Blinking molecules: Determination of Photo-Physical Parameters from the Intensity Correlation Function

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An explicit expression is given for the correlation function of blinking systems, i.e. systems exhibiting light and dark periods in their fluorescence. We show through the example of terrylene in a crystalline host that it is possible to determine by means of this explicit expression photo-physical parameters, like Einstein coefficients and the mean light and dark periods by a simple fit. In addition we obtain further parameters like the frequency of the various intensity periods and the probability density of photons scattered off the host crystal. It turns out that this approach is simpler and allows greater accuracy than previous procedures.

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I. INTRODUCTION

Since about twenty years it has been possible to observe and study the fluorescence of single ions in Paul traps [1] and, more recently, also of single molecules embedded in a crystal [2, 3, 4]. In the presence of metastable triplet levels the molecule can exhibit light and dark periods in its fluorescence (“blinking”) [5, 6], just as ions in the V or Λ configuration [7, 8, 9, 10, 11, 12, 13, 14]. Spectroscopy of single molecules is of fundamental importance both for basic quantum mechanical aspects like antibunching, quantum jumps or the dynamical Stark effect [5, 15, 16], as well as for applications in chemical and biophysics, cf. e.g. [4, 17]. For these applications a precise knowledge is required of the parameters characteristic of fluorescence, like Einstein coefficients and the mean duration of intensity periods. Often these parameters cannot be calculated directly but have to be determined indirectly from suitable experimentally accessible quantities.

One of the most important statistical quantities for the description of fluorescing quantum systems is the intensity correlation function, \( g(\tau) \) [18]. Its behavior for small times \( \tau \) yields insight into the nature, classical or quantum, of the photon statistics i.e. bunching (\( g(0) > 1 \)) or antibunching (\( g(0) < 1 \)), respectively, and it shows the effect of Rabi oscillations. In addition it may yield information on light and dark periods through long-time correlations. The importance of \( g(\tau) \) originates from its easy experimental accessibility as it does not depend on the detector efficiency. To obtain a deeper physical understanding of this important quantity, analytical results are often useful. By means of our recently proposed approach for an analytical calculation of photon correlation functions of arbitrary blinking quantum systems [19] we derive in this paper, for the first time, an explicit expression for the correlation function of the four-level scheme used to describe the fluorescence of single molecular systems like terrylene or pentacene. In contrast to previous work, our result depends directly on the relevant photo-physical parameters, such as Einstein coefficients, Rabi frequencies or the mean duration of the light and dark periods, with no further unknown quantities. This allows an easy determination of these in general unknown molecular parameters by a single fit to experimental data, where in comparison to previous approaches the fit is greatly facilitated through the explicit knowledge of \( g(\tau) \), as will be shown in the present paper for the example of a terrylene molecule embedded in p-terphenyl. This intensity correlation function has recently been measured in Refs. 20, 21, 22. In this paper we first derive an explicit expression of \( g(\tau) \) for terrylene, taking into account both its metastable levels, and then fit \( g(\tau) \) to the data of Ref. 22. From this we obtain the electronic Einstein coefficients, the mean light and dark periods and further fluorescence parameters and compare our results with those in the literature.

II. THE INTENSITY CORRELATION FUNCTION

The energy-level configuration of planar hydrocarbons, such as terrylene, can be described by an electronic three-level system [23, 24], with a singlet ground state, \( |1\rangle \), an excited singlet state, \( |3\rangle \), and a triplet state, \( |2\rangle \). Due to the interaction between the magnetic moments of the electron spins the metastable triplet state of terrylene splits into two metastable sub-levels with different population and depopulation rates (zero-field splitting) \( \tilde{B} \). Each electronic level is characterized by a host of vibrational degrees of freedom (cf. Fig. 1(a)). These vibrational states have a life time of about \( 10^{-12} \text{ s} \) \( \tilde{B} \). On the other hand, a transition from \( |3\rangle \) to the vibrational states of \( |1\rangle \) occur on a time scale of \( 10^{-8} \text{ s} \) and from \( |3\rangle \) to the triplet state \( |2\rangle \) about every \( 10^{-3} \text{ s} \). Therefore these transitions can be described by effective electronic Einstein coefficients \( A_{31}, A_{32}^{(i)}, A_{21}^{(i)}, i = 1, 2 \), and by the Rabi frequency \( \Omega_{31} \) of the laser driving the \( |1\rangle \leftrightarrow |3\rangle \) transition, while the vibrational levels can be neglected. Hence the
(b) The extremely fast relaxation of the vibrational levels into the metastable triplet state (with low probability).

