

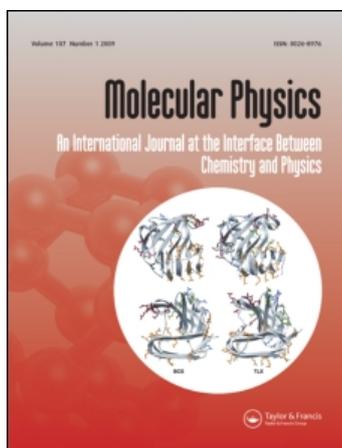
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On: 7 September 2009

Access details: Access Details: [subscription number 914485754]

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Molecular Physics

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713395160>

Quantum dynamics of individual molecules studied by photon distribution in blinking fluorescence

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First Published: January 2009

To cite this Article Osad'ko, I. S. (2009) 'Quantum dynamics of individual molecules studied by photon distribution in blinking fluorescence', *Molecular Physics*, 107:18, 1879 — 1888

To link to this Article: DOI: 10.1080/00268970902744326

URL: <http://dx.doi.org/10.1080/00268970902744326>

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INVITED ARTICLE

Quantum dynamics of individual molecules studied by photon distribution in blinking fluorescence

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(Received 6 August 2008; accepted 7 January 2009)

Various methods of photon counting in single molecule blinking fluorescence are considered and photon distribution functions, $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$ related to these methods are derived. It is shown that each exponential process $\exp(-\lambda_j t)$ in quantum dynamics of a single molecule manifests itself in the mathematical expressions for the photon distribution function via Poissonian function $P_N(-\lambda_j t)$ with the same rate constant. This relation enables one to avoid N-fold integration in the mathematical expressions for the functions, $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$ derived in previous works. Numerical calculations of the functions $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$ for blinking fluorescence are carried out. A relation between photon distribution and photo-electric pulse distribution is discussed. Thanks to relation found we can use photo-electric pulse distribution functions for studying photon distribution function and for studying quantum dynamics of single nanoparticle with blinking fluorescence.

Keywords: single molecule; photon statistics

1. Introduction

It is well known that intensity of fluorescence of atomic or molecular ensemble fluctuates even under CW excitation by laser field. These fluctuations are described by a probability $w_N(T)$ of finding N photons in time interval T . At first, the photon distribution has been studied in fluorescence of atomic and molecular ensembles. The photon distribution function in such fluorescence is a function of field operators [1–5]. The most general expression for the photon distribution function looks as follows [3]:

$$w_N(T) = \left\langle T: \frac{1}{N!} \left[\int_t^{t+T} dx \hat{I}(x) \right]^N \exp \left[- \int_t^{t+T} dx \hat{I}(x) \right] : \right\rangle. \quad (1)$$

The formula includes light intensity operators $\hat{I}(x)$ and quantum statistical average of the time and normally ordered operator expression. Equation (1) can be utilized for fluorescence of both atomic ensemble and single atom. Equation (1) relates to a special method of photon counting. In accordance with the method, the whole time axis is covered by equal time intervals T , and we count number N of photons in each time interval [3,6]. The beginning and the end of each time interval are not related to the instant of photon

emission. Such method of photon counting we shall call the method M.

Photon statistics in the fluorescence of molecular ensemble depends on both ensemble properties and statistics of single molecule emission. However, if we detect solely photons emitted by an individual molecule, we can study the dynamics of the individual molecule. The dynamics will manifest itself in statistics of single molecule fluorescence.

Indeed, each photon emitted by a molecule is a signal of quantum jump from the excited to the ground electronic state. Hence, photon statistics will reflect statistics of quantum jumps. In such an approach, the function $w_N(T)$ for photon distribution can be expressed via the probability of finding a molecule in the excited electronic state. Hence, the quantum dynamics of a single molecule driven by a CW laser field will be subject to consideration of the theory for the function $w_N(T)$.

Quantum dynamics of an atom or a molecule is determined by the Hamiltonian of the system and by initial conditions, i.e. we must know in which quantum state we find the atom or the molecule at $t=0$. Theoretical work on photon statistics in single molecule fluorescence is forced to introduce initial conditions to the theoretical expression for the

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function $w_N(T)$. Therefore, [7] considered solely time intervals T , the onset of which coincides with the instant of photon emission. This method of photon counting we shall call method Z. Other authors [8,9] considered solely time intervals, the onset and the end of which coincide with the photon emission. This method of photon counting we shall call method O. The photon distribution functions related to the three photon counting methods we shall denote $w_N^M(T)$, $w_N^Z(T)$, and $w_N^O(T)$, respectively.

The methods Z and O are more complicated than method M in experimental implementation and, therefore, it is not immediately clear why we need to consider these methods. However, from the point of view of a theorist, method O is the simplest because both the onset and end of the time interval are related to the molecule found in the ground electronic state. Therefore, it would be natural to start theoretical derivations by considering the method O of photon counting. The methods Z and M will be considered generalizations of the method O.

