



Matter and field spectral densities for multidimensional optical response



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ABSTRACT

In the semiclassical theory of multidimensional spectroscopy, which describes a classical field coupled to quantum matter, n -th order signals are calculated as a convolution of n spectral field envelopes and an n -th order matter response function which enforces the time-ordering of interactions. In quantum field spectroscopy, the electromagnetic field is in a nonclassical state and the product of spectral field envelopes is replaced by a correlation function of the associated field operators. In this paper, we introduce a complementary representation in which the roles of field and matter are interchanged and signals are given by an ordinary, correlation function of matter convoluted with a time-ordered response function of the field. This suggests an inverse spectroscopy which uses matter to probe the state of the field.

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1. Introduction

The key information extracted from spectroscopic signals is the energies and lifetimes of excitations. Multidimensional spectroscopy can access higher-order excitations and the couplings between their constituent single-excitations. In principle, this information is contained in a simple, non-time-ordered correlation function of material excitation operators (within the dipole approximation, the relevant operator is the transition dipole moment). We term the Fourier transform of such a correlation function the n -th order multidimensional spectral density $V^{(n)}$ in analogy to the linear case [1,2].

The actual calculation of spectroscopic signals must keep track of time-ordered interactions. This time-ordering is baked into the matter correlation function, resulting, in the frequency domain, in the n -th order nonlinear susceptibility $\chi^{(n)}$ [1,3]. Within the semiclassical theory, the fields may be taken as ordinary functions and the signal is then given as a convolution of the product of the spectral field envelopes with $\chi^{(n)}$. When spectroscopy is performed with quantum fields, one must instead replace the product of field spectral envelopes by a correlation function of frequency-domain field operators. A wide range of novel states of light have been created and analyzed [4–7] and performing spectroscopy with these states has been an area of active interest [8–14]. Since both field and matter are now quantum, a symmetric representation in the roles of field and matter is called for. We can write the associated

Heaviside theta functions that enforce time-ordering in the Fourier domain to obtain a function $h^{(n)}$ that connects the field and matter quantities via a double-convolution while encoding the time-ordering of interactions.

In this paper, we first derive a formula for multidimensional spectroscopy signals in terms of the “connection” function $h^{(n)}$. An explicit expression for $h^{(n)}$ is given. Importantly, the $h^{(n)}$ function is universal and all system-specific information is encoded in separate field or matter quantities. From this expression, one can recover the susceptibility via convolving $h^{(n)}$ with the material multidimensional spectral density. The relationship between the spectral density and the material response function is known as the Kramers–Kronig relation and is a well-known representation of linear signals [1]. Analogy has previously been made at the level of the third-order response [2] and is here extended to arbitrary order. In an alternate representation, one may convolve $h^{(n)}$ with the field correlation function to obtain a field-susceptibility $\tilde{\chi}^{(n)}$, the signal being then given by a convolution of the material multidimensional spectral density and $\tilde{\chi}^{(n)}$. This offers a new interpretation of spectroscopic signals that may be of particular use for interrogating complex quantum states of the electric field via simpler material systems with known multidimensional spectral densities.

2. Formalism

In the standard theory of multidimensional spectroscopy [2,15,16], signals are given as a convolution of a field correlation function and the matter susceptibility $\chi^{(n)}$, i.e.,

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$$S^{(n)}(\Lambda) = \Im \left[\int d\omega_{n+1} \dots \int d\omega_1 \chi^{(n)}(-\omega_{n+1}; \omega_n, \dots, \omega_1) \times \langle E(\omega_{n+1}) \dots E(\omega_1) \rangle \right]. \quad (1)$$

The signal depends on the parameters defining the field envelopes, collectively represented by Λ . Once one obtains the susceptibility, this formula is easily employed to predict the results of any experiment with a given set of classical, stochastic, or quantum fields [17,18]. Note that it is assumed that the field and matter are not initially entangled. When the field is classical, its correlation function reduces to the simple product of the spectral envelopes. The susceptibility encodes all details of the material and is given as the Fourier transform of a sum of dipole correlation functions with different time-orderings.

Eq. (1) is asymmetric in the roles of field and matter. The field enters as an ordinary, rather than time-ordered, correlation function whereas the matter enters as a response function, which is a specific combination of correlation functions with different time-orderings. This form is natural for the semiclassical description which is *causal*, i.e., the field is given and the matter responds to it. Once we consider quantum fields, the experiment involves coupled field and matter degrees of freedom. It may then be useful to reformulate the problem so that field and matter enter more symmetrically.

