(T + t_0)}{w_0^Z(t_0)}. \quad (19)$$

Using (16), we can derive the following expression for the sum of conditional probabilities:

$$\sum_{N=1}^{\infty} \rho_N(T + t_0, t_0|0) = w_0^Z(t_0) - w_0^Z(T + t_0). \quad (20)$$

This expression was derived taking into account that $\int_{t_0}^{T+t_0} dt_1 \int_{t_1}^{T+t_0} dt \ldots = \int_{t_0}^{T+t_0} dt \int_{t_0}^{t} dt_1 \ldots$. Using (19) and (20), we arrive at the law of conservation of conditional probabilities,

$$\sum_{N=0}^{\infty} w_N(T + t_0, t_0) = 1. \quad (21)$$

Clearly, these probabilities are reduced to the probabilities $w_N^Z(T)$ at $t_0 = 0$, i.e., $w_N(T + 0, 0) = w_N^Z(T)$.

If photons are detected by the method M, the probability density to observe the photonless time interval $(0, t_0)$ is

$$P(t_0) = \frac{w_0^Z(t_0)}{\int_0^{\infty} w_0^Z(t_0)dt_0} = \frac{w_0^Z(t_0)}{S}. \quad (22)$$

The probability of detecting an interval of the length T with N photons using the method M is defined by the following formula:

$$w_N^M(T) = \int_0^{\infty} w_N(T + t_0, t_0)P(t_0)dt_0 = \frac{1}{S}\int_0^{\infty} \rho_N(T + t_0, t_0, 0)dt_0. \quad (23)$$

Using formulas (22) and (23), we arrive at the law of conservation of probabilities $\sum_{N=0}^{\infty} w_N^M(T) = 1$.

Summarizing the consideration performed above, we can write the following expressions for the probabilities $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$:

for method O,

$$w_0^O(T) = s(T)/p(T),$$

$$w_N^O(T) = \int_0^T dt_N \int_0^{t_N} dt_{N-1} \ldots \int_0^{t_2} dt_1 P^O(T, t_N, t_{N-1}, \ldots t_1),$$

$$N \geq 1, \quad (24)$$

$$P^O(T, t_N, t_{N-1}, \ldots, t_1) = \frac{s(T-t_N)}{p(T)} \prod_{j=1}^{N-1} s(t_{j+1}-t_j) s(t_1),$$

$$(N>1), \quad P^O(T, t_1) = \frac{s(T-t_1)s(t_1)}{p(T)};$$

for method Z,

$$w_0^Z(T) = 1 - S(T),$$

$$w_N^Z(T) = \int_0^T dt_N \int_0^{t_N} dt_{N-1} \ldots \int_0^{t_2} dt_1 P^Z(T, t_N, t_{N-1}, \ldots, t_1)$$

$$(N \geq 1), \quad (25)$$

$$P^Z(T, t_N, t_{N-1}, \ldots, t_1) = w_0^Z(T-t_N) \prod_{j=1}^{N-1} s(t_{j+1}-t_j) s(t_1)$$

$$(N>1), \quad P^Z(T, t_1) = w_0^Z(T-t_1)s(t_1);$$

for method M,

$$w_0^M(T) = \frac{1}{S}\int_0^\infty dt_0 w_0^Z(T+t_0),$$

$$w_1^M(T) = \frac{1}{S}\int_0^T w_0^Z(T-t) w_0^Z(t) dt,$$

$$w_N^M(T) = \int_0^T dt_N \int_0^{t_N} dt_{N-1} \ldots \int_0^{t_2} dt_1 P^M(T, t_N, t_{N-1}, \ldots, t_1) \quad (26)$$

$$(N \geq 2),$$

$$P^M(T, t_N, t_{N-1}, \ldots, t_1) = \frac{w_0^Z(T-t_N)}{S} \prod_{j=1}^{N-1} s(t_{j+1}-t_j) w_0^Z(t_1).$$

It should be emphasized that formulas (24)–(26) are determined solely by the function $s(t)$, i.e., by the start–stop correlator. All physical specific features of a single nanoparticle emitting fluorescence photons are reflected in a particular form of the start–stop correlator. Therefore, formulas (24)–(26) can be used to consider fluorescence of nanoparticles that are described by different physical models. However, Eqs. (24)–(26) are inconvenient for use in practice due to multiple integration. The method that made it possible to obviate multiple integration was found in [16]. This method is as follows.