2. Mandel parameter

Equation (1) is a formal solution of the problem. Up to now, calculations of the photon distribution function in single molecule fluorescence have not been carried out with the help of Equation (1). However, L. Mandel has suggested using Equation (1) to calculate the value of the following parameter:

$$Q(T) = \frac{\langle N^{(2)} \rangle - \langle N \rangle^2}{\langle N \rangle} \quad (2)$$

called the Mandel parameter. Here $\langle N \rangle$ and $\langle N^{(2)} \rangle$ are the first and the second factorial moment of the photon distribution function $w_N(T)$. By using Equation (1) Mandel derived a very simple equation for $Q(T)$ [3]:

$$Q = \langle I \rangle \left[\frac{2}{T} \int_0^T dx \int_0^x dx_1 g^{(2)}(x - x_1) - T \right]. \quad (3)$$

Here, $g^{(2)}(t)$ is an autocorrelation function (AF) of fluorescence. It is important that AF can be measured by experiment and calculated theoretically for various microscopic models. A negative value of Q is evidence for sub-Poissonian photon statistics, and a positive value of Q is evidence for super-Poissonian photon statistics. A sub-Poissonian distribution is narrower and a super-Poissonian distribution is broader than a Poissonian distribution. Up to now, photon statistics in single molecule fluorescence have been investigated with the help of the Mandel parameter [10–15].

3. Methods of calculation of the photon distribution function

The Mandel parameter answers the question of the distribution function being narrower or broader than the Poissonian distribution, but it says nothing about the shape of the distribution. Therefore, some attempts were undertaken to calculate the shape of the distribution function.

For instance, Cook [16] and others [17,18] used the method of so called 'generating function' for calculation of the distribution function $w_N(T)$. In accordance with this approach the quantum dynamics of a single atom, but not the radiation field, was considered. The generating function $G(z, t)$ can be found from so called 'generalized Bloch equations' [15]. The photon distribution function for fluorescence of a two-level atom can be found with the help of the following equation [16]:

$$w_N(T) = \frac{1}{N!} \left(\frac{\partial^N}{\partial z^N} G(z, T) \right)_{z=0}. \quad (4)$$

The method based on the utilization of the generating function was used in a number of works [15–20]. By using this method Schenzle and Brewer [19] established a Poissonian distribution of photons in the fluorescence of a two-level atom in the limit of a strong and a weak driving laser field. Distribution of photons in blinking fluorescence was considered on a qualitative level. The question of which of the three methods of photon counting the generating function method relates to has not been discussed in these works. One can suppose that the generating function method relates to the method Z of photon counting because the generating function is calculated with initial condition relating to the molecule sitting in the ground electronic state. To date, calculations of the photon distribution function have not been carried out with the help of Equation (4) even for two-level atom fluorescence.

Zoller *et al.* [7] considered the method Z of photon counting. They derived an expression for the photon distribution function in the form of an N-fold integral. Carmichel *et al.* [6] found the photon distribution function in the form of N-fold integral for the method M of photon counting. However, N-fold integral form was inconvenient for use in practice. For instance, in order to find the distribution function in a time interval with an average number of photons of the order 100 we need to calculate 200-fold integrals.

It has recently been shown by the author [8,9] how one can avoid N-fold integration in this problem. It was established that each exponential process in the quantum dynamics of an individual molecule

corresponds to the Poissonian function with the same rate constant in the expression for the photon distribution function. Discovery of such a relation helps us to reduce N-fold integrals to one or two integrals of a few Poissonian functions [8,9] and avoid N-fold integration. New theoretical expressions enable one to calculate the photon distribution functions even for blinking fluorescence consisting of alternating bright and dark time intervals.

4. Distribution functions for various methods of photon counting

Final expressions for the distribution functions, $w_N^O(T)$, $w_N^Z(T)$ and $w_N^M(T)$ relating to the methods O, Z and M of photon counting were published in [21]. In Appendix A a detailed derivation of these probabilities is presented. In accordance with this derivation we arrive at the Equations (24A), (25A) and (26A). By carrying out Laplace transformation of these equations we arrive at the following expressions:

$$\begin{aligned} (w_N^O p(T))_\lambda &= s(\lambda)^{N+1}, \\ w_N^Z(\lambda) &= \frac{1}{-\lambda} [1 - s(\lambda)] s(\lambda)^N, \\ w_N^M(\lambda) &= \frac{1}{\lambda^2 \tau_0} [1 - s(\lambda)]^2 s(\lambda)^{N-1}, \quad (N \geq 1). \end{aligned} \tag{5}$$

Here, τ_0 defined by Equation (22A) in the Appendix A, is an average time interval between two consecutive events. Laplace transforms for three distribution functions are expressed via Laplace transform $s(\lambda)$ of the start-stop correlator $s(t)$ that defines a correlation of two consecutively emitted photons of fluorescence. After inverse Laplace transformation of Equation (5) we arrive at the following expressions:

For the method O:

$$w_N^O(T) = [s(\lambda)^{N+1}]_T / p(T). \tag{6}$$

Here $p(T) = s(T) + \sum_{N=1}^\infty s_N(T)$ is so-called full two-photon correlator [22,23].