FIG. 1: Level scheme of terrenylone. (a) Singlet ground state |1⟩, excited singlet state |3⟩, and triplet state |2⟩, associated with a host of vibrational states. ISC (intersystem crossing, singlet-triplet transition) with low probability. Zero-field splitting of the metastable triplet state into two sublevels with different population and depopulation rates. (b) The extremely fast relaxation of the vibrational levels leads to an effective four-level system with two metastable states, |2(1)⟩ and |2(2)⟩, and effective Einstein coefficients \( A_{21}^{(1)}, A_{21}^{(2)} \ll \Omega_{31}, \Omega_{31} \).

level configuration effectively consists of a four-level system as in Fig. 1(b), with two metastable states |2(1)⟩ and |2(2)⟩, and one has

\[
A_{21}^{(i)}, A_{32}^{(i)} \ll \Omega_{31}, \Omega_{31} , \quad i = 1, 2 .
\]

A fluorescence trajectory of such a system consists of light and dark periods. During a light period, the subsystem \{ |1⟩, |3⟩ \} behaves like a two-level system whose intensity is given by [23]

\[
I_L = \frac{\Omega_{31}^2}{A_{31}^2 + 2\Omega_{31}^2} .
\]

A transition from |3⟩ to one of the metastable states |2(1)⟩ or |2(2)⟩ each initiates a dark period (denoted by D(1) and D(2)) of mean duration \( A_{21}^{(1)} \) and \( A_{21}^{(2)} \), respectively. The transition rates from the light period to the two dark periods are denoted by \( p_{DL}^{(1)} \) and \( p_{DL}^{(2)} \), and those from the dark periods to the light period by \( p_{LD}^{(1)} \) and \( p_{LD}^{(2)} \). These transition rates can be calculated in a fully quantum mechanical way by the methods of Ref. [20], and they are given by (cf. Appendix A)

\[
p_{DL}^{(i)} = A_{21}^{(i)} \quad (\text{for } i = 1, 2) .
\]

\[
p_{LD}^{(i)} = \frac{A_{21}^{(i)} \Omega_{31}^2}{A_{31}^2 + \Omega_{31}^2} .
\]

A fluorescence trajectory of terrenylone is a Markovian jump process with three intensity steps, i.e., light, dark D(1), and dark D(2). Recently, the present authors [13] have derived a highly accurate expression for the intensity correlation function of arbitrary blinking systems which is given in Appendix B and takes here the form

\[
g(\tau) = \frac{1}{P_L} P_{LL}(\tau) g_2(\tau) ,
\]

where \( P_{LL}(\tau) \) is the conditional probability to have a light period at time \( t = \tau \) provided that at \( t = 0 \) there was also a light period, where

\[
P_L = \lim_{\tau \to \infty} P_{LL}(\tau)
\]

is the probability to find a light period at all, and where \( g_2(\tau) \) is the intensity correlation function of the \{ |1⟩, |3⟩ \} two-level subsystem. From Ref. [23] one has

\[
g_2(\tau) = 1 - e^{-\frac{1}{2}A_{31}^{(1)}} \sin \gamma \tau + \frac{3A_{31}^{(1)}}{4\gamma} \sin \gamma \tau
\]

where

\[
\gamma = \frac{1}{4} \sqrt{16\Omega_{31}^2 - A_{31}^2} .
\]