The Laplace transforms $\int_0^\infty dt F(t) e^{i(\omega + i0)t} = F(i\omega) = F(\lambda)$ of Eqs. (24)–(26) yield the following simple expressions:

$$(w_N^O p(T))_\lambda = s(\lambda)^{N+1}, \quad w_N^Z(\lambda) = \frac{1}{-\lambda}[1-s(\lambda)]s(\lambda)^N,$$

$$w_N^M(\lambda) = \frac{1}{\lambda^2 S}[1-s(\lambda)]^2 s(\lambda)^{N-1} \quad (N \geq 1). \quad (27)$$

These formulas were derived using the expressions

$$\int_0^\infty s(x_1+t_0)dt_0 = \int_{x_1}^\infty s(t)dt = 1 - \int_0^{x_1} s(t)dt = w_0^Z(x_1),$$

$$\left[\int_0^x f(x-y)g(y)dy\right]_\lambda = f(\lambda)g(\lambda).$$

It can be seen that all three types of photon distribution are determined by the Nth power of the Laplace transform of the start–stop correlator.

Let the expression for the inverse Laplace transform of the Nth power of the function $s(\lambda)$, i.e., the expression $[s(\lambda)^N]_t$, be known. Then, applying the inverse Laplace transform to formulas (27), we arrive at the following formulas:

for method O,

$$w_N^O(T) = [s(\lambda)^N]_T/p(T); \quad (28)$$

for method Z,

$$w_N^Z(T) = \int_0^T dt\{s[(\lambda)^N]_t - s[(\lambda)^{N+1}]_t\} \quad (N \geq 1), \quad (29a)$$

$$w_0^Z(T) = 1 - \int_0^T s(t)dt; \quad (29b)$$

and, finally, for method M,

$$w_N^M(T) = \frac{1}{S}\int_0^T (T-t) \times \{s[(\lambda)^{N-1}]_t - 2[s(\lambda)^N]_t + [s(\lambda)^{N+1}]_t\} dt \quad (30a)$$

$$(N \geq 1),$$

$$w_0^M(T) = \frac{1}{S}\int_0^\infty \left[1 - \int_0^{T+t} s(x)dx\right] dt. \quad (30b)$$

Formulas (28)–(30) are completely equivalent to formulas (24)–(26); however, they only contain one integration. However, as will be shown in the next section,

the formula for $[s(\lambda)^N]_t$ can also be expressed in terms of only one integral, which substantially eases the calculation of distribution functions by formulas (28)–(30).

EXPRESSING DISTRIBUTION FUNCTIONS VIA POISSON FUNCTIONS

Two-Level Nanoparticle

Consider initially the expression for the start–stop correlator for a two-level nanoparticle. These equations were already derived by the author in paper [21] and in chapter 2 of monograph [22]. It was shown there that the start–stop correlator is defined by the formula $s(t) = W_1(t)/T_1$, where the probability $W_1(t)$ should be found from the following system of equations:

$$\begin{aligned} \dot{W}_{10} &= -i(\Delta - i/2T_1)W_{10} + \chi(W_0 - W_1), \\ \dot{W}_{01} &= i(\Delta + i/2T_1)W_{01} + \chi(W_0 - W_1), \\ \dot{W}_1 &= -\chi(W_{10} - W_{01}) - W_1/T_1, \\ \dot{W}_0 &= \chi(W_{10} - W_{01}) \end{aligned} \tag{31}$$