For the method Z:

$$w_N^Z(T) = \int_0^T dt \{ [s(\lambda)^N]_t - [s(\lambda)^{N+1}]_t \}, \quad (N \geq 1) \tag{7}$$

$$w_0^Z(T) = 1 - \int_0^T s(t) dt. \tag{7a}$$

For the method M:

$$\begin{aligned} w_N^M(T) &= \frac{1}{\tau_0} \int_0^T (T-t) \{ [s(\lambda)^{N-1}]_t - 2[s(\lambda)^N]_t \\ &\quad + [s(\lambda)^{N+1}]_t \} dt, \quad (N \geq 1), \end{aligned} \tag{8}$$

$$w_0^M(T) = \frac{1}{\tau_0} \int_0^\infty \left[1 - \int_0^{T+t} s(x) dx \right] dt. \tag{8a}$$

The first way to use these equations in practice is to carry out N numerical Laplace inversions of N functions, $[s(\lambda)^N]_t$. However there is a more elegant way, which enables one to find an analytical expression for the functions $[s(\lambda)^N]_t$ avoiding numerical Laplace inversion. The method has already been used in [8,9]. The method enables one to express Equations (6), (7) and (8) via couple of integrals of a few Poissonian functions. Moreover, the method enables one to find a simple connection between the quantum dynamics of the system described by the start-stop correlator, on the one hand, and a few Poissonian functions in the final expressions for the distribution functions, $w_N^O(T)$, $w_N^Z(T)$ and $w_N^M(T)$, on the other hand. This is the main advantage of the method proposed.

If we carry out N numerical Laplace inversions of N functions, $[s(\lambda)^N]_t$ the relation between quantum dynamics and photon statistics of the system cannot be found in explicit form.

5. Start-stop correlator for three-level nanoparticle

How can we find dynamical equations for calculation of the start-stop correlator? This problem was discussed in detail in [22] and in Section 8 of the book [23]. It was shown that the start-stop correlator is described by the expression, $s(t) = W_1(t)/T_1$, for both CW fluorescence and blinking fluorescence. The energy diagram for finding the start-stop correlator of a nanoparticle with blinking fluorescence is shown in Figure 1.

Here k is rate of absorption and light induced emission, G is rate of non-radiation transitions and A and a are rate of transitions to dark state 2 and from dark state 2, $1/T_1$ is rate of spontaneous emission. The probability $W_1(t)$ can be found from the following equations:

$$\begin{aligned} \dot{W}_1 &= -(k + G + 1/T_1 + A)W_1 + kW_0, \\ \dot{W}_0 &= (k + G)W_1 - kW_0 + aW_2, \\ \dot{W}_2 &= AW_1 - aW_2, \end{aligned} \tag{9}$$

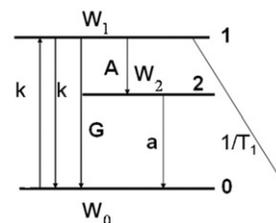


Figure 1. Energy diagram for finding the start-stop correlator of a nanoparticle with blinking fluorescence.

at $W_0(0)=1$. This initial condition relates to the fact of photon emission at $t=0$. Average values of on- and off-intervals in blinking fluorescence are given by [23,24]:

$$\frac{1}{\tau_{\text{on}}} = \frac{kA}{A + G + 1/T_1 + 2k}, \quad \frac{1}{\tau_{\text{off}}} = a. \quad (10)$$

After Laplace transformation $\int_0^\infty dt F(t)e^{i(\omega+i0)t} = F(i\omega) = F(\lambda)$ of Equation (9) we arrive at algebraic equations. By solving these equations with initial condition, $W_0(0)=1$, we find the following expression:

$$W_1(\lambda) = \frac{k(a - \lambda)}{(\lambda_0 - \lambda)(\lambda_1 - \lambda)(\lambda_2 - \lambda)}. \quad (11)$$

Here, λ_i are roots of the determinant of the set of the algebraic equations. Expressions for these roots are found in the Appendix B.

Carrying out inverse Laplace transformation of Equation (11), and taking into account that $ka/T_1 = \lambda_0\lambda_1\lambda_2$, we find the following expression for the start-stop correlator $s(t) = W_1(t)/T_1$:

$$s(t) = \lambda_1\lambda_2 \frac{\lambda_0}{a} \left[\frac{(a - \lambda_0)e^{-\lambda_0 t}}{(\lambda_2 - \lambda_0)(\lambda_1 - \lambda_0)} - \frac{(a - \lambda_1)e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_1 - \lambda_0)} + \frac{(a - \lambda_2)e^{-\lambda_2 t}}{(\lambda_2 - \lambda_1)(\lambda_2 - \lambda_0)} \right] \quad (12)$$

$$= \sum_{j=0}^2 s_j \exp(-\lambda_j t)$$

Three exponential functions describe dynamics of the three-level nanoparticle driven by CW laser field. Average values $\tau_{\text{on}} = 3 \times 10^{-3} \text{ s}$ and $\tau_{\text{off}} = 5 \times 10^{-3} \text{ s}$ of on- and off-intervals measured experimentally in ref. [24] can be obtained with the following set of rate constants:

$$k = 10^5 \text{ s}^{-1}, \quad 1/T_1 = 10^8 \text{ s}^{-1}, \quad G = 10^7 \text{ s}^{-1}, \quad (13)$$

$$A = 3.7 \times 10^5 \text{ s}^{-1}, \quad a = 200 \text{ s}^{-1}.$$

Calculation of the start-stop correlator with this set of rate constants yields the result shown in Figure 2.