To determine \( P_{LL}(\tau) \) we consider the conditional probability, \( P_{LL}^{(i)}(\tau) \), at that time \( t = \tau \) one has a dark period D(1) under the condition of a light period at \( t = 0 \) \( (i = 1, 2) \). These conditional probabilities satisfy the rate equations

\[
\dot{P}_{LL}(\tau) = \sum_{a=1}^{2} ( -\dot{P}_{LL}^{(a)} P_{LL}(\tau) + p_{DL}^{(a)} p_{LD}^{(a)} P_{LL}(\tau) )
\]

\[
\dot{P}_{LL}^{(i)}(\tau) = -p_{DL}^{(i)} P_{LL}^{(i)}(\tau) + p_{LD}^{(i)} P_{LL}(\tau) , \quad i = 1, 2
\]

which is easily seen by noting that the first terms on the r.h.s. describe the decrease of the probabilities and the second their increase. This can easily be generalized for an arbitrary number of light and dark periods as shown in Appendix B. With the initial condition \( P_{LL}(0) = 1 \) and \( P_{LL}^{(i)}(0) = 0 \) one finds in a straightforward way

\[
P_{LL}(\tau) = \frac{P_{DL} P_{DL}^{(2)}}{\mu_1 \mu_2} \left[ \frac{\mu_1 \mu_2}{\mu_1 (\mu_1 - \mu_2)} \right] \times \left( p_{DL}^{(1)} p_{LD}^{(1)} + \mu_2 \right) + p_{DL}^{(2)} p_{LD}^{(1)} + \mu_1 \right) + \frac{e^{\mu_1 \tau}}{\mu_1 (\mu_1 - \mu_2)} \times \left( p_{DL}^{(1)} p_{LD}^{(2)} + \mu_2 \right) + p_{DL}^{(2)} p_{LD}^{(2)} + \mu_2 \right) (11)
\]
where
\[
\mu_{1,2} = -\frac{1}{2} (p^{(1)}_{DL} + p^{(2)}_{DL} + p^{(2)}_{LD} + p^{(2)}_{DL}) \\
\pm \frac{1}{2} \left[ (p^{(1)}_{DL} + p^{(2)}_{LD} - p^{(2)}_{DL})^2 + 4 p^{(1)}_{DL} p^{(2)}_{LD} \right]^{\frac{1}{2}}.
\]
(12)

From this and from Eq. (6) one obtains
\[
P_L = \frac{p^{(1)}_{DL} p^{(2)}_{DL}}{\mu_1 \mu_2} = \frac{p^{(1)}_{DL} p^{(2)}_{DL}}{p^{(1)}_{DL} p^{(2)}_{DL} + p^{(1)}_{DL} p^{(2)}_{DL} + p^{(1)}_{DL} p^{(2)}_{DL}}.
\]
(13)

Thus the correlation function \( g(\tau) \) in Eq. (6) for the four-level system of Fig. 1(b) satisfying the inequalities in Eq. (1) is given in terms of the photo-physical parameters \( A_{31}, \Omega_{31}, A_{32}^{(1)}, A_{32}^{(2)}, A_{21}^{(1)}, \) and \( A_{21}^{(2)} \).

One can re-express \( g(\tau) \) through the mean durations of the three periods, denoted by \( T_L, T_D^{(1)} \) and \( T_D^{(2)} \), respectively, and by the branching ratios
\[
p_i = \frac{p^{(i)}_{DL}}{p^{(1)}_{DL} + p^{(2)}_{DL}}
\]
(14)
at the end of a light period, using \( p_L \)
\[
T_L = \frac{1}{p^{(1)}_{DL} + p^{(2)}_{DL}}
\]
(15)
\[
T_D^{(i)} = \frac{1}{p^{(i)}_{DL}}, \quad i = 1, 2.
\]
(16)

With these relations one obtains, after some calculation, the explicit expression
\[
g(\tau) = g_2(\tau) \left\{ 1 + \frac{1}{T_L} \exp \left[ \frac{1}{2} \left( \frac{1}{T_L} + \frac{1}{T_D^{(1)}} + \frac{1}{T_D^{(2)}} \right) \right] \tau \left[ (p^{(1)}_D T^{(1)}_D + p^{(2)}_D T^{(2)}_D) \cosh \Gamma \tau \\
+ \left( p_1 \left( \frac{T_L^{(1)}}{T_D^{(2)}} - \frac{T_L^{(1)}}{T_D^{(1)}} \right) + p_2 \left( \frac{T_L^{(2)}}{T_D^{(1)}} - \frac{T_L^{(2)}}{T_D^{(2)}} \right) - 1 \right) \left. \sinh \frac{\Gamma \tau}{2} \right] \right\}.
\]
(17)

One sees that the statistics of intensity periods leads to the well known bi-exponential tail in the intensity correlation function at a much larger time scale than where \( g_2(\tau) \) plays a role. Therefore one has a hump at intermediate times \( \tau \sim 10^{-7} \) s, where \( g_2(\tau) \approx 1 \) and \( P_L(\tau) \approx 1 \).

