Photon statistics: Nonlinear spectroscopy of single quantum systems

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A unified description of multitime correlation functions, nonlinear response functions, and quantum measurements is developed using a common generating function which allows a direct comparison of their information content. A general formal expression for photon counting statistics from single quantum objects is derived in terms of Liouville-space correlation functions of the material system by making a single assumption that a spontaneous emission is described by a master equation.

I. INTRODUCTION

Knowledge of the full density matrix of the radiation field allows to compute all its measurable properties. In particular, photon counting statistics which had proven to be a most valuable measure of coherence has been formulated in the sixties by Kelley and Kleiner, Glauber, and Mandel in terms of expectation values of normally ordered field operators [1–8]. A revived interest had emerged in the eighties when stochastic trajectory experiments on single quantum objects, atoms, ion traps, molecules, and quantum dots became feasible [9–17]. It is more convenient to formulate such measurements in terms of correlation functions of the material system, rather than of the radiation field. Various applications for specific few-level model systems have been investigated [9,18–21].

In this paper we develop correlation function expressions for photon statistics which apply to a general model of a quantum system driven by an external field and coupled to a bath. The normally ordered field expressions are remarkably general; the only assumption made in their derivation is that the photon detection is described by the Fermi golden rule. Similarly, our material correlation function expressions hold under a single assumption that spontaneous emission can be described by a master equation. The derivation of the master equation starting with the fully quantum description of the field is well documented [22–24]. No other properties of the radiation field enter explicitly in the present formulation. Computing the reduced density matrix of a single quantum system coupled to a bath has been a long standing goal of nonequilibrium statistical mechanics [24–26]. Various types of reduced equations of motion based on stochastic or microscopic models are well developed. The present approach is therefore particularly useful for single quantum systems since it can utilize any level of reduced equations of motion to predict the photon statistics. Computing the many-body density matrix of a macroscopic system is much more complex and a collective description using field operators [1–8] may then be more adequate.

We further develop some fundamental connections between multitime correlation functions of photon statistics and response functions of nonlinear spectroscopy [27]. Coherent experiments conducted using multiple pulses provide a wealth of information on electronic and nuclear dynamics [28]. These techniques can create and manipulate quantum coherences among selected states and the signals provide snapshots of their dynamics. There are numerous motivations for performing such measurements. (i) Novel spectroscopy: the ability to explore and access unusual regions of phase space. (ii) Coherent control: achieving a desired goal (e.g., optimize the branching ratio of a reaction towards a favorable product). (iii) Quantum computing: these applications depend on generating and retrieving information about coherences between several degrees of freedom prepared in correlated wave packets (such *entanglement* is a synonym to the old fashioned term *correlation*). (iv) Overcome coupling to a bath, e.g., selectively eliminating *dephasing* processes (or the more trendy term *decoherence*). We shall draw upon the analogy between photon statistics and nonlinear response and correlation functions to show important similarities and differences in their information content and simulation strategies.

In Sec. II we present the Liouville-space expressions for multipoint correlation functions and response functions. In Sec. III we discuss multipoint quantum equilibrium measurements and introduce a unified generating function that can be used to compute correlation, response, and measurements. This sets the stage for deriving the Liouville-space expressions for photon counting in Sec. IV. Finally, our results are summarized in Sec. V.

II. MULTIPOINT GENERATING FUNCTIONS FOR CORRELATION AND RESPONSE FUNCTIONS

The state of complex quantum systems may be conveniently characterized by multitime quantities which carry various levels of information and are easier to calculate, measure, or visualize compared to the many-body wave function [29]. In this section we present formal expressions for two such objects (correlation and response functions) using a Liouville-space (superoperator) approach. While the results of this section are not new, they establish the notation, setting the stage for calculating the successive measurements in Sec. III and eventually to the photon statistics in Sec. IV, which are our main results. Correlation and response functions can be defined in Hilbert space using ordinary operators. Quantum measurements on the other hand, must be formulated using density matrices in Liouville space. The notation introduced here is essential for expressing all of these quantities using a common generating function [Eq.

(26)] which unambiguously reveals their relative information content.