Exponential dependence looks like a smooth step in logarithmic time scale. The start-stop correlator exhibits three smooth steps and, hence, three exponential processes in quantum dynamics. The process with the rate constant, $\lambda_2 \cong 1/T_1 = 10^8 \text{ s}^{-1}$, determines growth of the correlator on a nanosecond time scale. Exponential functions with $\lambda_1 \cong k = 10^5 \text{ s}^{-1}$ and $\lambda_0 \cong a = 200 \text{ s}^{-1}$ determine two-stage decrease of the correlator as Figure 2 demonstrates.

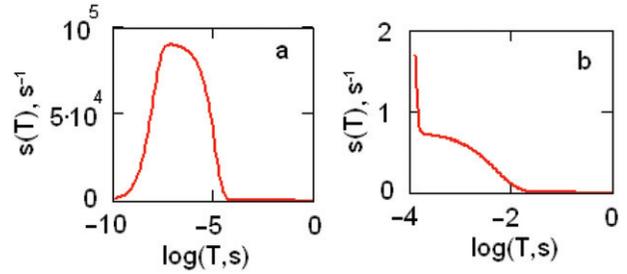


Figure 2. Start-stop correlator calculated by means of Equation (12) with the set of parameters (13).

By using Equation (11) we can arrive at the following expression:

$$s(\lambda)^N = \left(\frac{W_1(\lambda)}{T_1} \right)^N = \lambda_1\lambda_2 \left(\frac{\lambda_0}{a} \right)^N \left(\frac{a - \lambda}{\lambda_0 - \lambda} \right)^N \quad (14)$$

$$\times \frac{\lambda_1^{N-1}}{(\lambda_1 - \lambda)^N} \frac{\lambda_2^{N-1}}{(\lambda_2 - \lambda)^N}.$$

Two last ratios in this expression are Laplace transforms $P_{N-1}^{\lambda_i}(\lambda) = \lambda_i^{N-1}/(\lambda_i - \lambda)^N$ of Poissonian functions. The second ratio can be transformed to the following form:

$$\left(\frac{a - \lambda}{\lambda_0 - \lambda} \right)^N = \left(1 + \frac{a - \lambda_0}{\lambda_0} \frac{\lambda_0}{\lambda_0 - \lambda} \right)^N$$

$$= \sum_{m=0}^N \frac{N!}{m!(N-m)!} \left(\frac{a - \lambda_0}{\lambda_0} \right)^m \left(\frac{\lambda_0}{\lambda_0 - \lambda} \right)^m. \quad (15)$$

The sum is a power series in small parameter, $(a - \lambda_0)/\lambda_0$. The parameter is always much less than unity. By using Equation (2B) and the set of parameters (13) we find that $\lambda_0 = 199.221c^{-1} \cong a$, $\lambda_1 = 9.085 \times 10c^{-1} \cong k$, $\lambda_2 = 1.105 \times 10^8c^{-1} \cong 1/T_1$. Hence, $(a - \lambda_0)/\lambda_0 = 3.9 \times 10^{-3}$, i.e. the parameter is small indeed. By combining Equations (14) and (15), we arrive at the following expression:

$$s(\lambda)^N = \lambda_1\lambda_2 \left(\frac{\lambda_0}{a} \right)^N \sum_{m=0}^N C_N^m \left(\frac{a - \lambda_0}{\lambda_0} \right)^m$$

$$\times \lambda_0 \frac{\lambda_0^{m-1}}{(\lambda_0 - \lambda)^m} \frac{\lambda_1^{N-1}}{(\lambda_1 - \lambda)^N} \frac{\lambda_2^{N-1}}{(\lambda_2 - \lambda)^N}$$

$$= \lambda_1\lambda_2 \left(\frac{\lambda_0}{a} \right)^N \left[P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) + \lambda_0 \sum_{m=1}^N C_N^m \right.$$

$$\left. \times \left(\frac{a - \lambda_0}{\lambda_0} \right)^m P_{m-1}^{\lambda_0}(\lambda) P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) \right]. \quad (16)$$

The expression includes Laplace transforms of a few Poissonian functions. Carrying out the inverse Laplace transformation we arrive at the following expression:

$$\begin{aligned}
 [s(\lambda)^N]_t &= \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a}\right)^N \left\{ \int_0^t dx P_{N-1}[\lambda_1(t-x)] \right. \\
 &\quad \times P_{N-1}(\lambda_2 x) + \lambda_0 \sum_{m=1}^N C_N^m \left(\frac{a-\lambda_0}{\lambda_0}\right)^m \\
 &\quad \times \int_0^t dx P_{m-1}[\lambda_0(t-x)] \int_0^x dy P_{N-1}[\lambda_1(x-y)] \\
 &\quad \left. \times P_{N-1}(\lambda_2 y) \right\}. \quad (17)
 \end{aligned}$$

Here $P_{N-1}(\lambda_j t) = (\lambda_j t)^{N-1} \exp(-\lambda_j t) / (N-1)!$. If we insert this expression for the function $[s(\lambda)^N]_t$ into Equations (6), (7) and (8), we can calculate all three types of photon distribution function. Note that the transition to Poissonian functions enables one to avoid N -fold integration and to discover a relation between quantum dynamics and the photon distribution. Indeed, three Poissonian functions in the photon distribution function depend on the same rate constants, λ_0 , λ_1 , and λ_2 , which determine exponential processes in quantum dynamics, i.e. the following connection exists

$$\exp(-\lambda_j t) \rightarrow P_N(\lambda_j t). \quad (18)$$

Hence, each exponential process in quantum dynamics of the molecule manifests itself via a corresponding Poissonian function in the photon distribution function.