The height of this hump is given by \( 1/T_L \), according to Eq. (5) and to Eq. (17) for \( \tau \to 0 \) and \( g_2(\tau) \approx 1 \). Moreover, with the explicit form of \( g(\tau) \) in Eq. (17), all photo-physical parameters can be obtained by a single fit to experimental data, as shown in the following.

III. EXAMPLE: FIT AND RESULTS FOR TERRYLENE

We use the experimental data for the intensity correlation function of terrylene obtained in Ref. 22. Details of the experimental setup can be found in Ref. 23. Since some of the laser light is scattered off the embedding crystal, with intensity \( I_{sc} \), say, this gives rise to additional poissonian correlations. Therefore the intensity correlation function in a light period is modified to the weighted average
\[
g^{\text{mod}}_2(\tau) = \frac{I_L g_2(\tau) + I_{sc}}{I_L + I_{sc}}
\]
(19)
\[
= 1 - \frac{e^{-\frac{3}{2} A_{31} \tau}}{1 + I_{sc}/I_L} \left( \cos \gamma \tau + \frac{3 A_{31} \sin \gamma \tau}{4 \gamma} \right)
\]
(20)

with \( I_L \) given by Eq. (2). This has to be inserted into Eq. (17) instead of \( g_2(\tau) \).

The thus modified Eq. (17) has been fitted to the experimental data. In Eq. (17) there are two different time scales - for times \( \tau > 10^{-7} \) s the first factor, \( g^{\text{mod}}_2(\tau) \) is essentially 1 and for times \( \tau < 10^{-7} \) s the second factor is practically constant. Therefore, we have first fitted the second factor for \( \tau > 10^{-7} \) s and then fitted \( g^{\text{mod}}(\tau) \) multiplied by a constant for \( \tau < 10^{-7} \) s. Thus, in each of the two fits one has at most four free parameters, which reduces the numerical error. The fitted curve and the experimental data are shown in Fig. 2, and the resulting parameter values are listed in Table I.

With the results of Table I, one now could calculate \( A_{32}^{(i)} \) and \( A_{21}^{(i)} \) from Eqs. (3), (4), and (14) - (16). However, numerically it is better to insert the expressions for \( T_L, T_D^{(i)} \) and \( p_i \) into Eq. (17) and then again fit the second factor to the experimental data for \( \tau > 10^{-7} \) s. With this procedure one obtains all Einstein coefficients of the intersystem crossings, as listed in Table II.
The reason probably is that a direct determination of the period duration as done in Refs. [22, 27] depends sensitively on the choice of the time window employed [20].

TABLE I: Photo-physical parameters for terrylene in p-terphenyl, obtained by a fit of Eq. [17] to the data of Ref. [22] and compared with results in the literature.

|       | $A_{31}$ (10$^8$ s$^{-1}$) | $I_{sc}$ (10$^7$ s$^{-1}$) | $T_L$ (ms) | $T_D^{(1)}$ (ms) | $T_D^{(2)}$ (ms) | $p_1$ |
|-------|--------------------------|---------------------------|----------|----------------|----------------|------|
| This work | 3.3 ± 0.5 | 2.9 ± 0.1 | 7.7 ± 0.7 | 8.2 ± 0.3 | 2.3 ± 0.2 | 0.42 ± 0.03 | 0.12 ± 0.02 |
| Ref. [22] | – | – | – | 6.3 | 3 | 0.43 | – |
| Ref. [27] | 2.9 | – | – | 6.3 ± 0.1 | 3 ± 1 | 0.43 ± 0.01 | – |
| Ref. [5] | – | – | – | 4.5 | – | 0.4 | – |

Our value for $A_{31}$ agrees with that of Refs. [22, 27] within the error bars.

