Perturbation approach for computing frequency- and time-resolved photon correlation functions

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We propose an alternative formulation of the sensor method presented in Phys. Rev. Lett. **109**, 183601 (2012) for the calculation of frequency-filtered and time-resolved photon correlations. Our approach is based on an algebraic expansion of the joint steady state of quantum emitter and sensors with respect to the emitter-sensor coupling parameter ϵ. This allows us to express photon correlations in terms of the open quantum dynamics of the emitting system only and ensures that computation of correlations are independent on the choice of a small value of ϵ. Moreover, using time-dependent perturbation theory, we are able to express the frequency- and time-resolved second-order photon correlation as the addition of three components, each of which gives insight into the physical processes dominating the correlation at different time scales. We consider a bioinspired vibronic dimer model to illustrate the agreement between the original formulation and our approach.

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I. INTRODUCTION

Single-photon coincidence measurements have been recognized as a fundamental theoretical and experimental methodology to characterize quantum properties both of light [1–4] as well as those of the emitting source [5–7]. Particular focus has been placed on investigation of the second-order photon correlation function as the lowest order of correlations capable of probing nonclassical phenomena [2]. Formally, such a normally ordered two-photon correlation function is defined as [8]

$$g^{(2)}(t_1,t_2)=\frac{\langle \mathcal{T}_-[\hat{A}^\dagger(t_1)\hat{A}^\dagger(t_2)]\mathcal{T}_+[\hat{A}(t_2)\hat{A}(t_1)]\rangle}{\langle \hat{A}^\dagger(t_1)\hat{A}(t_1)\rangle\langle \hat{A}^\dagger(t_2)\hat{A}(t_2)\rangle}, \quad (1)$$

with $\hat{A}$ being the field operator and $\mathcal{T}_-$ and $\mathcal{T}_+$ the time-ordering and antiordering superoperators necessary for a consistent physical description [8]. Here $\mathcal{T}_-$ increases time arguments to the right in products of creation operators, while $\mathcal{T}_+$ increases time arguments to the left in products of annihilation operators.

In the context of photon counting experiments it has also become clearer that spectral filtering of optical signals—and its associated trade-off between frequency and time resolution—opens up the door for the investigation of a variety of phenomena in quantum optics [8–12]. The energy-time Fourier uncertainty relation imposes a constraint on the precision with which arrival time and frequency of a photon can be measured [13,14]. Rather than being a limitation, this uncertainty has shown to offer a potential for investigations of quantum phenomena ranging from the identification and manipulation of a variety of photon correlations [10,15–18] to the development of protocols for the preparation and readout of entangled photons [19,20]. It has also been shown that frequency- and time-resolved photon correlation measurements can provide deep insights into the dynamics of solid-state systems [21] and complex molecular systems [22–24]. For the latter it is argued that the information obtained through spectrally resolved correlations is complementary to that obtained by coherent multidimensional spectroscopy [25]—the ultrafast nonlinear technique capable of probing of quantum coherence dynamics in a variety of biomolecular and chemical systems (for a review, see [26]).

Filter-dependent correlation functions are defined in terms of filtered emission operators $\hat{A}_F(t)=\int_0^\infty F(t')\hat{A}(t-t')dt'$ and $\hat{A}_F^\dagger(t)=\int_0^\infty F(t')\hat{A}^\dagger(t-t')dt'$, with $F(t)$ the one-sided Fourier transform of the frequency filter function. The filtered two-time correlation function can be written as $g^{(2)}_{F_1,F_2}(T_1,T_2)$ and is defined identically to Eq. (1), but with the substitutions $\hat{A}^{(\dagger)}(t_1)\to\hat{A}^{(\dagger)}_{F_1}(T_1)$ and $\hat{A}^{(\dagger)}(t_2)\to\hat{A}^{(\dagger)}_{F_2}(T_2)$ with $F_j(t)$ the time and space filter functions for each detector [8,27–30]. Due to the convoluted definition of $\hat{A}^{(\dagger)}_{F_j}$, calculating $g^{(2)}_{F_1,F_2}(T_1,T_2)$ involves computing a four-dimensional integral with the time ordering applying within this set of integrals, thereby making such a calculation nontrivial. Higher-order correlations $g^{(n)}_{F_1\ldots F_n}(T_1\ldots T_n)$ are defined in a similar way, although their theoretical computation becomes more difficult. Thus a full theoretical understanding of the effects of such filters in the photon statistics has only recently been possible with the development of methods that can overcome the computational complexity [15,16,31].

In particular, Refs. [15,16] have put forward a general and powerful theoretical sensor method for calculating these frequency- and time-resolved correlation functions, which avoids the need to explicitly compute the multidimensional integral set. This formalism considers weak quantum coherent coupling between the quantum emitter and a set of sensors, each of which is represented as a two-level system. In the limit of vanishing system-sensor coupling, the sensor population correlations are shown to quantify the photon correlations of interest. One of the drawbacks of this approach is the fact that its more general computation requires solving the quantum dynamics of the joint emitter-sensors state and therefore the

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dimensionality of the Hilbert space in question can become a problem for quantum systems of large dimension and for higher-order correlations. This issue of having to consider the joined system-sensor Hilbert space has been highlighted and discussed in Ref. [31]. There the authors consider the specific problem of single-atom fluorescence and develop an interesting generalization of signal-processing methods applied to spectral filtering, where filters are treated as black boxes connected to the output. The analysis leads to formal expressions for higher-order spectral correlation functions that are resolved in time and frequency and are defined in the Hilbert space of the atom only. Within this framework the evaluation of time-resolved correlations does involve solving multidimensional integrals, though analytical solutions can be obtained under certain approximations.

In this paper, we report an alternative formulation of the sensor method [15,16] that allows us to derive photon correlations fully in terms of the quantum dynamics of the emitting system, thereby overcoming the need for solving the joint emitter-sensors quantum dynamics. By algebraically expanding the joint system-sensors state with respect to the weak system-sensor coupling parameter, we derive a hierarchy of auxiliary emitter-related matrices that allows efficient computation of photon correlations of arbitrary order at zero time delay. The hierarchy gives some insight into the physics of probing photon correlations with hypothetically weakly and coherently coupled sensors. Our formalism recovers the analytical expressions presented in the Supplemental Material of Ref. [15] and in Ref. [32] for the one- and two-photon spectrum, thereby showing full agreement between the approaches. Furthermore, using time-dependent perturbation theory, we derive a solution for the second-order photon correlation that can be expressed as the addition of three components, each of which provides insight into the physical processes dominating the emission dynamics at different time scales. The approach can be straightforwardly generalized to higher-order photon correlations where only one sensor has a time delayed detection.

The remaining of the paper is organized as follows. Section II summarizes the original presentation of the sensor method and motivates the development of an alternative formulation. Section III presents our algebraic approach to expand the steady state and derive the photon correlations at zero-time delay. Section IV explains the derivation of time-dependent correlation functions for finite detection delays. Section V illustrates the agreement between our approach and the original sensor method for a bioinspired vibronic dimer model, thereby highlighting the advantages filtered photon-counting statistics could offer for investigation of quantum dynamics in complex molecular systems. Section VI concludes.

II. MOTIVATION

As proposed in Ref. [15], the sensor method for calculating the M-photon correlation function involves simulating the dynamics of a quantum emitter with Hamiltonian H_0, weakly coupled to M sensors represented by two-level systems, labeled with $m = 1, \ldots, M$, and ground and excited states $|0_m\rangle$ and $|1_m\rangle$, respectively. Each sensor has an associated Hamiltonian $H_m = \omega_m \varsigma_m^\dagger \varsigma_m$ with annihilation operator

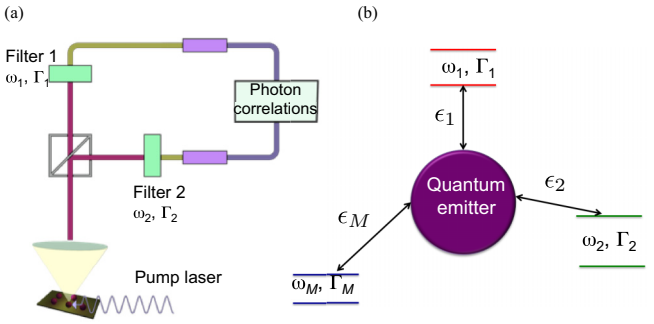

FIG. 1. (a) Schematic of an experimental setup to measure frequency-resolved photon correlations similar to the one used in Ref. [20]. (b) Diagram of the sensor method proposed in Ref. [15] to compute frequency-filtered correlations. Each sensor, represented by a two-level system, is quantum mechanically coupled to the quantum emitter with coupling strength ϵ_m with $m = 1, \ldots, M$. Photon correlations are given by normally ordered sensor operator correlations in the limit when $\epsilon_1, \ldots, \epsilon_M \to 0$.

$\varsigma_m = |0_m\rangle\langle 1_m|$ and transition frequency ω_m set to match the emission frequency to be measured. The interaction Hamiltonian between the quantum emitter and the mth sensor is given by $H_{e,m} = \epsilon_m(a_m \varsigma_m^\dagger + a_m^\dagger \varsigma_m)$, with the coupling strength ϵ_m being small enough to neglect backaction. For generality, we have considered that the emission operators a_j coupled to each sensor can be different. This is the case whenever local resolution is achievable in a multipartite quantum emitter or when emitting transitions can be distinguished via fluorescence polarization detection as it happens, for instance, in single light-harvesting complexes [33]. In such a scenario, the frequency filters illustrated in the envisioned experimental setup [see Fig. 1(a)] will also be polarizing filters.

Considering Markovian relaxation channels for both the emitter and the sensors, the joint emitter-sensors density matrix $\hat{\rho}$ satisfies the master equation $\frac{\partial}{\partial t}\hat{\rho} = \mathcal{L}(\hat{\rho})$, with the Liouvillian conveniently split as ($\hbar = 1$)

$$\mathcal{L}(\hat{\rho}) = \mathcal{L}_0(\hat{\rho}) + \sum_{m=1}^{M} (\mathcal{L}_m(\hat{\rho}) - i\,[H_{e,m}, \hat{\rho}]), \tag{2}$$

with

$$\mathcal{L}_0(\hat{\rho}) = -i\,[H_0, \hat{\rho}] + \sum_i \frac{1}{2}\gamma_{c_i}\mathcal{L}_{c_i}(\hat{\rho}), \tag{3}$$

$$\mathcal{L}_m(\hat{\rho}) = -i\,[H_m, \hat{\rho}] + \frac{1}{2}\Gamma_m \mathcal{L}_{\varsigma_m}(\hat{\rho}). \tag{4}$$

The superoperators on the right-hand side of Eq. (3) have the Lindblad form, i.e., $\mathcal{L}_{c_i}(\hat{\rho}) = 2c_i\hat{\rho}c_i^\dagger - c_i^\dagger c_i\hat{\rho} - \hat{\rho}c_i^\dagger c_i$ for a system jump operator c_i and a relaxation process at rate γ_{c_i}. Same holds for $\mathcal{L}_{\varsigma_m}$ in Eq. (4) describing the decay of the mth sensor with jump operator ς_m at a rate Γ_m. In the limit of ϵ_m satisfying $\epsilon_m \ll \sqrt{\Gamma\gamma_Q/2}$ with γ_Q the smallest transition rate within the emitter dynamics, and sensor populations satisfying $\langle n_m\rangle = \langle \varsigma_m^\dagger \varsigma_m\rangle \ll 1$, intensity-intensity correlations of the form $\langle : n_1 n_2 \ldots n_M : \rangle$ are directly related to the Mth-order

photon correlation functions [15,16]:

$$g^{(M)}_{\Gamma_1\ldots\Gamma_M}(\omega_1, T_1; \ldots; \omega_M, T_M) = \lim_{\epsilon_1,\ldots,\epsilon_M\to 0} \frac{\langle : n_1(T_1)\ldots n_M(T_M) : \rangle}{\langle n_1(T_1)\rangle \ldots \langle n_M(T_M)\rangle}, \quad (5)$$

$$\langle : n_1(T_1)\ldots n_M(T_M) : \rangle = \frac{\epsilon_1^2\ldots\epsilon_M^2}{\Gamma_1\ldots\Gamma_M}(2\pi)^M S^{(M)}_{\Gamma_1\ldots\Gamma_M}(\omega_1, T_1; \ldots; \omega_M, T_M), \quad (6)$$

with [8]

$$\begin{aligned} S^{(M)}_{\Gamma_1\ldots\Gamma_M}(\omega_1, T_1; \ldots; \omega_M, T_M) &= \int_{-\infty}^{\infty} dt_1' \int_{-\infty}^{\infty} dt_{M+1}' F_1^*(T_1 - t_1') F_1(T_1 - t_{M+1}') \ldots \\ &\int_{-\infty}^{\infty} dt_M' \int_{-\infty}^{\infty} dt_{2M}' F_M^*(T_M - t_M') F_M(T_M - t_{2M}') \\ &\times \langle \mathcal{T}_-[a_1^{(+)}(t_1') \ldots a_M^{(+)}(t_M')] \\ &\times \mathcal{T}_+[a_1^{(-)}(t_{M+1}') \ldots a_M^{(-)}(t_{2M}')]\rangle. \end{aligned} \quad (7)$$

The filter functions correspond to a Cauchy-Lorentz distribution, i.e., $F_m(t) = \theta(t)\Gamma_m/2 \exp[-(\Gamma_m/2 + i\omega_m)t]$ with $\theta(t)$ the Heaviside function, and can be realized, for instance, via a Fabry-Pérot interferometer when the reflection coefficient tends to unity [13]. The experimental setup we envision is sketched in Fig. 1(a) and the theoretical calculation of frequency-filtered photon correlations through the sensor method is illustrated in Fig. 1(b).