6. Photon distribution in blinking fluorescence under various methods of photon counting

How strong will the difference in photon distribution be when we count photons by the methods O, Z and M? This problem was studied in [21] for the CW fluorescence of a two-level nanoparticle. It was shown that the functions w_N^O , w_N^Z и w_N^M describe indistinguishable photon distributions for time intervals with $\langle N(T) \rangle > 5$. This result enables one to use the simplest expression w_N^O for comparison with experimental data obtained by photon counting method M. However, the photon distribution functions w_N^O , w_N^Z , and w_N^M have different shapes in blinking fluorescence. Figure 3 shows this difference.

In [25,26], a Poissonian distribution of photons emitted from the excited electronic state of a two-level molecule was postulated. In blinking fluorescence, we are facing another situation. Only the photon distribution function $w_N^O(T)$ in Figure 3(a) satisfies this

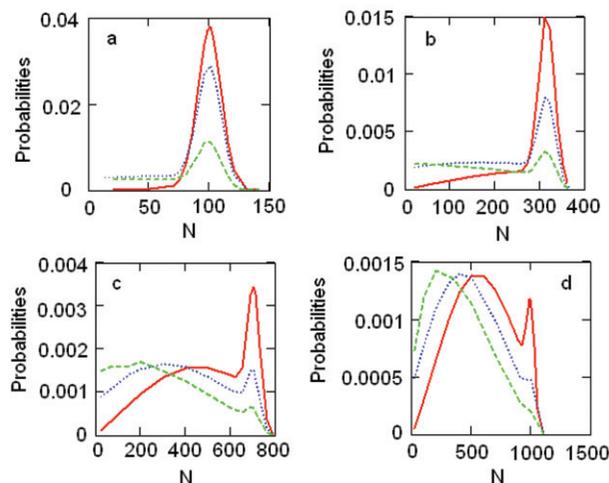


Figure 3. Probabilities $w_N^O(T)$ (solid line), $w_N^Z(T)$ (dotted line), and $w_N^M(T)$ (dashed line). Calculated with set of parameters (13) at $T =$ (a) 1 ms; (b) 3 ms; (c) 7 ms; (d) 10 ms.

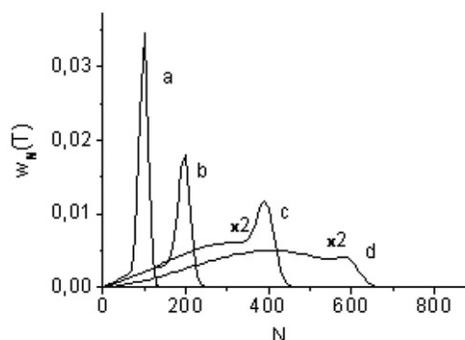


Figure 4. Photon distribution function $w_N(T) \equiv w_N^O(T)$ in blinking fluorescence with $\tau_{\text{on}} = \tau_{\text{off}} = 2 \times 10^{-5}$ s for time intervals $T = 10^{-5}$ s (a), 2×10^{-5} s (b), 4×10^{-5} s (c), 6×10^{-5} s (d) calculated with Equations (6) and (17).

assumption approximately. However, the distribution functions, $w_N^M(T)$, and $w_N^Z(T)$ in Figure 3(a), have tails ranging to small N . Hence, these distributions differ from the Poissonian distribution. These tails are not noise, but are signal.

7. Distribution of photo-electric pulses

Until now we supposed that each emitted photon causes a photo-electric pulse in PMT. However, the number N of photo-emissions and number n of electric pulses will differ considerably. Therefore, the question arises: how the photon distribution functions $w_N(T)$ will be related to the photo-electric pulse distribution function $w_n(T)$.

Consider first a Poissonian distribution. If we detect, for example, 10% of emitted photons, the average value $\langle n(T) \rangle$ of photo-electrons in interval T equals 10% of average value $\langle N(T) \rangle$ of emitted photons, i.e.

$$\langle n(T) \rangle = 0.1 \langle N(T) \rangle. \quad (19)$$

Losses of photons we can compensate by increasing the time interval, i.e. $\langle n(10T) \rangle = \langle N(T) \rangle$. Hence, we may write for Poissonian distributions of photons and electric pulses the following relation:

$$P(\langle N(T) \rangle) = P(\langle n(10T) \rangle). \quad (20)$$

This means that the distribution of photo-electrons on an enlarged time scale will coincide with the distribution of photons. Since we have the following relation: $\langle N(T) \rangle = \langle I \rangle T = kT$, we may rewrite the relation (20) in the following form:

$$w_N(k, T) = w_n\left(\frac{k}{10}, 10T\right). \quad (21)$$

This equation demonstrates some kind of scaling existing in emissions with Poissonian statistics.