Consider a dynamical variable of interest A which can represent, e.g., the dipole operator, the coordinate or the momentum of a tagged particle, or some collective coordinate. The simplest n-point object is the correlation function

$$C^{(n)}(\tau_n \ldots \tau_1) \equiv \text{Tr}[A(\tau_n) \ldots A(\tau_1)\rho_{eq}], \qquad (1)$$

where ρ_{eq} is the equilibrium density matrix of the system.

Classical correlation functions are given by moments of the joint distribution of successive measurements and are therefore directly observable. Quantum correlation functions, in contrast, are not connected to specific measurements in a simple way. Instead, response functions [25,27,29,30] which represent the reaction of the system to an external field $E(t)$ coupled to the variable A via $H_{int} = -E(t)A$ may be readily measured. In a response experiment the total Hamiltonian $H_T(\tau)$ consists of material Hamiltonian H and the coupling to the driving field

$$H_T(\tau) = H + H_{int}(\tau). \qquad (2)$$

We shall be interested in the expectation value of A at time t

$$U(t) = \text{Tr}[A\rho(t)] \equiv \langle\langle A | \rho(t)\rangle\rangle, \qquad (3)$$

where $|\rho(t)\rangle\rangle = \Sigma_{jk}\rho_{ik}(t)|jk\rangle\rangle$ is the density matrix of the system, and the ket $|jk\rangle\rangle$ denotes the Liouville-space operator $|j\rangle\langle k|$ [25,27,31].

Equation (3) can be recast in the form [32,33]

$$U(t) = \left\langle TA_+(t)\exp\left[\frac{i}{\hbar}\int_{-\infty}^t d\tau E(\tau)A_-(\tau)\right]\right\rangle. \qquad (4)$$

Here and below $\langle\cdots\rangle$ denotes averaging with respect to the equilibrium density matrix ρ_{eq}

$$\langle A\rangle \equiv \text{Tr}[A\rho_{eq}], \qquad (5)$$

$A_\pm$ are superoperators acting in Liouville space defined as follows: For any ordinary operator A, we define

$$A_- \equiv A_L - A_R \quad A_+ \equiv \frac{1}{2}(A_L + A_R), \qquad (6)$$

where A_L and A_R are the superoperators that act on the ket (left) and bra (right) of the density matrix ($A_L B \equiv AB$ and $A_R B \equiv -BA_R$).

The time evolution in Eq. (4) is given in the interaction picture. For an ordinary operator in Hilbert space this is defined by

$$A(\tau) \equiv \exp\left(\frac{i}{\hbar}H\tau\right)A\exp\left(-\frac{i}{\hbar}H\tau\right). \qquad (7)$$

Similarly, the time evolution of superoperators is governed by the Liouville operator H_- corresponding to the material Hamiltonian H

$$A_j(\tau) \equiv \exp\left(\frac{i}{\hbar}H_-\tau\right)A_j\exp\left(-\frac{i}{\hbar}H_-\tau\right), \quad j = +, -, L, R. \qquad (8)$$

T is the positive time ordering operator which rearranges all products of superoperators in order of decreasing time from left to right. The nonlinear response functions are obtained by expanding the exponent of Eq. (4) in powers of $E(\tau)$. The expectation value of A to $(n-1)$th order in the field is given by

$$U^{(n-1)}(\tau_n) = \int_{-\infty}^{\tau_n} dt_{\tau_{n-1}} \cdots \int_{-\infty}^{\tau_2} d\tau_1 R^{(n)}(\tau_n\cdots\tau_1)$$
$$\times \mathcal{E}(\tau_{n-1})\cdots\mathcal{E}(\tau_1), \quad n = 2,3,\ldots \qquad (9)$$

with the *nonlinear response function*

$$R^{(n)}(\tau_n\cdots\tau_1) \equiv \left(\frac{i}{\hbar}\right)^n \langle A_+(\tau_n)A_-(\tau_{n-1})\cdots A_-(\tau_1)\rangle. \qquad (10)$$

$R^{(n)}$ represents the response at time τ_n to $n-1$ very short pulses applied at times $\tau_1\cdots\tau_{n-1}$ [27]. Note that all time arguments are fully ordered $\tau_1 \leqslant \tau_2 \cdots \leqslant \tau_n$. The operator $A_+(\tau_n)$ corresponds to the observation time, the operators $A_-(\tau_j)$ $j = 1, \ldots, n-1$ represents interactions with the external field at times τ_j. We chose to label the response function corresponding to $U^{(n-1)}$ by $R^{(n)}$ rather than $R^{(n-1)}$ since it is an n-point function; this will facilitate the comparison with the other multitime quantities discussed below.