The original presentation of Eq. (5) in Ref. [15] omitted the normal order. Without the normal order this function yields unphysical results for a finite delay time. In an Erratum [16] the authors clarified that normal order is implied through the proof of Eq. (5), though it turns out to be unnecessary for zero time delay. Since Eq. (5) is the departing point of our work, we have carried out a consistency check of its proof as discussed in Appendix A.

The method as proposed in Ref. [15] is conceptually clear and mathematically equivalent to the integral form of correlations. Yet, in practice, its more general computation involves tackling some numerical challenges. Assuming that all the sensor couplings are identical, $\epsilon_j = \epsilon$, the numerical calculations of photon correlations rely on the choice of a system-sensor coupling ϵ that is numerically small, but not *so* small that adding or subtracting terms of order ϵ^{2M} to or from terms of order ϵ^0 causes problems within double precision arithmetic. The procedure then involves checking convergence and stability of the numerical results for different values of ϵ. Most importantly, computation of photon correlations at zero-time delay requires numerically finding the zero eigenvalue of the Liouvillian superoperator associated to the joint emitter system plus sensors. This means that computing $g^{(M)}_{\Gamma_1\ldots\Gamma_M}(\omega_1, T; \ldots; \omega_M, T)$ when $T \to \infty$ involves calculating the eigenvector with a zero eigenvalue of a matrix 4^M times larger than that of the quantum emitter alone [17]. Similarly, for time-resolved correlations, the calculation involves time propagation in the joint state space of the system and sensors. Evidently, as the dimensionality of the system is larger these numerical challenges become more demanding.

We were therefore motivated to find an approach that would allow us to avoid the issues above mentioned. In what follows we show that by expanding algebraically in ϵ one can propose an approach that eliminates the explicit numerical dependence on ϵ while at the same time reducing the dimensionality of the Hilbert space needed for computation.

III. FREQUENCY-FILTERED SPECTRUM AND PHOTON CORRELATIONS AT ZERO DELAY TIME

A. $M = 1$: Power spectrum

The weak coherent coupling assumption between quantum emitter and sensors implies that sensors probe the emitter dynamics without perturbing it. Following this physical rationale, we would then like to have a formalism that expresses the frequency-resolved photon correlations in terms of operators and dynamics defined in the Hilbert space of the system only.

We begin by demonstrating the basics of our derivation by considering the emitter system coupled to only one sensor. Let us denote $\hat{\rho}_{ss}$ the steady state of the joint emitter-plus-sensor system. From Eq. (6) we can calculate the power spectrum as

$$S^{(1)}_{\Gamma_1}(\omega_1) = \frac{\Gamma_1}{2\pi\epsilon^2}\langle n_1\rangle = \frac{\Gamma_1}{2\pi\epsilon^2}\,\mathrm{Tr}\,[n_1\hat{\rho}_{ss}]. \quad (8)$$

Considering the identity operator in the sensor Hilbert space, i.e., $\mathbb{1}_{s_1} = \sum_{j_1=0,1} |j_1\rangle\langle j_1|$, we can write the full steady state $\hat{\rho}_{ss}$ as

$$\hat{\rho}_{ss} = \mathbb{1}_{s_1}\hat{\rho}_{ss}\mathbb{1}_{s_1} = \sum_{j_1, j_1'=0,1} \hat{\rho}^{j_1'}_{j_1,} \otimes |j_1\rangle\langle j_1'|, \quad (9)$$

where the matrices $\hat{\rho}^{j_1'}_{j_1} = \langle j_1|\hat{\rho}_{ss}|j_1'\rangle$ are therefore only related to the degrees of freedom of the quantum emitter but are conditioned on specific sensor states. These matrices can then be interpreted as "auxiliary conditional states." Hermitian conjugates are obtained by swapping the upper and lower indices. Notice that each matrix $\hat{\rho}^{j_1'}_{j_1}$ is thus of order $\epsilon^{j_1+j_1'}$. With this definition the power spectrum given in Eq. (18) becomes

$$S^{(1)}_{\Gamma_1}(\omega_1) = \frac{\Gamma_1}{2\pi\epsilon^2}\,\mathrm{Tr}\left[\hat{\rho}_1^1\right]. \quad (10)$$

We now show that the relevant matrix $\hat{\rho}_1^1$ can be computed via a hierarchy of equations involving auxiliary matrices of lower order, which carry information on the emission properties of the steady state probed at the specific sensor frequency ω_1. We do this by considering the combined emitter plus sensor steady-state condition $\mathcal{L}(\hat{\rho}_{ss}) = 0$ and the action of the Liouvillian given in Eq. (2) ($M = 1$) on every term in Eq. (9):

$$\mathcal{L}\big(\hat{\rho}_0^0 \otimes |0\rangle\langle 0|\big) = \mathcal{L}_0\big(\hat{\rho}_0^0\big) \otimes |0\rangle\langle 0| - i\epsilon\big(a_1\hat{\rho}_0^0 \otimes |1\rangle\langle 0| - \hat{\rho}_0^0 a_1^\dagger \otimes |0\rangle\langle 1|\big), \quad (11)$$

$$\mathcal{L}\big(\hat{\rho}_1^0 \otimes |1\rangle\langle 0|\big) = (\mathcal{L}_0 - \Gamma_1/2 - i\omega_1)\big(\hat{\rho}_1^0 \otimes |1\rangle\langle 0| - i\epsilon\big(a_1^\dagger\hat{\rho}_1^0 \otimes |0\rangle\langle 0| - \hat{\rho}_1^0 a_1^\dagger \otimes |1\rangle\langle 1|\big), \quad (12)$$

$$\mathcal{L}\big(\hat{\rho}_1^1 \otimes |1\rangle\langle 1|\big) = (\mathcal{L}_0 - \Gamma_1)\big(\hat{\rho}_1^1 \otimes |1\rangle\langle 1|\big) + \Gamma_1\hat{\rho}_1^1 \otimes |0\rangle\langle 0| - i\epsilon\big(a_1^\dagger\hat{\rho}_1^1 \otimes |0\rangle\langle 1| - \hat{\rho}_1^1 a_1 \otimes |1\rangle\langle 0|\big), \quad (13)$$

and the expression for $\mathcal{L}(\hat{\rho}_0^1 \otimes |0_1\rangle\langle 1_1|)$ is the complex conjugate of Eq. (12). We can rewrite the sum of these expressions, in a similar way to Eq. (9), by grouping together terms related to populations or coherences of the sensor:

$$\mathcal{L}(\hat{\rho}_{ss}) = \sum_{j_1, j_1'=0,1} \hat{B}_{j_1,}^{j_1'} \otimes |j_1\rangle\langle j_1'| = \mathbf{0}, \tag{14a}$$

$$\hat{B}_{j_1,}^{j_1'} = \mathbf{0}, \quad \text{for all } j_1, j_1'. \tag{14b}$$

In this way we can see our problem reduces to solving the set of coupled equations for $\hat{\rho}_{j_1,}^{j_1'}$ such that the operators $\hat{B}_{j_1,}^{j_1'}$ of the system are null matrices (zero at every element). For instance, the equation $\hat{B}_0^0 = \mathbf{0}$ becomes

$$\hat{B}_0^0 = \mathcal{L}_0(\hat{\rho}_0^0) - i\epsilon\left(a_1^\dagger \hat{\rho}_1^0 - \hat{\rho}_0^1 a_1\right) + \Gamma_1 \rho_1^1 = \mathbf{0}. \tag{15}$$

For an arbitrary value of ϵ, Eq. (15) indicates that $\hat{\rho}_0^0$ depends on higher-order terms such that the sensors will not be just probing but affecting the system dynamics, and the set of coupled equations in Eq. (14b) will not have a simple solution. However, in the limit of weak coupling where $\epsilon \ll 1$ and sensors populations are very small, i.e., $\langle n_1\rangle = \mathrm{Tr}[\hat{\rho}_1^1] \ll 1$, we can neglect terms of the order of ϵ^2 in Eq. (15), that is, we discard the terms $\Gamma_1\hat{\rho}_1^1$ and $\|i\epsilon(a_1^\dagger\hat{\rho}_1^0 - \hat{\rho}_0^1 a_1)\|$. Likewise, for the equation of $\hat{B}_0^1 = \mathbf{0}$ (not shown) we have $\|a_1^\dagger\hat{\rho}_1^1\| \ll \|\hat{\rho}_0^0 a_1^\dagger\|$ such that terms depending on $\hat{\rho}_1^1$ can be neglected. These approximations, in which the sensor probes the system at a specific frequency and without affecting its dynamics, can be generalized to the concept of ignoring down coupling, that is, the prefactor matrix $\hat{B}_{j_1,}^{j_1'}$ for $|j_1\rangle\langle j_1'|$ has only contributions from terms that are of lower or the same order on ϵ, i.e., $\hat{\rho}_\ell^{\ell'}$ with $\ell + \ell' \leqslant j_1 + j_1'$. This is equivalent to a formal expansion in ϵ as all the $\hat{\rho}_\ell^{\ell'}$ matrices are of order $\epsilon^{\ell+\ell'}$. Using these approximations, we can write out the equations governing the steady state $\hat{B}_{j_1}^{j_1'} = 0$ as

$$\mathcal{L}_0(\hat{\rho}_0^0) \sim 0, \tag{16a}$$

$$\mathcal{L}_0(\hat{\rho}_1^0) - (\Gamma_1/2 + i\omega_1)\hat{\rho}_1^0 - i\epsilon a_1\hat{\rho}_0^0 \sim 0, \tag{16b}$$

$$\mathcal{L}_0(\hat{\rho}_0^1) - (\Gamma_1/2 - i\omega_1)\hat{\rho}_0^1 + i\epsilon\hat{\rho}_0^0 a_1^\dagger \sim 0, \tag{16c}$$

$$\mathcal{L}_0(\hat{\rho}_1^1) - \Gamma_1\hat{\rho}_1^1 - i\epsilon\left(a_1\hat{\rho}_0^1 - \hat{\rho}_1^0 a_1^\dagger\right) = 0. \tag{16d}$$

Notice Eq. (16d) has an equality as for that case all terms are of the same order so none is discarded. We can solve these equations in a chain from top to bottom, starting with $\hat{\rho}_0^0$. Formulating the problem in Liouville space, $|\hat{\rho}_0^0\rangle\!\rangle$ is the zero eigenvector of the (square) matrix $\mathcal{L}_0$ given in Eq. (3) and therefore it corresponds to the emitter steady state in the absence of any detector. The remaining equations can be solved as

$$|\hat{\rho}_1^0\rangle\!\rangle \sim \frac{i\epsilon a_1|\hat{\rho}_0^0\rangle\!\rangle}{\mathcal{L}_0 - (\Gamma_1/2 + i\omega_1)\mathbb{1}}, \tag{17a}$$

$$|\hat{\rho}_1^1\rangle\!\rangle = \frac{i\epsilon\left(a_1|\hat{\rho}_0^1\rangle\!\rangle - |\hat{\rho}_1^0\rangle\!\rangle a_1{}^\dagger\right)}{\mathcal{L}_0 - \Gamma_1\mathbb{1}}, \tag{17b}$$

where a_1 and $a_1^\dagger$ are written in the Liouville space form and $\mathbb{1}$ is the identity operator in the emitter Hilbert space. We need not solve for $\hat{\rho}_0^1$ as it is equal to $\hat{\rho}_1^{0\,\dagger}$. In the above equations $\hat{\rho}_1^0$ has a prefactor of ϵ; therefore, $\hat{\rho}_1^1$ has a prefactor of ϵ^2. Since the power spectrum given in Eq. (10) has a prefactor ρ_1^1/ϵ^2, then it is clear that its dependence on ϵ vanishes algebraically. The power spectrum is finally given by

$$S_{\Gamma_1}(\omega_1) = \frac{\Gamma_1}{2\pi}\mathrm{Tr}\left[\tilde{\hat{\rho}}_1^1\right], \tag{18}$$

where $\tilde{\hat{\rho}}_{j_1}^{j_1'} = \hat{\rho}_{j_1}^{j_1'}/\epsilon^{j_1+j_1'}$. Notice that substituting Eq. (17) in Eq. (18) leads to a semianalytical expression comparable to that presented in Ref. [32] for the one-photon spectrum, but here generalized for any open quantum system dynamics described by a superoperator $\mathcal{L}_0$. Moreover, the form of the hierarchy of equations in Eq. (17) gives us some physical insight on how the coherently coupled sensor probes the emission properties of the system steady state $\hat{\rho}_0^0$ by evaluating the action of the emission operators a_1 ($a_1^\dagger$) on "auxiliary states" $\hat{\rho}_0^1(\hat{\rho}_1^0)$, which in turn contain information of the emitting transitions filtered at frequency ω_1.