Consider now photon distribution functions in blinking fluorescence. We consider this problem by using distribution functions for the photon counting method O. The distribution function $w_N^O(T) \equiv w_N(T)$ calculated with the help of Equations (6) and (17) for four time intervals of various durations is shown in Figure 4. Ordinates of the curves c and d are multiplied by a factor 2 to improve details.

Shape of the distribution depends on values of physical parameters. Constants A and a determine rate of $on \Leftrightarrow off$ jumps in blinking fluorescence. The sum over m in Equation (17) determines the contribution of photons from various on-intervals. Since the dynamics of $on \Leftrightarrow off$ jumps influences the shape of the distribution function, we arrive at the following inequalities:

$$w_N(k, A, a, T) \neq w_n\left(\frac{k}{10}, A, a, T\right),$$

$$w_N(k, A, a, T) \neq w_n\left(\frac{k}{10}, A, a, 10T\right). \quad (22)$$

If the photon distribution function $w_N(k, A, a, T)$ is described by the curves shown in Figure 4, the photo-electric pulse distributions $w_n(\frac{k}{10}, A, a, T)$ on the same time intervals T and the functions $w_n(\frac{k}{10}, A, a, 10T)$ for the time intervals $10T$ will differ considerably in shape from the photon distribution function, $w_N(k, A, a, T)$, as Figure 5 shows.

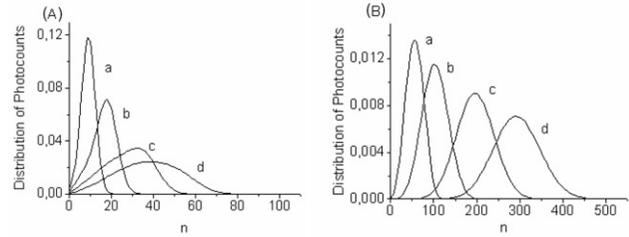


Figure 5. Distribution of photo-electric pulses $w_n(k/10, A, a, T)$ (A) and $w_n(k/10, A, a, 10T)$ (B) related to photon distribution functions shown in Figure 4.

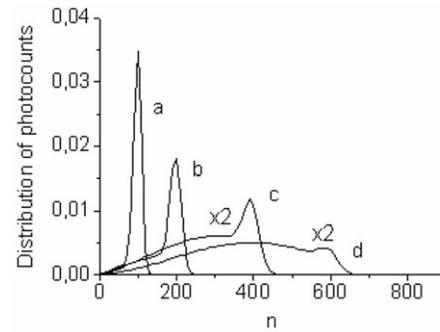


Figure 6. Function $w_n(\frac{k}{10}, \frac{A}{10}, \frac{a}{10}, 10T)$ of photo-electric pulse distribution.

However, if we know the percentage of photon losses, we can calculate the photon distribution function by using the shape of the photo-electric pulse distribution measured in an experiment. For instance, we know that 10% of photons create electric pulses. If the measured pulse distribution can be approximated by the function $w_n(\frac{k}{10}, A, a, T)$ calculated with Equations (6) and (17), we can calculate, using the same equations, a photon distribution function $w_N(k, A, a, T)$ relating to the measured pulse distribution function $w_n(\frac{k}{10}, A, a, T)$.

Notice that the scaling discussed above can be found even in blinking fluorescence with distribution functions of complex shape. The scaling is expressed by the following relation:

$$w_N(k, A, a, T) = w_n\left(\frac{k}{10}, \frac{A}{10}, \frac{a}{10}, 10T\right). \quad (23)$$

Comparison of Figure 4 with Figure 6 proves Equation (23).

8. Conclusions

Various methods of derivation of the photon distribution functions relating to various methods of photon

counting in single molecule blinking fluorescence were analysed. It was shown that a relation (18) exists between quantum dynamics of a single molecule driven by a CW laser field and the photon distribution function in blinking fluorescence.

The relation enables one

- (1) to avoid N-fold integration and, therefore, to calculate the photon distribution functions for time intervals of various durations;
- (2) to use the photon distribution function for studying quantum dynamics of single molecule with blinking fluorescence.

The shape of a photon distribution function differs from the shape of the photo-electric pulse distribution. The photon distribution function related to the measured photo-electric pulse distribution can be found if the percentage of photon losses is known.

Acknowledgement

The work was supported by the Russian Foundation for Basic Researches via grants 07-02-00181, 07-02-00547 and 08-07-00371.

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Appendix A

Information about quantum state of the molecule is obtained at the photon emission time moment. Therefore, it will be natural to start from consideration of method O in which each time interval is opened and closed by a photon emission event.

The method O of photon counting. Let

$$dS(t) = s(t)dt \quad (1A)$$

be the probability of finding a photon in time interval $(t, t+dt)$ if the preceding photon was emitted at $t=0$. The function $s(t)$ is the density of the probability and it is equivalent to the function $w_2(t)$ considered in [27]. The function $s(t)$ determines the correlation between two consecutively emitted photons. Therefore, it was named

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the start-stop correlator [22,23]. It is obvious, the function

$$S(T) = \int_0^T s(t)dt \quad (2A)$$

determines the probability of finding the second photon by time moment T . Hence, the integrals

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

determine the densities of the probability of finding $1, 2, \dots, N$ so called intermediate photons in time interval $[0, T]$ opened and closed by a photon. The density of the probability of finding N intermediate photons is expressed via a single function $s(T)$:

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

Consider an infinite sum

$$p(T) = s(T) + \sum_{N=1}^{\infty} s_N(T), \tag{5A}$$

that determines the density of the probability of finding any number of intermediate photons between the photon in the onset and in the end of time interval $[0, T]$. The function $p(T)$ determines correlation between two photons in the onset and in the end of time interval independently of the number of intermediate photons in the interval $[0, T]$. Therefore, the function $p(T)$ was named the full two-photon correlator [22,23]. In [27] this function was denoted $g_2(T)$.