In this paper, first we derive diagrammatically an alternative exact expression for optical signals of the form

$$S^{(n)}(\Gamma) = \Im \left[\int d\omega'_{n+1} d\omega_{n+1} \dots \int d\omega'_1 d\omega_1 \langle \hat{V}(\omega'_{n+1}) \dots \hat{V}(\omega'_1) \rangle_0 h^{(n)}(\omega'_{n+1}, \omega_{n+1}, \dots, \omega'_1, \omega_1) \langle \hat{E}(\omega_{n+1}) \dots \hat{E}(\omega_1) \rangle_0 \right] \quad (2)$$

where $\langle \dots \rangle_0 \equiv \langle \psi_0 | \dots | \psi_0 \rangle$ is the expectation value with respect to the initial state. In this form, the roles of the field and matter are completely symmetric. The function $h^{(n)}$ carries all the bookkeeping of the various time-ordered pathways that contribute to the response by connecting the unprimed (field) and primed (matter) frequency variables. Since it is entirely independent of the field and the material, we need only calculate this h -function once and may then freely apply it to any field-matter configuration. This approach formally simplifies the calculation of the n th-order signal by allowing the replacement of the matter susceptibility with the ordinary correlation function which, as will be shown below, has a simple form. Moreover, the resulting expression for the signal is insightful since it treats the field and matter in a symmetric fashion and neatly bundles the complicated path-order bookkeeping via the h -function. These three ingredients (material correlation function, field correlation function, and h -function) then carry all information necessary to reconstruct the signal. Carrying out the integrations over $d\omega'_i$ in Eq. (2) results in

$$\int d\omega'_{n+1} \dots \int d\omega'_1 \langle \hat{V}(\omega'_{n+1}) \dots \hat{V}(\omega'_1) \rangle h^{(n)}(\omega'_{n+1}, \omega_{n+1}, \dots, \omega'_1, \omega_1) = \chi^{(n)}(\omega_{n+1}, \dots, \omega_1), \quad (3)$$

and substitution into Eq. (2) then recovers Eq. (1). This approach is based on the idea of using simple fields, or fields with known properties, to study complicated material systems of interest (or those with unknown properties). However, Eq. (2) suggests that this step can be inverted; utilizing a simple material system with known properties to probe nontrivial electric field states (entangled photons, etc.). We therefore define the “field susceptibility”

$$\tilde{\chi}^{(n)}(\omega'_{n+1}, \dots, \omega'_1) = \int d\omega_{n+1} \dots \int d\omega_1 \langle \hat{E}(\omega_{n+1}) \dots \hat{E}(\omega_1) \rangle h^{(n)}(\omega'_{n+1}, \omega_{n+1}, \dots, \omega'_1, \omega_1) \quad (4)$$

which allows one to express the signal as

$$S^{(n)}(\Gamma) = \int d\omega'_{n+1} \dots \int d\omega'_1 \langle \hat{V}(\omega'_{n+1}) \dots \hat{V}(\omega'_1) \rangle \tilde{\chi}^{(n)}(\omega'_{n+1}, \dots, \omega'_1). \quad (5)$$

The signal is now expressible as an $(n+1)$ dimensional overlap integral of the field susceptibility with the material dipole correlation function. The present approach offers a new way of viewing the n -th order spectroscopic signal that may prove insightful, particularly when employing novel states of the electromagnetic field. To comprehend the structure of the non-time-ordered transition dipole correlation function, we begin by taking matrix elements of the dipole operator in the material eigenbasis

$$\langle a | \hat{V}(t) | b \rangle = V_{ab} e^{i\omega_{ab}t}. \quad (6)$$

The Fourier transform, the associated time integrations now being unrestricted, is therefore

$$\langle a | \hat{V}(\omega) | b \rangle = V_{ab} \delta(\omega + \omega_{ab}) \quad (7)$$

and the eigenbasis expansion of the material correlation function reads

$$\langle \hat{V}(\omega'_{n+1}) \dots \hat{V}(\omega'_1) \rangle_0 = \sum_{a_i} V_{a_0 a_n} \dots V_{a_1 a_0} \delta(\omega'_{n+1} + \omega_{a_0 a_n}) \dots \times \delta(\omega'_1 + \omega_{a_1 a_0}). \quad (8)$$

In analogy to the linear ($n=1$) case ($\langle \hat{V}(\omega'_2) \hat{V}(\omega'_1) \rangle = \langle \hat{V}(-\omega'_1) \hat{V}(\omega'_1) \rangle$), we term this the multidimensional spectral transition density [2]. It encodes the spectral density of material transitions at each of the ω'_j variables. For the field, the frequency domain correlation function is naturally obtained with a second-quantized representation of the field-operators given an arbitrary state of the field.

