Nonlinear spectroscopy with time- and frequency-gated photon counting: A superoperator diagrammatic approach

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We present a diagrammatic technique for calculating quantum-detected nonlinear optical signals using loop diagrams that act in the joint matter plus field space. This formalism, which is based on time-ordered superoperators keeps track of the entangled matter plus field state, making it most suitable for spectroscopy applications. Photon counting is recast as a time and frequency convolution of a bare signal, which is given by a correlation function of matter, and a gating spectrogram.

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I. INTRODUCTION

Rapid progress in pulse shaping technology [1–6] has made it possible to control the temporal as well as the spectral profiles of optical fields. The external optical field induces a polarization in matter that results in the electromagnetic response that is registered by the detection setup [7]. Time-resolved detection is natural when the incoming pulsed fields are much shorter than the relevant molecular time scales [3–5]. A frequency-resolved detection is used [6] for stationary fields.

A semiclassical formalism for describing the photon counting process was first derived by Mandel [8–10]. The full quantum mechanical description of the field and photon detection was developed by Glauber [11]. An ideal photon detector is a device that measures the radiation field intensity at a single point in space. The size of such a detector should be much smaller than spatial variations of the field. The response of an idealized time-domain photon detector does not depend on the frequency of the radiation.

The standard Glauber's theory of photon counting [11–13] is formulated in the radiation field space. It is based on the two-point field correlation function, convoluted with the time- and frequenc-gating spectrogram of the detector. This approach assumes that the detected field is given. Thus, it does not address the matter information and the way this field has been generated. Temporally and spectrally resolved measurements can reveal important matter information. Recent experimental results on single-photon spectroscopy of the single molecules [14–16] call for an adequate microscopic foundation where joint matter and field information could be retrieved by a proper description of the detection process.

The resolution of simultaneous frequency and time domain measurements is limited by the Fourier uncertainty $\Delta\omega\Delta t > 1$. A naive calculation of signals without proper time and frequency gating can work for slowly varying spectrally broad optical fields but otherwise may yield unphysical negative results [17]. In Ref. [18] the mixed time-frequency representation for the coherent optical measurements with interferometric or autocorrelation detection were calculated in terms of a mixed material response functions and a Wigner distribution for the incoming pulses, the detected field, and the gating device. Multidimensional gated fluorescence signals for single-molecule spectroscopy have been calculated in Ref. [19].

We consider signals generated by spontaneous emission in modes that are initially in the vacuum state. Adopting terminology used in spectroscopy, these are homodyne-detected signals [20]. Note that in quantum optics the homodyne (heterodyne) signal is interferometric detection with a local oscillator with the same (different) frequency than the signal. In spectroscopy the term homodyne (heterodyne) implies detection without (with) a local oscillator.

Here we develop a microscopic diagrammatic approach for calculating time- and frequency-gated photon counting measurements. The observed signal is represented by a convolution of the bare signal and detector spectrogram that contains the time- and frequency-gate functions. The bare signal is given by the product of two transition amplitude superoperators [21] (one for bra and one for ket of the matter plus field joint density matrix), each creating a coherence in the field between states with zero and one photon. By combining the transition amplitude superoperators from both branches of the loop diagram we obtain the photon occupation number that can be detected. The detection process is described in the joint space of the field and matter by a sum over pathways each involving a pair of quantum modes with different time orderings. The signal is recast using time-ordered superoperator products of matter and field. Ideal frequency domain detection only requires a single mode [19]. However, maintaining any time resolution requires a superposition of the field modes that contains the pathway information. This information is not directly accessible in the standard detection theory that works in the field space alone [11]. Finally in contrast with standard detection theory the present approach only involves a superoperator time ordering and does not require the normal ordering.

II. GATED SIGNALS

To good a approximation we can represent an ideal detector by two-level atom that is initially in the ground state b and is promoted to the excited state a by the absorption of a photon [see Fig. 1(a)]. At the same time, the detection of a photon brings the field from its initial state ψ_i to a final state ψ_f. The probability amplitude for photon absorption at time

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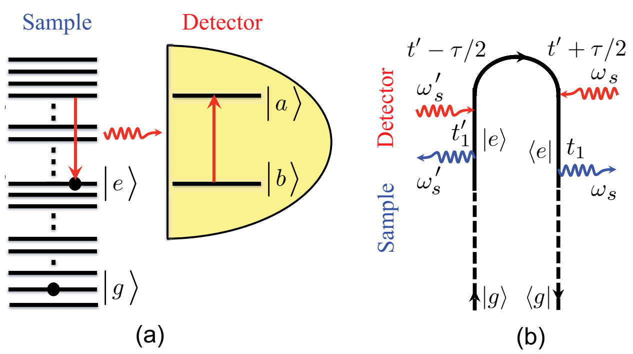