B. $M \geqslant 2$ zero-delay correlations

The normalized second-order ($M = 2$) photon correlation at zero delay time can be written as

$$g^{(2)}_{\Gamma_1\Gamma_2}(\omega_1, \omega_2) = \frac{S^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1, \omega_2)}{S^{(1)}_{\Gamma_1}(\omega_1)\, S^{(1)}_{\Gamma_2}(\omega_2)}, \tag{19}$$

where $S_{\Gamma_1}(\omega_1)$ and $S_{\Gamma_2}(\omega_2)$ are the mean count rates for the two sensors, as given in Eq. (18), and

$$S^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1, \omega_2) = \frac{\Gamma_1\Gamma_2}{(2\pi)^2\epsilon^4}\,\langle :n_1 n_2: \rangle. \tag{20}$$

Since time-independent sensor number operators n_j commute, normal order in Eq. (20) is unnecessary. Following the same procedure as before, we write our steady-state density matrix, with two sensors included, as

$$\hat{\rho}_{ss} = \sum_{j_1, j_2, j_1', j_2'=0,1} \hat{\rho}_{j_1,j_2}^{j_1',j_2'} \otimes |j_1\rangle\langle j_1'| \otimes |j_2\rangle\langle j_2'|, \tag{21}$$

where $\{j_1, j_1'\}$ and $\{j_2, j_2'\}$ are counters over the states of sensor 1 and sensor 2, respectively. As before, the matrices $\hat{\rho}_{j_1,j_2}^{j_1',j_2'} = \langle j_1 j_2|\hat{\rho}_{ss}|j_1' j_2'\rangle$ are defined in the Hilbert space of the quantum emitter alone. With this definition the second-order photon coincidence becomes

$$S^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1, \omega_2) = \frac{\Gamma_1\Gamma_2}{(2\pi)^2}\,\mathrm{Tr}\left[\tilde{\hat{\rho}}_{1,1}^{1,1}\right], \tag{22}$$

with the power spectrum given by

$$S^{(1)}_{\Gamma_1}(\omega_1) = \frac{\Gamma_1}{2\pi}\,\mathrm{Tr}\left[\tilde{\hat{\rho}}_{1,0}^{1,0}\right], \quad S^{(1)}_{\Gamma_2}(\omega_2) = \frac{\Gamma_2}{2\pi}\,\mathrm{Tr}\left[\tilde{\hat{\rho}}_{0,1}^{0,1}\right], \tag{23}$$

where $\tilde{\hat{\rho}}_{j_1,j_2}^{j_1',j_2'} = \hat{\rho}_{j_1,j_2}^{j_1',j_2'}/\epsilon^{j_1+j_1'+j_2+j_2'}$. To compute the matrices $\hat{\rho}_{j_1,j_2}^{j_1',j_2'}$ we solve for the steady state $\mathcal{L}(\hat{\rho}_{ss}) = 0$ with two sensors and by ignoring down coupling terms, that is, the matrix prefactor for $|j_1\rangle\langle j_1'| \otimes |j_2\rangle\langle j_2'|$ has only contributions from terms $\hat{\rho}_{\ell_1,\ell_2}^{\ell_1',\ell_2'}$ satisfying the condition $\ell_1 + \ell_2 + \ell_1' + \ell_2' \leqslant j_1 + j_2 + j_1' + j_2'$. This means we are neglecting matrices

depending on powers of ϵ higher than those in the matrix in question. The resultant hierarchy of linearly independent equations (besides those which are Hermitian conjugates of others) are then given by

$$\mathcal{L}_0\big(\tilde{\rho}^{0,0}_{0,0}\big) \sim 0, \tag{24a}$$

$$[\mathcal{L}_0 - \Gamma_1/2 - i\omega_1]\big(\tilde{\rho}^{0,0}_{1,0}\big) \sim i a_1 \tilde{\rho}^{0,0}_{0,0}, \tag{24b}$$

$$[\mathcal{L}_0 - \Gamma_2/2 - i\omega_2]\big(\tilde{\rho}^{0,0}_{0,1}\big) \sim i a_2 \tilde{\rho}^{0,0}_{0,0}, \tag{24c}$$

$$[\mathcal{L}_0 - \Gamma_1]\big(\tilde{\rho}^{1,0}_{1,0}\big) \sim i\big(a_1 \tilde{\rho}^{1,0}_{0,0} - \tilde{\rho}^{0,0}_{1,0} a_1^\dagger\big), \tag{24d}$$

$$[\mathcal{L}_0 - \Gamma_2]\big(\tilde{\rho}^{0,1}_{0,1}\big) \sim i\big(a_2 \tilde{\rho}^{0,1}_{0,0} - \tilde{\rho}^{0,0}_{0,1} a_2^\dagger\big), \tag{24e}$$

$$\begin{aligned}[\mathcal{L}_0 - (\Gamma_2 + \Gamma_1)/2 - i(\omega_1 + \omega_2)]\big(\tilde{\rho}^{0,0}_{1,1}\big)\\ \sim i\big(a_1 \tilde{\rho}^{0,0}_{0,1} + a_2 \tilde{\rho}^{0,0}_{1,0}\big),\end{aligned} \tag{24f}$$

$$\begin{aligned}[\mathcal{L}_0 - (\Gamma_2 + \Gamma_1)/2 - i(\omega_1 - \omega_2)]\big(\tilde{\rho}^{0,1}_{1,0}\big)\\ \sim i\big(a_1 \tilde{\rho}^{0,1}_{0,0} - \tilde{\rho}^{0,0}_{1,0} a_2^\dagger\big),\end{aligned} \tag{24g}$$

$$\begin{aligned}[\mathcal{L}_0 - (\Gamma_1/2 + \Gamma_2) - i\omega_1]\big(\tilde{\rho}^{0,1}_{1,1}\big)\\ \sim i\big(a_1 \tilde{\rho}^{0,1}_{0,1} + a_2 \tilde{\rho}^{0,1}_{1,0} - \tilde{\rho}^{0,0}_{1,1} a_2^\dagger\big),\end{aligned} \tag{24h}$$

$$\begin{aligned}[\mathcal{L}_0 - (\Gamma_2/2 + \Gamma_1) - i\omega_2]\big(\tilde{\rho}^{1,0}_{1,1}\big)\\ \sim i\big(a_1 \tilde{\rho}^{1,0}_{0,1} - \tilde{\rho}^{0,0}_{1,1} a_1^\dagger + a_2 \tilde{\rho}^{1,0}_{1,0}\big),\end{aligned} \tag{24i}$$

$$\begin{aligned}[\mathcal{L}_0 - (\Gamma_1 + \Gamma_2)]\big(\tilde{\rho}^{1,1}_{1,1}\big)\\ = i\big(a_1 \tilde{\rho}^{1,1}_{0,1} - \tilde{\rho}^{0,1}_{1,1} a_1^\dagger + a_2 \tilde{\rho}^{1,1}_{1,0} - \tilde{\rho}^{1,0}_{1,1} a_2^\dagger\big).\end{aligned} \tag{24j}$$

Again, $|\tilde{\tilde{\rho}}^{0,0}_{0,0}\rangle\!\rangle$ is the vector with zero eigenvalue for $\mathcal{L}_0$ and corresponds to the emitter steady state in the absence of coupling to the sensors. The solutions for the remaining matrices, in analogy to those in Eq. (17), are the following:

$$|\tilde{\tilde{\rho}}^{0,0}_{1,0}\rangle\!\rangle \sim \frac{i a_1 |\tilde{\tilde{\rho}}^{0,0}_{0,0}\rangle\!\rangle}{\mathcal{L}_0 - (i\omega_1 + \Gamma_1/2)\mathbb{1}}, \tag{25a}$$

$$|\tilde{\tilde{\rho}}^{0,0}_{0,1}\rangle\!\rangle \sim \frac{i a_2 |\tilde{\tilde{\rho}}^{0,0}_{0,0}\rangle\!\rangle}{\mathcal{L}_0 - (i\omega_2 + \Gamma_2/2)\mathbb{1}}, \tag{25b}$$

$$|\tilde{\tilde{\rho}}^{1,0}_{1,0}\rangle\!\rangle \sim \frac{i\left(a_1 |\tilde{\tilde{\rho}}^{1,0}_{0,0}\rangle\!\rangle - |\tilde{\tilde{\rho}}^{0,0}_{1,0}\rangle\!\rangle a_1^\dagger\right)}{\mathcal{L}_0 - \Gamma_1 \mathbb{1}}, \tag{25c}$$

$$|\tilde{\tilde{\rho}}^{0,1}_{0,1}\rangle\!\rangle \sim \frac{i\left(a_2 |\tilde{\tilde{\rho}}^{0,1}_{0,0}\rangle\!\rangle - |\tilde{\tilde{\rho}}^{0,0}_{0,1}\rangle\!\rangle a_2^\dagger\right)}{\mathcal{L}_0 - \Gamma_2 \mathbb{1}}, \tag{25d}$$

$$|\tilde{\tilde{\rho}}^{0,0}_{1,1}\rangle\!\rangle \sim \frac{i\left(a_1 |\tilde{\tilde{\rho}}^{0,0}_{0,1}\rangle\!\rangle - a_2 |\tilde{\tilde{\rho}}^{0,0}_{1,0}\rangle\!\rangle\right)}{\mathcal{L}_0 - (i\omega_1 + i\omega_2 + \Gamma_1/2 + \Gamma_2/2)\mathbb{1}}, \tag{25e}$$

$$|\tilde{\tilde{\rho}}^{0,1}_{1,0}\rangle\!\rangle \sim \frac{i\left(a_1 |\tilde{\tilde{\rho}}^{0,1}_{0,0}\rangle\!\rangle - |\tilde{\tilde{\rho}}^{0,0}_{1,0}\rangle\!\rangle a_2^\dagger\right)}{\mathcal{L}_0 - (i\omega_1 - i\omega_2 + \Gamma_1/2 + \Gamma_2/2)\mathbb{1}}, \tag{25f}$$

$$|\tilde{\tilde{\rho}}^{0,1}_{1,1}\rangle\!\rangle \sim \frac{i\left(a_1 |\tilde{\tilde{\rho}}^{0,1}_{0,1}\rangle\!\rangle + a_2 |\tilde{\tilde{\rho}}^{0,1}_{1,0}\rangle\!\rangle - |\tilde{\tilde{\rho}}^{0,0}_{1,1}\rangle\!\rangle a_2^\dagger\right)}{\mathcal{L}_0 - (i\omega_1 + \Gamma_1/2 + \Gamma_2)\mathbb{1}}, \tag{25g}$$

$$|\tilde{\tilde{\rho}}^{1,0}_{1,1}\rangle\!\rangle \sim \frac{i\left(a_1 |\tilde{\tilde{\rho}}^{1,0}_{0,1}\rangle\!\rangle - |\tilde{\tilde{\rho}}^{0,0}_{1,1}\rangle\!\rangle a_1^\dagger + a_2 |\tilde{\tilde{\rho}}^{1,0}_{1,0}\rangle\!\rangle\right)}{\mathcal{L}_0 - (i\omega_2 + \Gamma_2/2 + \Gamma_1)\mathbb{1}}, \tag{25h}$$

$$|\tilde{\tilde{\rho}}^{1,1}_{1,1}\rangle\!\rangle = \frac{i\left(a_1 |\tilde{\tilde{\rho}}^{1,1}_{0,1}\rangle\!\rangle - |\tilde{\tilde{\rho}}^{0,1}_{1,1}\rangle\!\rangle a_1^\dagger + a_2 |\tilde{\tilde{\rho}}^{1,1}_{1,0}\rangle\!\rangle - |\tilde{\tilde{\rho}}^{1,0}_{1,1}\rangle\!\rangle a_2^\dagger\right)}{\mathcal{L}_0 - (\Gamma_1 + \Gamma_2)\mathbb{1}}. \tag{25i}$$

Our derivation agrees with previous results [32]. Replacing Eqs. (25) in Eq. (22) leads to an analytical expression comparable to that presented in Ref. [32] for the two-photon spectrum at zero time delay. The hierarchy in Eq. (25) and, particularly, the compact form we obtain for the relevant matrix $\tilde{\tilde{\rho}}^{1,1}_{1,1}$ in Eq. (25i) gives some insight into the physics of probing the two-photon spectrum via weakly and coherently coupled sensors. The correlated sensors populations (given by $\mathrm{Tr}[\tilde{\tilde{\rho}}^{1,1}_{1,1}]$) evaluate the additive action of the emission operators a_1 and a_2 on respective "auxiliary conditional states," i.e., $\tilde{\tilde{\rho}}^{1,1}_{0,1}$ for a_1 and $\tilde{\tilde{\rho}}^{1,1}_{1,0}$ for a_2. Such auxiliary conditional states contain information on the correlations between emitting transitions of the system's steady state $\tilde{\tilde{\rho}}^{0,0}_{0,0}$, probed at frequencies ω_1 and ω_2.

