Quantum jumps and photon statistics in fluorescent systems coupled to classically fluctuating reservoirs

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Abstract

In this paper, we develop a quantum-jump approach for describing the photon emission process of single fluorophore systems coupled to complex classically fluctuating reservoirs. The formalism relies on an open quantum system approach where the dynamics of the system and the reservoir fluctuations are described through a density matrix whose evolution is defined by a Lindblad rate equation. For each realization of the photon-measurement processes it is possible to define a conditional system state (stochastic density matrix) whose evolution depends on both the photon detection events and the fluctuations between the configurational states of the reservoir. In contrast to standard fluorescent systems the photon-to-photon emission process is not a renewal one, being defined by a (stochastic) waiting time distribution that in each recording event parametrically depends on the conditional state. The formalism allows calculating experimental observables such as the full hierarchy of joint probabilities associated with the time intervals between consecutive photon recording events. These results provide a powerful basis for characterizing different situations arising in single-molecule spectroscopy, such as spectral fluctuations, lifetime fluctuations and light-assisted processes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A powerful theoretical formalism called the quantum-jump approach [1–11] was introduced by the quantum optics community to describe experimental realizations of single open quantum systems subjected to a continuous measurement process. Even when only one system is under observation, the quantum-jump approach allows us to define a system state (wave vector or density matrix) whose dynamics takes into account our change of information due to the continuous measurement action. Apart from new insights in the quantum measurement theory, the quantum-jump approach provides an alternative formalism for characterizing the radiation pattern of single fluorescent systems driven by a laser field.

While a wide class of quantum optical systems can be studied with the quantum-jump approach [1–3], it has been scarcely applied in the context of single-molecule (fluorescence) spectroscopy (SMS) [12–14], i.e. in the characterization of single fluorescent systems coupled to complex host classically fluctuating environments, such as those associated with biological or artificially designed nanoscopic reservoirs. The main task of SMS is to deduce the underlying environmental stochastic dynamics from the statistical properties of the scattered laser field [15–25]. In most of the experiments, the scattered electromagnetic field is measured with photon detectors. Hence, it can be resolved photon-to-photon.

For direct photon-detection measurement schemes the quantum-jump approach associates with each photon recording event a sudden disruptive change (wave vector collapse) in the system state, while in the middle intervals between consecutive events the conditional system evolution is smooth and non-unitary [1–6]. The formalism provides a simple technique for calculating and reproducing the photon
recording process. For Markovian two-level systems the emission process is a renewal one, i.e. the statistics of the (random) time intervals between consecutive photon emissions is always the same, being defined by a probability distribution called the waiting time distribution [1, 5].

The main obstacle for applying the quantum-jump approach for modelling SMS experiments comes from the description of the environmental fluctuations. As in general a full microscopic description is lacking, the complexity of the environment is taken into account by introducing effective time-dependent stochastic variables that may modify (parametrize) both the unitary and dissipative fluorophore evolution. In the context of the quantum-jump approach, it is not clear how these extra (classical) fluctuations must be introduced or consistently interpreted in terms of a continuous measurement action.

On the basis of stochastic models, the formalism of generalized Bloch equations [26–30] allows us to determine the photon counting probabilities, i.e. the probabilities of detecting \( n \) photons up to a given time. Nevertheless, from that approach it is not easy to know how the renewal property is broken by the external fluctuations, nor is it known which kind of stochastic dynamics may reproduce the photon emission process. Then, objects like the hierarchy of joint probabilities associated with the time intervals between consecutive photon detection events are also unknown. These statistical objects can be obtained, for example, from a time average along a single measurement trajectory (see equations (10) and (11)).

The main goal of this paper is to demonstrate that SMS experiments can be consistently described in the context of a quantum-jump approach. A general formalism that allows us to characterize the photon-to-photon emission process for a broad class of environmental fluctuations arising in SMS is developed. In each case, we provide (non-renewal) stochastic processes that reproduce the statistics of the photon recording events. The average of their associated dynamics in the system-bath Hilbert space recovers the density matrix evolution. As a central result, we obtain explicit analytical expressions for the set of joint probability densities defining the statistic of the time intervals between successive photon recording events. Therefore, our analysis allows us to quantify how, and by how much, the photon emission process departs from a renewal one.

The formulation of an alternative description of SMS experiments based on a quantum-jump approach relies on the possibility of describing both the fluorophore and the environmental fluctuations through a density matrix formalism. In [31] it was demonstrated that a broad class of SMS experiments can be studied through an open quantum system approach. The density matrix evolution is given by a Lindblad rate equation [32], which allows us to characterize in a unified way both the quantum nature of the fluorescent system and the classical nature of the environmental fluctuations. Based on those results, which are consistent [31] with the formalism of stochastic Bloch equations [26–30], we formulate the present treatment.

We remark that a similar analysis was developed in [33]. In contrast, our present analysis allows obtaining explicit expressions for the photon emission statistics, which is also analysed in the limit of slow and fast environmental fluctuations. Furthermore, an explicit formulation of the underlying stochastic photon emission process is presented. On the other hand, our results also clarify some of the assumptions introduced in the previous author’s works [34–36] as well as in other related contributions [37].

The paper is outlined as follows. In section 2, on the basis of the results developed in [31], we define the underlying density matrix formulation. In section 3, we develop the quantum-jump approach. Both the stochastic dynamics and the statistical characterization of the photon emission process are established. In section 4 we apply the formalism for the case in which the measurement apparatus only gives information about the photon emission events. Different specific cases, such as lifetime fluctuations and light-assisted processes, are analysed in detail. In appendix A we analyse the case of measurements that provide information about both the photon recording events and the configurational reservoir transitions. In section 5 we provide the conclusions.

### 2. Density matrix evolution

The description of SMS experiments based on a density matrix formalism relies on the possibility of finding analytically manageable microscopic interactions able to describe the environmental fluctuations as well as their dynamical influence over the system. In [31], following an argument developed by van Kampen [38], we modelled the environment through a set of (effective, coarse grained) macrostates, each representing the manifold of quantum bath states that lead to the same system dynamics. In our formalism, the underlying manifolds may be of infinite or finite dimension. The total microscopic dynamics is written in an effective Hilbert space defined by the external product of the Hilbert spaces of the system, the background electromagnetic field and the configurational space associated with the bath macrostates. The system is modelled by a two-level optical transition whose characteristic parameters, i.e. transition frequency and electric dipole, depend on the state of the environment. The dielectric constant of its local environment is also parametrized by the bath macrostates. After tracing out the electromagnetic field and the configurational states, the density matrix \( \rho_S(t) \) of the system can be written as [31]

\[
\rho_S(t) = \sum_{R=1}^{R_{\max}} \rho_R(t).
\]

Each auxiliary state \( \rho_R(t) \) defines the system dynamics given that the reservoir is in the \( R \)-configurational bath state. \( R_{\max} \) is the number of configurational states. The probability \( P_R(t) \) that the environment is in a given state at time \( t \) follows from

\[
P_R(t) = \text{Tr}_S[\rho_R(t)].
\]

where \( \text{Tr}_S[\cdots] \) denotes a trace operation in the system Hilbert space. Therefore, the set of states \( \{\rho_R(t)\} \) encodes both the
system dynamics and the fluctuations of the environment. Their dynamics is defined by a Lindblad rate equation [32]:

$$\frac{d\rho_R(t)}{dt} = -\frac{i}{\hbar}[H_R, \rho_R(t)] - \gamma_R [(D, \rho_R(t))] + J[\rho_R(t)]$$

$$- \sum_{R \neq R'} \frac{\hbar}{2} \left\{ A^{\dagger} A, \rho_R(t) \right\} + \sum_{R \neq R'} \eta_{RR'} A \rho_R(t) A^{\dagger}.$$ (3)

The first line of this equation defines the unitary and dissipative system dynamics given that the bath is in the configurational state $R$. The Hamiltonian $H_R$ reads

$$H_R = \frac{\hbar \omega_R}{2} \sigma_z + \frac{\hbar \Omega_R}{2} (\sigma^{+} e^{-i\omega_L t} + \sigma^{-} e^{i\omega_L t}),$$ (4)

where

$$\omega_R = (\omega_0 + \delta \omega_R).$$ (5)

The upper and lower states of the system are denoted as $|+\rangle$ and $|-\rangle$, respectively. Its transition frequency is $\omega_0$, $\sigma_z$ is the $z$-Pauli matrix in the basis $|+\rangle, |-\rangle$. Then, the contribution $\hbar \omega_0 \sigma_z/2$ defines the bare system Hamiltonian. The constants $\delta \omega_R$ define the spectral shifts associated with each bath state. The second contribution in equation (4) introduces the interaction between the system and the external laser excitation whose frequency is $\omega_L$. The operators $\sigma^\dagger = |+\rangle \langle -| \text{ and } \sigma = |-\rangle \langle +|$ are the raising and lowering operators acting on system eigenstates, respectively. The Rabi frequencies $\Omega_R$ measure the strength of the system–laser coupling for each configurational bath state. The rest of the system operators appearing in equation (3) are defined by

$$D = \sigma^\dagger \sigma^z/2, \quad J[\bullet] = \sigma \bullet \sigma^z,$$ (6)

while $[\bullet, \bullet]$ denotes an anticommutation operation. Then, the contribution proportional to the constant $\gamma_R$ defines the natural decay of the system associated with each reservoir state.

The second line in equation (3) introduces a coupling (with rates $\eta_{RR'}$) between all the states $| \rho_R(t) \rangle$, representing the fluctuations (transitions) between the configurational states of the environment. Depending on the definition of the system operator $A$, different cases are recovered. When $A = I$, where $I$ is the identity operator, the transitions between the configurational states do not depend on the system state. Hence, probabilities (2) are governed by a classical master equation whose structure follows straightforwardly from equation (3). This case allows us to describe situations such as spectral diffusion processes, conformational environmental fluctuations that affect the natural decay of the system as well as single fluorophore systems diffusing in a solution [31]. When $A \neq I$, the configurational fluctuations are statistically entangled with the state of the system. Depending on the structure of $A$ different kind of situations can be described such as for example light-assisted process, where the fluctuations of the bath depend on the external laser field intensity.

### 2.1. Vectorial representation

In order to establish a general formulation of the quantum-jump approach, we introduce a vectorial notation that allows us to simplify the presentation and calculations. The configurational bath states are associated with a vectorial space, defined by a basis $| R \rangle \rangle_{R=1}^R$, with $| R \rangle \rangle = \delta_{RR'}$, each vector $| R \rangle \rangle$ being related to a different configurational bath state. The set of auxiliary states $| \rho_R(t) \rangle$ allows us to define the vectors

$$| \rho_L \rangle \equiv \sum_R | \rho_R(t) \rangle \rangle, \quad | P_i \rangle \equiv \sum_R \text{Tr}_S[| \rho_R(t) \rangle \rangle | R \rangle \rangle].$$ (7)

These two objects encode both the system dynamics and the evolution of the configurational bath states. In fact,

$$\rho_S(t) = (1/| P_i \rangle \langle P_i |), \quad P_R(t) = (| R \rangle \langle R |),$$ (8)

where we have defined the $R$-vector $(1) \equiv \sum_R (| R \rangle \langle R |)$. These identities follow straightforwardly from equations (1) and (2), respectively. The normalization of the system state can be written as $\text{Tr}_S[(1 \langle P_i |) = 1$, while the normalization of the configurational populations reads $(1 \langle P_i |) = 1$.

With the vectorial notation, the Lindblad rate equation (3) can be rewritten as

$$\frac{d| \rho_L \rangle}{dt} = \hat{L}| \rho_L \rangle.$$ (9)

The structure of the matrix of system superoperators $\hat{L}$ follows from (3). From now on, with the hat symbol we denote vectors in the $R$-space whose components are superoperators acting on the system Hilbert space.

### 3. Quantum-jump approach

Our goal is to characterize the photon emission process associated with the fluorescent system. Of special interest is to determine how the environmental fluctuations broke the renewal property in successive photon emissions. This feature, for example, can easily be determined from a single experimental realization by measuring the successive time intervals $[\tau_i, \tau_{i+1}]$ between consecutive photon recording events occurring at times $\tau_i$ and $\tau_{i+1}$. Then, one can define the waiting time distribution

$$w^{(1)}(\tau) \equiv \langle \delta(\tau - \tau_i) \rangle_{\text{real}},$$ (10)

where $\langle \cdot \cdot \cdot \rangle_{\text{real}}$ denotes a time average along a single realization $[\langle f(\tau_i) \rangle_{\text{real}} = \lim_{t \to \infty} (1/t) \int_0^t f(\tau_i(\tau)) \rangle]$. Consequently, $w^{(1)}(\tau_i)$ defines the stationary probability density of the intervals $[\tau_i]$. It satisfies the normalization $\int_0^\infty d\tau w^{(1)}(\tau) = 1$. Similarly, one can define the (stationary) probability distribution $w^{(2)}(\tau_2, \tau_1)$ for two consecutive intervals $(\tau_i$ and $\tau_{i+1})$, i.e.,

$$w^{(2)}(\tau_2, \tau_1) \equiv \langle \delta(\tau_2 - \tau_{i+1}) \delta(\tau_1 - \tau_i) \rangle_{\text{real}}.$$ (11)

It fulfills $\int_0^\infty d\tau_2 \int_0^\infty d\tau_1 w^{(2)}(\tau_2, \tau_1) = 1$, and the consistency relations $\int_0^\infty d\tau_2 w^{(2)}(\tau_2, \tau_1) = w^{(1)}(\tau_1)$, and $\int_0^\infty d\tau_1 w^{(2)}(\tau_2, \tau_1) = w^{(1)}(\tau_2)$.