at the initial condition $W_0(0) = 1$, which means that, at time zero, the nanoparticle proved to be in the ground state; i.e., a fluorescence photon was emitted. Here, $\chi = \mathbf{dE}/\hbar$ is the Rabi frequency; $1/T_1$ is the rate of spontaneous emission of the electronically excited nanoparticle; and Δ is the difference between the frequency of the laser light and the resonance frequency of the purely electronic excitation. The system of equations (31) differs from Bloch equations in that the fourth equation does not contain the term $+W_1/T_1$. The system of equations (31) takes into account both incoherent and coherent effects. The latter effects manifest themselves at a high pumping intensity, i.e., at $\chi T_1 > 1$, as the well-known Rabi oscillations. Under weak pumping, when $\chi T_1 \ll 1$, the solutions to Eqs. (31) almost coincide with the solutions of the following system of balance equations:

$$\begin{aligned} \dot{W}_1 &= -(k + 1/T_1 + G)W_1 + kW_0, \\ \dot{W}_0 &= (k + G)W_1 - kW_0, \end{aligned} \tag{32}$$

which follow from the system of equations (31) at $\chi T_1 \ll 1$. This was shown in detail by the author in [16]. Here, $k = 4\chi^2 T_1/(4\Delta^2 T_1^2 + 1)$ is the rate of induced emission/absorption of laser photons by the nanoparticle; and G is the rate of nonradiative transitions, as a result of which the fluorescence quantum yield is smaller than unity. The initial condition $W_0(0) = 1$ means that a photon is emitted at $t = 0$. By solving Eqs. (32) with this initial condition, we arrive at the following expression for the start–stop correlator:

$$\begin{aligned} s(T) &= W_1(T)/T_1 \\ &= \frac{\lambda_1\lambda_2}{\lambda_2 - \lambda_1}[\exp(-\lambda_1 T) - \exp(-\lambda_2 T)], \end{aligned} \tag{33}$$

where $\lambda_1 = \gamma - R$, $\lambda_2 = \gamma + R$, and $\gamma = (\Gamma + k)/2$, $R = \sqrt{(\Gamma + k)^2/4 - k/T_1}$. Here, $\Gamma = k + G + 1/T_1$ is the total decay rate of the excited state. At a low excitation level at which the condition $k \ll 1/T_1$ is satisfied, we find that $\lambda_1 \cong k$ and $\lambda_2 \cong 1/T_1$.

The Laplace transform of function (33) has the form

$$s(\lambda) = \frac{\lambda_1\lambda_2}{(\lambda_1 - \lambda)(\lambda_2 - \lambda)}. \tag{34}$$

Therefore, the Nth power of the correlator can be represented as

$$\begin{aligned} s(\lambda)^N &= \lambda_1\lambda_2 \frac{\lambda_1^{N-1}}{(\lambda_1 - \lambda)^N} \frac{\lambda_2^{N-1}}{(\lambda_2 - \lambda)^N} \\ &= \lambda_1\lambda_2 P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda). \end{aligned} \tag{35}$$

Here, $P_M^\alpha(\lambda)$ is the Laplace transform of the Poisson function $P_N[\alpha t] = (\alpha t)^N \exp(-\alpha t)/N!$. Applying the inverse Laplace transform to formula (35), we arrive at the following expression:

$$[s(\lambda)^N]_t = \lambda_1\lambda_2 \int_0^t dx P_{N-1}[\lambda_1(t-x)] P_{N-1}[\lambda_2 x]. \tag{36}$$

We can see that the functions of time $[s(\lambda)^N]_t$ in formulas (28)–(30) are expressed only through the single integral. The integrand is the product of two Poisson functions, which depend on the same relaxation constants λ_1 and λ_1 that determine exponential processes in the dynamics of the nanoparticle.