FIG. 1. (Color online) (a) Schematic of time- and frequency-resolved measurement. (b) Loop diagram for the bare signal in a gated measurement (for rules see Ref. [21]).

t can be calculated in first-order perturbation theory, which yields [11]

$$\langle \psi_f|\mathbf{E}(t)|\psi_i\rangle \cdot \langle a|\mathbf{d}|b\rangle, \tag{1}$$

where $\mathbf{d}$ is the dipole moment of the atom and $\mathbf{E}(t) = E^\dagger(t) + E(t)$ is the electric field operator (we omit the spatial dependence). Clearly, only the annihilation part of the electric field contributes to the photon absorption process. The transition probability to find the field in state ψ_f at time t is given by the modulus square of the transition amplitude

$$\sum_{\psi_f} |\langle\psi_f|E(t)|\psi_i\rangle|^2 = \langle\psi_i|E^\dagger(t)\sum_{\psi_f}|\psi_f\rangle\langle\psi_f|E(t)|\psi_i\rangle$$
$$= \langle\psi_i|E^\dagger(t)E(t)|\psi_i\rangle. \tag{2}$$

Since the initial state of the field ψ_i is rarely known with certainty, we must trace over all possible initial states as determined by a density operator ρ. Thus, the output of the idealized detector is more generally given by $\mathrm{tr}[\rho E^\dagger(t)E(t)]$.

For simultaneous time- and frequency-resolved measurement a frequency (spectral) gate must be combined with time gate—a shutter that opens up for very short interval of time. The combined detector with input located at r_G is represented

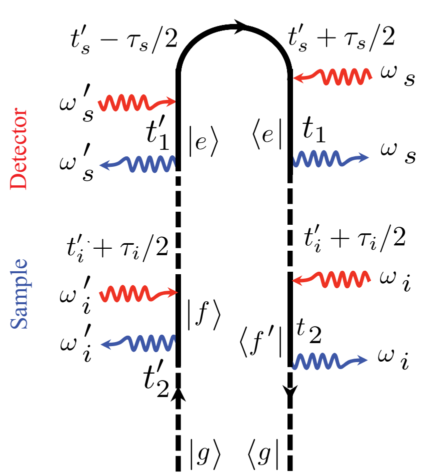

FIG. 2. (Color online) Loop diagram for correlated two-photon measurement. Dashed lines represent the the dynamics of the system driven by the field modes. τ_i and τ_s can be either positive or negative giving rise to four terms in Eq. (37).

by a time gate F_t centered at $\bar{t}$ followed by a frequency gate F_f centered at $\bar{\omega}$ [6]. First, the time gate transforms the electric field $E(r_G,t) = \sum_s \hat{E}_s(r_G,t)$ with $\hat{E}_s(r_G,t) = E(r_G,\omega_s)e^{-i\omega_s t}$ as follows:

$$E^{(t)}(\bar{t};r_G,t) = F_t(t,\bar{t})E(r_G,t). \tag{3}$$

Then, the frequency gate is applied $E^{(tf)}(\bar{t},\bar{\omega};r_G,\omega) = F_f(\omega,\bar{\omega})E^{(t)}(\bar{t};r_G,\omega)$ to obtain the time- and frequency-gated field. We assume that the time gate is applied first. Therefore, the combined detected field at the position r_D can be written as

$$E^{(tf)}(\bar{t},\bar{\omega};r_D,t) = \int_{-\infty}^{\infty} dt' F_f(t-t',\bar{\omega})F_t(t',\bar{t})E(r_G,t'), \tag{4}$$

where $E(t) \equiv \sum_s \sqrt{2\pi\hbar\omega_s/\Omega}\hat{a}_s e^{-\omega_s t}$ (Ω is a mode quantization volume) is understood. Similarly one can apply the frequency gate first and obtain frequency- and time-gated field $E^{(ft)}$.

$$E^{(ft)}(\bar{t},\bar{\omega};r_D,t) = \int_{-\infty}^{\infty} dt' F_t(t,\bar{t})F_f(t-t',\bar{\omega})E(r_G,t'). \tag{5}$$

The following discussion will be based on Eq. (4). Equation (5) can be handled similarly.