By knowing both probability distributions, one can quantify how much the photon emission process departs from

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1 In the context of [31], each vector $| R \rangle \rangle$ can be associated with a projector $| R \rangle \langle R |$, where the states $[| R \rangle \rangle]_{R=1}^R$ define the effective configurational Hilbert space.
a renewal one. The departure from zero of the dimensionless parameter
\[ \Lambda(t_2, t_1) = \frac{w^{(2)}_\infty(t_2, t_1)}{w^{(1)}_\infty(t_2)} - 1 \] (12)
measures the strength of the non-renewal effects induced by the bath fluctuations. In fact, in the absence of fluctuations the dynamics becomes Markovian. Furthermore, as the system is modelled through a two-level optical transition, each recording event resets the system to the same state, implying the renewal relation \( w^{(2)}_\infty(t_2, t_1) = w^{(1)}_\infty(t_2)w^{(1)}_\infty(t_1) \); then \( \Lambda(t_2, t_1) = 0 \). Note that in higher dimensional systems, a Markovian evolution does not guarantee the renewal property. On the other hand, non-Markovian system dynamics may also lead to a renewal emission process [33–35].

The possibility of finding analytical expressions for \( w^{(1)}_\infty(t_1) \) and \( w^{(2)}_\infty(t_2, t_1) \) is one of the central results of this contribution. We solve this task by extending the quantum-jump approach on the basis of equation (9) (equation (3)).

3.1. Measurement operators

The quantum-jump approach relies on a quantum measurement theory [1–3]. Here, the definition of a measurement operation must include both the system and the configurational bath states. If \( |\rho\rangle \) is the state previous to measurement, the state \( \hat{N}_\mu|\rho\rangle \) after measurement, consistently with the standard quantum measurement theory [3], must be defined as
\[ \hat{N}_\mu|\rho\rangle = \frac{\hat{J}_\mu|\rho\rangle}{\text{Tr}_S(1|\hat{J}_\mu|\rho\rangle)}. \] (13)
The vectorial superoperators \( \hat{J}_\mu \) determine the unnormalized transformation of \( |\rho\rangle \) due to the measurement action. As the underlying dynamics is defined by the fluorescent system and the configurational bath states, we introduced the subindex \( \mu \) for considering the possibility of having different measurement apparatus acting on each. When no measurement is performed over the configurational space, one must consider only one superoperator \( \hat{N}_\mu \) associated with the photon detection events, \( \mu \rightarrow \text{photon-detector} \) (see equations (42) and (69)).

When extra partial or complete information about the configurational transitions is available, the index \( \mu \) labels the corresponding measurement processes (see equations (A.2) and (A.10)). Consistently with the formulation of the standard quantum jump approach, equation (9) is discomposed as
\[ \frac{d|\rho_t\rangle}{dt} = \left( \hat{D} + \sum_\mu \hat{J}_\mu \right)|\rho_t\rangle. \] (14)

where \( \hat{D} \equiv \hat{L} - \sum_\mu \hat{J}_\mu \). In the Markovian case, i.e. when the configurational space is one dimensional, the (unique) superoperator \( \hat{J}_\mu \) is related to the wave vector collapse after a photon recording event, while \( \hat{D} \) defines the conditional dynamics between consecutive photon detections [1–3]. Here, the formalism must also take into account the fluctuations of the environment, i.e. the vectorial nature of \( |\rho_t\rangle \) and the existence of different channels (labelled by \( \mu \)) that may also provide information about the transitions between the bath states.

Equation (14) provides us the basis for characterizing the recording process. The following formulation is general, being independent of both the specific structure of equation (3) and the definition of the measurement channels \( \{\hat{N}_\mu\} \). Specific examples are worked out in section 4 and appendix A.

3.2. Statistics of the detection events

The statistic of the successive recording events can be obtained after writing the system dynamics as an integral over all possible measurement paths. The evolution (14) can formally be integrated as
\[ |\rho_t\rangle = e^{\hat{D}t}|\rho_0\rangle + \sum_\mu \int_0^t e^{\hat{D}(t-\tau)}\hat{J}_\mu|\rho_\tau\rangle d\tau, \] (15)

which can straightforwardly be rewritten in terms of the measurement operators \( \{\hat{N}_\mu\} \) as
\[ |\rho_t\rangle = P_0[t, 0; |\rho_0\rangle]\hat{T}(t, 0)|\rho_0\rangle + \sum_\mu \int_0^t P_0[t, \tau; \hat{N}_\mu|\rho_\tau\rangle]\hat{T}(t, \tau)\hat{N}_\mu|\rho_\tau\rangle F_\mu[|\rho_\tau\rangle] d\tau. \] (16)

Here, we have introduced the non-unitary propagator
\[ \hat{T}(t, \tau)|\rho\rangle \equiv \frac{e^{\hat{D}(t-\tau)|\rho\rangle}}{\text{Tr}_S(1|e^{\hat{D}(t-\tau)}|\rho\rangle)} \] (17)
and the scalar contribution
\[ F_\mu[|\rho\rangle] \equiv \text{Tr}_S(1|e^{\hat{D}(t-\tau)}|\rho\rangle). \] (18)

By associating the propagator \( \hat{T}(t, \tau) \) with the (vectorial) conditional system dynamics between consecutive recording events (photon detections or/and configurational transitions), the first line of equation (16) can be interpreted as the contribution of all measurement realizations where no detection event occurs up to time \( t \). Consistently, the weight \( P_0[t, \tau; |\rho_\tau\rangle] \) must be interpreted as the corresponding (survival) probability for not having any transition in the interval \( (\tau, t) \), given that the last one occurred at time \( \tau \), where the system state is \( |\rho_\tau\rangle \).

The second line (integral term) of equation (16) can be read as the contribution of all realizations where a measurement event occurs at time \( \tau \) (represented by the action of \( \hat{N}_\mu \) on \( |\rho_\tau\rangle \)) and no detection occurs up to time \( t \), which justifies the presence of \( \hat{T}(t, \tau) \) and the survival probability \( P_0[t, \tau; \hat{N}_\mu|\rho_\tau\rangle] \). Consistently, \( F_\mu[|\rho_\tau\rangle] \) must define the probability of having an event in the \( \mu \)-detector in the time interval \( (\tau, \tau + d\tau) \).

By expressing equation (16) as a sum over all possible measurement outcomes, the previous statistical interpretation can be explicitly demonstrated. By writing
\[ |\rho_t\rangle = \hat{G}(t)|\rho_0\rangle = \sum_{n=0}^\infty \hat{G}^{(n)}(t)|\rho_0\rangle. \] (20)
with $\hat{G}^{(0)}(t) = P_{0}(t, 0, |\rho_{0}\rangle)$, from equation (16) we obtain
\[
\hat{G}^{(m)}(t) = \sum_{\mu_{m}, \mu_{-m}} \int_{t_{m-1}}^{t} dt_{m} \cdots \int_{t_{2}}^{t} dt_{1} P_{n}[t_{n}, \{\mu_{i}\}^{n}] \\
\times \hat{T}(t_{n}, \tau_{n}; \nu_{m-1}, \{\mu_{i}\}^{n-1}) \cdots \hat{T}(t_{1}, \nu_{1}; \nu, \{\mu_{i}\}^{m}).
\] (21)

The intermediate states read
\[
|\rho_{i}\rangle_{\nu} = \hat{T}(t_{i+1}, \nu_{i}; \nu_{i+1}, |\rho_{i}\rangle),
\] (23)
with $|\rho_{i}\rangle_{\nu} = \hat{T}(t_{1}, 0; |\rho_{0}\rangle)$, while
\[
w_{\nu}[t, \tau; |\rho_{e}\rangle] = \text{Tr}_{S}(1|\hat{J}_{\mu}e^{\hat{H}(t-\tau)}|\rho_{e}\rangle).
\] (24)

Clearly, $\hat{G}^{(m)}(t)$ (equation (21)) can be associated with all trajectories where $n$-detection events occur up to time $t$, each at times $\{t_{i}\}^{n}_{i=1}$ in the $\{\mu_{i}\}^{n}$ detectors. The intermediate evolution between detection events $[\hat{M}_{\mu_{i}}]$ is given by $\hat{T}(t_{i+1}, \nu_{i}; \nu_{i+1})$. Consistently, $P_{n}[t, \{\mu_{i}\}^{n}]$ (equation (22)) defines the probability density of each trajectory. Thus, $w_{\nu}[t_{i}, \nu_{i-1}; \nu_{i}, \nu_{i+1}]$ can be read as the probability of having a detection event in the $\mu_{i}$-detector in the interval $(t_{i}, t_{i} + \Delta t_{i})$ given that the last detection event occurred at time $t_{i-1}$ in the $\mu_{i-1}$-detector, no event occurring in the interval $(t_{i-1}, t_{i})$.

By using the normalization of the vectorial state, $(d/d\tau)\text{Tr}_{S}[1|\rho_{e}\rangle] = 0$, from equation (14), the relation
\[
\text{Tr}_{S}[1|\rho_{e}\rangle] = -\sum_{\mu_{i}} \text{Tr}_{S}[|\hat{J}_{\mu_{i}}|\rho_{e}\rangle]
\] follows. Then, equation (18) can alternatively be written as
\[
P_{0}[t, \tau; |\rho_{e}\rangle] = 1 - \int_{0}^{t} w_{\nu}[t, \tau; |\rho_{e}\rangle] d\tau.
\] (25)

With this relation, we note that equation (22) has the same structure as a renewal process, i.e. there exists a probability distribution (waiting time distribution, $w_{\nu}[t, \tau; |\rho_{e}\rangle]$) that defines the statistics of the time interval between consecutive detection events. Nevertheless, here the waiting time distribution has a functional dependence on the system state following a detection event $[\hat{M}_{\mu_{i}}|\rho_{e}\rangle]$, which broke the renewal property.

By writing the states $|\rho_{i+1}\rangle$ (equation (23)) as
\[
|\rho_{i+1}\rangle = e^{\hat{H}(t_{i} - \tau_{i})} \hat{J}_{\mu_{i}}|\rho_{i}\rangle,
\] (26)
the $n$-joint probability density (22) can be rewritten as
\[
P_{n}[t, \{\mu_{i}\}^{n}] = \text{Tr}_{S}[1|e^{\hat{H}(t_{1} - \tau_{1})} \hat{J}_{\mu_{1}} \cdots e^{\hat{H}(t_{n} - \tau_{n})} \hat{J}_{\mu_{n}}|\rho_{0}\rangle].
\] (27)

This expression recovers the result of [33]. Note that its structure is similar to that obtained in the context of photon-measurement theory [1–3]. Nevertheless, here the underlying trajectories are vectorial and depend on the extra parameters $\mu_{i}, i = 1, \ldots, n$.

The probabilities $P_{n}(t)$ of having $n$-detection events up to time $t$ can be obtained by integrating the joint probability densities $P_{n}[t, \{\mu_{i}\}^{n}]$ over all possible detection paths:
\[
P_{n}(t) = \sum_{\mu_{m}, \mu_{-m}} \int_{0}^{t} dt_{m} \cdots \int_{0}^{t} dt_{1} P_{n}[t, \{\mu_{i}\}^{n}] \\
\times \hat{T}(t_{n}, \tau_{n}; \nu_{m-1}, \{\mu_{i}\}^{m-1}) \cdots \hat{T}(t_{1}, \nu_{1}; \nu, \{\mu_{i}\}^{m}).
\] (28)

In the context of SMS, objects of this kind are usually characterized through a generating function approach based on a stochastic Bloch equation [26–30]. Then, while the previous approaches are able to obtain these objects, the present treatment also allows us to obtain the underlying joint statistics defined by equation (22).