Equation (10) is an abbreviated notation for

$$R^{(n)}(\tau_n\cdots\tau_1) = \left(\frac{i}{\hbar}\right)^n \langle[\cdots([A(\tau_n),A(\tau_{n-1})],A(\tau_{n-2})),\ldots,A(\tau_1)]\rangle, \qquad (11)$$

or

$$R^{(n)}(\tau_n\cdots\tau_1) = \left(\frac{i}{\hbar}\right)^n \text{Tr}\{A(\tau_n)[A(\tau_{n-1}),\ldots,(A(\tau_2),[A(\tau_1),\rho_{eq}])\cdots]\}. \qquad (12)$$

$R^{(n)}$ is thus given by a combination of n-order ordinary (Hilbert space) correlation functions. Equation (12) contains 2^{n-1} terms representing all possible "left" and "right" actions of the various commutators. Each term corresponds to a

Liouville-space path and can be represented by a double-sided Feynman diagram [27]. The various pathways interfere, giving rise to many interesting effects such as new resonances. For a multilevel system $R^{(n)}$ is usually expanded in

the eigenstates of the free Hamiltonian H. Each path then consists of $n-1$ periods of free evolution separated by n couplings with A, which change the state of the system.

Using our superoperator notation, the correlation function Eq. (1) can be recast as

$$C^{(n)}(\tau_n \cdots \tau_1) = \text{Tr}[A_L(\tau_n) \cdots A_L(\tau_1)\rho_{eq}], \quad (13)$$

where the time evolution of $A_L(\tau)$ is given by Eq. (8).

Classical quantities are conveniently represented as moments of some *joint distribution functions* connected to measurements. The closest we can come up in quantum mechanics is through moments of *generating functions*. This is not only a convenient computational tool, but also provides insights and helps connect different measurements. The generating function for correlation functions is defined as

$$W_C^{(n)}(a_n \tau_n \cdots a_1 \tau_1) \equiv \langle \delta(a_n - A(\tau_n)) \cdots \delta(a_1 - A(\tau_1)) \rangle. \quad (14)$$

By comparing Eq. (1) and Eq. (14) we immediately find that

$$C^{(n)}(\tau_n \cdots \tau_1) = \int \cdots \int a_1 \cdots a_n$$
$$\times W_C^{(n)}(a_n \tau_n \cdots a_1 \tau_1) da_1 \cdots da_n. \quad (15)$$

Similarly we can define a generating function for response functions

$$W_R^{(n)}(a_n \tau_n \cdots a_1 \tau_1) = \langle [\delta(a_n - A(\tau_n)), \ldots, [\delta(a_2 - A(\tau_2)), [\delta(a_1 - A(\tau_1)), \rho_{eq}]]] \rangle, \quad (16)$$

so that the response function is given by

$$R^{(n)}(\tau_n \cdots \tau_1) = \int \cdots \int a_1 \cdots a_n$$
$$\times W_R^{(n)}(a_n \tau_n \cdots a_1 \tau_1) da_1 \cdots da_n. \quad (17)$$

Equations (14) and (16) play the role of a classical distribution functions even though they are generally complex and may be negative. Nevertheless, they serve as generating functions for correlation and response functions which are given by their first "moments," Eqs. (15) and (17).

So far we considered two n-point objects: Correlation functions and response functions. A third type of quantity which is more closely connected to photon statistics is the joint distribution of n successive measurements. This will be introduced next.