In order to maintain the bookkeeping for all interactions and develop a perturbative expansion for signals we describe the signal in terms of Liouville space "left" and "right" superoperators. For each ordinary operator A we define a pair of superoperators [22] $\hat{A}_L X = AX$, $\hat{A}_R X = XA$, and $\hat{A}_- = \hat{A}_L - \hat{A}_R$. To avoid the confusion and distinguish the ordinary operators (e.g., A) from the superoperator quantities we denote all superoperators by "hat" (e.g., $\hat{A}$). The gated signal is given by

$$S(\bar{t},\bar{\omega}) = \int_{-\infty}^{\infty} dt \sum_{s,s'} \left\langle \hat{E}^{(tf)\dagger}_{sR}(\bar{t},\bar{\omega};r_D,t)\hat{E}^{(tf)}_{s'L}(\bar{t},\bar{\omega};r_D,t)\right\rangle, \tag{6}$$

where the angular brackets denote $\langle\cdots\rangle \equiv \mathrm{Tr}[\rho(t)\ldots]$. The density operator $\rho(t)$ is defined in the joint field-matter space of the entire system. Note, that Eq. (6) represents the observable signal, and is always positive since it can be recast as a modulus square of an amplitude [Eq. (2)]. For clarity we hereafter omit the position dependence in the fields assuming that propagation between r_G and r_D is included in the spectral gate function.

A. Spectrogram-overlap representation

In the standard detection theory [6], the detected signal is given by a convolution of the spectrograms of the detector and bare signal. The detector spectrogram is an ordinary function of the gating parameters whereas the bare signal is related to the field prior to detection. We now show that when the process is described in the joint matter plus field space the signal can be brought to the same form, except that now the bare signal is given by a correlation function of matter that further includes a sum over the detected modes. We denote this the spectrogram-overlap (SO) representation of the signal. In the next section we present an alternative spectrogram-superoperator-overlap (SSO) representation that is more suitable for the counting of multiple photons. We first derive the signals in the time domain, which can be directly read of the diagram [Fig. 1(b)]. We then recast them using Wigner spectrograms, which depict simultaneously temporal and spectral profiles of the signal.

Starting with the gated signal (6), we define the bare time domain signal in terms of superoperators using the diagram shown in Fig. 1(b)

$$B(t',\tau) = \sum_{s,s'} \left\langle \mathcal{T} \hat{E}^{\dagger}_{sR}(t'+\tau/2)\hat{E}_{s'L}(t'-\tau/2)e^{-\frac{i}{\hbar}\int_{-\infty}^{\infty}\hat{H}'_{-}(T)dT}\right\rangle, \tag{7}$$

where $B(t',\tau)$ is an ordinary function since the trace in the right-hand side of the Eq. (7) implies the expectation value of the superoperators. The Hamiltonian superoperator is given by

$$\hat{H}'_{\nu}(t) = \hat{E}^{\dagger}_{\nu}(t)\hat{V}_{\nu}(t) + \text{H.c.}, \quad \nu = L,R. \tag{8}$$

$\mathcal{T}$ is our key bookkeeping device, which is responsible for the positive time ordering of superoperators

$$\mathcal{T}\hat{E}_{\nu}(t_1)\hat{E}_{\nu'}(t_2) = \hat{E}_{\nu}(t_1)\hat{E}_{\nu'}(t_2)\theta(t_1-t_2) + \hat{E}_{\nu'}(t_2)\hat{E}_{\nu}(t_1)\theta(t_2-t_1), \tag{9}$$

where $\theta(t)$ is the Heaviside step function. We next define the detector spectrogram

$$D(\bar{t},\bar{\omega};t',\tau) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega\tau}|F_f(\omega,\bar{\omega})|^2F_t^*(t'+\tau/2,\bar{t})F_t(t'-\tau/2,\bar{t}), \tag{10}$$

if the spectral gate applied first, using Eq. (5). The detector spectrogram is alternatively given by

$$D(\bar{t},\bar{\omega};t',\tau) = \int_{-\infty}^{\infty}dt|F_t(t,\bar{t})|^2F_f^*(t-t'-\tau/2,\bar{\omega})F_f(t-t'+\tau/2,\bar{\omega}). \tag{11}$$

Combining Eqs. (4)–(10) we obtain for the gated signal

$$S(\bar{t},\bar{\omega}) = \int_{-\infty}^{\infty}dt'd\tau D(\bar{t},\bar{\omega};t',\tau)B(t',\tau). \tag{12}$$

The signal is given by the temporal overlap of the bare signal and detector spectrogram. This is the conventional form [6] introduced originally for the field space alone. Equation (7) contains explicitly the multiple pairs of radiation modes s and s' that can be revealed only in the joint field plus matter space. Eventually this takes into account all the field-matter interactions that lead to the emission of the detected field modes. We can freely vary the parameters of F_f and F_t. The spectrogram will always satisfy the Fourier uncertainty $\Delta t\Delta\omega > 1$.