3.3. Stationary waiting time distributions

The joint probability density (equation (22)) is one of the central results of this section. It completely characterizes the statistics of the recording events. It can experimentally be determined from an ensemble average over measurement realizations having $n$-detection events in the interval $(0, t)$. Nevertheless, the stationary waiting time distributions (10) and (11) are defined by a time average along a single measurement realization. When the fluctuations of the environment are ergodic, objects of this nature can be studied by describing the measurement process after the occurrence of an infinite number of arbitrary recording events and that an infinite time elapsed since the initial condition, $|\rho_{0}\rangle$. By disregarding the information about the detector’s index in the stationary regime (first measured event), in appendix B we show that in that limit equation (22) remains valid under the replacement
\[
|\rho_{0}\rangle \rightarrow |\hat{\nu}(\rho_{\infty})\rangle,
\] (29)
where $|\rho_{\infty}\rangle$ corresponds to the stationary state
\[
|\rho_{\infty}\rangle = \lim_{t \to \infty} |\rho(t)\rangle.
\] (30)

It comes forth because a time-averaging procedure can only provide information about stationary observables. The measurement operator $\hat{M}$ is defined by
\[
\hat{M}(\rho) = \frac{\hat{J}(\rho)}{\text{Tr}_{S}[1|\hat{J}(\rho)|\rho_{\infty}\rangle]}, \quad \hat{J} \equiv \sum_{\mu_{i}} \hat{J}_{\mu_{i}},
\] (31)
and takes into account the occurrence of an arbitrary measurement event in the long-time regime. With these definitions, from equation (22) we introduce the first stationary waiting time distribution
\[
w_{\nu}^{(1)}(\tau, \mu) \equiv w_{\nu}[\tau, 0; \hat{M}(\rho_{\infty})],
\] (32)
as well as the second-order stationary waiting time distribution
\[
w_{\nu}^{(2)}(\tau_{2}, \mu_{2}; \tau_{1}, \mu_{1}) \equiv w_{\nu}[\tau_{2} + \tau_{1}, \tau_{1}; \hat{M}(\rho_{\infty})]w_{\nu}[\tau_{1}, 0; \hat{M}(\rho_{\infty})],
\] (33)
Higher objects, $w_{\nu}^{(n)}[\{\tau_{i}\}^{n}, \{\mu_{i}\}^{n}]$, can be written in a similar way. They define, in the stationary regime, the probability density of the time intervals $[\tau_{i}]^{n}$ between successive recording events occurring in the $\{\mu_{i}\}^{n}$ detectors. When the measurement process only involves a photon detector apparatus, $\mu \rightarrow$ photon-detector, equations (32) and (33) allow us to obtain analytical expressions for the distributions (10) and (11), respectively (see section 4).
3.4. Stochastic density matrix evolution

From the previous analysis, we obtained the statistic of the recording events associated with the density matrix evolution (equation (14)). The quantum-jump approach also allows building up the underlying stochastic dynamics that reproduce that statistic. The key ingredient is the definition of a stochastic process developing in the system Hilbert space and whose realizations can be mapped with the realizations of the measurement apparatus signals. The average over realizations must recover the system density matrix evolution. Then, in the present context we search for the definition of a stochastic vector \(|\rho^\mu_t\rangle\), such that \(|\bar{\rho}^\mu\rangle = |\rho_t\rangle\), where \(|\rho_t\rangle\) is defined by the evolution (14). From now on, the overbar denotes (ensemble) averaging over realizations.

Based on the path integral solution obtained previously (equation (20)), the stochastic evolution can be written as piecewise deterministic processes [3]:

\[
\frac{d}{dt} |\rho^\mu_t\rangle = \left[ \hat{D} - \text{Tr}_{s} (1|\hat{D}|\rho^\mu_t\rangle) \right] |\rho^\mu_t\rangle + \sum_{\mu} (\hat{\mathcal{N}}_{t_0} - 1) |\rho^\mu_t\rangle \frac{dN^\mu_t}{dt}, \tag{34}
\]

Here, the deterministic nonlinear term (first contribution on the rhs) corresponds to the conditional evolution in the intervals between consecutive measurement events, i.e. the dynamics defined by equation (17). On the other hand, the second term introduces the disruptive changes in the vectorial state after a measurement event, i.e. \(|\rho^\mu_t\rangle \rightarrow \hat{M}_\mu |\rho^\mu_t\rangle\). Consistently, the noisy terms are defined by \(dN^\mu_t\frac{d}{dt} \equiv \sum_{k} \delta(t - t^*_k)\), where \(t^*_k\) are the times where a measurement event occurs in the \(\mu\)-detector. By denoting with \(N^\mu_t\) the number of detection events up to time \(t\), it follows the alternative definition \(\frac{dN^\mu_t}{dt} = (N^\mu_{t', 0} - N^\mu_t)\), i.e. \(dN^\mu_t\) are the increments of the (Poisson) process \(N^\mu_t\) [3]. In agreement with the previous analysis, their average must recover equation (19), i.e.

\[
\frac{d}{dt} \text{Tr}_{s} (1|\hat{D}|\rho^\mu_t\rangle) = \text{Tr}_{s} (1|\hat{D}|\rho^\mu_t\rangle) \frac{d}{dt} |\rho^\mu_t\rangle. \tag{35}
\]

By using the property \(dN^\mu_t\frac{d}{dt} dN^\nu_t = \delta_{\mu\nu} dN^\mu_t\frac{d}{dt} dN^\mu_t\), which implies that a simultaneous detection in two different measurement apparatus is never observed and that \(\frac{dN^\mu_t}{dt} = dN^\mu_t\), in appendix C we show that equation (14) is recovered after averaging equation (34) over realizations.

The realizations associated with equation (34) can easily be determined after providing a recipe for calculating the random times where the detection events occur. Their numerical calculation relies on evaluating the statistical objects introduced in equation (16) along each trajectory. Given that the system is in the state \(|\rho^\mu_t\rangle\), the quantity \(\frac{d}{dt} \text{Tr}_{s} (1|\hat{D}|\rho^\mu_t\rangle)\) gives the probability of having an event in the \(\mu\)-detector in the time interval \((t, t + dt)\). This quantity defines an infinitesimal time step algorithm (see appendix D). In a similar way, \(P_0[t, t'; \hat{M}_\mu |\rho^\mu_t\rangle]\) (equation (18)) define the survival probability for the next detection event (at time \(t\)) given that a \(\mu\)-detection event occurred at time \(t'\). This object allows us to define a finite time step algorithm (see appendix D).

Independently of the method (algorithm) used to determine the times of the recording events (transitions), given that at time \(t\) measurement occurs, \(|\rho^\mu_t\rangle \rightarrow \hat{M}_\mu |\rho^\mu_t\rangle\), each transformation \(\hat{M}_\mu\) (equation (13)) must be chosen with the probability

\[
I_\mu(t) = \frac{F_\mu (|\rho^\mu_t\rangle)}{\sum_{\mu} F_\mu (|\rho^\mu_t\rangle)} = \frac{\text{Tr}_{s} (1|\hat{M}_\mu |\rho^\mu_t\rangle)}{\sum_{\mu} \text{Tr}_{s} (1|\hat{M}_\mu |\rho^\mu_t\rangle)}, \tag{36}
\]

which satisfies \(\sum_{\mu} I_\mu(t) = 1\). This rule corresponds to a selective measurement of the set of \(\mu\)-observables [3]. Between successive recording events, the evolution of \(|\rho^\mu_t\rangle\) is deterministic and defined by equation (17).

Through the relations

\[
\rho^\mu_S(t) = \text{Tr}_{s} (1|\hat{D} |\rho^\mu_t\rangle), \quad \rho^\mu(t) = \sum_{\mu} \text{Tr}_{s} (1|\hat{M}_\mu |\rho^\mu_t\rangle).
\]

(37)

the vectorial state \(|\rho^\mu_t\rangle\) provides a stochastic representation of both the system density matrix (equation (1)), \(\bar{\rho}^\mu(t)\) = \(\rho^\mu_S(t)\), and the occupation of the configurational bath states (equation (2)), \(\bar{R}P^{\nu}(t) = P^{\nu}(t)\). In contrast with the standard quantum-jump approach, in general it is not possible to obtain a simple dynamical evolution for \(\rho^\mu_S(t)\) (or to \(\bar{R}P^{\nu}(t)\)). In fact, here the formalism relies on the vectorial nature of \(|\rho^\mu_t\rangle\) (however see also appendix A).

3.5. Non-renewal recording realizations

The trajectories associated with equation (34) allow us to establish a simple scheme for understanding the non-renewal nature of the recording process. In fact, its underlying structure is similar to that of a renewal one. Given that the last event occurred at time \(t'\) in the \(\mu\)-detector, the random time \(t\) for the next event is defined by a waiting time distribution \(w_\mu(t, t', \mu)\), which reads

\[
w_\mu(t, t', \mu) \equiv -\frac{d}{dt} \rho^\mu_S(t, t'; \hat{M}_\mu |\rho^\mu_t\rangle), \quad \rho^\mu_S(t, t'; \hat{M}_\mu |\rho^\mu_t\rangle) = \text{Tr}_{s} (1|\hat{D} |\rho^\mu_t\rangle). \tag{38a}
\]

\[
= -\text{Tr}_{s} (1|\hat{D} |\rho^\mu_t\rangle) \frac{d}{dt} \rho^\mu_S(t, t'; \hat{M}_\mu |\rho^\mu_t\rangle), \tag{38b}
\]

By using the relation \(\text{Tr}_{s} (1|\hat{D} |\bullet\rangle) = -\sum_{\mu} \text{Tr}_{s} (1|\hat{J}_\mu |\bullet\rangle)\), it follows that

\[
w_\mu(t, t', \mu) = \text{Tr}_{s} (1|\hat{J}_\mu e^{\hat{H}(t' - t)} \hat{M}_\mu |\rho^\mu_t\rangle), \tag{39}
\]

where \(\hat{J}_\mu = \sum_{\nu} \hat{J}_\mu\) (equation (31)). At time \(t\), \(|\rho^\mu_t\rangle\) is updated with the conditional evolution (equation (17)) and the new recording event is selected with probabilities (36). The next events follow from the same rule (see appendix D). The average over realizations recovers the statistic defined by equation (22).

The departure of the recording realizations with respect to a renewal process comes from the dependence of \(w_\mu(t, t', \mu)\) on \(|\rho^\mu_t\rangle\). Only if \(\hat{M}_\mu |\rho^\mu_t\rangle\) is independent of \(|\rho^\mu_t\rangle\), one obtains a renewal recording process. Nevertheless, in general this does not occur, implying that \(w_\mu(t, t', \mu)\) randomly change between successive events. Then, in contrast with a renewal process, here the successive events are defined by a stochastic waiting time distribution that parametrically depends on the vectorial state \(|\rho^\mu_t\rangle\). Finally, we note that \(w_\mu(t, t', \mu)\) can consistently be written as \(w_\mu(t, t', \mu) = \sum_{\nu} w_{\nu}(t, t'; \hat{M}_\mu |\rho^\mu_t\rangle)\), where \(w_{\nu}(t, t'; \rho)\) is defined by equation (24).
4. Photon emission measurements

In the previous sections, we developed a general theory that allows us to characterize the measurement processes associated with a broad class of physical situations arising in SMS. The theory depends on which kind of measurement process is performed over both the system and the configurational states. In this section, we analyse the situation where there exists only one measurement process defined by a photon detector apparatus coupled to the scattered electromagnetic field. This is the standard situation in SMS, where any direct information about the configurational space is unavailable. Then, the parameter \( \mu \) includes only one term corresponding to the photon detector. Furthermore, our formalism is able to describe different kinds of environmental fluctuations. First, we analyse the case of self-fluctuating environments, i.e. when the transitions between the configurational states do not depend on the state of the system. As a second leading case, we analyse environmental fluctuations that depend on the intensity of the laser excitation.

4.1. Self-fluctuating environments

This case is covered by equation (3) by taking \( A = I \).

\[
\frac{d \rho_R(t)}{dt} = -\frac{i}{\hbar} [H_R, \rho_R(t)] - \gamma_R (\{D, \rho_R(t)\}_+ - J[\rho_R(t)]) - \sum_{R'} \phi_{R'RR} \rho_{R'R}(t) + \sum_{R'} \phi_{RR'R} \rho_{RR'}(t). \tag{40}
\]

For notational consistency we take \( \gamma_{RR} \to \Phi_{RR} \) [31]. From equation (40), the evolution of populations (equation (2)) is given by

\[
\frac{d}{dt} P_R(t) = -\sum_{R'} \phi_{R'R} P_{R'}(t) + \sum_{R'} \phi_{RR'} P_{R'}(t). \tag{41}
\]

Hence, the stochastic dynamics between the configurational states is governed by a classical master equation that does not depend on the state of the system. This case allows us to describe processes such as spectral fluctuations, lifetime fluctuations and molecules diffusing in a solution.

4.1.1. Photon-measurement operator

The measurement operator, equation (13), must take into account all contributions that, independently of the R-state of the reservoir, lead to a photon emission. Then, from equation (40), we write (\( \mu \to \text{ph} \)) \( |\rho\rangle = \sum_R |R\rangle \rho_R \):

\[
\hat{\mathcal{M}}_{\text{ph}} |\rho\rangle = \frac{\hat{J}_{\text{ph}} |\rho\rangle}{\text{Tr}_{S} (|\hat{J}_{\text{ph}} |\rho\rangle)} = \sum_R \gamma_R |R\rangle \sigma \rho \sigma^\dagger / \text{Tr}_{S} (\sigma^\dagger \sigma |\rho\rangle). \tag{42}
\]

Note that each contribution in the sum corresponds to the standard definition arising in Markovian fluorescent systems [1–3], i.e. \( \mathcal{M}_{\text{ph}} \rho = \sigma \rho \sigma^\dagger / \text{Tr}_{S} (\sigma^\dagger \sigma |\rho\rangle) \). The vectorial superoperator \( \hat{D} \) (equation (14)) here is defined from

\[
\hat{D} = \hat{\mathcal{L}} - \hat{J}_{\text{ph}}. \tag{43}
\]

where \( \hat{\mathcal{L}} \) follows from equations (9) and (40), while \( \hat{J}_{\text{ph}} \) from equation (42). Alternatively, \( \hat{D} \) can be explicitly defined through the non-unitary evolution generated by it:

\[
\frac{d}{dt} (R |\rho^u\rangle) = (R |\hat{D} |\rho^u\rangle), \tag{44}
\]

where the index \( u \) states that the auxiliary vector \( |\rho^u\rangle \) is not normalized to 1. In fact, its norm is related to the survival probability (equation (18)). By denoting \( \rho^u_R(t) = (R |\rho^u\rangle) \), we obtain

\[
\frac{d \rho^u_R(t)}{dt} = -\frac{i}{\hbar} [H_R, \rho^u_R(t)] - \gamma_R \{D, \rho^u_R(t)\}_+ + \sum_{R'} \phi_{R'R} \rho^u_{R'R}(t) + \sum_{R'} \phi_{RR'} \rho^u_{RR'}(t). \tag{45}
\]

The previous splitting relies on the assumption of a perfect photon detection efficiency. The extension to the case in which the detector efficiency \( \eta \) is less than 1 follows from the replacements [1, 2, 5]:

\[
\hat{D} \to \hat{D} + (1 - \eta) \hat{J}_{\text{ph}}, \quad \hat{J}_{\text{ph}} \to \eta \hat{J}_{\text{ph}}. \tag{46}
\]

Then, the superoperator \( \hat{\mathcal{M}}_{\text{ph}} \), equation (42), remains the same, while the conditional evolution, equation (45), is redefined with an extra diagonal contribution, \((1 - \eta) \gamma_R \sigma \rho \sigma^\dagger \). For simplifying the presentation, in the following analysis we will assume \( \eta = 1 \).