The derivation for the h -function is given in the appendix and results in

$$h^{(n)}(\omega_{n+1}, \omega'_{n+1}, \dots, \omega_1, \omega'_1) = \delta(\Omega_1 + \dots + \Omega_{n+1}) \sum_{k=0}^n \frac{(-1)^k \theta(\omega_{n-k+1})}{(2\pi)^{2n+1}} h_k^{(n)}(\Omega_{n+1}, \dots, \Omega_1) \quad (9)$$

with

$$h_k^{(n)}(\Omega_{n+1}, \dots, \Omega_1) = \prod_{j=0}^{k-1} \frac{1}{\sum_{j'=0}^j \Omega_{n+1-j'} - i\eta} \prod_{j=1}^{n-k} \frac{1}{\sum_{j'=1}^j \Omega_{j'} - i\eta} \quad (10)$$

where $\Omega_i \equiv \omega_i + \omega'_i$ and η is a positive infinitesimal. This expression has $n+1$ terms reflecting the fact that the expectation values are calculated via the wave-function picture. The auxiliary function $h_k^{(n)}$ can be easily rationalized by considering an expansion along the loop diagram shown in Fig. 1. In this figure, the frequencies on the ket branch accumulate in the denominators of the second product as one progresses up the ket branch. The frequencies on the bra branch then de-accumulate in the denominators of the first product as one descends the bra branch. One may thus easily convert the loop diagram associated with a particular experiment of interest into its corresponding $h_k^{(n)}$ (there may be one or several that contribute to a given spectroscopic signal). The relevant $h_k^{(n)}$ can then be combined with either matter or field to obtain the $\chi^{(n)}$ or $\tilde{\chi}^{(n)}$ that determines the signal.

The above discussion is predicated on a Hilbert-space description of the field-matter interaction, the natural language of which is the loop diagrams which maintain separate ket and bra time ordering. When the ket and bra evolve jointly, as when pure-dephasing and system-bath interactions are important, one must

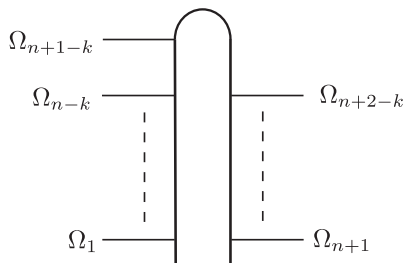


Fig. 1. This loop diagram represents $h_k^{(n)}$. Each period along the loop stands for a factor of $1/(\Omega - i\eta)$ where the frequency denominators accumulate as one goes up the ket branch and then de-accumulate as one goes down the bra branch of the loop. Time ordering is therefore kept separately on the ket and bra (i.e., along the loop). This results in Eq. (10).

switch to a fully time-ordered representation in which the density matrix evolves as a vector in Liouville space [1,19]. One must then split each partially time-ordered term, which maintains ket and bra orderings separately, into fully time-ordered terms, which maintain relative ordering of ket and bra interactions and are represented by ladder diagrams. Just as a given loop diagram may be expressed as a sum of ladder diagrams, the $h_k^{(n)}$ function can be recast into a sum of terms $\tilde{h}_k^{(n)}$ that maintain absolute time-ordering of ket and bra interactions, in contrast to $h_k^{(n)}$ which only maintains time-ordering on the ket and bra separately. This process results in $\binom{n}{k}$ “ladder” terms $\tilde{h}_k^{(n)}$ for each “loop” term $h_k^{(n)}$. This can be seen from Fig. 1 and considering that each of the k interactions on the bra may go anywhere in the $n - k + 1$ spaces between interactions on the ket. The ladder-based expansion therefore carries 2^n terms as opposed to the $n + 1$ terms when expanding along the loop and is less compact. Each ladder diagram represents a term in which the frequencies (in the denominators of the product) accumulate in real-time order as one progresses up the ladder. For concreteness, we use $\tilde{h}^{(n)}$ and $\tilde{h}_k^{(n)}$ to refer to expansions performed with the ladder diagrams. The conversion procedure is illustrated in Fig. 2 for $h_1^{(3)} \rightarrow \tilde{h}_1^{(3)}$ and results in

$$\begin{aligned}
 h_1^{(3)} &= \frac{1}{\Omega_1 - i\eta} \frac{1}{\Omega_1 + \Omega_2 - i\eta} \frac{1}{\Omega_4 - i\eta} \rightarrow \tilde{h}_1^{(3)} \\
 &= \frac{1}{\Omega_1 - i\eta} \frac{1}{\Omega_1 + \Omega_2 - i\eta} \frac{1}{\Omega_1 + \Omega_2 + \Omega_4 - i\eta} \\
 &\quad + \frac{1}{\Omega_1 - i\eta} \frac{1}{\Omega_1 + \Omega_4 - i\eta} \frac{1}{\Omega_1 + \Omega_4 + \Omega_2 - i\eta} \\
 &\quad + \frac{1}{\Omega_4 - i\eta} \frac{1}{\Omega_4 + \Omega_1 - i\eta} \frac{1}{\Omega_4 + \Omega_1 + \Omega_2 - i\eta}
 \end{aligned} \tag{11}$$

Unfortunately, in Liouville space, each of these $\tilde{h}_k^{(n)}$ is associated with a different material correlation function, corresponding to the possible positions of the k bra interactions. In Hilbert space, these material correlation functions are all the same, a key fact that permits the re-casting presented here. In Liouville space, it will not therefore be possible to write so compact an expression as Eq. (2), and the best one could do is write such a formula for each diagram.