Wigner spectrograms provide a more intuitive time and frequency representation of gated signals. The Wigner spectrogram of the bare signal reads

$$W_B(t',\omega') = \sum_{s,s'}\int_0^{\infty}d\tau e^{-i\omega'\tau}\left\langle\mathcal{T}\hat{E}^{\dagger}_{sR}(t'+\tau/2) \times\hat{E}_{s'L}(t'-\tau/2)e^{-\frac{i}{\hbar}\int_{-\infty}^{\infty}\hat{H}'_{-}(T)dT}\right\rangle, \tag{13}$$

Similarly the detector's spectrogram is given by

$$W_D(\bar{t},\bar{\omega};t',\omega') = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}|F_f(\omega,\bar{\omega})|^2W_t(t',\omega'-\omega,\bar{t}), \tag{14}$$

where

$$W_t(t',\omega) = \int_{-\infty}^{\infty}d\tau F_t^*(t'+\tau/2,\bar{t})F_t(t'-\tau/2,\bar{t})e^{i\omega\tau}. \tag{15}$$

Combining Eqs. (13)–(15) we can recast Eq. (12) in the form

$$S(\bar{t},\bar{\omega}) = \int_{-\infty}^{\infty}dt'\frac{d\omega'}{2\pi}W_D(\bar{t},\bar{\omega};t',\omega')W_B(t',\omega'). \tag{16}$$

The signal is given by the spectral and temporal overlap of the bare signal and the detector spectrograms.

B. Spectrogram-superoperator-overlap representation

So far we included the summation over the detected field modes in the bare signal, while treating the detection spectrogram as an ordinary function of gating parameters. This representation works quite well for a single detection. However for higher-order correlation measurements involving several photons, an easier bookkeeping of the numerous field modes can be achieved by redefining the detector spectrogram as a superoperator. In this case the observed signal is represented by the overlap of two spectrogram superoperators (SSOs) in time, frequency, and field mode space. We first define the reduced field density operator in the subspace of the detected modes s and s' $\text{Tr}'[\rho(t)] = \langle\rho(t)\rangle'$, where prime represents the partial trace over the matter and field degrees of freedom excluding the s and s' modes. Thus the quantity that contains all the information about the matter and field evolution up to detection point [see Fig. 1(b)] is the following two-time superoperator

$$\hat{\mathcal{B}}^{(s,s')}(t',\tau) = \left\langle\mathcal{T}e^{-\frac{i}{\hbar}\int_{-\infty}^{t'-\tau/2}\hat{H}'_L(T)dT}e^{\frac{i}{\hbar}\int_{-\infty}^{t'+\tau/2}\hat{H}'_R(T)dT}\right\rangle'. \tag{17}$$

We next define the detector superoperator

$$\hat{\mathcal{D}}^{(s,s')}(\bar{t},\bar{\omega};t',\tau) = D(\bar{t},\bar{\omega};t',\tau)\hat{E}_{s'L}(t'-\tau/2)\hat{E}^{\dagger}_{sR}(t'+\tau/2), \tag{18}$$

where $D(\bar{t},\bar{\omega};t',\tau)$ is defined in Eq. (10). Combining Eqs. (17) and (18) we obtain for the signal

$$S(\bar{t},\bar{\omega}) = \int_{-\infty}^{\infty}dt'd\tau\sum_{s,s'}\text{Tr}_{s,s'}[\hat{\mathcal{D}}^{(s,s')}(\bar{t},\bar{\omega};t',\tau)\hat{\mathcal{B}}^{(s,s')}(t',\tau)]. \tag{19}$$

The detected signal is represented by an overlap between detector spectrogram $\hat{\mathcal{D}}^{(s,s')}$ and bare signal $\hat{\mathcal{B}}^{(s,s')}$ superoperators.

Similarly, one can recast the results of SSO in the Wigner representation. To that end we introduce the Wigner superoperator for the bare signal

$$\hat{W}_B^{(s,s')}(t',\omega') = \int_{-\infty}^{\infty}d\tau e^{-i\omega'\tau}\left\langle\mathcal{T}e^{-\frac{i}{\hbar}\int_{-\infty}^{t'-\tau/2}\hat{H}'_L(T)dT}e^{\frac{i}{\hbar}\int_{-\infty}^{t'+\tau/2}\hat{H}'_R(T)dT}\right\rangle', \tag{20}$$

and for the detector

$$\hat{W}_{\mathcal{D}}^{(s,s')}(\bar{t},\bar{\omega};t',\omega') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} W_D(\bar{t},\bar{\omega};t',\omega)\hat{W}_E^{(s,s')}(t',\omega-\omega'), \tag{21}$$

where $W_D(\bar{t},\bar{\omega};t',\tau)$ is defined in Eq. (14) and Wigner superoperator for the field modes s and s' reads

$$\hat{W}_E^{(s,s')}(t',\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau}\hat{E}_{s'L}(t'-\tau/2)\hat{E}_{sR}^{\dagger}(t'+\tau/2). \tag{22}$$