4.1.2. Stochastic dynamics

Having the definition of the superoperators \( \hat{\mathcal{M}}_{\text{ph}} \) and \( \hat{D} \) we can apply the theory developed in the previous section. The dynamics of the stochastic state \( |\rho^u\rangle \) follows from equation (34). The disruptive transformation associated with a photon detection event, \( |\rho^u\rangle \to \hat{\mathcal{M}}_{\text{ph}} |\rho^u\rangle \), from expression (42), and by using \( \sigma = |\cdot \rangle \langle +|, \sigma^\dagger = |\cdot \rangle \langle -| \), can explicitly be written as

\[
|\rho^u\rangle \to \hat{\mathcal{M}}_{\text{ph}} |\rho^u\rangle = |\cdot \rangle \langle -| \sum_R p^u_R(t) |R\rangle. \tag{47}
\]

Here, the weights \( \{p^u_R(t)\} \) satisfy the normalization \( \sum_R p^u_R(t) = 1 \), and are defined as

\[
p^u_R(t) = \frac{\gamma_R (|\cdot \rangle \langle +| + |\cdot \rangle \langle -|)}{\sum_R \gamma_R (|\cdot \rangle \langle +| + |\cdot \rangle \langle -|)}. \tag{48}
\]

where the notation \( \rho^u_R(t) \to (R |\rho^u\rangle) \) was used. From equations (37) and (47), it is easy to obtain

\[
\rho^u_R(t) \to (R |\rho^u\rangle) = |\cdot \rangle \langle -| \sum_R p^u_R(t) |R\rangle. \tag{49}
\]

and that

\[
(R |\rho^u\rangle) \to |\rho^u\rangle = \text{Tr}_{S} (|R\rangle \hat{\mathcal{M}}_{\text{ph}} |\rho^u\rangle) = p^u_R(t). \tag{50}
\]

Equation (49) shows that in fact after a photon detection event the system collapses to its lower state \( |\cdot \rangle \). On the other hand, equation (50) states that \( p^u_R(t) \) is the value of the configurational populations after a photon recording event.

Between the detection events the stochastic dynamics is given by the conditional evolution defined by the superoperator \( \hat{D} \) (equations (43) and (45)). On the other hand, as there exists only one measurement apparatus, the weights \( \{p_R(t)\} \), equation (36), here reduce to \( p_R(t) = 1 \).

In the next figures, we consider a fluorophore system coupled to an environment characterized by a two-dimensional configurational space, \( R = A, B \), which only affects the decay rates \( \gamma_R \) of the system, i.e. the Rabi frequencies (equation (4)) do not depend on the configurational states, \( \Omega_A = \Omega_B \), and the spectral shifts (equation (5)) are null, \( \delta_{0A} = 0 \). Furthermore, the laser is in resonance with the system, i.e. \( \omega_L = \omega_0 \).
In figure 1(a) we show a realization of the upper population of the system \( |+\rangle |\rho_S(t)\rangle + \rangle \) (equation (37)). The realizations were determined by using the finite time step algorithm defined in appendix D. Each collapse of the upper population to zero is related to a photon emission (see equation (49)).

In figure 1(b), we show the realization of the configurational population \( \langle R | P^u \rangle \) for \( R = A \) (equation (37)). As the configurational space is two dimensional, \( \langle A | P^u \rangle + \langle B | P^u \rangle = 1 \). We remark that these realizations are associated with a measurement process that only gives information about the photon emission events. No information is provided about the configurational states of the bath. Therefore, the realizations of \( \langle R | P^u \rangle \) are the best estimation [39] about the configurational state of the reservoir that can be obtained by knowing the master equation (40) and a given realization of the photon detector apparatus.

In figure 1(c) we plot \( \langle R | P^u \rangle \) (for \( R = A \)) over a larger time interval. For the chosen parameter values, the configurational populations develop a quasi-dichotomic behaviour. When \( \langle R | P^u \rangle \approx 1 \), we can affirm that it is highly probable that the bath is in the configurational state \( |R\rangle \).

In figure 1(d), we plot the scattered intensity, which is defined by \( I(t) = [n(t + \delta t) - n(t)]/\delta t \), where \( n(t) \) is the number of photon recording events up to time \( t \) and \( \delta t \) is an adequate time flag averaging. Its fluctuations are highly correlated with the values of \( \langle R | P^u \rangle \). In fact, the intensity fluctuates around two well-defined values \( I_R \), which are defined by the intensity of a Markovian fluorescent system [1–3] characterized by the parameters corresponding to each configurational state [31], i.e.

\[
I_R = \frac{\gamma_R \Omega_R^2}{\gamma_R^2 + 2 \Omega_R^2 + 4 \delta_R^2},
\]

where \( \delta_R = \Delta - \omega_R \). The dichotomic behaviour arises because the system is able to emit a large number of photons before the occurrence of a transition between the configurational bath states, i.e. \( \sum_R \phi_{RR} \ll I_R \).

In figure 2(a) we plot the upper population \( |+\rangle |\rho_S(t)\rangle + \rangle \) that follows from equation (40), as well as an average over \( \approx 10^3 \) realizations of \( |+\rangle |\rho_S^u(t)\rangle + \rangle \) (see figure 1(a)). In figure 2(b), we plot the analytical solution of the configurational populations \( \langle R | P_r \rangle \) defined by equation (41) as well as an average over realization of \( \langle R | P^u \rangle \) (see figures 1(b) and (c)). In both cases the ensemble averages recover the dynamics dictated by the corresponding master equations, showing the consistency of the developed approach.
4.1.3. Photon emission process. The recording events are characterized by the stochastic waiting time distribution (39). Then, we write

\[ w_{st}(t, t') = \text{Tr}_{s} \left[ \langle 1 | \hat{J}_s e^{\hat{H}_{t-t'}^{\nu} - \nu} \hat{M}_{ph} | p^o_{R} \rangle \right] \]  

(52)

Note that here \( \hat{J}_s \equiv \hat{J}_{ph} \). The function \( w_{st}(t, t') \) defines the statistics of the time intervals between consecutive photon emissions. From equations (42) and (47) it follows that

\[ w_{st}(t, t') = \sum_{R} \gamma_{R} \langle + | e^{\hat{H}_{t-t'}^{\nu} R} [(-|p^o_{R}(t')\rangle] [+]. \]  

(53)

This expression allows us to obtain an analytical expression for \( w_{st}(t, t') \) (not provided due to its extension) that parametrically depends on the set \( \{ p^o_{R}(t') \} \), equation (48).

As the set of weights \( \{ p^o_{R}(t') \} \) corresponds to the configurational populations after a photon recording event (see equation (50)), the waiting time distribution changes between consecutive photon emissions. The successive (stochastic) values of \( \{ p^o_{R}(t') \} \) can be read from the realization of \( \{ R | P^o_{R} \} \) shown in figure 1(b). Note that in each event, defined by the collapses \( ( + | p^o_{R}(t') \rangle + \rightarrow 0 \) (figure 1(a)), \( \{ R | P^o_{R} \} \) suffer an abrupt change in its slope.

In figure 3(a), we plot \( w_{st}(t, t') \) (as a function of \( t - t' \)) for different values of \( p^o_{R}(t') \). As the configurational space is two dimensional, the two parameters satisfy the normalization \( p^o_{A}(t') + p^o_{B}(t') = 1 \). We note that \( w_{st}(t, t') \) has a strong dependence on the values of the configurational populations \( \{ p^o_{R}(t') \} \), which in turn state that the photon emission process strongly departs from a renewal one. For Markovian (two-level) fluorescent systems, the set \( \{ p^o_{R}(t') \} \) reduces only to one parameter with a value equal to 1 (the configurational space is one dimensional). Therefore, \( w_{st}(t, t') \) is the same object along a measurement trajectory, recovering a renewal process.

4.1.4. Stationary waiting time distributions. By measuring the time intervals between successive photon emissions along a given trajectory one can determine the stationary waiting time distribution (10). The analytical expression for this object can be read from equation (32). We obtain

\[ w^{(1)}(\tau) = \sum_{R} \gamma_{R} \langle + | e^{\hat{H}_{R}^{\nu} \tau} [-] (-| p_{R}^{\infty} \rangle | +) \]  

(54)

where the weights \( p_{R}^{\infty} \) are defined from the relation

\[ \hat{N}_{ph} | \rho_{\infty} \rangle = [-] (-| \sum_{R} p_{R}^{\infty} | R \rangle \]  

(55)

delivering the expression

\[ p_{R}^{\infty} = \frac{\gamma_{R} \langle + | \rho_{\infty}^{\infty} \rangle +}{\sum_{R} \gamma_{R} \langle + | \rho_{R}^{\infty} \rangle +} \]  

(56)

Here, \( \rho_{R}^{\infty} \equiv \lim_{\nu \to \infty} \rho_{R}(\nu) = \langle R | \rho_{\infty} \rangle \) (equation (30)). By comparing equation (54) with equation (53), we realize that \( w^{(1)}(\tau) \) follows from \( w_{st}(t, t') \) after the replacements \( p_{R}^{o}(t') \rightarrow p_{R}^{\infty} \) and \( (t - t') \rightarrow \tau \).

In figure 3(b) we plot the analytical expression for \( w^{(1)}(\tau) \) that follows from equation (54). Furthermore, we show a numerical distribution determined from the time average (10). The theoretical distribution correctly fits the numerical result. Consistently, we also checked that the time average of \( \{ p_{R}^{\infty}(t') \} \) along a single trajectory recovers the weights \( \{ p_{R}^{\infty} \} \), equation (56).

The analytical expression for the second waiting time distribution (equation (11)) can be obtained from equation (33), delivering

\[ w^{(2)}(\tau_2, \tau_1) = \sum_{R} \gamma_{R} \langle + | e^{\hat{H}_{R}^{\nu} \tau_2} [-] (-| \varphi_{R}(\tau_1) \rangle | +), \]  

(57)

where the functions \( \varphi_{R}(\tau_1) \) read

\[ \varphi_{R}(\tau_1) = \gamma_{R} \sum_{R} \langle + | e^{\hat{H}_{R}^{\nu} \tau_1} [-] (-| p_{R}^{\infty} \rangle | +). \]  

(58)

In figure 4(a) we plot the analytical expression for \( w^{(2)}(\tau_2, \tau_1) \) that follows from equation (57) for different values of \( \tau_1 \). Furthermore, we show the numerical result that follows by determining the probability distribution of two consecutive time intervals between successive photon emissions along a single trajectory, equation (11). The theoretical result correctly fits the numerical distribution.

In figure 4(b) we plot the dimensionless parameter \( \Lambda(\tau_2, \tau_1) \) (equation (12)) determined from equations (54) and (57), for different values of \( \tau_1 \). For almost all values of \( \tau_2 \) and \( \tau_1 \), \( \Lambda(\tau_2, \tau_1) \) departs appreciably from zero, indicating the departure of the photon emission process from a renewal one. We also note that there exist special values of the consecutive
different values of $\tau$ (equation (12)) determined from equations (54) and (57), for the parameters are the same as in figure 1. From top to bottom we take $\Omega_1/\omega_1\tau$ than the average time between photon emissions, $\{w(t)\}$. Figure 4.

4.1.5. Slow and fast environmental fluctuations. The expressions for the stochastic waiting distribution $w_{st}(t, t')$ (equation (53)), and the first ($w_{st}(t)$, equation (54)) and second ($w_{st}(t_2, t_1)$, equation (57)) stationary waiting time distributions allow us to characterize the photon emission process as well as its departure with respect to a renewal one. Here, we provide simple analytical expressions for these objects in the limit of both fast and slow environmental fluctuations.

The characteristic time of the bath fluctuations is measured by the rates $\{\phi_{RR}\}$, equations (40) and (41). On the other hand, the average time between photon emissions is measured by the inverse of the intensities $\{I_R\}$, equation (51). When the bath fluctuations are much slower than the average time between photon emissions, $\{\phi_{RR}\} \ll \{I_R\}$, it is valid to approximate the conditional evolution defined by the superoperator $\hat{D}$ (equations (43) and (44)) as

$$
\hat{D}_{RR}^{(t-t')}\left[|\phi|^2\right] \approx \delta_{RR}^{(t-t')}\left[|\phi|^2\right] = \delta_{RR}^{(t-t')}\left[|\phi|^2\right].
$$

Time intervals where $\Lambda(t_2, t_1) = 0$. From the definition (12), we deduce that when $\Lambda(t_2, t_1) > 0$, the frequency of the successive intervals $t_1$ and $t_2$ is greater than that in the renewal case. The situation $\Lambda(t_2, t_1) < 0$ admits the inverse interpretation. For clarifying the structure of both $w_{st}^{(1)}(t_2, t_1)$ and $\Lambda(t_2, t_1)$, we show their contour plots in figure 5. As can be deduced from figures 4 and 5, $\Lambda(t_2, t_1)$ reaches its maximal values for higher values of both $t_2$ and $t_1$.