In case of the Einstein coefficients of the intersystem crossings our values qualitatively agree with those of Ref. [1, 22, 27], where the results of Refs. [22, 27] depend on the same data as ours. There is overall agreement in so far as the population rates $A_{32}^{(i)}$ of the metastable states are an order of magnitude smaller than the corresponding depopulation rates $A_{21}^{(i)}$ and that the values for $i = 1$ are an order of magnitude smaller than those for $i = 2$. As a consequence, the metastable state $|2^{(1)}\rangle$ is occupied considerably less often than $|2^{(2)}\rangle$, a fact also mirrored in the largely different branching ratios $p_1$ and $p_2$. Hence the dark period associated with the state $|2^{(1)}\rangle$ occurs much less frequently than the other one, and hence a statistical determination may be more error prone than our fit procedure. In Table II, somewhat larger differences are seen for $A_{21}^{(1)}$, the population rate of the less frequently occupied metastable state.

IV. CONCLUSIONS AND OUTLOOK

In this paper an explicit expression for the intensity correlation function of blinking systems has been applied to a four-level system with two metastable states. Using terrylene in p-terphenyl as an example it has been shown that the relevant photo-physical parameters can be obtained from a single fit to experimental data for the correlation function. This is a considerable simplification compared to previous procedures, and it can also result in smaller error bars. In this way we have obtained the Einstein coefficient of the fast transition, the mean durations of the light and dark periods, as well as the population and depopulation rates of the metastable levels. Our results qualitatively agree with values given in the literature. In addition we have obtained further parameters like the Rabi frequency $\Omega_{31}$ and the contribution, $T_{sc}$, to the correlation function due to the light back-scattered off the crystal.

It should also be possible to apply our approach of an explicit calculation of the correlation function not only to terrylene but also to other blinking systems with a more complicated statistics of light and dark peri-

The mean durations of the light and dark periods obtained here essentially agree with those of Ref. [22, 27], with a difference of about 23% in the case of $T_L$ and with a drastically reduced error bar in our value for $T_D^{(1)}$. The reason probably is that a direct determination of the period duration as done in Refs. [22, 27] depends sensitively on the choice of the time window employed [20].

FIG. 2: The intensity correlation function of a single fluorescent terrylene molecule embedded in a host crystal of p-terphenyl. Shown are the experimental data from Ref. [22] (×) and the fit function obtained with Eq. (17) (solid line). This function contains both the Rabi oscillations for small times as well as the long time correlations (hump) due to the metastable levels.
ods. Particularly interesting in this context would be the recently performed fluorescence measurement of two dipole-interacting molecules and to determine the interaction parameters of such a system by the present methods.

**APPENDIX A**

We indicate here the derivation of Eqs. (3) and (11) for the transition rates between the different fluorescence periods of the level system in Fig. 1(b). To do this we use the method of Ref. [26]. During a dark period D for the transition rates between the different fluorescence methods.

To evaluate this we use the Bloch equations which can be written in the form [29, 30] and the super-operator \( \rho \) by

\[
\rho_D^{(i)} = |2^{(i)}⟩⟨2^{(i)}| , \quad (A1)
\]

and during a light period in the steady state of the \( |1⟩, |3⟩ \) subsystem, with the density matrix

\[
\rho_L = \frac{1}{A_{31}^2 + 2\Omega_{31}^2} \left( (A_{31}^2 + \Omega_{31}^2) |1⟩⟨1| \\
+ \Omega_{31}^2 |3⟩⟨3| + i A_{31} \Omega_{31} (|1⟩⟨3| − |3⟩⟨1|) \right) . \quad (A2)
\]

Starting from one of these density matrices, the increase in occupation of the other subsystems during a time \( \Delta t \) yields the transition rates; here \( \Delta t \) has to satisfy

\[
(A_{32}^{(l)})^{-1}, (A_{21}^{(l)})^{-1} \ll \Delta t \ll A_{31}^{-1}, \Omega_{31}^{-1} . \quad (A3)
\]