III. UNIFIED GENERATING FUNCTION FOR CORRELATION, RESPONSE, AND EQUILIBRIUM MEASUREMENTS

We consider a sequence of n measurements of a dynamical variable A performed on the system at times $\tau_1 \leq \tau_2 \leq \tau_3 \cdots \leq \tau_n$ and yielding the outcomes $a_1 \cdots a_n$. We would like to compute the following ensemble average over many such measurements

$$S^{(n)} \tau_n \cdots \tau_1 \equiv \overline{A(\tau_n) \cdots A(\tau_1)}. \quad (18)$$

This quantity is common to classical and quantum systems alike. Equation (18) is a shorthand notation for

$$S^{(n)}(\tau_n \cdots \tau_1) = \int \cdots \int a_1 \cdots a_n$$
$$\times W_S^{(n)}(a_n \tau_n, \ldots, a_1 \tau_1) da_1 \cdots da_n, \quad (19)$$

where the joint distribution function $W_S^{(n)}$ can be computed using the theory of quantum measurements [34–38]. To that end, we define the eigenstates $|\alpha_j\rangle$ of A with eigenvalues a_j, and represent the operator A in the form of an expansion in projection operators $\hat{A}_j$

$$A = \sum_j a_j \hat{A}_j, \quad (20)$$

with

$$\hat{A}_j \equiv |\alpha_j\rangle\langle\alpha_j|. \quad (21)$$

We next define the Liouville-space projection operator onto the diagonal elements of A

$$\hat{P}(a) \equiv \sum_j \delta(a - a_j)|\hat{A}_j\rangle\rangle\langle\langle\hat{A}_j|. \quad (22)$$

The Liouville-space bracket $\langle\langle F|G\rangle\rangle \equiv \text{Tr}' FG$ denotes a scalar product computed by a partial trace over the measured degrees of freedom of the operator A. Using this projection, the joint distribution function of successive measurements may be recast in the form [34–37,39]

$$W_S^{(n)}(a_n \tau_n \cdots a_1 \tau_1) = \text{Tr}[\hat{P}(a_n, \tau_n) \cdots \hat{P}(a_1, \tau_1)\rho_{eq}], \quad (23)$$

where the time evolution of $\hat{P}(a, \tau)$ is given by the interaction picture [Eq. (8)]. The compact Liouville-space notation used in Eq. (23) will help establish the connection between photon counting and other multitime quantities. Note that both W_C and W_S are normalized as

$$\int W_j^{(n)}(a_n \tau_n \cdots a_1 \tau_1) da_1 \cdots da_n = 1, \quad j = C, S, \quad (24)$$

whereas W_R, which represents the deviation of the density matrix from equilibrium, has a zero trace [40]

$$\int W_R^{(n)}(a_n\tau_n\cdots a_1\tau_1)da_1\cdots da_n=0. \qquad (25)$$

So far, we introduced three different generating functions to describe correlation functions, response functions, and the joint probability of measurements [Eqs. (14), (16), and (23), respectively]. To establish the connection between these

quantities it will be useful to compute all three using a single fundamental object. This is possible by using the following generating function:

$$W^{(n)}(a_na_n'\tau_n,a_2a_2'\tau_2\cdots a_1a_1'\tau_1)$$
$$\equiv \mathrm{Tr}\{\delta(a_n-A(\tau_n))\cdots\delta(a_1-A(\tau_1))\rho_{eq}$$
$$\times\delta(a_1'-A(\tau_1))\cdots\delta(a_n'-A(\tau_n))\}. \qquad (26)$$

The density matrix underlying Eq. (26) is

$$\rho^{(n)}(a_na_n'\tau_n\cdots a_1a_1'\tau_1)=\mathcal{G}_{a_na_n'a_{n-1}a_{n-1}'}(\tau_n-\tau_{n-1})\cdots\mathcal{G}_{a_2a_2'a_1a_1'}(\tau_2-\tau_1)\rho_{a_1a_1'}(\tau_1), \qquad (27)$$

where

$$\mathcal{G}(\tau)\equiv\exp\left(-\frac{i}{\hbar}H_-\tau\right), \qquad (28)$$

is the interaction-picture propagator.