This approximation corresponds to disregarding the non-diagonal contributions between photon recording events. By inserting this condition in equation (53) we obtain

$$
w_{st}(t, t') \simeq \sum_R \gamma_R \{e^{\phi_{RR}(t-t')}|\rangle -$$. (59)

Then, $w_{st}(t, t')$ can be written as a linear combination of the waiting time distributions $\{w_R(t)\}$, each being defined by the expression

$$
w_R(t) = \gamma_R \{e^{\phi_{RR}(t-t')}|\rangle -$$. (60)

This function corresponds to the waiting time distribution associated with a Markovian fluorescent system [1, 5] with decay rate $\gamma_R$, and whose Hamiltonian is given by $\hat{H}_R$, equation (4), i.e. its transition frequency is $\omega_R = (\omega_0 + \delta \omega_R)$, and its coupling to the external laser is measured by $\Omega_R$. This result can straightforwardly be read from equations (44) and (45) under the replacement $\phi_{RR} \to 0$. In the Laplace domain, $t \to u$, it can be written as [34]

$$
w_R(u) = \frac{\gamma_R/2}{u + \gamma_R/2} \left( \frac{\Omega_R^2 h_R(u)}{u^2 + u\gamma_R + \Omega_R^2 h_R(u)} \right).
$$

\[ (61) \]
where the auxiliary function \( h_R(u) \) is
\[
h_R(u) = \frac{(u + \gamma_R/2)^2}{(u + \gamma_R/2)^2 + \delta_R},
\]
and \( \delta_R = \omega_L - \omega_R \). After the Laplace inversion, we obtain
\[
w_R(t) = \frac{2\gamma_R\Omega_R^2}{\xi_R} \exp(-\gamma_R t/2) \left[ \cosh(\xi_R t) - \cosh(\xi_R t) \right].
\]
(64)

where \( \xi_R = \left\{ \frac{\gamma_R^2 - 4(\Omega_R^2 + \delta_R^2) \pm \xi_R}{2\sqrt{2}} \right\}^{1/2} \), with \( \xi_R = \left\{ (\gamma_R^2 + 4(\Omega_R^2 + \delta_R^2))^2 - 16\gamma_R^2\Omega_R^2 \right\}^{1/2} \). When \( \delta_R = 0 \), the expression of \([1, 5]\) is recovered.

We have checked that equation (60) combined with equation (64) provides an excellent approximation to the exact functions plotted in figure 3(a). On the other hand, equation (59) is also useful for approximating the stationary waiting time distributions. Equation (54) leads to
\[
w^{(1)}(\tau) \simeq \sum_R w_R(\tau) \rho_R^\infty,
\]
while from equation (57), we obtain
\[
w^{(2)}(\tau_2, \tau_1) \simeq \sum_R w_R(\tau_2)w_R(\tau_1) \rho_R^\infty.
\]
(65)
(66)

Furthermore, under the hypothesis of slow fluctuations, from equation (40) we can approximate \( \gamma_R(\pm|\rho_R^{\infty}|) \simeq I_R \rho_R^\infty \). The constants \( I_R \) (equation (51)) are the intensities associated with each configurational state \( R \). On the other hand, \( P_R^\infty \) are the stationary values of the configurational populations equation (41), i.e. \( P_R^\infty \equiv \lim_{t \to \infty} P_R(t) \). Therefore, from equation (56) we obtain the approximate expression
\[
P_R^\infty \simeq \frac{I_R \rho_R^\infty}{\sum_R I_R \rho_R^\infty}.
\]
(67)

Equations (65)–(67) also provide an excellent approximation to the exact analytical results plotted in figures 3–5. Moreover, they have a clear physical meaning. In the slow limit each bath state establishes an intensity regime defined by equation (51). Hence, the statistics of the non-renewal photon emission process follows from an average of the renewal statistics associated with each state (defined by \( w_R(\tau) \)). The weight of each contribution is \( \rho_R^\infty \). Consistently, these factors, which are the average configurational populations after a detection event (equation (55)), are proportional to the intensities \( I_R \) and the stationary populations \( P_R^\infty \) related to each bath state.

Equation (66) also allows us to interpret the structure of \( \Lambda(\tau_2, \tau_1) \) shown in figures 4 and 5. Note that consistently with that equation, this argument, as well as \( w^{(2)}(\tau_2, \tau_1) \), is symmetric in its time arguments, \( \Lambda(\tau_2, \tau_1) = \Lambda(\tau_1, \tau_2) \). Its behaviour at short times is related to the antibunching property inherited from the waiting time distributions \( w_R(\tau) \). On the other hand, \( \Lambda(\tau_2, \tau_1) \) reaches its maximal value for higher values of both \( \tau_2 \) and \( \tau_1 \). Its contour plot always reaches a plateau regime characterized by the value \( \Lambda_\infty \equiv \lim_{\tau_2, \tau_1 \to \infty} \Lambda(\tau_2, \tau_1) \). These properties arise because in the long-time regime \( (\int_0^\infty t w_R(t) dt) \), each waiting time distribution can be approximated by an exponential behaviour, \( w_R(\tau) \simeq I_R \exp[-I_R \tau] \), where the constants \( I_R \)

are defined by \( I_R^{-1} = \int_0^\infty t w_R(t) dt = -(d/d\tau)\ln w_R(\tau)|_{\tau=0} \), i.e. equation (51). Furthermore, from equations (65) and (66), in combination with the definition of \( \Lambda(\tau_2, \tau_1) \), equation (12), one can obtain \( \Lambda_\infty \equiv \langle p_R^\infty \rangle^{-1} - 1 \), where \( p_R^\infty \) is defined by equation (67), and \( R_c \) is the value of \( R \) such that \( I_R \) is the minimal value of the set \( \{I_R\}_{R_c} \). For the example defined by the parameters of figure 1, we obtain \( R_{c} = B \), delivering \( \Lambda_\infty \approx 1.1 \), which correctly fits the plateau regime of \( \Lambda(\tau_2, \tau_1) \), the upper-right corner of figure 5.

When the bath fluctuations are much faster than the average time between photon emissions, \( \{\rho_R \} \gg \{I_R \} \), the configurational populations reach their stationary values, \( P_R^\infty = \lim_{t \to \infty} P_R(t) \), before the occurrence of many photon emissions. Hence, the fluorophore behaves like a Markovian fluorescent system with the decay rate \( \bar{\gamma} \equiv \sum_R \gamma_R P_R^\infty \), Rabi frequency \( \bar{\Omega} \equiv \sum_R \Omega_R P_R^\infty \) and detuning \( \delta \equiv \sum_R \delta_R P_R^\infty \). The photon emission process becomes a renewal one, being defined by the waiting time distribution (64) with \( \{\gamma_R, \Omega_R, \delta_R \} \rightarrow \{\bar{\gamma}, \bar{\Omega}, \bar{\delta} \} \). Near this limit, for two-dimensional configurational spaces, \( w^{(2)}(\tau_2, \tau_1) \) develops small asymmetries on its arguments \( w^{(2)}(\tau_2, \tau_1) \neq w^{(2)}(\tau_1, \tau_2) \). In general, this property may arise in the intermediate regime between fast, \( w^{(1)}(\tau_2, \tau_1) \simeq w^{(2)}(\tau_2, \tau_1)w^{(2)}(\tau_1, \tau_2) \), and slow bath fluctuations, equation (66).

The previous results can be extended to the case in which the photon detector efficiency is less than 1, \( \eta < 1 \), equation (46). From equation (59), we deduce that the analysis for slow environmental fluctuations remains the same after the replacement \( w_R(\tau) \rightarrow \eta w_R^\eta(\tau) \), where \( w_R^\eta(\tau) \) is the photon waiting time distribution of a Markovian system, with parameters corresponding the bath state \( R \), in the presence of a detector with efficiency \( \eta \) [5]. The limit of fast environmental fluctuations is redefined in a similar way.

The configurational fluctuations are frozen when equation (40) is defined with \( \{\rho_R \} = \{0 \} \). This case was partially addressed in [34, 35]. Our present treatment provides a general description. Evidently, the configurational populations remain unaffected during all the evolution, \( |P_\eta \rangle = |P_0 \rangle \). The results of [34, 35] follow from the approximation \( |P_\eta \rangle \approx |P_0 \rangle \), which is valid in a weak laser intensity regime and when the dynamics develops two different time scales induced by an infinite-dimensional configurational space.

4.2. Light-assisted environmental fluctuations

The general evolution (3) may also cover the case in which the statistical properties of the radiation pattern as well as the environmental fluctuations depend on the external laser intensity [31, 36], i.e. light-assisted processes. By taking \( \Lambda = \sigma, \) and \( \eta_{RR} \rightarrow \gamma_R \), we write
\[
\frac{d \rho_{\eta}(t)}{dt} = \frac{-i}{\hbar} \left[ H_{\eta}, \rho_{\eta}(t) \right] - \gamma_{\eta}(|D, \rho_{\eta}(t)\rangle_\eta - \mathcal{J}[\rho_{\eta}(t)])
\]
\[ - \sum_R \gamma_{R}\langle D, \rho_{\eta}(t)\rangle_\eta + \sum_R \gamma_{RR} \mathcal{J}[\rho_{\eta}(t)].
\]
(68)
divided by \( D \) and \( \mathcal{J} \) follow from equation (6). We remark that this kind of equations provides a generalization of triplet blinking models [12, 31, 36], where the system is incoherently
coupled to an extra (dark) state. The evolution of the configurational populations (equation (2)) that follows from equation (68) strongly depends on the state of the system. In fact, here the configurational transitions may only occur when a photon emission occurs. Thus, in general it is not possible to write a simple equation for their evolution. Only when \( \gamma_{RR} \ll \gamma_{\delta} \), a classical rate equation similar to equation (41) can be derived [31, 36].

4.2.1. Photon-measurement operator. Here, the photon-measurement superoperator \( \hat{N}_{\text{ph}}(\rho) = \hat{J}_{\text{ph}}(\rho)/Tr_{S}(1|\hat{J}_{\text{ph}}|\rho) \), from equation (68), reads

\[
\hat{N}_{\text{ph}}(\rho) = \sum_{R} \left\{ \gamma_{R} |\rho_{R}\rangle\langle \rho_{R}| + \sum_{R'} \gamma_{RR'} |\rho_{R'}\rangle\langle \rho_{R'}| - \sum_{R'} \gamma_{R'} |\rho_{R'}\rangle\langle \rho_{R'}| \right\},
\]

(69)

where \( |\rho\rangle = \sum_{R} |R\rangle \rho_{R} \), and we have defined the rate

\[
\gamma_{R} = \gamma_{R} + \sum_{R'} \gamma_{RR'}. \tag{70}
\]

As in the previous case (equation (42)), equation (69) takes into account all possible configurational paths that lead to a photon emission. The conditional evolution defined by the operator \( \hat{D} = \hat{L} - \hat{J}_{\text{ph}} \), expressed through the evolution of the unnormalized state \( |\rho_{\text{i}}\rangle \) (equation (44)), reads

\[
\frac{d\rho_{\text{ph}}(t)}{dt} = -\frac{i}{\hbar} [H_{R}, \rho_{\text{ph}}(t)] - \gamma_{R} [D, \rho_{\text{ph}}(t)]. \tag{71}
\]

Note that in contrast with equation (45), here the conditional evolution is diagonal in the \( \rho \)-space. This property is broken if the detector efficiency \( \eta \) considerably departs from 1, equation (46). In fact, in such a case, the evolution of \( \rho_{\text{ph}}^{\text{et}}(t) \) must involve the extra contribution \((1-\eta)\gamma_{R} |\rho_{R}\rangle\langle \rho_{R}| + \sum_{R'} \gamma_{RR'} |\rho_{R'}\rangle\langle \rho_{R'}| \). In the following analysis we assume \( \eta = 1 \).

4.2.2. Stochastic dynamics. The structure of the stochastic dynamics of the vectorial state \( |\rho_{\text{i}}\rangle \), equation (34), is similar to that of the previous case. When a photon detection event occurs, it implies the transformation

\[
|\rho^{\text{st}}_{\text{i}}\rangle \rightarrow \hat{N}_{\text{ph}}(\rho^{\text{st}}_{\text{i}}) = |\text{?}\rangle \sum_{R} \rho_{R}(t)|R\rangle,
\]

(72)

where the weights satisfy \( \sum_{R} \rho_{R} = 1 \). From equation (69), here they read

\[
\rho^{\text{st}}_{R}(t) = \frac{\gamma_{R} |+\rangle\langle +| + \sum_{R'} \gamma_{RR'} |+\rangle\langle +|}{\sum_{R'} \gamma_{RR'} |+\rangle\langle +|} \rho^{\text{et}}_{R'}(t) |+\rangle\langle +|, \tag{73}
\]

From equation (37) it is simple to demonstrate that equations (49) and (50) are also valid in this case. Therefore, in each photon recording event the system collapses to its ground state while \( \rho^{\text{st}}_{R}(t) \) define the posterior value of the configurational populations.