With initial state \( \rho(t_0) = \rho_L \), one then has

\[
P_{LD}^{(i)} = \frac{d}{dt} ⟨2^{(i)}|ρ(t)|2^{(i)}⟩_{t=t_0+\Delta t} \quad (A4)
\]

and for \( \rho(t_0) = \rho_D^{(i)} \) one has

\[
P_{DL}^{(i)} = \frac{d}{dt} ⟨3|ρ|3⟩ + (1|ρ|1)⟩_{t=t_0+\Delta t} . \quad (A5)
\]

To evaluate this we use the Bloch equations which can be written in the form [29, 30]

\[
\frac{d}{dt} \rho(t) = -\frac{i}{\hbar} \left( H_C ρ(t) − ρ(t) H_C^† \right) + \mathcal{R}(ρ(t)) \quad (A6)
\]

where the so-called conditional Hamiltonians \( H_C \) is given by

\[
H_C = \frac{\hbar}{21} \left( A_{31} |3⟩⟨3| + A_{21}^{(1)} |2^{(1)}⟩⟨2^{(1)}| + A_{21}^{(2)} |2^{(2)}⟩⟨2^{(2)}| \right) \\
+ \frac{\hbar \Omega_{31}}{2} \left( |1⟩⟨3| + |3⟩⟨1| \right) \quad (A8)
\]

and the super-operator \( \mathcal{R} \) by

\[
\mathcal{R}(ρ) = \sum_{i=1}^2 |1⟩⟨A_{31} (3|ρ⟩⟨3| + A_{21}^{(1)} |2^{(1)}⟩⟨2^{(1)}| + A_{21}^{(2)} |2^{(2)}⟩⟨2^{(2)}|)⟩ |1⟩ \\
+ A_{32}^{(1)} |2^{(1)}⟩⟨3|ρ⟩⟨3|2^{(1)}⟩ |1⟩ . \quad (A9)
\]

Using Eq. (A8) one can show that Eqs. (A4) and (A5) can be written as

\[
P_{LD}^{(i)} = A_{32}^{(i)} ⟨3|ρ(t_0+\Delta t)⟩3 − A_{21}^{(2)} |2^{(2)}⟩⟨2^{(2)}|ρ(t_0+\Delta t)⟩2^{(2)} \quad (A10)
\]

\[
P_{DL}^{(i)} = \sum_{α=1}^2 \left( A_{21}^{(α)} |2^{(α)}⟩⟨2^{(α)}|ρ(t_0+\Delta t)⟩2^{(α)} \right. \\
− A_{32}^{(α)} ⟨3|ρ(t_0+\Delta t)⟩3 \right) . \quad (A11)
\]

The necessary matrix elements of \( ρ(t_0+\Delta t) \) are obtained from the Bloch equations written as in of Eq. (A3). Writing L in the obvious form

\[
L = L_0(A_{31}, Ω_{31}) + L_1(A_{32}, A_{21}^{(1)}) \quad (A12)
\]

one obtains in a way analogous to the usual quantum mechanical perturbation theory, to first order in \( A_{32}^{(1)} \) and \( A_{21}^{(1)} \),

\[
ρ(t_0+\Delta t) = e^{L_{0}\Delta t} ρ(t_0) \\
= e^{L_0_{\alpha}} e^{i L_1 t_1} e^{L_0 t} ρ(t_0) . \quad (A13)
\]

Since \( ρ(t_0) \) is a stationary state of subsystems one has \( L_0 ρ(t_0) = 0 \) and hence \( e^{L_0_{\alpha}} ρ(t_0) = ρ(t_0) \). After a change of variable one thus obtains

\[
ρ(t_0+\Delta t) = ρ(t_0) + \int_0^{\Delta t} dτ e^{L_1} e^{L_0 (\Delta t − τ)} L_{1} e^{L_0 t} ρ(t_0) . \quad (A14)
\]

Now \( L_1 ρ(t_0) \) can be decomposed into a component parallel to the null space of \( L_0 \) and a component belonging to the subspace for nonzero eigenvalues,

\[
L_1 ρ(t_0) = \mathbb{P}_∥ L_1 ρ(t_0) + (\mathbb{I} - \mathbb{P}_∥) L_1 ρ(t_0) . \quad (A15)
\]