Our proposed formalism allows going beyond the second order and leads to a compact form of the hierarchy defining the M-order frequency-resolved correlation at $\tau = 0$. It requires writing out the general steady state for the emitter and M sensors in the form analogous to Eqs. (9) and (21):

$$\hat{\rho}_{ss} = \sum_{j_1, j_1', \ldots, j_M, j_M' = 0,1} \hat{\rho}^{j_1' \ldots j_m' \ldots j_M'}_{j_1 \ldots j_m \ldots j_M} \otimes |j_1\rangle\langle j_1'| \otimes \cdots \otimes |j_M\rangle\langle j_M'|, \tag{26}$$

where $\{j_m, j_m'\}$ are counters over the state of sensor m and $\hat{\rho}^{j_1' \ldots j_m' \ldots j_M'}_{j_1 \ldots j_m \ldots j_M} = \langle j_1 \ldots j_m \ldots j_M | \hat{\rho_{ss}} | j_1 \ldots j_m' \ldots j_M' \rangle$. The Mth-order photon coincidence at zero-delay time is given in terms of the trace of matrix with $j_m = j_m' = 1$ for all m,

$$S^{(M)}_{\Gamma_1 \ldots \Gamma_M}(\omega_1, \ldots \omega_m, \ldots \omega_M) = \frac{\Gamma_1 \ldots \Gamma_m \ldots \Gamma_M}{(2\pi)^M} \mathrm{Tr}\big[\tilde{\tilde{\rho}}^{1 \ldots 1 \ldots 1}_{1 \ldots 1 \ldots 1}\big], \tag{27}$$

and the power spectrum for each sensor m is given by the trace of the matrix with $j_m = j_m' = 1$ for m and $j_y = j_y' = 0$ from $y \neq m$:

$$S^{(1)}_{\Gamma_m}(\omega_m) = \frac{\Gamma_m}{2\pi} \mathrm{Tr}\big[\tilde{\tilde{\rho}}^{0 \ldots 1 \ldots 0}_{0 \ldots 1 \ldots 0}\big], \tag{28}$$

where $\tilde{\tilde{\rho}}^{j_1' \ldots j_m' \ldots j_M'}_{j_1 \ldots j_m \ldots j_M} = \hat{\rho}^{j_1' \ldots j_m' \ldots j_M'}_{j_1 \ldots j_m \ldots j_M} / \epsilon^{j_1 + j_1' + \cdots + j_m + j_m' \cdots + j_M + j_M'}$. The general equation satisfied by the matrices $\tilde{\tilde{\rho}}^{j_1' \ldots j_m' \ldots j_M'}_{j_1 \ldots j_m \ldots j_M}$ such that $\mathcal{L}(\hat{\rho}_{ss}) = 0$ becomes

$$\begin{aligned}\left[\mathcal{L}_0 - \sum_{m=1}^{M} \{(j_m + j_m')\Gamma_m/2 + (j_m - j_m')i\omega_m)\}\right] \tilde{\tilde{\rho}}^{j_1' \ldots j_m' \ldots j_M'}_{j_1 \ldots j_m \ldots j_M}\\ = i \sum_{m=1}^{M} \big[\delta_{j_m,1} a_m \tilde{\tilde{\rho}}^{j_1' \ldots j_m' \ldots j_M'}_{j_1 \ldots j_m (1 - \delta_{j_m,1}) \ldots j_M}\\ - \delta_{j_m',1} \tilde{\tilde{\rho}}^{j_1' \ldots j_m' (1 - \delta_{j_m',1}) \ldots j_M'}_{j_1 \ldots j_m \ldots j_M} a_m^\dagger\big].\end{aligned} \tag{29}$$

Here $\delta_{u,v}$ is the Kronecker delta function, equal to zero if $u \neq v$ or unity if $u = v$. The derivation of Eq. (29) is discussed in Appendix B.

We conclude this section by highlighting that our approach to compute multiphoton correlations in the frequency domain is quite efficient as it depends on the Liouvillian of the emitter alone $\mathcal{L}_0$. This should provide an important advantage for quantum emitters of large Hilbert space dimension such as multichromophoric complexes [34]. Notice also that, while we have assumed a Lindblad form for $\mathcal{L}_0$ [see Eq. (4)], the relation in Eq. (29) does not explicitly depend on this fact. Hence, if one is able to generalize the proof for the equivalence between the sensor method and the integral methods beyond the Markovian and quantum regression restriction presented in the Supplemental Material of [15], our result in Eq. (29) will apply to open quantum systems undergoing non-Markovian, nonperturbative dynamics.

IV. FREQUENCY-FILTERED CORRELATIONS AT FINITE DELAY TIME

In this section we will use time-dependent perturbation theory to construct solutions for the correlation functions at finite time delay. We focus on the second-order correlation function at finite delay denoted $g^{(2)}_{\Gamma_1\Gamma_2}(\omega_1, T, \omega_2, T+\tau)$. In the steady state $\hat{\rho}_{ss}$, the explicit time dependence on T vanishes and we can simply write $g^{(2)}_{\Gamma_1\Gamma_2}(\omega_1, \omega_2, \tau)$. In terms of the sensor operators, this correlation is expressed as

$$g^{(2)}_{\Gamma_1\Gamma_2}(\omega_1, \omega_2, \tau) = \frac{S^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1, \omega_2, \tau)}{S^{(1)}_{\Gamma_1}(\omega_1)\, S^{(1)}_{\Gamma_2}(\omega_2)}, \tag{30}$$

where the numerator is given by

$$S^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1, \omega_2, \tau) = \frac{\Gamma_1\Gamma_2}{(2\pi)^2\epsilon^4}\, \langle \varsigma_1^\dagger \varsigma_2^\dagger(\tau)\varsigma_2(\tau), \varsigma_1\rangle \tag{31}$$

and the functions in the denominator are given in Eq. (23). We consider the correlations in Eq. (31) when $\tau > 0$, meaning sensor 1 first registers a detection, then sensor 2 does so a time τ later. Here the normal time ordering is of crucial importance as the sensor operators do not commute at different times. Correlations for $\tau < 0$ are obtained by exchanging $\varsigma_1 \to \varsigma_2$ and $\varsigma_2(\tau) \to \varsigma_1(\tau)$. Expressed in Liouville space, the correlation given in Eq. (31) is written as

$$\begin{aligned}\langle \varsigma_1^\dagger \varsigma_2^\dagger(\tau)\varsigma_2(\tau)\varsigma_1\rangle &= \mathrm{Tr}\{\varsigma_2^\dagger\varsigma_2\, \mathcal{G}(\tau)\varsigma_1\hat{\rho}_{ss}\varsigma_1^\dagger\} \\ &\equiv \langle\!\langle \varsigma_2^\dagger\varsigma_2|\mathcal{G}(\tau)\varsigma_1\hat{\rho}_{ss}\varsigma_1^\dagger\rangle\!\rangle,\end{aligned} \tag{32}$$

with $\mathcal{G}(\tau) = \exp(\mathcal{L}t)$, the time propagator operator for the joint sensor plus emitter with $\mathcal{L}$ given in Eq. (2). The term $\varsigma_1\hat{\rho}_{ss}\varsigma_1^\dagger$ represents a photon detection on sensor 1 which resets this sensor to its ground state and leaves the emitter and sensor 2 in a joint "conditional state," that is,

$$\hat{\rho}(0) = \varsigma_1\hat{\rho}_{ss}\varsigma_1^\dagger = \sum_{j_2, j_2'=0,1} \hat{\rho}^{1,j_2'}_{1,j_2} \otimes |j_2\rangle\langle j_2'| \otimes |0_1\rangle\langle 0_1|. \tag{33}$$

Notice that $\hat{\rho}(0)$ is not normalized but has a trace equal to $\langle\varsigma_1^\dagger\varsigma_1\rangle$. Let us define $|\hat{\rho}(\tau)\rangle\!\rangle = \mathcal{G}(\tau)|\hat{\rho}(0)\rangle\!\rangle$ with the initial condition $|\hat{\rho}(0)\rangle\!\rangle = |\varsigma_1\hat{\rho}_{ss}\varsigma_1^\dagger\rangle\!\rangle$. In principle, one can perform this explicit time propagation. Since sensor 1 is now in the ground state, only the interaction Hamiltonian with sensor 2, $H_{e,2} = \epsilon\,(a_2\varsigma_2^\dagger + a_2^\dagger\varsigma_2)$, contributes to the joint dynamics and the propagation requires one to test for convergence in ϵ. Alternatively, since we are interested in the regime where ϵ is small, we can evaluate such dynamics by using time-dependent perturbation theory with respect to $H_{e,2}$. We then proceed to expand $|\hat{\rho}(\tau)\rangle\!\rangle$ as [35]

$$|\hat{\rho}(\tau)\rangle\!\rangle = |\hat{\rho}^{(0)}(\tau)\rangle\!\rangle + |\hat{\rho}^{(1)}(\tau)\rangle\!\rangle + |\hat{\rho}^{(2)}(\tau)\rangle\!\rangle + \cdots. \tag{34}$$

The zeroth-order term corresponds to the dynamics given by the emitter and sensors Liouvillians without interaction, that is, $|\hat{\rho}^{(0)}(\tau)\rangle\!\rangle = \mathcal{G}_0(t)|\hat{\rho}(0)\rangle\!\rangle$ with $\mathcal{G}_0(t) = \exp([\mathcal{L}_0 + \mathcal{L}_1 + \mathcal{L}_2]t)$ and $\mathcal{L}_0$, $\mathcal{L}_1$, and $\mathcal{L}_2$ as in Eqs. (3) and (4). For the initial condition considered, the sensor 1 (2) will not contribute to the dynamics for $\tau > 0$ ($\tau < 0$) and can thus be traced over. The kth-order solution requires k interactions with $H_{e,2}$, but time propagation occurs only in terms of $\mathcal{G}_0(t)$:

$$|\hat{\rho}^{(k)}(\tau)\rangle\!\rangle = -i\int_0^\tau dt\; H^\times_{e,2}\mathcal{G}_0(\tau - t)|\hat{\rho}^{(k-1)}(t)\rangle\!\rangle, \tag{35}$$

with $H^\times_{e,2}|\rho\rangle\!\rangle \equiv [H_{e,2}, \rho]$ denoting a commutator superoperator in Liouville space. Notice that $\hat{\rho}(0)$ contains $\hat{\rho}^{1,j_2'}_{1,j_2}$, which has terms of order $\epsilon^{2+j_2+j_2'}$, that is, from ϵ^2 up to ϵ^4. This indicates that to compute the second-order correlation function we need to consider up to second-order perturbation theory as this will be the first term that, by requiring two iterations of $H_{e,2}$, will be of the same order ϵ^2. Third-order perturbation will result in terms of the order of ϵ^5 or higher, which are negligible under the weak-coupling assumption. The time-resolved photon correlation can thus be written as

$$\langle \varsigma_1^\dagger\varsigma_2^\dagger(\tau)\varsigma_2(\tau)\varsigma_1\rangle = \langle\!\langle \varsigma_2^\dagger\varsigma_2|\hat{\rho}(\tau)\rangle\!\rangle = I_0(\tau) + I_1(\tau) + I_2(\tau), \tag{36}$$

where $I_k(\tau) = \langle\!\langle \varsigma_2^\dagger\varsigma_2|\hat{\rho}^{(k)}(\tau)\rangle\!\rangle = \mathrm{Tr}\{\varsigma_2^\dagger\varsigma_2\hat{\rho}^{(k)}(\tau)\}$.