The $\tilde{h}_k^{(n)}$ would then enforce the time-ordering while the k -index would label a particular string of n L 's and R 's that specifies whether each transition dipole operator acts on the ket or bra. Such a representation may still be useful, as it would still be possible to convolve the $\tilde{h}_k^{(n)}$ with the field correlation function to obtain the Liouville-space equivalent of Eq. (5). The limitation is that this must then be done separately for each diagram. Under Hamiltonian evolution, i.e., when the Liouvillian is a simple commutator, the L and R operators commute at all times and one can recombine these

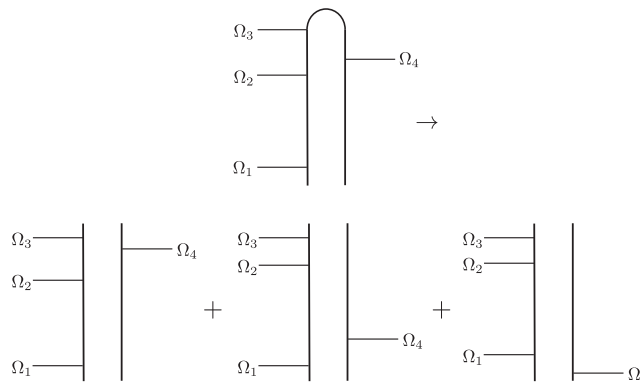


Fig. 2. This figure illustrates the conversion $h_k^{(n)} \rightarrow \tilde{h}_k^{(n)}$. For the ladder diagrams, each period up the loop stands for a factor of $1/(\Omega - i\eta)$ where the frequency denominators accumulate as one goes up the ladder. A general formula for $\tilde{h}_k^{(n)}$ (in the same spirit as Eq. (10)) is not convenient. We therefore simply illustrate the conversion process. This results in Eq. (11).

fully time-ordered terms into the separately ket- and bra-ordered terms associated with the Hilbert-space description. It is however possible to account for finite excited state lifetimes by allowing the transition frequencies to become complex and modifying the $h_k^{(n)}$. This alteration is somewhat subtle, in that it requires that real and imaginary parts of the transition frequencies be incorporated differently, and is described in the appendix resulting in Eq. (B8).

In summary, the present formalism allows one to put the entire burden of time ordering either on the matter (Eq. (1)), the field (Eq. (5)), or neither (Eq. (2)). Non-time-ordered correlation functions are easier to calculate and have fewer terms compared to time-ordered response functions. This approach thus offers a compact representation of nonlinear spectroscopies that is symmetric in field and matter quantities. Moreover, the ability to place the time-ordering on the matter or field part gives a valuable flexibility in the theoretical treatment of nonlinear signals. By convolving the h -function with the field quantity, one obtains a field-susceptibility (Eq. (4)) and the signal can then be viewed as a “matter spectroscopy”. That is, one may apply a given complicated external electric field state to a variety of simple material systems, possibly generated by alterations to some zero-order material system. One then interrogates the response of the field to different materials rather than vice versa as is ordinarily done. This can be done, e.g., by the Ramsay setup whereby a molecular beam passes through a series of optical cavities and the final molecular state is detected say by fluorescence [20,21].

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Appendix A. Deriving the h -function

The Hamiltonian is given by the sum of the bare matter and field Hamiltonian and the matter–field interaction.

$$H = H_0 + H'(t). \tag{A1}$$

Throughout, we will work in the interaction picture with respect to this $H'(t)$ (we also employ atomic units so that $\hbar = 1$). The interaction is assumed to be dipolar

$$H'(t) = - \int d\mathbf{r} \hat{\mathbf{V}}(\mathbf{r}, t) \cdot \hat{\mathbf{E}}(\mathbf{r}, t) \quad (\text{A2})$$

To make the resulting expressions less cluttered, we take $\hat{\mathbf{V}}$ to be the component of the transition dipole along the electric field. This amounts to omitting the sum over cartesian components that arises from the dot product $\mathbf{V} \cdot \mathbf{E}$. These omissions can be easily reinstated when the need arises (as in polarization spectroscopy). In the interest of conciseness of the resulting expressions, we derive the h -function for a sample consisting of an isolated particle of size much less than the wavelength of the interacting light. Under these conditions, we may simply write

$$H'(t) = -\hat{\mathbf{V}}(t)\hat{\mathbf{E}}(t) \quad (\text{A3})$$

Omitting polarization, the transverse electric field operator is given by

$$\hat{\mathbf{E}}(t) = i \sum_{\mathbf{i}} \sqrt{\frac{\omega}{8\pi V}} [\hat{a}_{\mathbf{i}} e^{i\mathbf{k}_{\mathbf{i}} \cdot \mathbf{r} - i\omega t} - \hat{a}_{\mathbf{i}}^{\dagger} e^{-i\mathbf{k}_{\mathbf{i}} \cdot \mathbf{r} + i\omega t}] \equiv \hat{\mathcal{E}}(t) + \hat{\mathcal{E}}^{\dagger}(t). \quad (\text{A4})$$