Three-Level Nanoparticle

Consider now the start–stop correlator for a nanoparticle with two singlet levels 0 and 1 and one triplet level 2 that is located between the singlet levels. In this case, it is necessary to add another equation to system (32), and the resultant system will take the form

$$\begin{aligned} \dot{W}_1 &= -(k + G + 1/T_1 + A)W_1 + kW_0, \\ \dot{W}_0 &= (k + G)W_1 - kW_0 + aW_2, \\ \dot{W}_2 &= AW_1 - aW_2. \end{aligned} \tag{37}$$

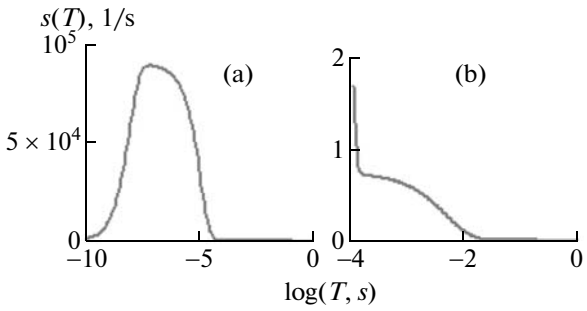

Fig. 2. Start–stop correlator calculated by formula (40) with parameters (41).

Here, G is the rate of nonradiative transitions between levels 0 and 1, which are involved in fluorescence, while A and a are the rates of transitions to and from dark state 2. The role of the dark state is played by the triplet level, upon transition to which the fluorescence of the molecule ceases and the off-interval occurs. In this case, the average durations of the on and off intervals are defined by the following formulas:

$$\frac{1}{\tau_{on}} = \frac{kA}{A+G+1/T_1+2k}, \quad \frac{1}{\tau_{off}} = a. \tag{38}$$

Performing the Laplace transforms of the left- and right-hand sides of Eq. (37) and solving the obtained algebraic equation with the initial condition $W_0(0) = 1$, which means that, at the time zero, a photon was emitted, we arrive to the following expression for the Laplace transform of the probability W_1:

$$W_1(\lambda) = \frac{k(a-\lambda)}{(\lambda_0-\lambda)(\lambda_1-\lambda)(\lambda_2-\lambda)}. \tag{39}$$

Here, λ_i are the roots of the determinant of system of equations (37), which are presented in the Appendix.

Now, performing the inverse Laplace transform in formula (39) and taking into account that $ka/T_1 = \lambda_0\lambda_1\lambda_2$, we can find the following expression for the start–stop correlator $s(t) = W_1(t)/T_1$:

$$s(t) = \lambda_1\lambda_2\frac{\lambda_0}{a}\left[\frac{(a-\lambda_0)e^{-\lambda_0 t}}{(\lambda_2-\lambda_0)(\lambda_1-\lambda_0)}\right.$$
$$\left. - \frac{(a-\lambda_1)e^{-\lambda_1 t}}{(\lambda_2-\lambda_1)(\lambda_1-\lambda_0)} + \frac{(a-\lambda_2)e^{-\lambda_2 t}}{(\lambda_2-\lambda_1)(\lambda_2-\lambda_0)}\right] \tag{40}$$
$$= \sum_{j=0}^{2} s_j \exp(-\lambda_j t).$$

Let us use the constants

$$k = 10^5\ \mathrm{s}^{-1}, \quad 1/T_1 = 10^8\ \mathrm{s}^{-1}, \quad G = 10^7\ \mathrm{s}^{-1},$$
$$A = 3.7\times 10^5\ \mathrm{s}^{-1} \text{ и } \quad a = 200\ \mathrm{s}^{-1}, \tag{41}$$

which correspond to the average durations $\tau_{on} = 3 \times 10^{-3}$ s and $\tau_{off} = 5 \times 10^{-3}$ s of the on- and off-intervals calculated by formula (38). The calculation of the start–stop correlator by formula (40) with constants (41) yields the result, which is presented in Fig. 2.

The exponential dependence on the logarithmic time scale looks like as a smooth step, which approximately covers one order of magnitude. The correlator that has three such steps demonstrates three exponential processes, namely, the process with the constant $\lambda_2 = 1/T_1 = 10^8\ \mathrm{s}^{-1}$, which determines the rise of the correlator in the range $T = 10^{-8}$ s, and the processes with the constants $\lambda_1 \cong k = 10^5\ \mathrm{s}^{-1}$ and $\lambda_0 \cong a = 200\ \mathrm{s}^{-1}$, which determine two falls of the correlator in Figs. 2a and 2b.