In the next figures we consider a fluorophore system whose evolution is defined by equation (68) and a two-dimensional configurational space, \( R = A, B \). The Rabi frequencies (equation (4)) do not depend on the configurational states, \( \Omega_{R} = \Omega \), and the spectral shifts (equation (5)) are null, \( \delta_{\Omega R} = 0 \). Therefore, the bath states only affect the decay rates \( \gamma_{R} \) of the system. The laser is in resonance with the system, i.e. \( \Omega_{L} = \omega_{0} \).

**Figure 6.** Stochastic realizations of a fluorophore system defined by the evolution (68). The configurational space is two dimensional, \( R = A, B \). The parameters are \( \Omega_{R} = \Omega, \delta_{\Omega R} = 0, \gamma_{A} / \Omega = 1.8, \gamma_{B} / \Omega = 0.15, \gamma_{AB} / \Omega = 0.35, \gamma_{BA} / \Omega = 0.2 \). The laser is in resonance with the system, i.e. \( \omega_{L} = \omega_{0} \). (a) Realization of the upper population of the system \( |+\rangle \rho^{\text{ph}}_{R}(t) |+\rangle \). (b), (c) Realization of the configurational population of the bath \( |R\rangle P^{\text{ph}}_{R} \), for \( R = A \). (d) Intensity realization. \( I_{\infty} \) is defined by equation (74).

In figure 6(a) we show a realization of the upper population of the system \( |+\rangle \rho^{\text{ph}}_{R}(t) |+\rangle \) (equation (37)). The times of the photon emission events correspond to the collapse of the upper population to zero. Figure 6(b) shows the realization of the configurational population of the bath \( |R\rangle P^{\text{ph}}_{R} \), for \( R = A \) (equation (37)). Due to the chosen parameter values, at any time it is not possible to predict with total certainty \( \{ |R\rangle P^{\text{ph}}_{R} \approx 1 \} \) the configurational state of the reservoir. This fact is evident from figure 6(c), where we plot \( |R| P^{\text{ph}}_{R} \) (for \( R = A \)) over a larger time interval. In figure 6(d), we plot the scattered intensity. Consistently with the behaviour of \( |R| P^{\text{ph}}_{R} \), the intensity does not develop any dichotomic behaviour. The intensity fluctuates around the value \( I_{\infty} \) defined by (see equation (55) in [31])

\[
I_{\infty} = \sum_{R} \gamma_{R} |+\rangle\langle +| + \rho^{\infty}_{R} |+\rangle\langle +|, \tag{74}
\]

where as before \( \rho^{\infty}_{R} = \lim_{t \rightarrow \infty} \rho_{R}(t) \).

In figures 7(a) and (b) we plot the analytical solutions of the upper population \( |+\rangle \rho_{R}(t) |+\rangle \) and the configurational populations \( |R\rangle P^{\text{ph}}_{R} \) that follow from equation (68) (and equation (2)). The noisy curves correspond to an average over
realizations like those shown in figure 6. Note that here, the behaviour of the configurational population strongly departs from an exponential one, indicating that their underlying dynamics is highly non-Markovian. The physical origin of this characteristic is the dependence of the configurational transitions on the system state.

4.2.3. Photon emission process. In this case it is also possible to define a stochastic waiting time distribution that parametrically depends on the configurational populations after a photon detection event, i.e., $w_a(t, t') = \text{Tr}_S[1(R|\hat{P}|)]$, equation (52). From equations (69) and (72) we obtain

$$w_a(t, t') = \sum_{R'R} \gamma_R\langle \hat{P}_R^{t-t'}| -| -\hat{P}_{R'}^{t-t'}| \rangle\langle +| +\rangle ,$$

(75)

where $\hat{P}_R^{t-t'}(t')$ is given by equation (73). As the vectorial superoperator $\hat{D}$ is diagonal (see equation (71)), this expression can be written as

$$w_a(t, t') = \sum_R \bar{w}_R(t-t') p_R^{t-t'}(t'),$$

(76)

where $\bar{w}_R(t)$ is defined by equation (64) after the replacement $\gamma_R \rightarrow \bar{\gamma}_R$ (equation (70)). While equation (60) is an approximation valid in the limit of slow environmental fluctuations, here equation (76) is valid independently of the values of any of the parameters that define the system evolution, equation (68).

In figure 8(a), we plot $w_a(t, t')$ (as a function of $t - t'$) for different values of the parameters $p_R^{t-t'}(t')$. As in the previous case, $w_a(t, t')$ has a strong dependence on the values of the configurational populations $\{p_R^{t-t'}(t')\}$, implying strong departures from a renewal process. In fact, note that depending on $p_R^{t-t'}(t')$, $w_a(t, t')$ may or may not develop oscillatory behaviours.

4.2.4. Stationary waiting time distributions. The first stationary waiting time distribution (10) from equation (32) can be written as $w_{\infty}^{(1)}(\tau) = \sum_R \gamma_R\langle | -\rangle\langle | -| \hat{P}_R^{\infty}\rangle\langle +| +\rangle$. After using the definition of the conditional evolution (equation (71)), it follows that

$$w_{\infty}^{(1)}(\tau) = \sum_R \bar{w}_R(\tau) p_R^{\infty},$$

(77)

where the weights $p_R^{\infty}$ are determined from the relation $\gamma_R\langle | -\rangle\langle | -| \hat{P}_R^{\infty}\rangle\langle +| +\rangle$, delivering

$$p_R^{\infty} = \gamma_R\langle | -\rangle\langle | -| \hat{P}_R^{\infty}\rangle\langle +| +\rangle + \sum_{R'} \gamma_{R'}\langle | +\rangle\langle | +| \hat{P}_{R'}^{\infty}\rangle\langle +| +\rangle.$$

(78)

In figure 8(b) we plot the analytical expression for $w_{\infty}^{(1)}(\tau)$ (equation (77)) and the numerical distribution (noisy curve) obtained as the probability distribution of the time intervals between successive photon emissions along a single trajectory, equation (10). The theoretical and numerical results match between them.
The second waiting time distribution \( w^{(2)}_{\infty}(t_2, t_1) \) follows from equation (33). After some calculations we obtain

\[
\begin{align*}
\sum_R \left[ \tilde{w}_R(t_2)q_R + \sum_{R'} \tilde{w}_{R'}(t_2)q_{R'R} \right] \tilde{w}_R(t_1)p_R^{-1} & = \sum_R \sum_{R'} \tilde{w}_{R'}(t_2)q_{R'R} \tilde{w}_R(t_1) p_R^{-1}. \\
q_R & = \frac{\gamma_R}{\bar{\gamma}_R}, \quad q_{R'R} = \frac{\gamma_{R'R}}{\bar{\gamma}_R},
\end{align*}
\]

which for any \( R \) satisfy the normalization \( q_R + \sum_{R'} q_{R'R} = 1 \).

The physical content of equation (79) can be read as follows. After a first photon emission (contribution \( \tilde{w}_R(t_1) p_R^{-1} \)), the second one occurs without a configurational transition with probability \( q_R \), while with probability \( q_{R'R} \) it is endowed with the configurational transition \( R \rightarrow R' \). This interpretation is consistent with the results presented in [36] (see also appendix A). On the other hand, while in general \( w^{(2)}_{\infty}(t_2, t_1) \neq w^{(2)}_{\infty}(t_1, t_2) \), here for two-dimensional configurational spaces \( w^{(2)}_{\infty}(t_2, t_1) \) is symmetric on its arguments.

In figure 9(a) we plot \( w^{(2)}_{\infty}(t_2, t_1) \) (equation (79)) for different values of \( t_1 \). We also show the numerical distribution (11). In figure 9(b) we plot the dimensionless parameter \( \Lambda(t_2, t_1) \) (equation (12)) determined from equations (77) and (79), for different values of \( t_1 \). From top to bottom \( \Omega \tau_1 = 10, 0.25, 0.85 \) and 2. For clarity, the curves corresponding to the last three values were shifted by \(-0.25, -0.75 \) and \(-1 \), respectively. The parameters are the same as in figure 6.

Figure 9. (a) Stationary two-time waiting time distribution \( w^{(2)}_{\infty}(t_2, t_1) \) (equation (79)) for different values of \( t_1 \). From top to bottom we take \( \Omega \tau_1 = 2, 0.85, 5, 0.25 \) and 10. The noisy curves correspond to the time average (11). (b) Parameter \( \Lambda(t_2, t_1) \) (equation (12)) determined from equations (77) and (79), for different values of \( t_1 \). From top to bottom \( \Omega \tau_1 = 10, 0.25, 0.85 \) and 2. For clarity, the curves corresponding to the last three values were shifted by \(-0.25, -0.75 \) and \(-1 \), respectively. The parameters are the same as in figure 6.

Figure 10. Contour plot of \( w^{(2)}_{\infty}(t_2, t_1)/\Omega^2 \) (upper panel) and \( \Lambda(t_2, t_1) \) (lower panel) corresponding to the plots of figure 9.
dynamics, by increasing the external laser intensity the renewal departure measure $\Lambda(t_2, t_1)$ develops a richer structure.

When the radiation pattern develops a blinking phenomenon [31], i.e. for slow (light-assisted) environmental fluctuations, $\gamma_{RR} \ll \gamma_R$, equation (78) becomes

$$p_R^\infty \simeq \frac{\hat{I}_R}{\sum_R \hat{I}_R P_R^\infty}$$

where as before $\hat{I}_R$ follows from equation (51) under the replacement $\gamma_R \rightarrow \gamma_R$ (equation (70)), and the probabilities $P_R^\infty$ are the stationary solution of a classical master equation obtained from equation (41) under the replacement $\phi_{RR} \rightarrow \Gamma_{RR} = q_{RR} \hat{I}_R$ (see equations (81) and (82) in [31]). In the limit of fast environmental fluctuations, $\gamma_{RR} \gg \gamma_R$, the photon emission process becomes a renewal one.

5. Summary and conclusions

In this paper, we formulated a quantum-jump approach for describing the radiation patterns of single fluorescent systems coupled to complex fluctuating environments. Our results rely on a density matrix formulation of the problem. The master equation (3) takes into account both the system dynamics and a wide class of environmental fluctuations.

The quantum-jump approach relies on a quantum measurement theory. Here, after introducing general measurement transformations acting on the system and the configurational bath space (equation (13)), the density matrix evolution was written as an average over measurement trajectories, equation (20). The weight of each trajectory is measured by its associated $n$-joint probability, equation (22). The hierarchy of these objects completely characterizes the statistical properties of the measurement processes. Its functional form in an asymptotic time regime provides information about observables defined from a time average along a single measurement trajectory. Equations (32) define the stationary probability distribution for the time interval between consecutive measurement events, while equations (33) define the joint probability for two consecutive intervals. These two objects allow measuring the departure of the measurement process from a renewal one.

The decomposition of the density matrix evolution into a set of measurement trajectories leads to a stochastic representation of the system dynamics, equation (34). Each stochastic realization can be related to a particular measurement trajectory. Their structure allowed us to define how the measurement process occurs event-to-event. The waiting time distribution (39) defines the probability density for consecutive recording events. In contrast with a renewal process, it depends on the stochastic state of the system property that breaks the renewal character of the measurement process. This dependence encodes the influence of the bath fluctuations.

The case when there exists only one measurement process, providing information about the photon emission events, was analysed in detail. Independently of the underlying bath dynamics (and the measurement processes, see appendix A) the photon-to-photon emission process is defined by a stochastic waiting time distribution that parametrically depends on the configurational bath populations. The analysis based on equation (40) allows us to describe situations such as spectral diffusion process, lifetime fluctuations and molecules diffusing in a solution. The stochastic waiting time distribution, equation (53), and the first and second stationary waiting time distributions, equations (54) and (57), respectively, provide a deep characterization of the photon emission process. These general expressions assume a simple form when the environmental fluctuations are much slower than the optical system transitions. In fact, in such a case those objects can be written as linear combinations of the waiting time distribution associated with a Markovian fluorescent system characterized by the parameters corresponding to each configurational state, equations (60), (65) and (66). The case of a light-assisted process, equation (68), admits a similar description, equations (76), (77) and (79).

The developed results provide an alternative theoretical tool for analysing single fluorescent systems coupled to classically fluctuating environments. In fact, the explicit analytical characterization of statistical observables like the stationary waiting time distributions, equations (10) and (11), and the renewal departure function, equation (12), may provide a power tool for deducing the underlying structure of complex nanoscopic reservoirs analysed through fluorescence spectroscopy.

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Appendix A. Measuring photon emissions and configurational transitions

In section 4 we characterized the quantum-jump approach (for both self-environmental fluctuations and light-assisted processes) when the measurement action only gives information about the photon emission events. While that is the standard situation in SMS, the formalism developed in section 3 allows us to analyse the case in which there exist extra measurement channels (apparatus) that give information about the configurational states of the reservoir. Besides its theoretical interest and potential applications, the following analysis also allows us to understand some previous results [36].