The signal at time t is defined by

$$S(t) = \langle \hat{N} \rangle \quad (\text{A5})$$

where $N = \sum_{\mathbf{i}} \hat{a}_{\mathbf{i}}^{\dagger} \hat{a}_{\mathbf{i}}$ is the photon number operator. Assuming that $[H_0, N] = 0$, it is readily verified that

$$\langle \hat{N} \rangle = i[H'(t), N] = 2\Im \left[\langle \hat{\mathbf{V}}(t) \hat{\mathcal{E}}^{\dagger}(t) \rangle \right]. \quad (\text{A6})$$

In order to obtain an expression of the form given in Eq. (2), we will expand this expectation value using the wavefunction-based approach (in the interaction picture):

$$\langle \hat{\mathbf{V}}(t) \hat{\mathcal{E}}^{\dagger}(t) \rangle = \langle \psi(t) | \hat{\mathbf{V}}(t) \hat{\mathcal{E}}^{\dagger}(t) | \psi(t) \rangle \quad (\text{A7})$$

We could of course approach the problem via the density matrix but the result then has 2^n terms versus $n+1$ and a certain kind of path-ordering (due to the commutators between the dipole operators and the density matrix) cannot then be built into the h -function but continues to reside with the correlation functions. This difficulty can be overcome and the 2^n terms may be combined into $n+1$ but this exactly reproduces the result obtained more simply from a direct application of the wavefunction-based approach. We may of course extend this formalism to mixed states by averaging over the distribution of initial wavefunctions at the end. Expanding to n -th order, we have

$$S^{(n)}(t) = 2\Im \left[\sum_{k=0}^n \langle \psi^{(k)}(t) | \hat{\mathbf{V}}(t) \hat{\mathcal{E}}^{\dagger}(t) | \psi^{(n-k)}(t) \rangle \right] \quad (\text{A8})$$

Using the time-ordered expansion for $|\psi\rangle$

$$|\psi^{(k)}(t)\rangle = (i)^k \int_{-\infty}^t d\tau_k \int_{-\infty}^{\tau_k} d\tau_{k-1} \dots \times \int_{-\infty}^{\tau_2} d\tau_1 \hat{\mathbf{V}}(\tau_k) \hat{\mathbf{E}}(\tau_k) \dots \hat{\mathbf{V}}(\tau_1) \hat{\mathbf{E}}(\tau_1) | \psi(-\infty) \rangle \quad (\text{A9})$$

we obtain

$$\langle \psi^{(k)}(t) | \hat{\mathbf{V}}(t) \hat{\mathcal{E}}^{\dagger}(t) | \psi^{(n-k)}(t) \rangle = (-1)^k (i)^n \int d\tau_n \dots \int d\tau_1 \theta(\tau_{n-1} - \tau_n) \dots \theta(t - \tau_{n-k+1}) \theta(t - \tau_{n-k}) \dots \theta(\tau_2 - \tau_1) \langle \hat{\mathbf{V}}(\tau_n) \hat{\mathbf{E}}(\tau_n) \dots \hat{\mathbf{V}}(\tau_{n-k+1}) \hat{\mathbf{E}}(\tau_{n-k+1}) \hat{\mathbf{V}}(t) \hat{\mathcal{E}}^{\dagger}(t) \hat{\mathbf{V}}(\tau_{n-k}) \hat{\mathbf{E}}(\tau_{n-k}) \dots \hat{\mathbf{V}}(\tau_1) \hat{\mathbf{E}}(\tau_1) \rangle_0 \quad (\text{A10})$$

where we have extended the integrals to all time by adding theta functions to enforce the proper time-ordering. We also suppress the integration limits for brevity and use the shorthand

$\langle \dots \rangle_0 \equiv \langle \psi(-\infty) | \dots | \psi(-\infty) \rangle$. It is convenient to symmetrize the notation by $t \rightarrow \tau_{n+1}$. We now substitute the fourier representation for each of the time-dependent operators in the above:

$$\hat{\mathbf{E}}(\tau_j) = \int \frac{d\omega_j}{2\pi} \hat{\mathbf{E}}(\omega_j) e^{i\omega_j \tau_j}, \quad \hat{\mathbf{V}}(\tau_j) = \int \frac{d\omega'_j}{2\pi} \hat{\mathbf{V}}(\omega'_j) e^{i\omega'_j \tau_j} \quad (\text{A11})$$

Through the use of a theta function, we may write \mathcal{E}^{\dagger} in terms of E :

$$\hat{\mathcal{E}}^{\dagger}(\tau_j) = \int \frac{d\omega_j}{2\pi} \hat{\mathbf{E}}(\omega_j) e^{i\omega_j \tau_j} \theta(\omega_j). \quad (\text{A12})$$