Using formula (39) and the relation $ka/T_1 = \lambda_0\lambda_1\lambda_2$ for the roots of the cubic equation, we can write

$$s(\lambda)^N = \left(\frac{W_1(\lambda)}{T_1}\right)^N$$
$$= \lambda_1\lambda_2\left(\frac{\lambda_0}{a}\right)^N\left(\frac{a-\lambda}{\lambda_0-\lambda}\right)^N\frac{\lambda_1^{N-1}}{(\lambda_1-\lambda)^N}\frac{\lambda_2^{N-1}}{(\lambda_2-\lambda)^N}. \tag{42}$$

Two latter fractions of this expression are Laplace transforms $P^{\lambda}_{N-1}(\lambda) = \lambda_i^{N-1}/(\lambda_i - \lambda)^N$ of Poisson functions. The second fraction can be transformed as follows:

$$\left(\frac{a-\lambda}{\lambda_0-\lambda}\right)^N = \left(1+\frac{a-\lambda_0}{\lambda_0}\frac{\lambda_0}{\lambda_0-\lambda}\right)^N$$
$$= \sum_{m=0}^{N}\frac{N!}{m!(N-m)!}\left(\frac{a-\lambda_0}{\lambda_0}\right)^m\left(\frac{\lambda_0}{\lambda_0-\lambda}\right)^m. \tag{43}$$

This sum is the expansion of the initial fraction in terms of the small parameter $(a-\lambda_0)/\lambda_0$. This parameter is always significantly smaller than unity. Using set of constants (41) and formulas (A.2), we can find the following values for the roots of Eq. (A.1): $\lambda_0 = 199.221\ \mathrm{s}^{-1} \cong a$, $\lambda_1 = 9.085\times 10^4\ \mathrm{s}^{-1} \cong k$, and $\lambda_2 = 1.105 \times 10^8\ \mathrm{s}^{-1} \cong 1/T_1$. This yields $(a-\lambda_0)/\lambda_0 = 3.708 \times 10^{-3}$; i.e., the expansion parameter is indeed very small. Substituting expansion (43) into formula (42), we arrive at the following expression:

$$s(\lambda)^N = \lambda_1\lambda_2\left(\frac{\lambda_0}{a}\right)^N \sum_{m=0}^{N} C_N^m \left(\frac{a-\lambda_0}{\lambda_0}\right)^m \times \lambda_0 \frac{\lambda_0^{m-1}}{(\lambda_0-\lambda)^m}\frac{\lambda_1^{N-1}}{(\lambda_1-\lambda)^N}\frac{\lambda_2^{N-1}}{(\lambda_2-\lambda)^N} = \lambda_1\lambda_2\left(\frac{\lambda_0}{a}\right)^N \left[P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) + \lambda_0 \sum_{m=1}^{N} C_N^m \left(\frac{a-\lambda_0}{\lambda_0}\right)^m P_{m-1}^{\lambda_0}(\lambda) P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) \right], \quad (44)$$

which contains the Laplace transforms only of Poisson functions. Performing the inverse Laplace transform in (44), we obtain

$$[s(\lambda)^N]_t = \lambda_1\lambda_2\left(\frac{\lambda_0}{a}\right)^N \left\{ \int_0^t dx P_{N-1}[\lambda_1(t-x)] P_{N-1}[\lambda_2 x] + \lambda_0 \sum_{m=1}^{N} C_N^m \left(\frac{a-\lambda_0}{\lambda_0}\right)^m \int_0^t dx P_{m-1}[\lambda_0(t-x)] \times \int_0^x dy P_{N-1}[\lambda_1(x-y)] P_{N-1}[\lambda_2 y] \right\}. \quad (45)$$

Substituting this expression for $[s(\lambda)^N]_t$ into formulas (28)–(30) makes it possible to numerically calculate photon distribution functions in blinking fluorescence, which will be shown below. This passage to Poisson functions not only simplifies numerical calculations of distribution functions, but also uncovers a very important relation between the quantum dynamics of a nanoparticle and the statistics of its radiation. The three Poisson functions in formula (45) correspond to the three exponentials that determine the time dependence of the start–stop correlator. Consequently, each exponential process in the dynamics of the nanoparticle is represented by its own Poisson function in the formula for the distribution of fluorescence photons.