The generating function for correlation functions [Eq. (14)] is recovered by integrating Eq. (26) over the primed variables

$$W_C^{(n)}(a_n\tau_n,\ldots,a_1\tau_1)$$
$$=\int W^{(n)}(a_na_n'\tau_n,a_2a_2'\tau_2,\ldots,a_1a_1'\tau_1)$$
$$\times da_1'da_2'\cdots da_n' \qquad (29)$$

and the correlation function is given by Eq. (15). Similarly, the response function is obtained by the following integration

$$R^{(n)}(\tau_n\cdots\tau_1)=\int da_1\cdots da_n\int da_1'\cdots da_n'$$
$$\times(a_n-a_n')\cdots(a_1-a_1')$$
$$\times W^{(n)}(a_na_n'\tau_n\cdots a_1a_1'\tau_1). \qquad (30)$$

Comparing Eq. (26) with Eq. (23), it is clear that the joint probability of measurements is related to the diagonal elements of Eq. (26), i.e., $a_j=a_j'$. However we cannot simply set $a_j=a_j'$ in Eq. (26) since it will diverge. In order to properly obtain Eq. (26) from Eq. (23) we need to add a finite resolution for the measurement defined by a normalized function $f(a-a')$ sharply peaked at zero. We can then write

$$W_S^{(n)}(a_n\tau_n\cdots a_1\tau_1)=\int\cdots\int da_1'\cdots da_n'$$
$$\times W(a_1a_1'\tau_1,a_2a_2'\tau_2\cdots a_na_n'\tau_n)$$
$$\times f(a_1-a_1')\cdots f(a_n-a_n'). \qquad (31)$$

Note that the definition of $W_S^{(n)}$ is more clean in Liouville-space [Eq. (23)] but requires some care in Hilbert space.

We can now better appreciate the fundamental differences between these various multitime quantities. W_C (and $C^{(n)}$) depend only on a_j, where a_j' are integrated out. This follows from Eq. (13) which only contains "left" superoperators. Due to the a_j-a_j' factors in Eq. (30) $R^{(n)}$, on the other hand, depends only on the off-diagonal elements of W with $a_j\neq a_j'$ (diagonal elements do not contribute). Finally, W_S (and $S^{(n)}$) depends solely on the diagonal elements of W with $a_j=a_j'$. W_S is the basic quantity in the consistent history description of quantum dynamics [36–38] and has all the properties of a classical joint probability distribution. At each time τ_j the system is in the state $|\alpha_j\rangle$ and its density matrix is $|\alpha_j\rangle\langle\alpha_j|,j=0,\ldots,n$. In contrast, in a nonlinear response measurement as described by $R^{(n)}$ we only measure A at the last time τ_n; at the earlier times $\tau_j(j=1,\ldots,n-1)$ we only "pass through" α_j, but the density matrix could be either $|\alpha_j\rangle\langle\alpha_k|$ or $|\alpha_k\rangle\langle\alpha_j|$ with $k\neq j$. W_R is thus not a joint probability; even though we perform some operation on the system at n points ($n-1$ interactions with the fields and the time of observation), only the last interaction corresponds to an actual measurement. In the other times we merely perturb the system. It should be emphasized that even though the response functions (and $W_R^{(n)}$) are experimental observables that may be obtained from multiple pulse experiments with heterodyne detection [27], they may not be represented by the joint probability $W_S^{(n)}$ since it does not carry enough information for representing this type of observables.

The response function carries information that depends on delicate interferences among events that occur at various points in time. This interference may be understood in terms of sums over pathways which differ by their time ordering, i.e., $\langle A(\tau_1)A(\tau_2)A(\tau_3)\rangle$, $\langle A(\tau_2)A(\tau_1)A(\tau_3)\rangle$, etc. It is less obvious that a similar interference does exist in classical mechanics as well. Classically, of course, time ordering is immaterial since all operators commute and it suffices to calculate $\langle A(\tau_1)A(\tau_2)A(\tau_3)\rangle$, for $\tau_1\leqslant\tau_2\cdots\leqslant\tau_n$. Quantum mechanically, each of the $n!$ permutations of the time arguments in an n-point correlation function is distinct and carries a different information. Classical correlation functions

then carry less information than their quantum counterparts. The classical interference takes place between closely lying trajectories [41,42].

IV. CORRELATION FUNCTION EXPRESSIONS FOR PHOTON STATISTICS

Photon counting statistics as well as shot noise statistics of electrons [43] are most closely related to $W_S^{(n)}$ (or $S^{(n)}$) since they involve n real measurements. However, photon counting is a more complex operation than described by $W_S^{(n)}$ since it is performed under nonequilibrium conditions where the system is strongly driven by an external field. Furthermore, the material system is not closed since photons are emitted. Thirdly, the measurement does change the state of the system, not by merely projecting onto a diagonal element. All of these complications can be adequately addressed and Eq. (23) can be modified to account for photon statistics, as will be shown below.