The second-order autocorrelation function $g^{(2)}(T)$ of fluorescence can be expressed via full two-photon correlator as follows [22,23,28]:

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

Here, $p(\infty)$ equals an average intensity $\langle I \rangle$ of fluorescence appearing in the Mandel's expressions for the first and the second factorial moments:

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

The full two-photon correlator $p(T)$ and the start-stop correlator $s(T)$ are related by the following integral equation:

$$p(T) = s(T) + \int_0^T s(T-t)p(t)dt. \tag{8A}$$

This integral equation can be easily derived using Equations (3A) and (5A). Since correlator $p(T)$ takes into account intervals with any number of intermediate photons, the following ratios

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

can be considered as probabilities of finding interval $[0, T]$ with no intermediate photon and with N intermediate photons. The sum of all probabilities equals unit:

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

Equations (9A) were derived in [8].

The method Z of photon counting. In this method we deal with semi-open time intervals $[0, T)$ opened by an emitted photon. The probability of finding time interval with no photon is given by:

$$w_0^Z(T) = 1 - S(T). \tag{11A}$$

The probability of finding interval $[0, T)$ with one photon and with N photons is given by

$$w_1^Z(T) = \int_0^T dt_1 w_0^Z(T - t_1) s(t_1),$$

$$w_N^Z(T) = \int_0^T dt_N \int_0^{t_N} dt_{N-1} \dots \int_0^{t_2} dt_1 w_0^Z(T - t_N) \times s(t_N - t_{N-1}) \dots s(t_2 - t_1) s(t_1). \tag{12A}$$

These probabilities are expressed solely via the start-stop correlator. The sum of all probabilities equals unity:

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

The method M of photon counting. Consider, first, an auxiliary method. It differs from the method Z because now we are interested in the probability of finding a photon in time interval $(t_0, T + t_0)$, whose onset is separated by time t_0 from the moment $t = 0$ at which a photon was emitted. This situation is shown in Figure 1A.

The probability of finding a photon in the interval $(t_0, T + t_0)$ at the additional condition (conditional probability), that a preceding photon was emitted at time moment $t = 0$, is given by:

$$\rho_1(T + t_0, t_0|0) = \int_{t_0}^{T+t_0} \left(1 - \int_{t_1}^{T+t_0} s(t - t_1) dt \right) s(t_1) dt_1$$

$$= \int_{t_0}^{T+t_0} dt_1 w_0^Z(T + t_0 - t_1) s(t_1). \tag{14A}$$

The conditional probability of finding 2 and N photons in time interval $(t_0, T + t_0)$ is given by:

$$\rho_2(T + t_0, t_0|0) = \int_{t_0}^{T+t_0} dt_2 w_0^Z(T + t_0 - t_2) \times \int_{t_0}^{t_2} dt_1 s(t_2 - t_1) s(t_1) \tag{15A}$$

$$\rho_N(T + t_0, t_0|0) = \int_{t_0}^{T+t_0} dt_N w_0^Z(T + t_0 - t_N) \times \int_{t_0}^{t_N} dt_{N-1} s(t_N - t_{N-1}) \dots \int_{t_0}^{t_2} dt_1 s(t_2 - t_1) s(t_1)$$

$$= \int_0^T dx_N \int_0^{x_N} dx_{N-1} \dots \int_0^{x_2} dx_1 w_0^Z(T - x_N) \times s(x_N - x_{N-1}) \dots s(x_2 - x_1) s(x_1 + t_0) \tag{16A}$$

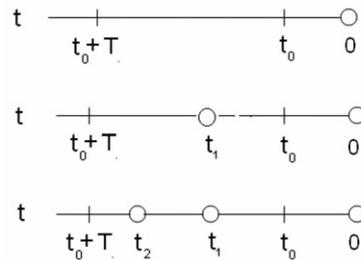


Figure 1A. Time intervals with photons (circles).

The conditional probability $\rho_N(T + t_0, t_0|0)$ can be written in the following form:

$$\rho_N(T + t_0, t_0|0) = w_N(T + t_0, t_0)\rho_0(t_0|0), \quad N \geq 1. \quad (17A)$$

Here, $\rho_0(t_0|0) = 1 - S(t_0)$ is the probability of finding no photons in time interval $(0, t_0)$ and $w_N(T + t_0, t_0)$ is the probability of finding N photons in time interval $(t_0, T + t_0)$ independently of the photon history preceding time t_0 . Therefore, we shall call $w_N(T + t_0, t_0)$ the unconditional probability. By operating in the same fashion, we can write the following expression for the probability $\rho_0(T + t_0|0) = 1 - S(T + t_0)$ of finding no photon in the interval $(0, T + t_0)$ if the preceding photon was emitted at $t = 0$:

$$\rho_0(T + t_0|0) = w_0(T + t_0, t_0)\rho_0(t_0|0). \quad (18A)$$

Here $w_0(T + t_0, t_0)$ is an unconditional probability of finding interval $(t_0, T + t_0)$ with no photons.