CALCULATION OF PHOTON DISTRIBUTION FUNCTIONS

Initially, we will consider continuous the fluorescence of a two-level nanoparticle. Substituting formula (36) into formulas (28)–(30), we can calculate the photon distribution functions $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$. It was shown in [1] that these functions only differ from each other for short intervals T in which the average number of photons $\langle N \rangle$ is smaller than five. For longer time intervals, the shapes of all three distribution functions are nearly the same. This is demonstrated by Fig. 3.

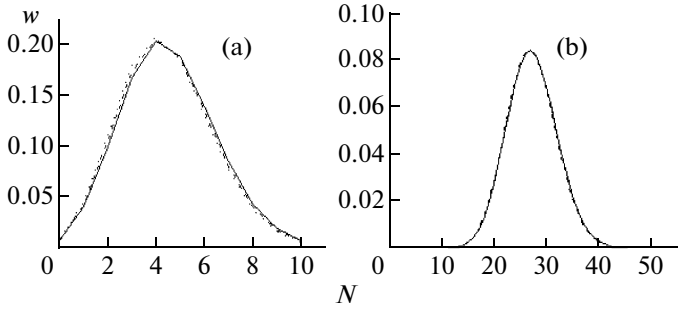

Fig. 3. Comparison of the three photon distributions in a time interval with (a) $\langle N(T) \rangle \approx 5$ and (b) $\langle N(T) \rangle \approx 30$. $\lambda_1/\lambda_2 \cong kT_1 = 0.1$. The solid, dashed, and dotted curves correspond, respectively, to the photon distribution functions w^M, w^Z, and w^O.

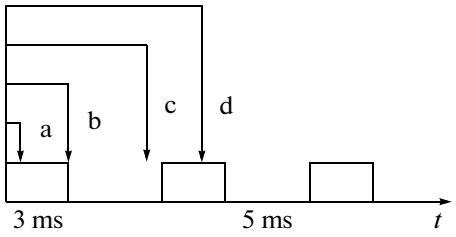

Fig. 4. Relations between the average durations of on- and off-intervals and the duration of the measurement interval T = (a) 1, (b) 3, (c) 7, and (d) 10 ms.

Consider now the blinking fluorescence of a three-level nanoparticle. Substituting formula (45) into formulas (28)–(30), we can calculate the photon distribution functions $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$ for blinking fluorescence, which consists of on and off intervals. We consider the distribution photons of blinking fluorescence for set of parameters (41). This distribution sharply depends on the relation between the signal accumulation time T and the average duration of on and off intervals. Figure 4 shows the average durations of on and off intervals and four different time intervals T denoted as a, b, c, and d. The distributions calculated for these four different intervals are presented in Fig. 5.

The shapes of the photon distributions w_N^O, w_N^Z, and w_N^M for blinking fluorescence are different. This result for blinking fluorescence fundamentally differs from the result for continuous fluorescence presented in Fig. 3. The distribution of photons is the closest to the Poisson distribution in the 1-ms interval only if