The *zeroth-order* term becomes

$$I_0(\tau) = \langle\!\langle n_2|\mathcal{G}_0(\tau)\hat{\rho}(0)\rangle\!\rangle = e^{-\Gamma_2\tau}\mathrm{Tr}\big[\hat{\rho}^{1,1}_{1,1}\big]. \tag{37}$$

Here it is relevant to notice that this term contains the same information as $g^{(2)}(0)$ at zero time delay [see Eqs. (19) and (22)], while the exponential time dependence provides no information about the emitter dynamics as it only relates to the uncertainty in detection time.

The next term arises from the *first-order* perturbation theory, in the form

$$I_1(\tau) = -i\int_0^\tau dt_1 \langle\!\langle n_2|\mathcal{G}_0(\tau - t_1)H^\times_{e,2}\mathcal{G}_0(t_1)\hat{\rho}(0)\rangle\!\rangle. \tag{38}$$

We can act the first $\mathcal{G}_0(\tau - t_1)$ to the left, giving $\langle\!\langle n_2|\mathcal{G}_0(\tau - t_1) = \langle\!\langle n_2|\exp[-\Gamma_2(\tau - t_1)]$. The only elements to the right which will contribute are $a_2\hat{\rho}^{1,1}_{1,0}(t_1)\exp[-(\Gamma_2/2 + i\omega_2)t_1]$ and $\hat{\rho}^{1,0}_{1,1}(t_1)a_2^\dagger\exp[-(\Gamma_2/2 - i\omega_2)t_1]$, with $|\hat{\rho}^{1,j_2'}_{1,j_2}(t)\rangle\!\rangle \equiv \Theta[t]\exp(\mathcal{L}_0 t)|\hat{\rho}^{1,j_2'}_{1,j_2}(0)\rangle\!\rangle$ defined via the evolution of the emitter alone. As these two terms are complex conjugates, we can write

$$I_1(\tau) = 2\epsilon\,\mathrm{Im}\left(\int_0^\tau dt_1 e^{-\Gamma_2(\tau - t_1/2) + i\omega_2 t_1}\mathrm{Tr}\big[a_2\hat{\rho}^{1,1}_{1,0}(t_1)\big]\right). \tag{39}$$

This is essentially a finite-time Laplace transform of a complex number, which is simple enough to perform numerically.

Here the density matrix $\hat{\rho}^{1,1}_{1,0}(t_1)$ evolves under the action of Liouvillian $\mathcal{L}_0$.

Finally, the *second-order* term, $I_2(\tau)$, reads

$$I_2(\tau) = -\int_0^\tau dt_2 \int_0^{t_2} dt_1 \langle\langle n_2|\mathcal{G}_0(\tau - t_2) \times H^{\times}_{e,2}\mathcal{G}_0(t_2 - t_1)H^{\times}_{e,2}\mathcal{G}_0(t_1)|\hat{\rho}(0)\rangle\rangle. \quad (40)$$

Because we have two applications of $H_{e,2}$, both $\hat{\rho}^{1,0}_{1,0} \otimes |0_2\rangle\langle 0_2|$ and $\hat{\rho}^{1,1}_{1,1} \otimes |1_2\rangle\langle 1_2|$ terms can contribute. However, since $\mathrm{Tr}[\hat{\rho}^{1,1}_{1,1}] \ll \mathrm{Tr}[\hat{\rho}^{1,0}_{1,0}]$, we need only to consider $\hat{\rho}^{1,0}_{1,0} \otimes |0_2\rangle\langle 0_2|$ in our initial condition. Hence, to lowest order in ϵ, we have

$$\begin{aligned} I_2(\tau) &= -\epsilon^2 \int_0^\tau dt_2 \int_0^{t_2} dt_1 e^{-\Gamma_2(\tau - t_2)} \\ &\quad \times \langle\langle n_2|\overrightarrow{a_2\varsigma_2^\dagger}\mathcal{G}_0(t_2 - t_1)\overleftarrow{a_2^\dagger\varsigma_2}\mathcal{G}_0(t_1)|\rho(0)\rangle\rangle + \mathrm{H.c.} \\ &= -2\epsilon^2 \mathrm{Re} \int_{t_1}^\tau dt_2 \int_0^{t_2} dt_1 e^{-\Gamma_2[\tau - (t_2+t_1)/2] + i\omega_2(t_2 - t_1)} \\ &\quad \times \mathrm{Tr}\{a_2(t_2 - t_1)\hat{\rho}^{1,0}_{1,0}(t_1)a_2^\dagger\}, \end{aligned} \quad (41)$$

with H.c. meaning Hermitian conjugate, $\overrightarrow{O}|\rho\rangle\rangle \equiv \hat{O}\hat{\rho}$ and $\overleftarrow{O}|\rho\rangle\rangle \equiv \hat{\rho}\hat{O}$. We have used the Heisenberg and Schrödinger pictures such that $a_2(t)$ is the time-dependent operator, propagating under the adjoint of $\mathcal{L}_0$. The double integral over the two-dimensional simplex is numerically more complex, but can be performed.

Equation (31) for the time-resolved two-photon coincidence becomes

$$S^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1, \omega_2, \tau > 0) = \frac{\Gamma_1\Gamma_2}{(2\pi)^2\epsilon^4}[I_0(\tau) + I_1(\tau) + I_2(\tau)]. \quad (42)$$

Notice that $I_0(\tau)$, $I_1(\tau)$, and $I_2(\tau)$ will all feature a prefactor ϵ^4. Hence the ϵ dependence in Eq. (42) cancels out algebraically, as expected. The time-resolved photon coincidence can therefore be written as

$$S^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1, \omega_2, \tau > 0) = \frac{\Gamma_1\Gamma_2}{(2\pi)^2}[\tilde{I}_0(\tau) + \tilde{I}_1(\tau) + \tilde{I}_2(\tau)], \quad (43)$$

with $\tilde{I}_k(\tau) = \epsilon^{-4} I_k(\tau)$ the kth-order term, which requires k interactions with the coupling Hamiltonian $H_{e,2}$. The final expression for the second-order correlation at a finite-time delay reads

$$g^{(2)}_{\Gamma_1\Gamma_2}(\omega_1, \omega_2, \tau > 0) = \frac{\tilde{I}_0(\tau) + \tilde{I}_1(\tau) + \tilde{I}_2(\tau)}{\langle\tilde{n}_1\rangle\langle\tilde{n}_2\rangle}, \quad (44)$$

with $\langle\tilde{n}_1\rangle = \mathrm{Tr}[\tilde{\rho}^{1,0}_{1,0}]$ and $\langle\tilde{n}_2\rangle = \mathrm{Tr}[\tilde{\rho}^{0,1}_{0,1}]$. The correlation for $\tau < 0$ is obtained by taking $\hat{\rho}(0) = \varsigma_2\hat{\rho}_{ss}\varsigma_2^\dagger$ and doing time-dependent perturbation theory with respect to $H_{e,1}$. This results in making the replacements $\Gamma_2 \to \Gamma_1$, $\omega_2 \to \omega_1$, $a_2 \to a_1$, $\hat{\rho}^{1,1}_{1,0}(t_1) \to \hat{\rho}^{1,1}_{0,1}(t_1)$, and $\hat{\rho}^{1,0}_{1,0}(t_1) \to \hat{\rho}^{0,1}_{0,1}(t_1)$ in Eqs. (37), (39), and (41). At this point it is worth noting that, in general, the time-resolved correlation function can exhibit time asymmetry whenever the two frequencies detected are different from each other ($\omega_1 \neq \omega_2$), even if $a_1 = a_2$. This is evident from the definition of I_1 in Eq. (39) and the definition of I_2 in Eq. (41): both I_1 and I_2 have exponentials in their integrands that explicitly depend on ω_2 or ω_1 for positive or negative times, respectively. Similar arguments apply to the specific matrix operators involved for the different time regimes. Time-symmetrical functions are expected when we have identical system emission operators ($a_1 = a_2$), identical frequencies ($\omega_1 = \omega_2$), and identical sensor decay rates ($\Gamma_1 = \Gamma_2$).

Behaviors at short- and large-time delays

We first consider the short-time delay regime. As we discussed above, $\tilde{I}_0\tau \propto e^{-\Gamma_2\tau}$ for all $\tau \geqslant 0$, indicating that its time dependence simply captures the uncertainty in the detection. When τ is smaller than any relevant system time scales, we have, to lowest order, $\tilde{I}_1(\tau) \sim 2\tau\,\mathrm{Im}(\mathrm{Tr}[a_2\tilde{\rho}^{1,1}_{1,0}])$ and $\tilde{I}_2(\tau) \sim \tau^2\,\mathrm{Re}(\mathrm{Tr}[a_2\tilde{\rho}^{1,0}_{1,0}a_2^\dagger])$. The most interesting information is thus given by the short-time behavior of $\tilde{I}_2(\tau)$. Since this function involves a propagation in time after a first iteration with $H_{e,2}$ [see Eq. (40)], its short-time behavior can have contributions from coherent dynamics within the excited manifold of the system of interest. In fact, the proportionality of $\tilde{I}_2(\tau)$ to τ^2 is suggestive that quantum speed-up processes are being captured by this function [36]. For $\tau < 0$, the sensor ordering is reversed and we have instead $\tilde{I}_1(\tau) \sim 2\tau\,\mathrm{Im}(\mathrm{Tr}\{a_1\tilde{\rho}^{1,1}_{0,1}\})$ and $\tilde{I}_2(\tau) \sim \tau^2\,\mathrm{Re}(\mathrm{Tr}\{a_1\tilde{\rho}^{0,1}_{0,1}a_1^\dagger\})$. In general, $\mathrm{Re}(\mathrm{Tr}\{a_1\tilde{\rho}^{0,1}_{0,1}a_1^\dagger\}) \neq \mathrm{Re}(\mathrm{Tr}\{a_2\tilde{\rho}^{1,0}_{1,0}a_2^\dagger\})$ and likewise $\mathrm{Im}(\mathrm{Tr}\{a_2\tilde{\rho}^{1,1}_{1,0}\}) \neq \mathrm{Im}(\mathrm{Tr}\{a_1\tilde{\rho}^{1,1}_{0,1}\})$. Hence we will expect an asymmetry in $g^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1, \omega_2, \tau)$ for positive and negative τ, even in the case when $a_1 = a_2$.

We now investigate $\tilde{I}_1(\tau)$ and $\tilde{I}_2(\tau)$ in the regime where τ becomes large relative to the emitter or sensor linewidth time scales. Let us call γ_{sys} the largest emitter decay rate linked to the field operator a_2. If $\gamma_{\mathrm{sys}} \gg \Gamma_2$ and $\tau\gamma_{\mathrm{sys}} \gg 1$, we can make the approximation

$$\tilde{I}_1(\tau) \sim 2e^{-\Gamma_2\tau}\,\mathrm{Im}\left(\int_0^\infty dt_1 e^{+\Gamma_2 t_1/2 + i\omega_2 t_1}\mathrm{Tr}\left[a_2\tilde{\rho}^{1,1}_{1,0}(t_1)\right]\right), \quad (45)$$

where the integral, now independent of τ, can be identified as the infinite Laplace transform $F(s)$ of $\mathrm{Tr}[a_2\tilde{\rho}^{1,1}_{1,0}(t_1)]$ and $s = \Gamma_2/2 + i\omega_2$, i.e., $\tilde{I}_1(\tau) \sim 2e^{-\Gamma_2\tau}\mathrm{Im}\{F(\Gamma_2/2 + i\omega_2)\}$; thus time dependence is only due to uncertainty in the detection time. Since $I_1(0) = 0$, we expect the full form of $\tilde{I}_2(\tau)$ to undergo an initial rise, followed by an exponential decay. On the other hand, if $\gamma_{\mathrm{sys}} \ll \Gamma_2$, we can approximate $\tilde{\rho}^{1,1}_{1,0}(t)$ as having a single dominant coherent transition frequency ω_{sys}, that is, $\tilde{\rho}^{1,1}_{1,0}(t) \simeq \exp(+\gamma_{\mathrm{sys}}t - i\omega_{\mathrm{sys}}t)\tilde{\rho}^{1,1}_{1,0}(t)$ and slowly varying. Let us define $\tilde{t}_1 = \tau - t_1$ so we can write

$$\begin{aligned} &\tilde{I}_1(\tau) \\ &= 2\,\mathrm{Im}\left(\int_0^\tau d\tilde{t}_1 e^{-\Gamma_2(\tilde{t}_1 + \tau)/2 + i\omega_2(\tilde{t}_1 - \tau)}\mathrm{Tr}\left[a_2\tilde{\rho}^{1,1}_{1,0}(\tau - \tilde{t}_1)\right]\right) \\ &\sim 2\,\mathrm{Im}\left(\frac{e^{-(\Gamma_2 + \gamma_{\mathrm{sys}})\tau/2 - i(\omega_{\mathrm{sys}} - \omega_2)\tau} - e^{-\Gamma_2\tau}}{(\Gamma_2 - \gamma_{\mathrm{sys}})/2 + i(\omega_2 - \omega_{\mathrm{sys}})}\mathrm{Tr}\left[a_2\tilde{\rho}^{1,1}_{1,0}(\tau)\right]\right), \end{aligned} \quad (46)$$

where, by assumption, the dominant term is the numerator of the fraction resulting in a damped oscillatory function. The approximation of a single frequency breaks down when the sensor linewidth is smaller than the emission spectrum.