Combining Eqs. (20)–(22) we obtain the final SSO expression for the signal

$$S(\bar{t},\bar{\omega}) = \int_{-\infty}^{\infty} dt' \frac{d\omega'}{2\pi}\sum_{s,s'} \mathrm{Tr}_{s,s'}\left[\hat{W}_{\mathcal{D}}^{(s,s')}(\bar{t},\bar{\omega};t',\omega')\hat{W}_{\mathcal{B}}^{(s,s')}(t',\omega')\right]. \tag{23}$$

The detected signal is given by the trace of a convolution of two Wigner superoperators for the detector $\hat{W}_{\mathcal{D}}^{(s,s')}$ and bare signal $\hat{W}_{\mathcal{B}}^{(s,s')}$.

III. BARE SIGNAL

The bare signal contains all relevant information for calculating photon counting measurement. Below we present several schemes for calculating the bare signal, using superoperator diagrammatic techniques. This will be done using both SO and SSO representations.

The bare signal is given by the closed path time-loop diagram shown in Fig. 1 [22]. We assume arbitrary field-matter evolution starting from the matter ground state g that promotes the system up to some excited state. Then the system emits a photon with frequency ω_s that leaves the matter in the state e. This photon is later absorbed by the detector.

A. Bare signal expressed as a product of two transition amplitudes

We first calculate the time-dependent bare signal (7) in the interaction picture where we factorize the detected field and matter correlation functions

$$\left(-\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t'+\tau/2} dt_1 \int_{-\infty}^{t'-\tau/2} dt_1' \langle \mathcal{T}\hat{V}_L(t_1')\hat{V}_R^{\dagger}(t_1)\rangle \times\langle \mathcal{T}\hat{E}_{sR}^{\dagger}(t'+\tau/2)\hat{E}_{s'L}(t'-\tau/2)\hat{E}_{s'L}^{\dagger}(t_1')\hat{E}_{sR}(t_1)\rangle. \tag{24}$$

Since both $\hat{E}_{s'L}$ and $\hat{E}_{sR}$ are initially in the vacuum state, the field correlation function reads

$$\langle \hat{E}_{sR}^{\dagger}(t'+\tau/2)\hat{E}_{s'L}(t'-\tau/2)\hat{E}_{s'L}^{\dagger}(t_1')\hat{E}_{sR}(t_1)\rangle = \left(\frac{2\pi\hbar}{\Omega}\right)^2 \omega_s\omega_s' e^{i\omega_s(t'+\tau/2-t_1)-i\omega_s'(t'-\tau/2-t_1')}. \tag{25}$$

In the absence of dissipation (unitary evolution) we can factorize the matter correlation function as

$$\langle \mathcal{T}\hat{V}_L(t_1')\hat{V}_R^{\dagger}(t_1)\rangle = \sum_e \langle\langle \hat{V}_L(t_1')|ge\rangle\rangle\langle\langle ge|\hat{V}_R^{\dagger}(t_1)\rangle\rangle = \sum_e \langle\langle e(t'+\tau/2)g|\hat{V}_L(t_1')\mathcal{T}\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{t_1'}\hat{H}_L'(T)dT\right]|gg\rangle\rangle \times\langle\langle gg|\hat{V}_R^{\dagger}(t_1)\mathcal{T}\exp\left[\frac{i}{\hbar}\int_{-\infty}^{t_1}\hat{H}_R'(T)dT\right]|e(t'+\tau/2)g\rangle\rangle, \tag{26}$$

where we denote $\langle\langle eg|\hat{A}|gg\rangle\rangle \equiv \mathrm{Tr}[|g\rangle\langle e|\hat{A}|g\rangle\langle g|]$. We next define the transition amplitude

$$T_{eg}(t) = -\frac{i}{\hbar}\sum_s \frac{2\pi\hbar\omega_s}{\Omega}\int_{-\infty}^{t} dt_1' e^{-i\omega_s(t-t_1')-i\omega_{eg}t} \times\langle\langle e(t)g|\hat{V}_L(t_1')\mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{-\infty}^{t_1'}\hat{H}_L'(T)dT\right)|gg\rangle\rangle. \tag{27}$$