To proceed further we introduce the master equation, derived by tracing the density matrix over the radiation field [22–24]. We shall denote by $\Gamma_{\nu\nu'}$ the spontaneous emission rate from state ν' to the lower energy state ν. The total decay rate (inverse radiative lifetime) of state ν' will then be

$$\gamma_{\nu'} \equiv \sum_{\nu \neq \nu'} \Gamma_{\nu\nu'}. \tag{32}$$

The effects of spontaneous emission are then incorporated by the master equation

$$\frac{d\rho_{\nu\nu'}}{dt} = -\frac{1}{2}(\gamma_\nu + \gamma_{\nu'})\rho_{\nu\nu'}, \quad \nu \neq \nu',$$

$$\frac{d\rho_{\nu\nu}}{dt} = -\gamma_\nu \rho_{\nu\nu} + \sum_{\nu' \neq \nu} \Gamma_{\nu\nu'}\rho_{\nu'\nu'}. \tag{33}$$

Adopting Liouville-space (tetradic) notation, the master equation reads

$$\frac{d\rho}{dt} = -\gamma\rho - \Gamma\rho, \tag{34}$$

with

$$\gamma = \sum_{\nu,\nu'} |\nu\nu'\rangle\rangle \frac{1}{2}(\gamma_\nu + \gamma_{\nu'})\langle\langle\nu\nu'|, \tag{35}$$

and

$$\Gamma = \sum_{\nu \neq \nu'} |\nu\nu\rangle\rangle \Gamma_{\nu\nu'}\langle\langle\nu'\nu'|. \tag{36}$$

The quantities defined in the previous section correspond to a closed-system and may be described either in Hilbert space or in Liouville-space [44,45]; the choice is a matter of convenience. The master equation allows us to avoid the explicit

treatment of the field degrees of freedom when describing an open system. This can only be done by using the density matrix in Liouville space.

We consider a single quantum system coupled to a bath, driven by an external field and subjected to spontaneous emission. The Liouville equation will be partitioned as

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}L(t)\rho - \Gamma\rho. \tag{37}$$

Here the Liouville operator $L(t) \equiv H_-(t)$ includes our single multilevel system, any other bath degrees of freedom, as well as the driving field. It also includes the γ matrix [Eq. (35)] which represents the diagonal (in Liouville space) part of the master equation. Γ, on the other hand [Eq. (36)], is the off-diagonal part of the master equation which describes the transitions among states ν and ν'.

We define the Green function solution of Eq. (37) with $\Gamma = 0$

$$\mathcal{G}(\tau_2, \tau_1) \equiv T \exp\left[-\frac{i}{\hbar}\int_{\tau_1}^{\tau_2} d\tau L(\tau)\right], \tag{38}$$

and introduce the off-diagonal radiative-decay operator in the interaction picture

$$\Gamma(\tau) \equiv \mathcal{G}^\dagger(\tau,0)\Gamma\mathcal{G}(\tau,0). \tag{39}$$

The solution of Eq. (37) in the interaction picture then reads

$$\rho(t) = T \exp\left[-\int_{t_0}^t d\tau\Gamma(\tau)\right]\rho(t_0). \tag{40}$$

The total probability density of emitting a photon between t_0 and $t_0 + dt_0$ and another photon between t and $t+dt$ is

$$W(t,t_0) = \text{Tr}\left(T\Gamma(t)\exp\left[-\int_{t_0}^t d\tau\Gamma(\tau)\right]\Gamma(t_0)\rho(t_0)\right). \tag{41}$$

Expanding the solution of Eq. (40) to nth order in Γ, yields

$$\rho(t) = \sum_{n=0}^\infty \rho^{(n)}(t), \tag{42}$$

where

$$\rho^{(n-1)}(\tau_n) = \int_0^{\tau_n} d\tau_{n-1}\cdots\int_0^{\tau_2} d\tau_1$$

$$\times \mathcal{G}(\tau_n, \tau_{n-1})\Gamma\cdots\Gamma\mathcal{G}(\tau_2, \tau_1)\Gamma\rho(\tau_1). \tag{43}$$

$\rho^{(n-1)}$ describes $n-1$ photon emission processes at times $\tau_1\cdots\tau_{n-1}$.