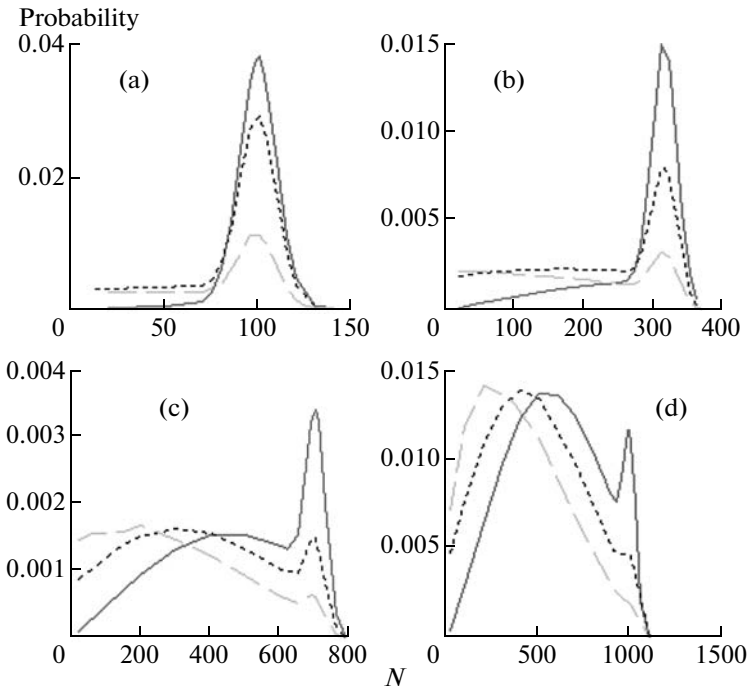

Fig. 5. Probabilities $w_N^O(T)$ (solid curve), $w_N^Z(T)$ (dotted curve), and $w_N^M(T)$ (dashed curve) calculated with parameters (41) at $T =$ (a) 1, (b) 3, (c) 7, and (d) 10 ms.

photons are counted by the method *O*. The distributions w_N^Z and w_N^M have appreciable tails in the range of small *N*. Consequently, these distributions appreciably differ from the Poisson distribution. These tails are not noise, but rather they describe the signal. Their origin can be explained using the scheme shown in Fig. 6. If the interval of measurement T exceeds the average time interval $1/k$ between photons in the on interval and the interval T falls on the end of an on interval, as is shown in Fig. 6, then the probability of detecting a single photon by the method *M* or *Z* is nonzero, whereas, for the counting method *O*, it is nearly zero because, in this method, both the beginning and the end of the interval should coincide with the instant of emission of a photon. This explains the occurrence of tails in the distributions $w_N^Z(T)$ and $w_N^M(T)$ and the absence of a tail in the distribution $w_N^O(T)$.

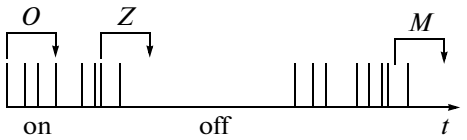

Fig. 6. Scheme explaining the appearance of tails in distributions $w_N^Z(T)$ and $w_N^M(T)$. Vertical lines correspond to photons in the on-interval. The probability of detecting a single photon in a long interval T using the *Z* and *M* counting methods is nonzero, whereas that using the counting method *O* is nearly zero.

The areas under the curves in Fig. 5 are the sums $\sum_{N=1}^{\infty} w_N^O(T)$, $\sum_{N=1}^{\infty} w_N^Z(T)$, and $\sum_{N=1}^{\infty} w_N^M(T)$. For one and the same T, these sums differ from each other because the probabilities $w_0^O(T)$, $w_0^Z(T)$, and $w_0^M(T)$ to detect a photonless interval are also different for the three counting methods. However, the sum over all *N* obeys the law of conservation of probability; i.e., $w_0^i(T) + \sum_{N=1}^{\infty} w_N^i(T) = 1$, where $i = O$, Z, and M.

Clearly, photons emitted in different on-intervals can be detected in the interval T. This circumstance manifests itself in formula (45) via two factors, namely, via the multiplier $(\lambda_0/a)^N$ in front of the brace and via the sum over *m* in the braces. For continuous fluorescence of two-level nanoparticles, we have $(\lambda_0/a)^N = 1$, while the sum over *m* is absent, and only the first term remains in the braces of formula (45).

As the interval of observation increases, the contribution to the distribution function from photons emitted in different on-intervals will increase; i.e., the sum over *m* in formula (45) will play an increasingly greater role. The influence of this effect is demonstrated in Fig. 5d. Since the contribution of photons emitted in different on-intervals increases, the tails of the distri-

bution functions in the range of relatively small N begin to play a dominating role.

These tails in the photon distribution functions begin to dominate, if the observation interval exceeds not only the average duration of on-intervals but also the average duration of off intervals. As the length of intervals increases, the narrow peak of the sub-Poissonian shape vanishes, which is especially clearly seen in the distribution $w_N^M(T)$. This narrow peak is formed by photons emitted from only one on-interval. It vanishes nearly completely at $T = 10$ ms, as is shown in Fig. 5d.