Since all interactions are from the left (L), we can also write the transition amplitude using ordinary operators in Hilbert space

$$T_{eg}(t) = -\frac{i}{\hbar}\sum_s \frac{2\pi\hbar\omega_s}{\Omega}\int_{-\infty}^{t} dt_1' e^{-i\omega_s(t-t_1')-i\omega_{eg}t} \times\langle e(t)|V(t_1')\mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{-\infty}^{t_1'}H'(T)dT\right)|g\rangle. \tag{28}$$

This gives for the bare signal (7)

$$B(t',\tau) = -\sum_e T_{eg}(t'-\tau/2)T_{eg}^*(t'+\tau/2). \tag{29}$$

The corresponding Wigner function is given by

$$W_B(t',\omega') = -\sum_e \int_0^{\infty} d\tau e^{-i\omega'\tau}T_{eg}(t'-\tau/2)T_{eg}^*(t'+\tau/2). \tag{30}$$

Together with the gated spectrogram (10) the bare signal (29) represents the time- and frequency-resolved gated signal. The final result can be recast in Hilbert space without using superoperators. The Wigner representation is very convenient and intuitive for time- and frequency-resolved measurements. The drawback is that for general photon correlation measurements, the definition of the signals and spectrograms will require a derivation for each new type of measurement. This is not very convenient for higher-order correlation measurements, where we would like to introduce a modular detection anytime we need. This will be done next.

Note, that in the presence of a bath, the signal (30) is no longer given by a product of two amplitudes. $T_{eg}(t)$ is then an operator in the space of the bath degrees of freedom. Therefore, Eq. (30) yields

$$W_B(t',\omega') = -\sum_e \int_0^\infty d\tau e^{-i\omega'\tau} \langle T_{eg}(t'-\tau/2)T^*_{eg}(t'+\tau/2)\rangle, \tag{31}$$

where $\langle\cdots\rangle$ corresponds to averaging over the bath degrees of freedom.

B. Transition amplitude superoperator

We start with the bare signal superoperator (17). Similar to Eq. (24) we factorize the matter correlation function

$$\left(-\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t'+\tau/2} dt_1 \int_{-\infty}^{t'-\tau/2} dt_1' \langle \mathcal{T}\hat{V}_L(t_1')\hat{V}_R^\dagger(t_1)\rangle' \hat{E}^\dagger_{s'L}(t_1')\hat{E}_{sR}(t_1). \tag{32}$$

The matter correlation function can be further factorized into a product of two amplitudes according to Eq. (26). We next define the transition superoperator. For the ket

$$\hat{T}^{(s')}_{eg,L}(t) = -\frac{i}{\hbar}\int_{-\infty}^t dt_1' \hat{E}^\dagger_{s'L}(t_1')e^{-i\omega_{eg}t} \times \langle\langle e(t)g|\hat{V}_L(t_1')\mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{-\infty}^{t_1'}\hat{H}'_L(T)dT\right)|gg\rangle\rangle, \tag{33}$$

and for the bra

$$\hat{T}^{(s)\dagger}_{eg,R}(t) = \frac{i}{\hbar}\int_{-\infty}^t dt_1 \hat{E}_{sR}(t_1)e^{i\omega_{eg}t} \times \langle\langle gg|\hat{V}_R(t_1)\mathcal{T}\exp\left(\frac{i}{\hbar}\int_{-\infty}^{t_1}\hat{H}'_R(T)dT\right)|e(t)g\rangle\rangle. \tag{34}$$

Note that Eq. (33) represents a transition amplitude that includes all the field-matter interactions, but excluding the detection. On the other hand $T_{eg}(t)$ in Eq. (27)

$$T_{eg}(t) = \sum_s \mathrm{Tr}_s\left[\hat{E}_s(t)\hat{T}^{(s)}_{eg}(t)\right] \tag{35}$$

does include the detection.

The bare signal superoperator is thus given by

$$\hat{\mathcal{B}}^{(s,s')}(t',\tau) = -\sum_e \hat{T}^{(s')}_{eg,L}(t'-\tau/2)\hat{T}^{(s)\dagger}_{eg,R}(t'+\tau/2). \tag{36}$$

The corresponding Wigner superoperator reads

$$\hat{W}^{(s,s')}_{\mathcal{B}}(t',\omega') = -\sum_e \int_{-\infty}^\infty d\tau e^{-i\omega'\tau} \times \hat{T}^{(s')}_{eg,L}(t'-\tau/2)\hat{T}^{(s)\dagger}_{eg,R}(t'+\tau/2). \tag{37}$$

Together with Eqs. (18) and (19), the bare signal spectrogram superoperator (36) represents the time- and frequency-resolved gated signals. Note that the bare superoperator (36) depends explicitly on the initial and final states of matter. In addition the convolution of two amplitudes T_{eg} reveals the multiple pathways between these initial and final states that allows to observe them through the simultaneous time and frequency resolution. Both the bare and the detector spectrograms contain the superoperator of the field s and s' modes. This follows immediately from the diagrammatic representation of Fig. 1(b). As was done in Eq. (31) bath correlations can be added to Eq. (37).