With these substitutions, Eq. (A10) becomes

$$\begin{aligned} & \langle \psi^{(k)}(\tau_{n+1}) | \hat{\mathbf{V}}(\tau_{n+1}) \hat{\mathcal{E}}^{\dagger}(\tau_{n+1}) | \psi^{(n-k)}(\tau_{n+1}) \rangle \\ &= (-1)^k (i)^n \int d\omega_{n+1} d\omega'_{n+1} \dots \int d\omega_1 d\omega'_1 \frac{\theta(\omega_{n+1})}{(2\pi)^{2n+2}} \\ & \langle \hat{\mathbf{V}}(\omega'_n) \hat{\mathbf{E}}(\omega_n) \dots \hat{\mathbf{V}}(\omega'_{n-k+1}) \hat{\mathbf{E}}(\omega_{n-k+1}) \hat{\mathbf{V}}(\omega'_{n+1}) \hat{\mathbf{E}}(\omega_{n+1}) \\ & \times \hat{\mathbf{V}}(\omega'_{n-k}) \hat{\mathbf{E}}(\omega_{n-k}) \dots \hat{\mathbf{V}}(\omega'_1) \hat{\mathbf{E}}(\omega_1) \rangle_0 \int d\tau_n \dots \\ & \times \int d\tau_1 \theta(\tau_{n-1} - \tau_n) \dots \theta(\tau_{n+1} - \tau_{n-k+1}) \theta(\tau_{n+1} - \tau_{n-k}) \dots \\ & \times \theta(\tau_2 - \tau_1) e^{i(\Omega_1 \tau_1 + \dots + \Omega_{n+1} \tau_{n+1})} \end{aligned} \quad (\text{A13})$$

where we have defined $\Omega_j = \omega_j + \omega'_j$. The integrals over $d\tau_1 \dots d\tau_n$ can now be carried out. This amounts to Fourier transforms of the theta function and results in:

$$\begin{aligned} & \int d\tau_n \dots \int d\tau_1 \theta(\tau_{n-1} - \tau_n) \dots \theta(\tau_{n+1} - \tau_{n-k+1}) \theta(\tau_{n+1} \\ & - \tau_{n-k}) \dots \theta(\tau_2 - \tau_1) e^{i(\Omega_1 \tau_1 + \dots + \Omega_{n+1} \tau_{n+1})} \\ &= (-i)^n e^{i(\Omega_1 + \dots + \Omega_{n+1}) \tau_{n+1}} \prod_{j=0}^{k-1} \frac{1}{\sum_{j'=0}^j \Omega_{n+1-j'}} - i\eta \prod_{j=1}^{n-k} \frac{1}{\sum_{j'=1}^j \Omega_j - i\eta} \end{aligned} \quad (\text{A14})$$

with η a positive infinitesimal. We now make the substitutions $\omega'_{n+1} \rightarrow \omega'_{n-k+1}$ and $\omega'_{n-k+j} \rightarrow \omega'_{n-k+j+1}$ for $j=1 \rightarrow k$. This reorders the $\omega^{(j)}$ to be in increasing order from right to left and results in

$$\begin{aligned} & \langle \psi^{(k)}(\tau_{n+1}) | \hat{\mathbf{V}}(\tau_{n+1}) \hat{\mathcal{E}}^{\dagger}(\tau_{n+1}) | \psi^{(n-k)}(\tau_{n+1}) \rangle \\ &= (-1)^k \int d\omega_{n+1} d\omega'_{n+1} \dots \int d\omega_1 d\omega'_1 \frac{\theta(\omega_{n-k+1})}{(2\pi)^{2n+2}} \\ & \langle \hat{\mathbf{V}}(\omega'_{n+1}) \hat{\mathbf{E}}(\omega_{n+1}) \dots \hat{\mathbf{V}}(\omega'_1) \hat{\mathbf{E}}(\omega_1) \rangle_0 \\ & \times e^{i(\Omega_1 + \dots + \Omega_{n+1}) \tau_{n+1}} \prod_{j=0}^{k-1} \frac{1}{\sum_{j'=0}^j \Omega_{n+1-j'}} - i\eta \prod_{j=1}^{n-k} \frac{1}{\sum_{j'=1}^j \Omega_j - i\eta} \end{aligned} \quad (\text{A15})$$