Here, we assume that at any time one knows which is the configurational state of the bath. Under this condition, the stochastic dynamics of $|\rho_s^a\rangle$ and $|P_t^s\rangle$ assume the structure

$$|\rho_s^a\rangle = \rho_s^a(t) |R_s^a\rangle, \quad |P_t^a\rangle = |R_t^a\rangle,$$

where $\text{Tr}_s[\rho_s^a(t)] = 1$, and $R_s^a$ randomly change over the set of possible values $R = 1, 2, \ldots, R_{max}$. Therefore, here the vectorial nature of $|\rho_s^a\rangle$ can be avoided. In fact, all relevant information is encoded in $\rho_s^a(t)$ and $|P_t^a\rangle = \delta_{RR'}$.
(see equation (37)). While the underlying master equations are different, the results of [37] also rely on the previous assumption. On the other hand, here we also assume perfect detection efficiency. The extension to the case \( \eta < 1 \) also relies on the replacements defined by equation (46).

### A.1. Self-fluctuating environments

First we analyse the case of self-fluctuating environments, equation (40). The parameter \( \mu \) includes one term corresponding to the photon detector, \( \mu = \text{ph} \), and \( \mu = 1, \ldots, R_{\text{max}} \) terms that detect (measure) when a transition to a given conformational state \( R \) occurs.

#### A.1.1. Measurement operators.

The measurement operators (equation (13)) read

\[
\hat{\mathcal{M}}_{\text{ph}}|\rho\rangle = \frac{\sum_{R} \gamma_{R} |R\rangle \sigma_{R} \rho_{\sigma}^{|R\rangle}}{\sum_{R} \gamma_{R} |TR_{\sigma}\sigma_{R}\rangle}, \tag{A.2a}
\]

\[
\hat{\mathcal{M}}_{R}|\rho\rangle = \frac{|R\rangle \sum_{R} \phi_{R} \rho_{R}}{\sum_{R} \phi_{R} |TR_{R}\rangle \rho_{R} \langle R\rangle}, \tag{A.2b}
\]

where \( |\rho\rangle = \sum_{R} |R\rangle \rho_{R} \). The (unnormalized) conditional evolution (equation (44)) is diagonal in the \( R \)-space and reads

\[
\frac{d\rho_{R}^{\nu}(t)}{dt} = -\frac{i}{\hbar} [H_{R}, \rho_{R}^{\nu}(t)] - \gamma_{R} \{ D, \rho_{R}^{\nu}(t) \} + \phi_{R} \rho_{R}^{\nu}(t), \tag{A.3}
\]

where the rate \( \phi_{R} \) is defined by

\[
\phi_{R} = \sum_{R} \phi_{R}^{\nu}. \tag{A.4}
\]

These definitions provide a splitting of equation (40) that allows us to formulate the quantum-jump approach, equation (14). \( \hat{\mathcal{M}}_{\text{ph}} \) corresponds to the transformation associated with a photon detection event. On the other hand, \( \hat{\mathcal{M}}_{R} \) takes into account all transitions \( R' \rightarrow R \) that leave the bath in the configurational state \( R \).

#### A.1.2. Stochastic dynamics.

The measurement operators (equation (A.2)) imply the transformations \([|\rho_{R}^{\nu}\rangle \rightarrow \rho_{R}^{\nu}(t) |R\rangle\])

\[
|\rho_{R}^{\nu}\rangle \rightarrow \hat{\mathcal{M}}_{\text{ph}}|\rho_{R}^{\nu}\rangle = -(-|R_{\text{th}}^{\nu}\rangle), \tag{A.5a}
\]

\[
|\rho_{R}^{\nu}\rangle \rightarrow \hat{\mathcal{M}}_{R}|\rho_{R}^{\nu}\rangle = \rho_{R}^{\nu}(t) |R\rangle. \tag{A.5b}
\]

The first transformation collapses the system to its ground state and does not affect the configurational state. The measurement operator \( \hat{\mathcal{M}}_{R} \) leaves invariant the system state \( \rho_{R}^{\nu}(t) \), while produces the configurational transition \( |R_{\text{th}}^{\nu}\rangle \rightarrow |R\rangle \). On the other hand, note that the dynamics between recording events, i.e. equation (A.3), does not affect the configurational bath state.

From equations (19) and (A.2), it follows

\[
F_{\text{ph}}[|\rho_{R}^{\nu}\rangle] = \gamma_{R} R_{\text{th}}^{\nu} |+\rho_{R}^{\nu}(t)\rangle |+\rangle, \tag{A.6a}
\]

\[
F_{R}[|\rho_{R}^{\nu}\rangle] = \phi_{R} R_{\text{th}}^{\nu}. \tag{A.6b}
\]

Consistently with the classical evolution equation (41), the probability by unit of time for observing the configurational transition \( |R_{\text{th}}^{\nu}\rangle \rightarrow |R\rangle \) (i.e. \( \phi_{R} R_{\text{th}}^{\nu} \)) is independent of the state of the system \( \rho_{R}^{\nu}(t) \).

When a recording event occurs, each transformation (equations (A.5)) must be selected in agreement with the transition probabilities \( t_{R} (t) \), equation (36). They read

\[
t_{\text{ph}}(t) = \frac{\gamma_{R} R_{\text{th}}^{\nu} |+\rho_{R}^{\nu}(t)\rangle |+\rangle}{\gamma_{R} R_{\text{th}}^{\nu} |+\rho_{R}^{\nu}(t)\rangle |+\rangle + \phi_{R} R_{\text{th}}^{\nu}}, \tag{A.7a}
\]

\[
t_{R}(t) = \frac{\phi_{R} R_{\text{th}}^{\nu} (|+\rho_{R}^{\nu}(t)\rangle |+\rangle + \phi_{R} R_{\text{th}}^{\nu})}{\gamma_{R} R_{\text{th}}^{\nu} |+\rho_{R}^{\nu}(t)\rangle |+\rangle + \phi_{R} R_{\text{th}}^{\nu}}. \tag{A.7b}
\]

where \( \phi_{R} R_{\text{th}}^{\nu} \) follows from equation (A.4). Note that when a configurational transition occurs, \( |R_{\text{th}}^{\nu}\rangle \rightarrow |R\rangle \), the different possible final states \( |R\rangle \) are chosen with probabilities \( t_{R} R_{\text{th}}^{\nu} = t_{R}(t)/\sum_{R} t_{R}(t) = \phi_{R} R_{\text{th}}^{\nu}/\phi_{R} R_{\text{th}}^{\nu} \). This result can straightforwardly be read from the classical master equation (41).

In figure A1 we show the realizations associated with the measurement transformations (A.5) and the evolution (40).
They were built up by using the finite time step algorithm (appendix D).

Figure A1(a) shows a realization of the upper population of the system $|+\rho^u(t)|$ (equation (37)). In contrast with figure 1, here each event may correspond to a photon detection event, $|+\rho^u(t)| \rightarrow 0$ (equation (A.5a)), or to a configurational transition (vertical dotted lines), equation (A.5b). In these last events the upper population remains unaffected. In figure A1(b), we show the realization of $(R[P^u_R])$, for $R = A$. In contrast with figure 1, here at all times we know with total certainty $[(R[P^u_R]) = 1 \text{ or } 0]$ the configurational state of the bath.

In figures A1(c) and (d) we show the realization of $|+\rho^u(t)|$ and the scattered intensity $I(t)$. The parameters are the same as in figure 1. In A1(d), the telegraphic signal corresponds to $\sum_R I_R(R[P^u_R])$, where the intensities $\{I_R\}$ are defined by equation (51). This function assumes the value $I_R$ when the bath is in the configurational state $R$. The plot shows the direct correlation between the value of the intensity and the configurational bath state.

### A.1.3. Recording process

Given that a recording event occurs in the $\mu$-detector at time $t'$, the waiting time distribution for the next event at time $t$ is given by $w_a(t, t', \mu)$, equation (39). The event at time $t$ is selected with probabilities $t_a(t)$, equation (A.7). Here, $w_a(t, t', \mu)$ can be expressed in a shorter way through its associated survival probability, i.e. $w_a(t, t', \mu) = -d/dt P^\mu_R(t', t_R)$, equation (38). From equations (A.3) and (A.5), we obtain

$$P_0[t', t; \hat{M}_\mu | \rho^u_R] = e^{-\phi \omega(t-t')} W_{\mu}^u[t - t'; |\cdot\rangle\langle \cdot|], \quad \text{(A.8)}$$

and for $R = 1, 2, \ldots, R_{\text{max}}$

$$P_0[t', t; \hat{M}_R | \rho^u_R] = e^{-\phi \omega(t-t')} W_{\mu}^u[t - t'; \rho^u_R(t')]. \quad \text{(A.9)}$$

Here, $W_{\mu}^u[t; \rho] = \text{Tr}[\rho^u_R(t)]$, where $\rho^u_R(t)$ is the solution of the equation $(\partial t/\partial t) \rho^u_R(t) = -i(\hat{H}_R, \rho^u_R(t)) - \gamma_R \{ \rho^u_R(t), \rho^u_R(t) \}$, solved with the initial condition $\rho^u_R(0) = \rho$. Thus, $W_{\mu}^u[t; \rho]$ is the photon survival probability of a Markovian system that begins in the state $\rho$, and whose characteristic parameters are $\gamma_R$, $\omega_R$ and $\Omega_R$. In fact, the waiting time distribution (61) can also be written as $w_{\mu}(t) = -(d/dt) W_{\mu}^u[t; |\cdot\rangle\langle \cdot|]$. The interpretation of the survival probabilities (A.8) and (A.9) is very simple. The exponential factors take into account the possibility of having no any configurational transition in the time interval $(t', t)$. On the other hand, the factors defined by $W_{\mu}^u[t; \rho]$ measure the probability of not having any photon emission in $(t', t)$. In equation (A.9), $W_{\mu}^u[t - t'; \rho^u_R(t') \rangle \langle \cdot|]$ is the photon survival probability of a Markovian system (with parameters corresponding to the configurational state $R$) that begins in the (arbitrary) state $\rho^u_R(t')$. Consistently, in equation (A.8) the factor $W_{\mu}^u[t - t'; |\cdot\rangle\langle \cdot|]$ corresponds to the photon survival probability after the occurrence of a photon detection event at time $t'$, i.e. $\rho^u_R(t') = |\cdot\rangle\langle \cdot|$. Hence, here the associated stochastic waiting time distributions $\{w_a(t, t', \mu)\}$ change when a configurational transition or when a photon recording event occurs. Added to its dependence on the configurational state $R$, in contrast with the result of section 4, $w_a(t, t', \mu)$ may also depend on the system state $\rho^u_R(t')$, i.e. its functional form depends parametrically on the matrix elements of $\rho^u_R(t')$.

We have checked that the stochastic dynamics of $|\rho^u_R| \rangle \langle \cdot|$ defined by equations (A.8) and (A.9), like in figure 2, also recovers the density matrix evolution defined by equation (40). As the dynamics of the configurational states is classical, the statistical properties of the photon-emission process remain the same. This fact is clearly seen by comparing figures 1(d) and A1(d). In both cases the intensity is characterized by the same telegraphic behaviour.

### A.2. Light-assisted processes

Here we analyse the quantum-jump approach associated with equation (68) when both the photon emissions and the configurational transitions are measured, equation (A.1).

#### A.2.1. Measurement operators

From equation (68) the measurement transformations read

$$\hat{M}_\mu \rho) = \frac{\sum_R \gamma_R \rho(R)|\sigma_R \rho R^u|}{\sum_R \gamma_R \rho(R)|\sigma_R \rho R^u|}, \quad \text{(A.10a)}$$

$$\hat{M}_R \rho) = \frac{|\rho(R)| \sum_R \gamma_R \rho(R)|\sigma_R \rho R^u|}{\sum_R \gamma_R \rho(R)|\sigma_R \rho R^u|}, \quad \text{(A.10b)}$$

where $R \in (1, R_{\text{max}})$, while the conditional evolution here is also defined by equation (71).

#### A.2.2. Stochastic dynamics

The equations (A.10) imply the transformations $[|\rho^u_R| \rangle \langle \cdot|] 

$$|\rho^u_R| \rangle \langle \cdot|] \rightarrow \hat{M}_\mu \rho^u_R| \rangle \langle \cdot|], \quad \text{(A.11a)}$$

$$|\rho^u_R| \rangle \langle \cdot|] \rightarrow \hat{M}_R \rho^u_R| \rangle \langle \cdot|], \quad \text{(A.11b)}$$

While $\hat{M}_\mu$ collapses the system to its ground state and leaves invariant the configurational state, the superoperators $\hat{M}_R$ produce both the system collapse and the configurational transition $R^u \rightarrow R$. Therefore, here any recording event (due to $\hat{M}_\mu$ or to $\hat{M}_R$) implies a photon detection event.

The transformations defined by equation (A.11) must be selected in agreement with the transition probabilities $t_{a}(t)$, equation (36). From equations (19) and (A.10), we obtain

$$F_{\text{ph}}[|\rho^u_R|] = \gamma_R \rho(R)|\sigma_R \rho R^u|] \langle +| \rho^u_R| \rangle \langle +|, \quad \text{(A.12a)}$$

$$F_{\text{R}}[|\rho^u_R|] = \rho(R)|\sigma_R \rho R^u|] \langle +| \rho^u_R| \rangle \langle +|, \quad \text{(A.12b)}$$

Then, the transition probabilities read

$$t_{\text{det}}(t) = \frac{\gamma_R \rho^u_R}{\gamma_R R^u}, \quad t_R(t) = \frac{\gamma_R R^u}{\gamma_R R^u}. \quad \text{(A.13)}$$

Note that these objects are independent of the state $\rho^u_R(t')$. Furthermore, they are closely related to the definitions introduced in equation (80).