We expect $g^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1,\omega_2,\tau)\to 1$ when $\Gamma_2\tau\gg$ and $\gamma_{\rm sys}\tau\gg$. Since $\tilde{I}_0(\tau)$ and $\tilde{I}_1(\tau)$ decay exponentially in this regime, $\tilde{I}_2(\tau)$ must therefore tend to a constant value. To see this we rewrite $\tilde{I}_2$ in terms of $\tilde{t}_1=\tau-(t_2+t_1)/2$ and $\tilde{t}_2=t_2-t_1$ as

$$\tilde{I}_2(\tau)=2\,\mathrm{Re}\int_0^{\tau}d\tilde{t}_2\int_0^{\tau-\tilde{t}_2/2}d\tilde{t}_1 e^{-\Gamma_2\tilde{t}_1+i\omega_2\tilde{t}_2}\times\mathrm{Tr}\{a_2(\tilde{t}_2)\tilde{\rho}^{1,0}_{1,0}(\tau-\tilde{t}_1-\tilde{t}_2/2)a_2^{\dagger}\}. \tag{47}$$

As $\tau\to\infty$, $\tilde{\rho}^{1,0}_{1,0}(\tau)$ will approach the functional form of our original steady state for the emitter, and so we can write $\tilde{\rho}^{1,0}_{1,0}(\tau-\tilde{t}_1/2-\tilde{t}_2)\to\langle\tilde{n}_1\rangle[\tilde{\rho}^{0,0}_{0,0}-\Delta\tilde{\rho}_{ss}(\tau-\tilde{t}_1/2-\tilde{t}_2)]$. We also expect the trace of the difference term $\Delta\rho_{ss}$ to be exponentially small when $\tau\to\infty$, and the variation in terms of $\tilde{t}_1$ and $\tilde{t}_2$ to be slow enough to neglect. We can therefore take the integral over $\tilde{t}_1$ and obtain

$$\tilde{I}_2(\tau)\sim\frac{2\langle\tilde{n}_1\rangle}{\Gamma_2}\mathrm{Re}\int_0^{\tau}d\tilde{t}_2(1-e^{-\Gamma_2(\tau-\tilde{t}_2/2)})e^{+i\omega_2\tilde{t}_2}\times\mathrm{Tr}\big[a_2(\tilde{t}_2)\{\tilde{\rho}^{0,0}_{0,0}-\Delta\tilde{\rho}_{ss}(\tau-\tilde{t}_2/2)\}a_2^{\dagger}\big]. \tag{48}$$

If we take the integral over $\tilde{t}_2$ to infinity (assuming $\gamma_{\rm sys}\tau\gg 1$), the term dependent on $\tilde{\rho}^{0,0}_{0,0}$ will tend to $\langle\tilde{n}_1\rangle\langle\tilde{n}_2\rangle$ and the remainder term, which is a function of $\Delta\tilde{\rho}_{ss}(\tau-\tilde{t}_2/2)$, tends to zero, giving $g^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1,\omega_2,\tau)\to 1$. Assuming $\Delta\tilde{\rho}_{ss}(t)$ does not have rapidly oscillating components, we expect Eq. (48) to be a good general approximation for a wide range of τ.

We conclude this section by noting that the second-order time-dependent perturbation approach described above can also be used in the calculation of higher-order photon correlations when only one sensor has a time delayed detection, i.e., $g^{(M)}_{(\Gamma_1,\ldots\Gamma_m\ldots\Gamma_M)}(\omega_1,\ldots,\omega_m,\tau,\ldots,\omega_M)$. The generalization to multiple time delays is, however, more elaborate. For instance, computation of the third-order correlations for different delay times will require the application of second-order perturbation theory with respect to the interactions with sensors 2 and 3, $H_{e,2}$ and $H_{e,3}$, respectively, but at different stages in the dynamics. This will lead to a four-dimensional numerical integration. In this case one can instead take advantage of the efficient method to compute the auxiliary matrices defining the steady state [see Eq. (29)] and propagate in time without perturbation.

V. COMPARISON OF ORIGINAL AND PROPOSED METHOD

To compare our approach and the original formulation of the sensor method, we consider a toy model for a prototype vibronic dimer as in Refs. [37–39]. We are motivated by the experimental measurements of room-temperature photocounting statistics of similar bichromophoric [40,41] and multichromophoric systems [34], all of which have given evidence of antibunching. In our toy model, each chromophore has an excited electronic state $|k\rangle$ with energy α_k, $k=1,2$, and is locally coupled with strength g to a quantized vibrational mode of frequency $\omega_{\rm vib}$. Interchromophore coupling is generated by dipole-dipole interaction of strength V. The electronic Hamiltonian and the bare vibrational Hamiltonian read $H_{\rm el}=\alpha_1|1\rangle\langle 1|+\alpha_2|2\rangle\langle 2|+V(|1\rangle\langle 2|+|2\rangle\langle 1|)$ and $H_{\rm vib}=\omega_{\rm vib}(d_1^{\dagger}d_1+d_2^{\dagger}d_2)$, respectively. Linear coupling of electronic excited states to their corresponding local vibration is described via $H_{\text{el-vib}}=g\sum_{k=1,2}|k\rangle\langle k|(d_k^{\dagger}+d_k)$, where $d_k^{\dagger}(d_k)$ creates (annihilates) a phonon of the vibrational mode of chromophore k. We denote $|X_1\rangle$ and $|X_2\rangle$ the exciton eigenstates of $H_{\rm el}$, with corresponding eigenvalues E_1 and E_2 yielding an average energy $E=(E_1+E_2)/2$ and a splitting $\Delta E=\sqrt{(\Delta\alpha)^2+4V^2}$, with $\Delta\alpha=\alpha_1-\alpha_2$ being the positive difference between the on-site energies. Including the electronic ground state $|G\rangle$ with energy set to zero, we define the electronic basis $\{|G\rangle,|X_1\rangle,|X_2\rangle\}$. Transformation of this electronic-vibrational Hamiltonian into normal mode coordinates [37,42] shows that only the relative displacement mode, with creation operator $D^{(\dagger)}=(d_1^{(\dagger)}-d_2^{(\dagger)})/\sqrt{2}$, couples to the excitonic system. The effective Hamiltonian for the prototype dimer takes the form of a generalized quantum Rabi model [43]:

$$H_0=E\,\tilde{M}+\frac{\Delta E}{2}\tilde{\sigma}_z+\omega_{\rm vib}D^{\dagger}D+\frac{g}{\sqrt{2}}[\cos(2\theta)\,\tilde{\sigma}_z-\sin(2\theta)\,\tilde{\sigma}_x](D+D^{\dagger}). \tag{49}$$

Here we have defined the collective electronic operators $\tilde{M}=|X_1\rangle\langle X_1|+|X_2\rangle\langle X_2|$, $\tilde{\sigma}_z=|X_1\rangle\langle X_1|-|X_2\rangle\langle X_2|$, and $\tilde{\sigma}_x=|X_2\rangle\langle X_1|+|X_1\rangle\langle X_2|$, and the mixing angle $\theta=1/2\arctan(2|V|/\Delta\alpha)$ satisfies $0<\theta<\pi/4$. The vibrational eigenstates of $D^{\dagger}D$ are denoted as $|l\rangle$, which for the purpose of numerical computation, are set to a maximum number L, i.e., $l=0,1,\ldots,L$. Hence the ground electronic-vibrational eigenstates of H_0 are of the form $|G,l\rangle\equiv|G\rangle\otimes|l\rangle$, while the excited vibronic eigenstates, labeled $|F_v\rangle$, can be written as quantum superpositions of states $|X_i,l\rangle\equiv|X_i\rangle\otimes|l\rangle$, i.e., $|F_v\rangle=\sum_{l=0}^{L}\sum_{i=1,2}C_{il}(v)|X_i,l\rangle$. We assume each local electronic state undergoes pure dephasing at a rate γ_{pd} and associated with jump operator $A_k=|k\rangle\langle k|$, while the collective vibrational mode undergoes thermal emission and absorption processes with rates $\Gamma_{\rm th}[\eta(\omega_{\rm vib})+1]$ and $\Gamma_{\rm th}\eta(\omega_{\rm vib})$, respectively. Here $\eta(\omega)=(e^{\beta\omega}-1)^{-1}$ with $\beta=1/K_BT$ the thermal energy scale. The system is subjected to incoherent pumping of the highest-energy exciton $|X_1\rangle$ state, with transition operator $\sigma^{\dagger}_{X_1}=|X_1\rangle\langle G|$ and rate P_{X_1}. Radiative decay processes from excited vibronic states to the ground are given at rate γ and are described by jump operators of the form $\sigma_{vl}=|G,l\rangle\langle F_v|$. The Liouvillian of the emitter system in the absence of coupling to any sensor is given by [see Eq. (3)]

$$\mathcal{L}_0(\hat{\rho})=-i\,[H_0,\hat{\rho}]+\sum_{k=1,2}\frac{\gamma_{pd}}{2}\mathcal{L}_{A_k}(\hat{\rho})+\frac{\Gamma_{\rm th}[\eta(\omega_{\rm vib})+1]}{2}\mathcal{L}_D(\hat{\rho})+\frac{\Gamma_{\rm th}\eta(\omega_{\rm vib})}{2}\mathcal{L}_{D^{\dagger}}(\hat{\rho})+\frac{\gamma}{2}\sum_{v=1}^{2L}\sum_{l=1}^{L}\mathcal{L}_{\sigma_{vl}}(\hat{\rho})+\frac{P_{X_1}}{2}\mathcal{L}_{\sigma^{\dagger}_{X_1}}(\hat{\rho}). \tag{50}$$

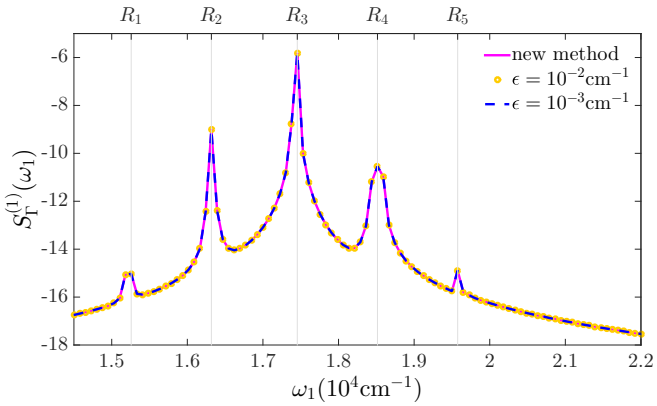

FIG. 2. Power spectra $S_\Gamma(\omega_1)$ in log scale vs ω_1 for our vibronic dimer as predicted both by the method proposed in this paper and by the ϵ-dependent sensor method.

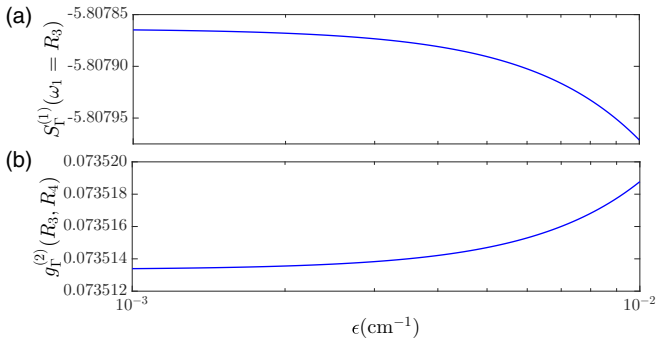

FIG. 3. (a) Intensity of power spectrum at a fixed frequency, $S_\Gamma(\omega_1 = R_3)$ in log-log scale, and (b) zero-delay time second-order correlation $g_\Gamma^{(2)}(R_4, R_3)$ in semilog scale, as functions of ϵ. Both functions are calculated with the ϵ-dependent method for our vibronic dimer.