The probability density $K^{(n)}$ of emitting n photons at times $\tau_1\cdots\tau_n$ is obtained by multiplying the integrand by Γ from the left and taking a trace. This gives

$$K^{(n)}(\tau_n\cdots\tau_1) = \text{Tr}[\Gamma(\tau_n)\cdots\Gamma(\tau_1)\rho(\tau_1)]. \tag{44}$$

This general expression for photon statistics in terms of system variables is equivalent to the standard normally ordered expression of field variables [1–4,6]. To see that, we consider the probability of emitting n photons between times t_i and t_f

$$P_n(t_f,t_i) = \int_{t_i}^{t_f} d\tau_n \int_{t_i}^{\tau_n} d\tau_{n-1} \cdots \int_{t_i}^{\tau_2} d\tau_1 K^{(n)}(\tau_n \cdots \tau_1).$$

(45)

As can be seen from Eq. (40), this is normalized as

$$\sum_{n=0}^{\infty} P_n(t_f,t_i) = \mathrm{Tr}\,\rho(t) = 1.$$

(46)

To compute P_n, we introduce the generating function

$$G(t_f,t_i;U) \equiv \sum_{n=0}^{\infty} P_n(t_f,t_i)U^n.$$

(47)

It then follows from Eqs. (44) and (45) that

$$G(t_f,t_i,U) = \left\langle \mathrm{T}\exp\left[U\int_{t_i}^{t_f} d\tau \Gamma(\tau)\right]\rho(t_i)\right\rangle,$$

(48)

G thus satisfies the equation of motion

$$\frac{dG(t,t_i;U)}{dt} = -\frac{i}{\hbar}L(t)G(t,t_i,U) - U\Gamma G(t,t_i,U).$$

(49)

Using Eq. (48), we have

$$P_n(t,t+T) = \frac{1}{n!}\frac{d^n}{dU^n}G(U)\bigg|_{U=0}$$

(50)

and Eq. (47) gives

$$\frac{d^m}{dU^m}G(U)\big|_{U=1} = \sum_{n=0}^{\infty} P_n(t,t+T)\frac{n!}{(n-m)!}$$

$$\equiv \langle n(n-1)\cdots(n-m+1)\rangle,$$

(51)

which is the nth factorial moment of P_n. Setting $m=1$ and $m=2$ in Eq. (51), we get

$$\langle n\rangle = \frac{dG(U)}{dU}\bigg|_{U=1},$$

$$\langle n^2\rangle - \langle n\rangle = \frac{d^2G(U)}{dU^2}\bigg|_{U=1}.$$

(52)

Higher moments may be calculated similarly.

The most commonly used measure of photon statistics, the Mandel parameter, has been shown to be related to $K^{(2)}$ [1,9,20] in simple kinetic models of single quantum systems. Photon statistics has been calculated using the simplest reduced descriptions such as the Bloch equations [21]. The present approach opens up the use of a broad class of reduced descriptions and stochastic models [26] for computing $K^{(2)}$. One interesting application will be the photon statistics in super-radiance of aggregates [46]. Equation (44) may be easily generalized to describe more refined, frequency resolved, measurements whereby at each time we monitor a different (preselected) transition. This can be done simply by using a different element of Γ at each time $\Gamma(\tau_j)$ to represent the desired transition. Equation (44) could then provide more detailed information about the system.

V. DISCUSSION

We have introduced several types of multipoint functions commonly used in experimental observations and their theoretical analysis. Using the Liouville-space superoperator notation, we can recast these various quantities in a formally similar form that facilitates their comparison. Equation (13) can be written as

$$C^{(n)}(\tau_n \cdots \tau_1) = \mathrm{Tr}[A_L \mathcal{G}(\tau_n - \tau_{n-1})A_L \cdots \mathcal{G}(\tau_2 - \tau_1)A_L \rho_{eq}],$$