IV. LIMITING CASES: TIME- OR FREQUENCY-RESOLVED SIGNALS

We now consider two limiting cases. In the absence of a frequency gate, then $F_f(\omega,\bar{\omega}) = 1$ we get $W_D(\bar{\omega},\bar{t};t,\tau) = \delta(\tau)F_t^*(t+\tau/2,\bar{t})F_t(t-\tau/2,\bar{t})$. For the narrow time gate $|F_t(t,\bar{t})|^2 = \delta(t-\bar{t})$ we then obtain the time-resolved measurement

$$S(\bar{\omega},\bar{t}) = -\sum_e |T_{eg}(\bar{t})|^2. \tag{38}$$

In the opposite limit if there is no time gate [i.e., $F_t(t,\bar{t}) = 1$] and the frequency gate is very narrow, such that $F_f(t,\bar{\omega}) = \frac{\sqrt{\gamma}}{\pi}e^{-i\bar{\omega}t-\gamma t}\theta(t)$ at $\gamma \to 0$, then $W_D(\bar{\omega},\bar{t};t,\tau) = e^{-i\bar{\omega}\tau}$. In this case we obtain the frequency-resolved measurement

$$S(\bar{\omega},\bar{t}) = -\sum_e |T_{eg}(\bar{\omega})|^2, \tag{39}$$

where $T_{eg}(\omega) = \int_{-\infty}^\infty dt e^{i\omega t}T_{eg}(t)$. Equations (38) and (39) indicate that if the measurement is either purely time-resolved or purely frequency-resolved, the signal can be expressed in terms of the modulus square of a transition amplitude. Interference can then occur only within T_{eg} in Hilbert space but not between the two amplitudes. Simultaneous time and frequency gating also involves interference between the two amplitudes; the pathway is in the joint ket plus bra density matrix space. In the presence of a bath, the signal can be written as a correlation function in the space of bath coordinates $\langle T^*_{eg}(\bar{t})T_{eg}(\bar{t})\rangle$ for Eq. (38) and $\langle T^*_{eg}(\bar{\omega})T_{eg}(\bar{\omega})\rangle$ for Eq. (39).

V. MULTIPLE DETECTIONS

The present formalism is modular and may be easily extended to any number of detection events. To that end it is more convenient to use the time domain, rather than Wigner representation. For coincidence counting of two photons measured by first detector with parameters $\bar{\omega}_i,\bar{t}_i$ followed by second detector characterized by $\bar{\omega}_s,\bar{t}_s$ (see Fig. 2) the time- and frequency-resolved measurement in SO representation is given by

$$S(\bar{t}_s,\bar{\omega}_s;\bar{t}_i,\bar{\omega}_i) = \int_{-\infty}^\infty dt_s' d\tau_s \int_{-\infty}^\infty dt_i' d\tau_i D^{(s)}(\bar{t}_s,\bar{\omega}_s;t_s',\tau_s) \times D^{(i)}(\bar{t}_i,\bar{\omega}_i;t_i',\tau_i')B(t_s',\tau_s;t_i',\tau_i'), \tag{40}$$

where the detector spectrogram for mode $\nu = i,s$ reads

$$D(\bar{t}_\nu,\bar{\omega}_\nu;t_\nu',\tau_\nu) = \int_{-\infty}^\infty \frac{d\omega_\nu}{2\pi}e^{-i\omega_\nu\tau_\nu}|F_f(\omega_\nu,\bar{\omega}_\nu)|^2 \times F_t^*(t_\nu'+\tau_\nu/2,\bar{t}_\nu)F_t(t_\nu'-\tau_\nu/2,\bar{t}_\nu). \tag{41}$$

The bare signal is given by

$$B(t_s',\tau_s;t_i',\tau_i) = -\sum_e T_{eg}(t_s'-\tau_s/2,t_i'-\tau_i/2) \times T_{eg}^*(t_s'+\tau_s/2,t_i'+\tau_i/2). \quad (42)$$