The sensors, each with bare Hamiltonian $H_m = \omega_m \varsigma_m^\dagger \varsigma_m$, are assumed to have identical linewidths Γ and are coupled with equal strength ϵ to bare exciton states through the operator $a = \sigma_{X_1} + \sigma_{X_2}$ such that $H_{e,m} = \epsilon[(\sigma_{X_1} + \sigma_{X_2})\varsigma_m^\dagger + (\sigma_{X_1}^\dagger + \sigma_{X_2}^\dagger)\varsigma_m]$. The second term for the Liouvillian superoperator in Eq. (2) then becomes

$$\mathcal{L}_I(\hat{\rho}) = \sum_{m=1}^{M} \left(\frac{\Gamma}{2} \mathcal{L}_{\varsigma_m}(\hat{\rho}) - i\,[H_m + H_{e,m}, \hat{\rho}] \right). \tag{51}$$

In the right-hand side of Eqs. (50) and (51) $\mathcal{L}_c(O) = (2cOc^\dagger - c^\dagger cO - Oc^\dagger c)$. We consider bioinspired parameters for our toy model [37,44]. The electronic coupling takes the value $V = 92\ \text{cm}^{-1}$, while the on-site energy difference is $\Delta\alpha = 1042\ \text{cm}^{-1}$ [37] such that the average exciton energy becomes $E = 18\,000\ \text{cm}^{-1}$ [44] and the exciton energy splitting $\Delta E = 1058.2\ \text{cm}^{-1}$. The latter is comparable with $\omega_{\text{vib}} = 1111\ \text{cm}^{-1}$. The thermal energy scale $K_B T = 200\ \text{cm}^{-1}$ is on the scale of the coupling strength $g = 267.1\ \text{cm}^{-1}$ but much smaller than ω_{vib}. Hence a maximum vibrational level of $L = 5$ yields converged results. For clarity, in our numerical calculations all wave numbers are multiplied by $2\pi c$, where c is the speed of light. The electronic pure dephasing is $\gamma_{pd} = [1\ \text{ps}]^{-1}$. We consider an enhanced radiative decay rate $\gamma = [0.5\ \text{ns}]^{-1}$ and a pumping rate $P_{X_1} = [0.6\ \text{ns}]^{-1}$. Thermal relaxation is set to $\Gamma_{\text{th}} = [4.8\ \text{ps}]^{-1}$ and equal to the sensor linewidth $\Gamma = [4.8\ \text{ps}]^{-1}$.

Figure 2 presents the power spectra $S_\Gamma(\omega_1)$ for our vibronic dimer as predicted by our approach and by the original method with different values of ϵ satisfying $\epsilon \ll \sqrt{\Gamma\gamma_Q/2} \sim 10^{-1}\ \text{cm}^{-1}$. The highest peak, given at the emission frequency $\omega_1 = R_3 = 17455\ \text{cm}^{-1}$, captures transitions from the excited vibronic states with the largest amplitude on $|X_2, l\rangle$ to the ground state with the same vibrational quanta $|G, l\rangle$. It also includes transitions from excited states quasilocalized on $|X_1, l\rangle \to |G, l+1\rangle$. The peak at $\omega_1 = R_4 = 18\,515\ \text{cm}^{-1}$ accounts for transitions from excited vibronic states quasilocalized on $|X_1, l\rangle \to |G, l\rangle$, as well as transitions from states quasilocalized on $|X_2, l\rangle \to |G, l-1\rangle$. The ϵ-dependent method tends to underestimate the spectrum as can be seen in Fig. 3(a), with differences of the order of ϵ. Converged results are obtained for $\epsilon \sim 10^{-3}\ \text{cm}^{-1}$.

The second-order correlation function at zero delay time $g_\Gamma^{(2)}(\omega_1, \omega_2)$ is shown in Fig. 4(a). There we have fixed $\omega_2 = R_3$ and scan ω_1 over the domain of frequencies in the power spectrum. Antibunching is observed for the whole frequency regime with larger offsets from zero for the frequency pair (R_5, R_3), indicating transitions corresponding to this pair are weakly correlated. The predictions of the two methods agree up to differences that scale with ϵ^2 as can be seen in Fig. 4(b). This figure plots $|\Delta g_\epsilon^{(2)}(0)|$, the absolute value of the difference between the values obtained with our approach

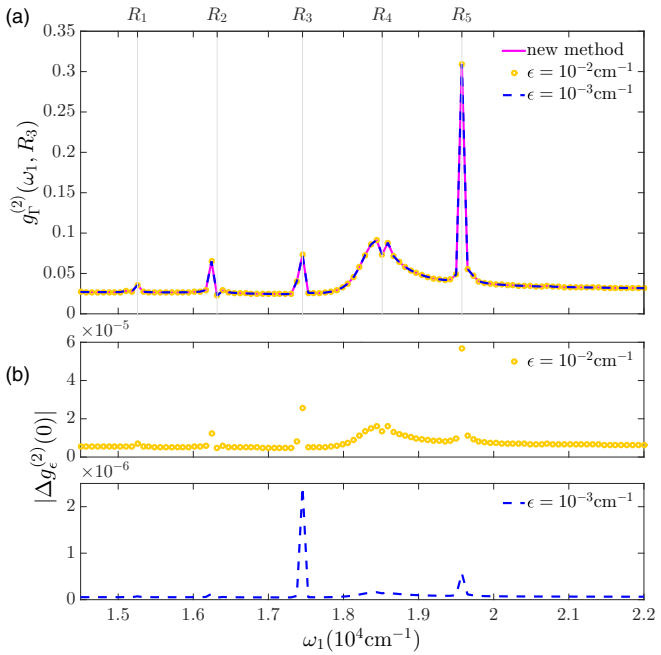

FIG. 4. (a) Second order at zero time delay $g_\Gamma^{(2)}(\omega_1, R_3)$ vs ω_1 computed with the proposed method and the ϵ-dependent sensor method for different values of ϵ. (b) $|\Delta g_\epsilon^{(2)}(0)|$, the absolute difference value between the predictions of the two methods, vs ω_1 for two values of ϵ.

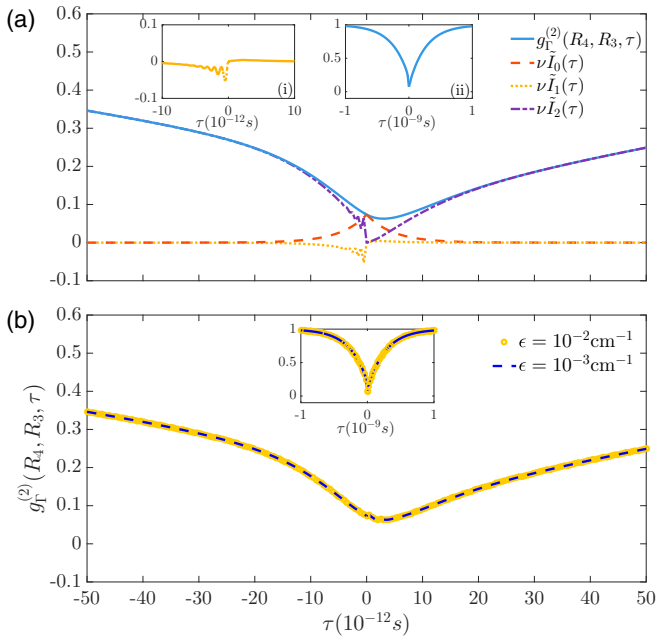

FIG. 5. Frequency- and time-resolved correlation function $g_\Gamma^{(2)}(R_4, R_3, \tau)$ versus τ predicted with (a) the proposed method and (b) the ϵ-dependent method. Inset (i) in panel (a) shows the short-time behavior of $\nu\tilde{I}_0(\tau)$ as defined in the text. Inset (ii) in (a) and inset in (b) show the long-time regime of $g_\Gamma^{(2)}(\omega_1, \omega_2, \tau)$.

[solving Eq. (24)] and the ϵ-dependent method. The latter tends to overestimate the second-order photon correlations as can be seen in Fig. 3(b), which plots $g_\Gamma^{(2)}(R_4, R_3)$ as a function of ϵ.

We now turn our attention to the function $g_\Gamma^{(2)}(R_4, R_3, \tau)$ depicted in Figs. 5(a) and 5(b), which show the correlation between photodetections of the frequency pair $(\omega_1 = R_4, \omega_2 = R_3)$ as a function of the delay time. We compute this time-resolved correlation in two ways. First, using Eq. (44), we perform the numerical integration for the contributions $\tilde{I}_0(\tau)$, $\tilde{I}_1(\tau)$, and $\tilde{I}_2(\tau)$ and add them together [Fig. 5(a)]. Second, we use the ϵ-dependent method [Fig. 5(b)]. The agreement between the predictions of the two methods is evident for both short-time (main panels) and long-time regimes [inset (ii) in Fig. 5(a) and inset in Fig. 5(b)].

The figures highlight the asymmetric behavior of $g_\Gamma^{(2)}(R_4, R_3, \tau)$ with respect to τ, which appears in the time scale of the vibronic decoherence in our model (set mainly by Γ_{th}). The components $\nu\tilde{I}_k(\tau)$ $(k = 0, 1, 2)$ with $\nu = [\langle\tilde{n}_1\rangle\langle\tilde{n}_2\rangle]^{-1}$ are also plotted in Fig. 5(a). As predicted, $\tilde{I}_0(\tau)$ decays exponentially from the initial value set by $g_\Gamma^{(2)}(R_4, R_3, \tau = 0)$. $\tilde{I}_1(\tau)$ is linear in τ in the short-time regime and evolves to take negative values [see Fig. 5(a), inset (i)], reflecting an overdamped oscillation that decays to zero in the long-time regime, in agreement with the behaviors discussed in Sec. IV. The negative values of $\tilde{I}_1(\tau)$ are counteracted by $\tilde{I}_0(\tau)$ and $\tilde{I}_2(\tau)$ such that a physical $g_\Gamma^{(2)}(R_4, R_3, \tau)$ is always obtained. Figure 5 also shows that the short-time asymmetry in $g_\Gamma^{(2)}(R_4, R_3, \tau)$ can be traced back, as expected, to $\tilde{I}_1(\tau)$ and $\tilde{I}_2(\tau)$, indicating that the correlation function is capturing coherent processes in this time scale. Depending on which frequency is probed first, such coherent processes set a different rate for approaching the uncorrelated steady-state emission at large times [see inset (ii) in Fig. 5(a)].

In summary, we have shown the method here proposed is equivalent to the ϵ-dependent sensor method to compute frequency-filtered correlation functions. In our method the dependence of correlation functions on ϵ vanishes algebraically. It therefore avoids both the need to test for convergence for different values of ϵ and the possible numerical instabilities associated to the smallness of this factor. Identifying *a priori* when the original method will lead to instabilities is difficult, as it is case dependent.

VI. CONCLUSION

We have developed an alternative formulation of the sensor method for the calculation of M-photon correlations at zero-time delay as well as for the filtered and time-resolved second-order photon correlation. Our main results are summarized by Eqs. (27)–(29) and (44). Our approach, being based on perturbation theory, leads to a formalism that redefines the problem of computing photon correlations in terms of a hierarchy of auxiliary matrices defined in the Hilbert space of the emitter only. This hierarchy gives some insight into the physics of probing photoemission correlations via hypothetically weakly and coherently coupled sensors. We recover previously reported analytical results for the one- and two-photon spectral correlations at zero delay time [15–17,32], which highlights the validity of our approach. Provided that one can relax the quantum regression assumption that was used in Refs. [15,16] for proving the equivalence between the sensor and integral methods for evaluating M-photon correlations, the relations in Eqs. (27)–(29) and (44) apply to a general non-Markovian, nonperturbative open quantum dynamics of the emitter.

A further advantage of the proposed approach is that the numerical evaluation of the correlations does not depend explicitly on the small value of ϵ and then eliminates the need of evaluating convergence and stability with respect to it. We note here that it has recently been shown that the results based on the weakly and coherently coupled sensors in Refs. [15,16] are mathematically equivalent to considering cascaded incoherent coupling, of finite strength, between emitter and sensors [45,46]. This provides an alternative method to evaluate photon correlations and implies equivalence with our approach.

Our proposed derivation of time-resolved correlations is based on time-dependent perturbation and leads to the expression of the second-order correlation $g^{(2)}_{\Gamma_1,\Gamma_2}(\omega_1, \omega_2, \tau)$ in Eq. (44) as the sum of three components $\tilde{I}_0$, $\tilde{I}_1$, and $\tilde{I}_2$, each of which gives insight into the physical processes dominating the correlations at different time scales. The trade-off is that computation of two of these components requires numerical integration of manageable single and double integrals. The method can be systematically generalized for higher order when there is delay in only one of the detectors. Its extension to multiple time delays is more elaborated. In that case one can still take the advantage of computing the auxiliary matrix operators given in Eq. (29) but propagate in time without perturbation, thereby combining the advantages of both our approach and the original sensor method.