The photon distribution in Fig. 5d is mainly determined by the sum over m in formula (45). Although this sum contains powers of the small parameter $(a - \lambda_0)/\lambda_0$, the coefficients C_N^m increase with increasing m at $m < N/2$. The greater the number N, the greater the coefficients C_N^m. Nevertheless, the value of the coefficient $C_N^m(a - \lambda_0)^m/\lambda_0^m$ becomes negligibly small already at m on the order of 10 even for the longest interval $T = 10$ ms, which corresponds to Fig. 5d. According to Fig. 5d, if the duration of the photon accumulating interval exceeds the total duration of the average on- and off-intervals, the photon distribution proves to be very broad, i.e., sub-Poissonian. This distribution strongly differs in shape from the Poisson distribution.

CONCLUSIONS

We derived mathematical expressions corresponding to the three different counting methods of fluorescence photons of a single nanoparticle excited by light from a cw laser. It should be especially emphasized that formulas (24)–(26) and formulas (28)–(30) equivalent to them are valid for an arbitrary microscopic model of a nanoparticle.

The three photon distribution functions $w_N^M(T)$, $w_N^Z(T)$, and $w_N^O(T)$, which correspond to these three counting methods, were expressed via Poisson functions for two particular models of a nanoparticle, namely, for a two-level nanoparticle, whose fluorescence is continuous, and for a three level nanoparticle, whose fluorescence is blinking. This made it possible, first, to cardinally ease the numerical calculation of the photon distributions in continuous and blinking fluorescence by replacing the N-fold integration with two- or threefold integration and, second, to find that each exponential process in the dynamic of a nanoparticle excited by continuous light has its own Poisson function in the mathematical expression for the photon distribution.

We found that all three photon-counting methods yield identical photon distributions for continuous fluorescence and different distributions for blinking fluorescence.

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APPENDIX

The equation $\mathrm{Det}_W = 0$ has the form

$$\mathrm{Det}_W = [\lambda - (A + k + 1/T_1 + G)](\lambda - k)(\lambda - a) - \lambda k(k + G) + ka(A + k + G) = 0. \quad \text{(A.1)}$$

By solving this cubic equation, we can find the following expressions for its roots:

$$\lambda_0 = M - \frac{2}{3}\sqrt{P}\cos\left[\frac{1}{3}a\cos\left(\frac{-Q}{2P^{1.5}}\right)\right], \quad \text{(A.2a)}$$

$$\lambda_1 = M - \frac{2}{3}\sqrt{P}\sin\left[\frac{1}{3}a\sin\left(\frac{Q}{2P^{1.5}}\right)\right], \quad \text{(A.2b)}$$

$$\lambda_2 = M + \frac{2}{3}\sqrt{P}\sin\left[\frac{1}{3}a\sin\left(\frac{Q}{2P^{1.5}}\right) + \frac{\pi}{3}\right], \quad \text{(A.2c)}$$

where

$$P = A^2 + A[k - a + 2(1/T_1 + G)] + 4k^2 - k(2a - 1/T_1 - 4G) + a^2 - a(1/T_1 + G) + (1/T_1 + G)^2, \quad \text{(A.3)}$$

$$M = \frac{A + 2k + a + 1/T_1 + G}{3}, \quad \text{(A.4)}$$

$$Q = 2A^3 + 3A^2[k - a + 2(1/T_1 + G)] + 3A[2k^2 - k(7a - 2/T_1 - 5G) - a^2 - 2(a - 1/T_1 - G)(1/T_1 + G)] + 16k^3 - 6k^2(2a - 1/T_1 - 4G) - 3k[2a^2 + 2a(2G - 1/T_1) - (1/T_1)^2 - G(5/T_1 + 4G)] + (a + 1/T_1 + G)[2a^2 - 5a(1/T_1 + G) + 2(1/T_1 + G)^2]. \quad \text{(A.5)}$$

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