Here

\[
\mathbb{P}_∥ = \frac{1}{2\pi i} \oint_{C_0} dz (z - L_0)^{-1} , \quad (A16)
\]

where \( C_0 \) is a path in the complex plane enclosing no other eigenvalue than zero. The integral can be calculated by the residue method. In view of Eq. (A3), the contribution to Eq. (A15) of the \( \mathbb{P}_∥ \) term in Eq. (A16) is negligible. The contribution to Eq. (A14) of the \( (\mathbb{I} - \mathbb{P}_∥) \) term is governed by the nonzero eigenvalues of \( L_0 \) which possess a (large) negative real part of the order of \( A_{31} \) and \( Ω_{31} \). Therefore the integrand in Eq. (A14) is strongly damped in \( τ \), and in view of Eq. (A3), the upper integration limit can be replaced by \( \infty \), yielding

\[
ρ(t_0+\Delta t) = ρ(t_0) + \int_0^{\infty} dτ e^{L_0 t} (\mathbb{I} - \mathbb{P}_∥) L_1 ρ(t_0) \\
= ρ(t_0) + (e - L_0)^{-1} (\mathbb{I} - \mathbb{P}_∥) L_1 ρ(t_0) , \quad (A17)
\]
with $\epsilon \to +0$. Inserting this into Eqs. (A11) and (A10) one obtains, after some calculations involving $16 \times 16$ matrices, the transition rates of Eqs. (3) and (4). These hold to first order in $A_{21}^{(i)}$ and $A_{32}^{(i)}$.

**APPENDIX B**

We give here generalized expressions for the intensity correlation function of fluorescing systems with an arbitrary number of different intensity periods with intensity $I_i$. A detailed discussion can be found in Ref. [19].

Let $P_i$ be the probability for the occurrence of period $i$ and let $P_{ij}(\tau)$ be the probability to have period $j$ at time $\tau$ provided one had period $i$ at $\tau = 0$. Then it can be shown, that a highly accurate expression for the normalized intensity correlation function is

$$g(\tau) = \frac{\sum_{ij} P_i I_i I_j P_{ij}(\tau) g_j(\tau)}{\left(\sum_\alpha P_\alpha I_\alpha\right)^2},$$

where $g_i(\tau)$ is the correlation function within a given period $i$ and usually easier to calculate than that of the complete system. In the case of only one light period and two dark periods Eq. (B1) reduces to Eq. (5).

Let $p_{ij}$ be the transition rates from period $i$ to $j$. Then the $P_{ij}(\tau)$ are easily seen to obey rate equations, e.g.

$$\dot{P}_{11}(\tau) = \left(-\sum_k p_{1k}\right) P_{11}(\tau) + p_{21} P_{12}(\tau) + \cdots + p_{1n} P_{1n}(\tau).$$

In general, with the matrix $B = (B_{ij})$,

$$B_{ij} = p_{ij} - \delta_{ij} \sum_k p_{ik},$$

and the matrix

$$P(\tau) = \begin{pmatrix} P_{11}(\tau) \\ & & \vdots \\ & & P_{nn}(\tau) \end{pmatrix},$$

one has

$$\dot{P} = PB,$$

with the initial condition $P_{ij}(0) = \delta_{ij}$, or

$$P(0) = I.$$

The solution of equation (B5) with this initial condition can be written as

$$P(\tau) = e^{B\tau}.$$

If $\mu_0, \ldots, \mu_{n-1}$ are the eigenvalues of $B$ (assumed distinct) then [32]

$$e^{B\tau} = \sum_{i=0}^{n-1} e^{\mu_i \tau} \prod_{\alpha \neq i} \frac{B - \mu_\alpha}{\mu_i - \mu_\alpha}.$$

The properties of the matrix $B$ are closely related to those of stochastic matrices [32], and under quite general conditions $B$ has a single eigenvalue $\mu_0 = 0$ and eigenvalues $\mu_1, \ldots, \mu_{n-1}$ with negative real part.

To find the $P_i$’s, we note that for $\tau \to \infty$ the memory to the initial condition is in general lost. Therefore, for any $k$,

$$P_i = P_{\kappa}(\infty).$$

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