To illustrate the agreement between our approach and the original method, we have compared their predictions for the frequency-filtered photon statistics of a toy model that has been inspired in a light-harvesting vibronic dimer. The focus here has been on highlighting the equivalence between the predictions of the two approaches rather than a detailed analysis of the physical insight of the photon correlations for the system under consideration. We would however like to point out that the results presented here already suggest that frequency-filtered and time-resolved photon-counting statistics can provide a powerful approach to probe coherent contributions to the emission dynamics in complex molecular systems [34]. An in-depth analysis of frequency-filtered photon correlations for the prototype system considered here will be presented in a separate forthcoming manuscript.

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APPENDIX A: CONSISTENCY CHECK OF THE PROOF OF THE EQUIVALENCE BETWEEN THE SENSING AND THE INTEGRAL METHODS

In Ref. [15] and in its Supplemental Material it is shown that the sensor method to evaluate M-photon correlation functions is identical to the integral method with Lorentzian frequency filter functions for the sensors. Originally, in Ref. [15] the normal order for sensor intensity correlations given in Eq. (5) was omitted. This could lead to the confusion that the normal order for sensor operators was, in general, unnecessary. In an Erratum [16] the authors have clarified that their proof assumes normal order all throughout. Since our proposed approach is equivalent to the sensor method, as long as the normal order of the sensor operators is taken into consideration, we have made a consistency check of the proof presented in the Supplemental Material of Ref. [15].

We begin by considering Eq. (42) in the Supplemental Material of Ref. [15]:

$$\begin{aligned}&\partial_\tau \langle n_1(0) n_2(\tau)\rangle \\ &\quad = -\Gamma_2 \langle n_1(0) n_2(\tau)\rangle + 2\,\mathrm{Re}[i\epsilon_2 \langle n_1(0)(\varsigma_2 a^\dagger)(\tau)\rangle], \end{aligned} \tag{A1}$$

with $n_j = \varsigma_j^\dagger \varsigma_j$ the sensor number operator and $\langle n_1(0) n_2(\tau)\rangle \equiv \mathrm{Tr}[n_2(\tau)\hat{\rho}_{ss} n_1]$. This equation, which does not consider normal ordering as written, leads to spurious results such as negative values in $g^{(2)}(\omega_1, \omega_2, \tau)$. To see this, we write the steady-state density matrix for the joint emitter and sensors as in Eq. (21) in our manuscript. In this form the difference between using normally ordered operators and the number operator is evident:

$$\varsigma_1 \hat{\rho}_{ss} \varsigma_1^\dagger = \sum_{j_2, j_2' = 0,1} \hat{\rho}_{1,j_2}^{1,j_2'} \otimes |j_2\rangle\langle j_2'| \otimes |0_1\rangle\langle 0_1|, \tag{A2}$$

$$\begin{aligned}\hat{\rho}_{ss} \varsigma_1^\dagger \varsigma_1 = \sum_{j_2, j_2' = 0,1} |j_2\rangle\langle j_2'| \otimes \big(&\hat{\rho}_{1,j_2}^{1,j_2'} \otimes |1_1\rangle\langle 1_1| \\ &+ \hat{\rho}_{0,j_2}^{1,j_2'} \otimes |0_1\rangle\langle 1_1|\big). \end{aligned} \tag{A3}$$

First, notice that while these two expressions are different, their traces are identical, i.e., $\mathrm{Tr}[n_2 \hat{\rho}_{ss} n_1] = \mathrm{Tr}[n_2 \varsigma_1 \hat{\rho}_{ss} \varsigma_1^\dagger]$, which means at $\tau = 0$ the normal order for computation of the second-order photon correlation can be waived. However, the difference in these expressions does have an impact for $\tau \neq 0$. The second expression has the term $\hat{\rho}_{1,j_2}^{1,j_2'} \otimes |1_1\rangle\langle 1_1|$ rather than $\hat{\rho}_{1,j_2}^{1,j_2'} \otimes |0_1\rangle\langle 0_1|$ in the first one; it also contains an additional term $\hat{\rho}_{0,j_2}^{1,j_2'} \otimes |0_1\rangle\langle 1_1|$, which makes the expression not Hermitian (the Hermitian conjugate term with $|1_1\rangle\langle 0_1|$ vanishes due to the action of n_1). The impact of this difference becomes clear when we consider $\langle n_1(0) n_2(\tau)\rangle \equiv \mathrm{Tr}[n_2(\hat{\rho}_{ss} n_1)(\tau)]$. This equation indicates the population of sensor 1 decays exponentially in time with a rate Γ_1. In terms of derivatives in τ this means the $\hat{\rho}_{1,j_2}^{1,j_2'} \otimes |j_2\rangle\langle j_2'|$ in $(\hat{\rho}_{ss} \varsigma_1^\dagger \varsigma_1)(\tau)$ will acquire an extra factor of $-\Gamma_1$ when compared to those in $(\varsigma_1 \hat{\rho}_{ss} \varsigma_1^\dagger)(\tau)$, which is not included in Eq. (A1). This then disproves Eq. (A1).

On the other hand, a similar equation for the normally ordered correlation does hold, that is,

$$\begin{aligned}&\partial_\tau \langle \varsigma_1^\dagger(0) n_2(\tau) \varsigma_1(0)\rangle \\ &\quad = -\Gamma_2 \langle \varsigma_1^\dagger(0) n_2(\tau) \varsigma_1(0)\rangle \\ &\qquad + 2\,\mathrm{Re}[i\epsilon_2 \langle \varsigma_1^\dagger(0)(\varsigma_2 a^\dagger)(\tau) \varsigma_1(0)\rangle] + O\big(\epsilon_1^2, \epsilon_2^2\big). \end{aligned} \tag{A4}$$

The solution of this normally ordered derivative in τ can be found starting from a vector analogous to $\mathbf{w}'[11, \mu_2\nu_2](\tau)$ given by Eq. (43) in the Supplemental Material of [15] but that contains the terms in normal order:

$$\tilde{\mathbf{w}}[11, \mu_2\nu_2](\tau) = \begin{bmatrix} \langle \varsigma_1^\dagger (\varsigma_2^{\dagger,\mu_2} \varsigma_2^{\nu_2})(\tau) \varsigma_1\rangle \\ \langle \varsigma_1^\dagger (\varsigma_2^{\dagger,\mu_2} \varsigma_2^{\nu_2} a)(\tau) \varsigma_1\rangle \\ \langle \varsigma_1^\dagger (\varsigma_2^{\dagger,\mu_2} \varsigma_2^{\nu_2} a^\dagger)(\tau) \varsigma_1\rangle \\ \langle \varsigma_1^\dagger (\varsigma_2^{\dagger,\mu_2} \varsigma_2^{\nu_2} a^\dagger a)(\tau) \varsigma_1\rangle \\ \vdots \end{bmatrix}. \tag{A5}$$

The time derivatives of the elements in $\tilde{\mathbf{w}}[11, \mu_2\nu_2](\tau)$ are of the form

$$\begin{aligned}&\partial_\tau \langle \varsigma_1^\dagger (\varsigma_2^{\dagger\mu_2} \varsigma_2^{\nu_2} a^{\dagger\nu} a^{\nu'})(\tau) \varsigma_1\rangle \\ &\quad = \mathrm{Tr}\{(\varsigma_2^{\dagger,\mu_2} \varsigma_2^{\nu_2} a^{\dagger\nu} a^{\nu'})(\tau) \mathcal{L}(\varsigma_1 \rho_{ss} \varsigma_1^\dagger)\}, \end{aligned} \tag{A6}$$

where the Liouvillian is defined as in Eq. (2) in this manuscript. In particular, we are interested in obtaining an equation when $\mu_2 = 0$ and $\nu_2 = 1$.

Following the formalism either of the Supplemental Material of [15] or a time-dependent perturbation approach as we propose in our manuscript, one can show that, in the limit $\langle n_{1(2)}\rangle \ll 1$, the solution for the normally ordered correlation is formally identical to Eq. (44) in Ref. [15] (Supplemental

Material):

$$\partial_\tau \tilde{\mathbf{w}}[11,01](\tau) = [\mathbf{M} - (i\omega_2 + \Gamma_2/2)\mathbb{1}]\tilde{\mathbf{w}}[11,01](\tau) - i\epsilon_2 \mathcal{T}_- \tilde{\mathbf{w}}[11,00](\tau), \tag{A7}$$

where $\mathbf{M}$ is the matrix that rules the dynamical evolution of the emitter. This means the equations governing the normally ordered vector $\tilde{\mathbf{w}}[11, \mu_2\nu_2](\tau)$ [Eq. (A5)] are exactly the same as those presented in the proof given in Ref. [15] (Supplemental Material), in agreement with the clarification stated in the Erratum [16].

APPENDIX B: NUMERICAL PROCEDURE TO COMPUTE ZERO DELAY TIME CORRELATIONS OF ORDER $M > 2$

Starting with the steady state for the joint emitter and M sensors written as in Eq. (26), the Mth-order photon correlation at $\tau = 0$ depends on the rescaled matrix $\tilde{\beta}^{1\dots1}_{1\dots1} = \langle 1_1, \dots, 1_M|\tilde{\beta}_{ss}|1_1, \dots, 1_M\rangle$. To find this matrix we solve $\mathcal{L}(\hat{\rho}_{ss}) = 0$ which, in analogy to Eq. (14), can be rewritten as

$$\mathcal{L}(\hat{\rho}_{ss}) = \sum_{j_1, j_1'\dots j_M, j_M'} \hat{B}^{j_1'\dots j_m'\dots j_M'}_{j_1\dots j_m\dots j_M} \otimes |j_1\rangle\langle j_1'| \cdots \otimes |j_m\rangle\langle j_m'| \cdots \otimes |j_M\rangle\langle j_M'| = 0. \tag{B1}$$

We derive the set of equations satisfying $\hat{B}^{j_1'\dots j_m'\dots j_M'}_{j_1\dots j_m\dots j_M} = \mathbf{0}$ with the approximation of ignoring down coupling as discussed in the main text. This leads to a hierarchy satisfied by the matrices $\tilde{\beta}^{j_1'\dots j_m'\dots j_M'}_{j_1\dots j_m\dots j_M}$. Careful inspection of the sets in Eqs. (16) and (24) allows one to identify the pattern for such a set. Let us define $J = j_1 + j_1' + \cdots + j_m + j_m' \cdots + j_M + j_M'$ the sum of all matrix indexes. Notice that for $J = 0$ the solution is simply given by $\mathcal{L}_0(\tilde{\beta}^{0,\dots,0}_{0,\dots,0}) \sim 0$. In general, the form for the left-hand side terms for each equation will be given by

$$\left[\mathcal{L}_0 - \sum_{m=1}^{M}\{(j_m + j_m')\Gamma_m/2 + (j_m - j_m')i\omega_m\}\right]\tilde{\beta}^{j_1'\dots j_m'\dots j_M'}_{j_1\dots j_m\dots j_M}. \tag{B2}$$

This term is simply down to the evolution under the Liouvillian of the emitter and the decay and phase evolution of the sensors. Each matrix with $J \geqslant 1$ is coupled only to matrices with $J - 1$. Hence the solution of the $J = 2M$ matrix $\tilde{\beta}^{1,\dots,1}_{1,\dots,1}$ involves only matrices with $J = 2M - 1$ and so on [cf. Eq. (24j)]. The total number of tier-below matrices required equals J and each of these matrices differs only in one index j_m or j_m' which will be zero rather than unity. Let us call these tier-below matrices $\tilde{\beta}^{\ell_1'\dots\ell_m'\dots\ell_M'}_{\ell_1\dots\ell_m\dots\ell_M}$. The matrix that differs in the mth component such that $j_m = 1$ and $\ell_m = 0$, with all others equal, will add a term of the form $ia_m\tilde{\beta}^{j_1'\dots j_m'\dots j_M'}_{j_1\dots j_m=0\dots j_M}$. Likewise if $j_m' = 1$ but $\ell_m' = 0$ and $\ell_y' = j_y'$ and $\ell_y = j_y$ for $y \neq m$, we have a contribution of the form $-i\tilde{\beta}^{j_1'\dots j_m'=0\dots j_M'}_{j_1\dots j_m\dots j_M}a_m^\dagger$. Therefore, the right-hand side term, to which Eq. (B2) is approximated to, will be of the form

$$i\sum_{m=1}^{M}\left[\delta_{j_m,1}a_m\tilde{\beta}^{j_1'\dots j_m'\dots j_M'}_{j_1\dots j_m(1-\delta_{j_m,1})\dots j_M} - \delta_{j_m',1}\tilde{\beta}^{j_1'\dots j_m'(1-\delta_{j_m',1})\dots j_M'}_{j_1\dots j_m\dots j_M}a_m^\dagger\right]. \tag{B3}$$

Here $\delta_{u,v}$ is the Kronecker δ function, equal to zero if $u \neq v$ or unity if $u = v$.

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