We see then that this reordering has freed us from the need for a k -index with regards to the correlation function. From a density-matrix representation, one may see this re-ordering as a cyclic permutation of the trace so as to re-order all bra operators to act on the ket. The fact that the joint field-matter expectation values of these various re-orderings differ only by a theta function that

picks out the $\hat{\mathbf{E}}$ operator associated with the emission is the central fact that permits the re-formulation presented in this paper. We may therefore immediately identify the h -function as

$$\begin{aligned}
h^{(n)}(\tau_{n+1}, \omega_{n+1}, \omega'_{n+1}, \dots, \omega_1, \omega'_1) \\
= e^{i(\Omega_1 + \dots + \Omega_{n+1})\tau_{n+1}} \sum_{k=0}^n \frac{(-1)^k \theta(\omega_{n-k+1})}{(2\pi)^{2n+2}} \prod_{j=0}^{k-1} \frac{1}{\sum_{j'=0}^j \Omega_{n+1-j'} - i\eta} \\
\times \prod_{j=1}^{n-k} \frac{1}{\sum_{j'=1}^j \Omega_{j'} - i\eta} \quad (\text{A16})
\end{aligned}$$

$$\langle \hat{V}(t) \hat{\mathcal{E}}^\dagger(t) \rangle = \left\langle \left\langle \mathbb{1} \mid \hat{V}_+(t) \hat{\mathcal{E}}^\dagger(t) \mathcal{T} e^{-i \int_{-\infty}^t H'_-(\tau) d\tau} \mid \rho(-\infty) \right\rangle \right\rangle. \quad (\text{B1})$$

The n th order signal is then

$$\begin{aligned}
S^{(n)} = \Im \left[\sum_{\pm_i} \int d\omega'_{n+1} d\omega_{n+1} \dots d\omega'_1 d\omega_1 \left\langle \left\langle \mathbb{1} \mid \hat{V}_+(\omega'_{n+1}) \hat{E}_+(\omega_{n+1}) \hat{V}_{\mp n}(\omega'_n) \hat{E}_{\pm n}(\omega_n) \dots \hat{V}_{\mp 1}(\omega'_1) \hat{E}_{\pm 1}(\omega_1) \right\rangle \right\rangle_0 \right. \\
\left. \times \frac{\theta(\omega_{n+1})}{(2\pi)^{2n+2}} e^{i(\Omega_1 + \dots + \Omega_{n+1})\tau_{n+1}} \prod_{j=1}^n \frac{1}{\sum_{j'=1}^j \Omega_{j'} - i\eta} \right] \quad (\text{B2})
\end{aligned}$$

with which the signal may be given by

$$\begin{aligned}
S^{(n)}(\tau_{n+1}) = \Im \left[\int d\omega_{n+1} d\omega'_{n+1} \dots \int d\omega_1 d\omega'_1 \left\langle \hat{V}(\omega'_{n+1}) \dots \hat{V}(\omega'_1) \right\rangle \right. \\
\left. \times \left\langle \hat{E}(\omega_{n+1}) \dots \hat{E}(\omega_1) \right\rangle h^{(n)}(\tau_{n+1}, \omega_{n+1}, \omega'_{n+1}, \dots, \omega_1, \omega'_1) \right] \quad (\text{A17})
\end{aligned}$$

Since Eq. (A16) was obtained from the wavefunction perspective, it may be viewed as originating from an expansion along loop diagrams. The k -th term in the summation giving h is then represented by the loop diagram given in Fig. 1 For concreteness, we let

$$\begin{aligned}
h^{(n)}(\tau_{n+1}, \omega_{n+1}, \omega'_{n+1}, \dots, \omega_1, \omega'_1) \\
= e^{i(\Omega_1 + \dots + \Omega_{n+1})\tau_{n+1}} \sum_{k=0}^n \frac{(-1)^k \theta(\omega_{n-k+1})}{(2\pi)^{2n+2}} h_k^{(n)}(\Omega_{n+1}, \dots, \Omega_1) \quad (\text{A18})
\end{aligned}$$

which defines $h_k^{(n)}$. The loop diagram given in Fig. 1 then directly stands for $h_k^{(n)}$. It is expanded by writing $1/(\Omega - i\eta)$ for each propagation period along the loop with the Ω accumulating as one goes up the ket (left branch of the loop) and de-accumulating as one goes down the bra (right branch of the loop). The integrated signal

$$S^{(n)} \equiv \int d\tau_{n+1} S^{(n)}(\tau_{n+1}) \quad (\text{A19})$$

corresponding to the frequency-dispersed photon gain or loss, is easily obtained from Eqs. (A17) and (A18). Since the only dependence on τ_{n+1} is through the phase factor in the h -function, this integration results in a delta function that enforces conservation of energy. Formally, we write

$$\begin{aligned}
S^{(n)} = \Im \left[\int d\omega_{n+1} d\omega'_{n+1} \dots \int d\omega_1 d\omega'_1 \left\langle \hat{V}(\omega'_{n+1}) \dots \hat{V}(\omega'_1) \right\rangle \right. \\
\left. \times \left\langle \hat{E}(\omega_{n+1}) \dots \hat{E}(\omega_1) \right\rangle h^{(n)}(\omega_{n+1}, \omega'_{n+1}, \dots, \omega_1, \omega'_1) \right] \quad (\text{A20})
\end{aligned}$$

with

$$\begin{aligned}
h^{(n)}(\omega_{n+1}, \omega'_{n+1}, \dots, \omega_1, \omega'_1) \\
= \delta(\Omega_1 + \dots + \Omega_{n+1}) \sum_{k=0}^n \frac{(-1)^k \theta(\omega_{n-k+1})}{(2\pi)^{2n+1}} h_k^{(n)}(\Omega_{n+1}, \dots, \Omega_1) \quad (\text{A21})
\end{aligned}$$