Figure A2 shows the realizations associated with the measurement transformations (A.11) and the evolution (68). The realizations were determined by using the finite time
The parameters are the same as in equation (64) after the replacement $\gamma_R \to \tilde{\gamma}_R$ (equation (70)), i.e. they are the waiting time distribution of a Markovian fluorescent system with decay rate $\tilde{\gamma}_R$, detuning $\delta_R$ and Rabi frequency $\Omega_R$.

The expressions written in equation (A.14) only differ in their subindex $(R^a_c$ or $R)$. After a recording event, the indexes must be chosen with probabilities (A.13). Therefore, $w_{\mu}(t, t', \mu)$ during successive photon recording events is randomly selected over the set of functions $\{\tilde{w}_R(t)\}$. This result recovers the analysis developed in [36]. For the example shown in figure A2, the two functions $\tilde{w}_R(t-t')$ and $\tilde{w}_R(t-t')$ can be read from figure 8(a) by taking $p_{\mu}(t') = 1$ and $p_{\mu}(t') = 0$, respectively. On the other hand, from equations (A.13) and (A.14), one can deduce that here the stationary photon waiting time distributions are also defined by equations (77) and (79).

Appendix B. Stationary n-joint probabilities

The probabilities (22) define the ensemble statistics of the measurement process. They depend on the initial condition $|\rho_0\rangle$. The statistical information that can be obtained from a time average along a single realization can be obtained from the stationary n-joint probabilities $P_n^{\infty}[t, \{\tau_i\}^n, \{\mu_i\}^n]$. They define the statistic of the measurement events after the occurrence of an infinite number of transitions and that an infinite time elapsed since the initial condition,

$$P_n^{\infty}[t, \{\tau_i\}^n, \{\mu_i\}^n] \equiv \lim_{N \to \infty} \lim_{t_N \to \infty} \int_0^{t_N} dt_{N-1} \cdots \int_0^{t_i} dt_1 \cdots \sum_{\nu_N \cdots \nu_1} P_n^{\infty}[t, \{\tau_i\}^n, \{\nu_i\}^n].$$

The new time variables are defined as $\tau \equiv t - t_N$, $\tau_i \equiv t_{i+1} - t_N$. The measurement apparatus indexes are $\mu_i = \nu_{i+N}$. By working in a Laplace domain, from equation (27) it is possible to obtain

$$P_n^{\infty}[t, \{\tau_i\}^n, \{\mu_i\}^n] = \text{Tr}_S[\lim_{N \to \infty} \lim_{t_N \to \infty} \int_0^{t_N} dt_{N-1} \cdots \int_0^{t_i} dt_1 \cdots \sum_{\nu_N \cdots \nu_1} P_n^{\infty}[t, \{\tau_i\}^n, \{\nu_i\}^n] e^{\tilde{\gamma}_R(t - \tau)} \hat{J}_1 \cdots \hat{J}_n].$$

Here, we introduced the index $\rho_\infty \equiv \nu_N$. The measurement operator $\hat{\mathcal{M}}_{\mu_\infty}$ and the constant $F_{\mu_\infty}$ are defined by equations (13) and (19), respectively. The stationary state $|\rho_\infty\rangle$ is defined by equation (30).

From equation (B.1), by performing the inverse calculation steps to those done in the derivation of equation (27), it follows that

$$P_n^{\infty}[t, \{\tau_i\}^n, \{\mu_i\}^n] = P_0^\infty[t, \tau_n; \hat{\mathcal{M}}_{\mu_n}; \rho_\infty] \times \prod_{j=2}^{n} w_{\mu_j}^{\infty}[\tau_j, \tau_{j-1}; \hat{\mathcal{M}}_{\mu_{j-1}}; \rho_{\tau_{j-1}}] \times w_{\mu_1}^{\infty}[\tau_1, 0; \hat{\mathcal{M}}_{\mu_1}; \rho_\infty] F_{\mu_\infty}. \quad \text{(B.2)}$$

The auxiliary states $|\rho_{\tau_{i+1}} = \mathcal{T}(\tau_{i+1}, \tau_i) \hat{\mathcal{M}}_{\mu_i} |\rho_{\tau_i}\rangle$, where $|\rho_{\tau_i}\rangle = \mathcal{T}(\tau_i, 0) \hat{\mathcal{M}}_{\mu_i} |\rho_{\tau_i}\rangle$. The interpretation (and structure) of equation (B.2) is similar to that of equation (22). Nevertheless, here the factor $F_{\mu_\infty}$ takes into account the probability by unit of time of

A.2.3. Recording process. The stochastic waiting time distributions (39), from equations (71) and (A.11), here read

$$w_{\mu}(t, t', \text{ph}) = \tilde{w}_{\mu}^{ph}(t - t'), \quad \text{(A.14a)}$$

$$w_{\mu}(t, t', R) = \tilde{w}_{\mu}(t - t'), \quad \text{(A.14b)}$$

where $\tilde{w}_{\mu}(t)$ follows from equation (64) after the replacement $\gamma_R \to \tilde{\gamma}_R$ (equation (70)), i.e. they are the waiting time distribution of a Markovian fluorescent system with decay rate $\tilde{\gamma}_R$, detuning $\delta_R$ and Rabi frequency $\Omega_R$.
having a detection in the \( \mu_{\infty} \)-detector in the long-time regime. The associated measurement operator is \( \hat{\mathcal{M}}_{\mu_{\infty}} \). Furthermore, in contrast to equation (22), the first contribution (waiting time distribution) in equation (B.2) is defined by the state \( \hat{\mathcal{M}}_{\mu_{\infty}}(\rho_0) \), i.e. the state after a \( \mu_{\infty} \)-detection occurring in the stationary regime.

From equations (B.2) and (B.1), the expressions (32) and (33) follow straightforwardly after replacing \( \tau_1 \rightarrow \tau_s \) and \( \tau_2 \rightarrow \tau_1 + \tau_2 \). In fact, the variables \( \{\tau_i\} \) of the stationary waiting time distributions \( w_\infty(\mu_1; \mu_1, \mu) \) denote the time interval between consecutive recording events. Furthermore, for simplicity, we define these objects as the waiting time distributions after the occurrence of an arbitrary event in the stationary regime. Therefore, in equation (B.2) the information given by the index \( \mu_{\infty} \) must be ‘traced out’. By using

\[
\sum_{\mu_{\infty}} \hat{\mathcal{M}}_{\mu_{\infty}}(\rho_0)|F_{\mu_{\infty}} = \hat{\mathcal{M}}(\rho_0)|F_{\infty}, \tag{B.3}
\]

where \( F_{\infty} \equiv \sum_{\mu} F_{\mu} |(\rho_0) = \text{Tr}_S(1|\hat{J}_\mu|\rho_0) \), the appearance of the operators \( \hat{J} = \sum_{\mu} \hat{J}_\mu \) and \( \hat{\mathcal{M}} \) (equation (31)) is justified. Evidently, \( F_{\infty} \) can be read as the probability by unit of time of occurrence of an arbitrary event in the long-time regime.

**Appendix C. Averaging over realizations**

Here, we demonstrate that the deterministic evolution (14) is recovered after averaging equation (34) over realizations of the Poisson processes \( N^\mu_t \).

First, by using that \( (dN^\mu_t)^{\delta} = dN^\mu_t \) and the property \( dN^\mu_t dN^\nu_t = \delta_{\mu\nu} dN^{\mu\nu}_t \), it is possible to obtain the relation [3]

\[
\mathbb{E}(\{N^\mu_t\}) dN^\nu_t = \mathbb{E}(\{N^\nu_t\}) \text{Tr}_S(1|\hat{J}_\mu|\rho_0)|d \mu, \tag{C.1}
\]

where \( \mathbb{E}(\{N^\mu_t\}) \) is an arbitrary function of the Poisson processes \( \{N^\mu_t\} \). This equality can be immediately deduced by introducing a series expansion of \( \mathbb{E} \). Now, we split the average of equation (34) as

\[
\frac{d}{dt} |(\rho_t) = \frac{d}{dt} |(\rho_t) + \frac{d}{dt} |(\rho_t) - \text{Tr}_S(1|\hat{D}|\rho_0)|\rho_0^\nu t, \tag{C.2}
\]

where the first contribution is associated with the conditional deterministic dynamics and the second one with the disruptive measurement changes. Then, trivially it follows

\[
\frac{d}{dt} |(\rho_t) = \hat{\mathcal{D}}(\rho_t) - \text{Tr}_S(1|\hat{D}|\rho_0)|\rho_0^\nu t. \tag{C.3}
\]

On the other hand, by using the definition (13) and the relation (C.1), we obtain

\[
\frac{d}{dt} |(\rho_t) = \hat{\mathcal{J}}_{\mu}(\rho_t) - \sum_{\mu} \text{Tr}_S(1|\hat{J}_{\mu}|\rho_0)|\rho_0^\nu t. \tag{C.4}
\]

After introducing the relation \( \text{Tr}_S(1|\hat{D}|\bullet) = -\sum_{\mu} \text{Tr}_S(1|\hat{J}_{\mu}|\bullet) \) in equations (C.3) and (C.4), the evolution (14) follows straightforwardly.

**Appendix D. Algorithms associated with the stochastic evolution**

Two different algorithms allow us to build up the realizations associated with the stochastic evolution (34).

**D.1. Infinitesimal time step algorithm**

In the first algorithm, the stochastic state \( |\rho_{t+\Delta t}^\nu t \rangle \) is obtained from \( |\rho_0^\nu t \rangle \), where \( \Delta t \) is the time discretization step. By introducing the quantity

\[
F(t) = \sum_{\mu} F_{\mu} |(\rho_0^\nu t) = \sum_{\mu} \text{Tr}_S(1|\hat{J}_{\mu}|\rho_0^\nu t), \tag{D.1}
\]

the probability \( \Delta P \) of having a measurement event is defined by \( \Delta P = \Delta t F(t) \). Then, a random number \( r \) in \( (0, 1) \) is generated and compared with \( \Delta P \). If \( r > \Delta P \), no recording event occurs, so the vectorial state evolves deterministically as (equation (17))

\[
|\rho_{t+\Delta t}^\nu t \rangle = \hat{\mathcal{F}}(t + \Delta t, t)|\rho_0^\nu t \rangle \approx \frac{(1 + \Delta t)|\rho_0^\nu t \rangle}{1 + \text{Tr}_S(1|\hat{D}|\rho_0^\nu t)}. \tag{D.2}
\]

If \( r < \Delta P \), there is a measurement event. Then, the system state at \( t + \Delta t \) is defined by (equation (13))

\[
|\rho_{t+\Delta t}^\nu t \rangle = \hat{\mathcal{M}}_{\mu_i}|\rho_i^\nu t \rangle = \frac{\hat{\mathcal{J}}_{\mu_i}|\rho_i^\nu t \rangle}{\text{Tr}_S(1|\hat{J}_{\mu_i}|\rho_i^\nu t)}. \tag{D.3}
\]

Here, the index \( \mu \) is chosen with the probability \( t_{\mu}(t) \), equation (36). Due to the relation \( F_{\mu} |(\rho_0) = t_{\mu}(t) F(t) \), the generated realizations satisfy equation (34).

**D.2. Finite time step algorithm**

An alternative and more efficient algorithm can be defined by using the survival probability (equation (18)) (see also equation (38)). Given that the state of the system after measurement at time \( t_i \) is \( \hat{\mathcal{M}}_{\mu_i}|\rho_i^\nu t \rangle \), the time \( t_{i+1} \) of the next event is obtained from the equation

\[
P_r(t_i, t_{i+1}; |\rho_i^\nu t \rangle = \text{Tr}_S(1|e^{\hat{D}(t_{i+1} - t_i)}\hat{\mathcal{M}}_{\mu_i} |\rho_i^\nu t \rangle) = r, \tag{D.4}
\]

where as before \( r \) is a random number in the interval \( (0, 1) \). For \( t \in (t_i, t_{i+1}) \), the stochastic state evolves deterministically as (equation (17))

\[
|\rho_i^\nu t \rangle = \hat{\mathcal{F}}(t, t_i)|\rho_i^\nu t \rangle = \frac{e^{\hat{D}(t_{i+1} - t)}\hat{\mathcal{M}}_{\mu_i} |\rho_i^\nu t \rangle}{\text{Tr}_S(1|e^{\hat{D}(t_{i+1} - t)}\hat{\mathcal{M}}_{\mu_i} |\rho_i^\nu t \rangle)}. \tag{D.5}
\]

At time \( t = t_{i+1} \), an index \( \mu_{i+1} \) is chosen with the probability \( \{t_{\mu}(t_{i+1})\} \), equation (36), and then the sudden transformation

\[
|\rho_{i+1}^\nu t \rangle \rightarrow \hat{\mathcal{M}}_{\mu_{i+1}}|\rho_{i+1}^\nu t \rangle = \frac{\hat{\mathcal{J}}_{\mu_{i+1}}|\rho_{i+1}^\nu t \rangle}{\text{Tr}_S(1|\hat{J}_{\mu_{i+1}}|\rho_{i+1}^\nu t \rangle)}, \tag{D.6}
\]

is applied. The first event follows from equation (D.4) with \( \hat{\mathcal{M}}_{\mu_i} |\rho_i^\nu t \rangle \rightarrow |\rho_i^\nu t \rangle \). The realizations generated with this algorithm are also consistent with the evolution (34).
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