The expression for $w_N(T + t_0, t_0)$ can be written in the following form:

$$\begin{aligned} w_0(T + t_0, t_0) &= \frac{\rho_0(T + t_0|0)}{\rho_0(t_0|0)} = \frac{1 - S(T + t_0)}{1 - S(t_0)} \\ &= \frac{w_0^Z(T + t_0)}{1 - S(t_0)}. \end{aligned} \quad (19A)$$

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

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

taking into account that

$$\int_{t_0}^{T+t_0} dt_1 \int_{t_1}^{T+t_0} dt \dots = \int_{t_0}^{T+t_0} dt \int_{t_0}^t dt_1 \dots$$

Making use of Equations (19A) and (20A) we arrive at the following law of conservation for the unconditional probabilities:

$$\begin{aligned} \frac{1 - S(T + t_0)}{1 - S(t_0)} + \sum_{N=1}^{\infty} \frac{\rho_N(T + t_0, t_0|0)}{1 - S(t_0)} \\ = \sum_{N=0}^{\infty} w_N(T + t_0, t_0) = 1. \end{aligned} \quad (21A)$$

At $t_0 = 0$, these probabilities coincide with the probabilities $w_N^Z(T)$, i.e. $w_N(T + 0, 0) = w_N^Z(T)$.

If we detect photons with the help of the method M, we find time interval $(0, t_0)$ with no photons with the following density of the probability:

$$P(t_0) = \frac{1 - S(t_0)}{\int_0^{\infty} (1 - S(t_0))dt_0} = \frac{1 - S(t_0)}{\tau_0}. \quad (22A)$$

Here, τ_0 is an average time interval between two consecutive events. Therefore, the probability of finding interval T with N photons is determined by the following expression:

$$\begin{aligned} w_N^M(T) &= \int_0^{\infty} w_N(T + t_0, t_0)P(t_0)dt_0 \\ &= \frac{1}{\tau_0} \int_0^{\infty} \rho_N(T + t_0, t_0|0)dt_0 \end{aligned} \quad (23A)$$

This is the photon distribution function for the method M of photon counting. Making use of Equations (21A) and (25A), we arrive at the law of the probability conservation: $\sum_{N=0}^{\infty} w_N^M(T) = 1$.

By summing we can write the following expressions for the probabilities, $w_N^O(T)$, $w_N^Z(T)$ and $w_N^M(T)$.

For the method O:

$$\begin{aligned} w_0^O(T) &= s(T)/p(T), \quad w_N^O(T) = \int_0^T dt_N \int_0^{t_N} dt_{N-1} \dots \\ &\times \int_0^{t_2} dt_1 P^O(T, t_N, t_{N-1}, \dots, t_1), \quad N > 1, \end{aligned}$$

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

$$(N > 1), \quad P^O(T, t_1) = \frac{s(T - t_1)s(t_1)}{p(T)}. \quad (24A)$$

For the method Z:

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

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

$$(N > 1),$$

$$P^Z(T, t_N, t_{N-1}, \dots, t_1)$$

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

$$P^Z(T, t_1) = w_0^Z(T - t_1)s(t_1). \quad (25A)$$

For the method M:

$$w_0^M(T) = \frac{1}{\tau_0} \int_0^{\infty} dt_0 w_0^Z(T + t_0),$$

$$w_1^M(T) = \frac{1}{\tau_0} \int_0^T w_0^Z(T - t)w_0^Z(t)dt,$$

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

$$(N \geq 2),$$

$$P^M(T, t_N, t_{N-1}, \dots, t_1)$$

$$= \frac{w_0^Z(T - t_N)}{\tau_0} \prod_{j=1}^{N-1} s(t_{j+1} - t_j)w_0^Z(t_1) \quad (26A)$$

Equation (25A) for the probability $P^Z(T, t_N, t_{N-1}, \dots, t_1)$ coincides with the expression found in [7]. Carmichael [6] introduced the function, $\rho_1(t_2, [t_1, t_2])$, determined as the density of the probability that, "if observation begins at t_1 , the first photoelectric count is recorded in the interval $(t_2, t_2 + \Delta t_2)$ ". If we substitute $\rho_1(t_2, [t_1, t_2])$ by the function, $s(t_2 - t_1)w_0^Z(t_1)$, the Equation (6) in [6] will coincide with the function $P^M(T, t_N, t_{N-1}, \dots, t_1)$ found here.

Appendix B

The determinant of Equation (5) is as follows:

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

By solving this cubic equation we arrive at the following formulas for roots:

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

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

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

Here,

$$\begin{aligned} P = & A^2 + A[k - a + 2(1/T_1 + G)] + 4k^2 - k(2a - 1/T_1 - 4G) \\ & + a^2 - a(1/T_1 + G) + (1/T_1 + G)^2, \end{aligned} \quad (3B)$$

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

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