(53)

where $\mathcal{G}(\tau)$ is given by Eq. (28). The nonlinear response function [Eq. (10)] can be similarly recast in the form

$$R^{(n)}(\tau_n \cdots \tau_1)$$

$$= \mathrm{Tr}[A_+\mathcal{G}(\tau_n,-\tau_{n-1})A_- \mathcal{G}\cdots A_-\mathcal{G}(\tau_2,-\tau_1)A_-\rho_{eq}].$$

(54)

The joint distribution of successive measurements [Eq. (23)] is written as

$$W_S^{(n)}(a_n\tau_n \cdots a_1\tau_1) = \mathrm{Tr}[\hat{P}(a_n)\mathcal{G}(\tau_n-\tau_{n-1})\hat{P}(a_{n-1})\cdots$$

$$\times \hat{P}(a_2)\mathcal{G}(\tau_2-\tau_1)\hat{P}(a_1)\rho_{eq}].$$

(55)

The probability density of observing consecutive photons [Eq. (44)] is

$$K^{(n)}(\tau_n \cdots \tau_1) = \mathrm{Tr}[\Gamma \mathcal{G}(\tau_n,\tau_{n-1})\cdots\Gamma \mathcal{G}(\tau_2,\tau_1)\Gamma\rho(\tau_1)],$$

(56)

where $\mathcal{G}(\tau,\tau')$ is given by Eq. (38). Finally, the probability density of measuring n photons at times $\tau_1 \cdots \tau_n$ (regardless of how many photons are emitted in between) is

$$P^{(n)}(\tau_n \cdots \tau_1) = \mathrm{Tr}[\Gamma \tilde{\mathcal{G}}(\tau_n,\tau_{n-1})\cdots\tilde{\mathcal{G}}(\tau_2,\tau_1)\Gamma\rho(\tau_1)],$$

(57)

where $\tilde{\mathcal{G}}$ is the Green function solution of Eq. (37) for the driven system

$$\rho(t) = \tilde{G}(t,t_0)\rho(t_0).$$

(58)

We note several marked differences between the photon statistics observables [Eqs. (56) and (57)] and the other quantities [Eqs. (53)–(55)]. Since the latter are equilibrium properties, the Green function is translationally invariant and only depends on the time difference $\mathcal{G}(\tau_j - \tau_k)$ rather than on τ_j and τ_k separately, $\mathcal{G}(\tau_j,\tau_k)$. Also the initial density matrix $\rho(\tau_1)$ in photon statistics measurements is generally a more complex object than ρ_{eq} since it requires computing the

preparation stage leading to a nonequilibrium steady state. This does not cause any problem in stochastic models where the bath evolution does not depend on the state of the system. $\rho(\tau_1)$ is then completely specified since the first photon emission at τ_1 determines the state of the system (the final state of the emission) and the bath is always in equilibrium. However, fully microscopic modeling will require a separate calculation of $\rho(\tau_1)$.

Equation (56) is very similar to the general expression for n successive measurements [Eq. (55)]. However, the Γ matrix is off-diagonal since photon emission is accompanied by a transition in the system, as opposed to the diagonal $\hat{P}(a)$ in Eq. (55) which represents ordinary measurements. Were we to use a diagonal $\Gamma = |\nu\nu\rangle\rangle\langle\langle\nu\nu|$ it would represent the probability of measuring the system at state ν at times $\tau_1 \cdots \tau_n$. Photon counting, however, implies that the system is at state ν prior to the count but it changes to state ν' after the count; this is the initial state for the next period of propagation. Apart from this, Eq. (56) or Eq. (57) is equivalent to n-point measurements [Eq. (55)]. These differences stem from the nonequilibrium nature of photon counting performed on open driven systems.

Finally we note that Eqs. (56) and (57) are reminiscent of the normally ordered expressions with field operators [1,3] where Γ represents the detector rather than spontaneous emission. In the present approach we do not need normal ordering since in Liouville-space time ordering is enough to maintain the bookkeeping of interactions. We also note that $L(\tau)$ in Eq. (38) contains the γ matrix, and the Green function therefore contains some diagonal signatures of the photon emission. This is required for maintaining the trace of the density matrix. Such terms should also be present in the field formulation, but are usually neglected and the Green function represents the pure system (without the detector) [1,3]. Adding these corrections could improve the standard theory of photon statistics.

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