The transition amplitude for the ket reads

$$T_{eg}(t_s,t_i) = \left(-\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t_s} dt_1' \int_{-\infty}^{t_i} dt_2' e^{-i\omega_{eg}t_s} \times \langle\langle e(t_s)g|\hat{V}_L(t_1')\hat{V}_L(t_2') \times \mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{-\infty}^{\max[t_1',t_2']} \hat{H}_L'(T)dT\right)|gg\rangle\rangle, \quad (43)$$

and for the bra

$$T_{eg}^*(t_s,t_i) = \left(\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t_s} dt_1 \int_{-\infty}^{t_i} dt_2 e^{i\omega_{eg}t_s} \times \langle\langle gg|\hat{V}_R^\dagger(t_1)\hat{V}_R^\dagger(t_2) \times \mathcal{T}\exp\left(\frac{i}{\hbar}\int_{-\infty}^{\max[t_1,t_2]} \hat{H}_R'(T)dT\right)|e(t_s)g\rangle\rangle. \quad (44)$$

Similarly, one can derive multiple detection measurement using SSO formalism. The coincidence signal is given by

$$S(\bar{t}_s,\bar{\omega}_s;\bar{t}_i,\bar{\omega}_i) = \int_{-\infty}^{\infty} dt_s' d\tau_s \int_{-\infty}^{\infty} dt_i' d\tau_i \sum_{s,s'}\sum_{i,i'} \times \text{Tr}_{s,s',i,i'}[\hat{\mathcal{D}}^{(s,s')}(\bar{t}_s,\bar{\omega}_s;t_s',\tau_s)\hat{\mathcal{D}}^{(i,i')} \times(\bar{t}_i,\bar{\omega}_i;t_i',\tau_i)\hat{\mathcal{B}}^{(s,s',i,i')}(t_s',\tau_s;t_i',\tau_i)], \quad (45)$$

where the detector spectrogram superoperator reads

$$\hat{\mathcal{D}}^{(\nu,\nu')}(\bar{t}_\nu,\bar{\omega}_\nu;t_\nu',\tau_\nu) = D(\bar{t}_\nu,\bar{\omega}_\nu;t_\nu',\tau_\nu)\hat{E}_{\nu' L}(t_\nu'-\tau_\nu/2)\hat{E}_{\nu R}^\dagger(t_\nu'+\tau_\nu/2) \quad (46)$$

and the detection spectrogram $D(\bar{t}_\nu,\bar{\omega}_\nu;t_\nu',\tau_\nu)$ is defined in Eq. (41). The bare signal superoperator yields

$$\hat{\mathcal{B}}^{(s,s',i,i')}(t_s',\tau_s;t_i',\tau_i) = -\sum_e \hat{T}_{egL}^{(s',i')}(t_s'-\tau_s/2,t_i'-\tau_i/2) \times \hat{T}_{egR}^{(s,i)\dagger}(t_s'+\tau_s/2,t_i'+\tau_i/2), \quad (47)$$

where the transition superoperator for the left branch, the ket, is

$$\hat{T}_{egL}^{(s',i')}(t_s,t_i) = \left(-\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t_s} dt_1' \int_{-\infty}^{t_i} dt_2' e^{-i\omega_{eg}t_s} \times \hat{E}_{s'L}^\dagger(t_1')\hat{E}_{i'L}^\dagger(t_2')\langle\langle e(t_s)g|\hat{V}_L(t_1')\hat{V}_L(t_2') \times \mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{-\infty}^{\max[t_1',t_2']} \hat{H}_L'(T)dT\right)|gg\rangle\rangle. \quad (48)$$

and for the bra (right branch)

$$\hat{T}_{egR}^{(s,i)\dagger}(t_s,t_i) = \left(\frac{i}{\hbar}\right)^2 \int_{-\infty}^{t_s} dt_1 \int_{-\infty}^{t_i} dt_2 e^{i\omega_{eg}t_s} \times \hat{E}_{sR}(t_1)\hat{E}_{iR}(t_2)\langle\langle gg|\hat{V}_R^\dagger(t_1)\hat{V}_R^\dagger(t_2) \times \mathcal{T}\exp\left(\frac{i}{\hbar}\int_{-\infty}^{\max[t_1,t_2]} \hat{H}_R'(T)dT\right)|e(t_s)g\rangle\rangle. \quad (49)$$

Note, that in the presence of a bath bare signal (42) and (47) will contain the correlation function of two transition operators in the bath space similarly to Eq. (31).

VI. CONCLUSION

We have developed a diagrammatic approach in the joint matter plus field space for calculating time- and frequency-gated photon counting measurements. Unlike standard detection theory the present approach does not require the normal ordering of the field operators, it only employs superoperator time ordering. The result is given by the temporal and spectral overlap of the bare and detector spectrograms. The detector is governed by the time and frequency gates. The bare signal is represented by the product of two transition amplitudes, each corresponding to the side of the loop diagram. The transition amplitude superoperator creates a coherence in the field between states with zero and one photon. The detection of photons occurs by combining two transition amplitude superoperators—one for bra and one for ket in the joint field plus matter space. The detection involves an interference of two pathways with different time orderings.

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