Appendix B. Liouville space expression

We may also choose to expand the signal in Liouville space utilizing the density matrix $\rho \equiv |\psi\rangle\langle\psi|$ ($\rho \equiv \sum_k P_k |\psi_k\rangle\langle\psi_k|$ for a statistical mixture). In this case, Eq. (A7) becomes:

By expanding the \pm operators into L/R operators, we may bring this expression for the signal to the same form as before

$$\begin{aligned}
S^{(n)}(\tau_{n+1}) = \Im \left[\int d\omega_{n+1} d\omega'_{n+1} \dots \int d\omega_1 d\omega'_1 \left\langle \hat{V}(\omega'_{n+1}) \dots \hat{V}(\omega'_1) \right\rangle \right. \\
\left. \times \left\langle \hat{E}(\omega_{n+1}) \dots \hat{E}(\omega_1) \right\rangle \tilde{h}^{(n)}(\omega_{n+1}, \omega'_{n+1}, \dots, \omega_1, \omega'_1) \right]. \quad (\text{B3})
\end{aligned}$$

However, this requires the assumption that L operators commute with R operators at all times, which, in the interaction picture, is only true under Hamiltonian evolution. A general Liouvillian propagator between the interactions would prohibit this recasting. With the Liouville space h -function (which we denote \tilde{h} for clarity) given by

$$\begin{aligned}
\tilde{h}^{(n)}(\omega'_{n+1}, \omega_{n+1}, \dots, \omega'_1, \omega_1) \\
= \delta(\Omega_1 + \dots + \Omega_{n+1}) \sum_{k=0}^n \frac{\theta(\omega_{n+1-k})}{(2\pi)^{2n+1}} \tilde{h}_k^{(n)}(\Omega_{n+1}, \dots, \Omega_1) \quad (\text{B4})
\end{aligned}$$

and $\tilde{h}_k^{(n)}$ is now represented by a sum of ladder diagrams. Specifically, $\tilde{h}_k^{(n)}$ corresponds to the ladder diagrams whose sum is the loop diagram representing $h_k^{(n)}$. There are therefore $\binom{n}{k}$ terms in $\tilde{h}_k^{(n)}$ (for a total of 2^n terms for the signal expressed with ladder diagrams versus the $n+1$ terms when using the loop diagrams) and it is expanded by considering all possible interaction orders (subject to the separate time-ordering of ket-bra constraint) and writing $1/(\Omega - i\eta)$ for each propagation period with the Ω accumulating as one goes up the ladder. This is illustrated for $\tilde{h}_1^{(3)}$ in Fig. 2 and results in:

$$\begin{aligned}
\tilde{h}_1^{(3)} = \frac{1}{\Omega_1 - i\eta} \frac{1}{\Omega_1 + \Omega_2 - i\eta} \frac{1}{\Omega_1 + \Omega_2 + \Omega_4 - i\eta} \\
+ \frac{1}{\Omega_1 - i\eta} \frac{1}{\Omega_1 + \Omega_4 - i\eta} \frac{1}{\Omega_1 + \Omega_4 + \Omega_2 - i\eta} \\
+ \frac{1}{\Omega_4 - i\eta} \frac{1}{\Omega_4 + \Omega_1 - i\eta} \frac{1}{\Omega_4 + \Omega_1 + \Omega_2 - i\eta} \quad (\text{B5})
\end{aligned}$$

as compared to

$$h_1^{(3)} = \frac{1}{\Omega_1 - i\eta} \frac{1}{\Omega_1 + \Omega_2 - i\eta} \frac{1}{\Omega_4 - i\eta} \quad (\text{B6})$$

obtained from expansion along the loop.

It is important to note that, since the derivation of the above requires the assumption that ket and bra operators commute at all times, it is not capable of accounting for pure dephasing which depends on the joint ket-bra combination. However, the formalism can be extended to account for finite lifetimes of states. First, one allows the transition frequencies to be complex so that Eq. (7) becomes

$$\langle a | \widehat{V}(\omega) | b \rangle = V_{ab} \delta(\omega + \zeta_{ab}), \quad \zeta_{ab} \equiv \omega_{ab} + i\gamma_a \quad (\text{B7})$$

where γ_a is the lifetime of state $|a\rangle$. There is a subtlety in that, while the transition frequencies accumulate, only the last lifetime is active in any given spectral propagator. Thus, the modified $h_k^{(n)}$ is then given by

$$h_k^{(n)}(\Omega_{n+1}, \dots, \Omega_1) = \prod_{j=0}^{k-1} \frac{1}{\sum_{j'=0}^j \Re[\Omega_{n+1-j'}] - i|\Im[\Omega_{n-j}]|} \times \prod_{j=1}^{n-k} \frac{1}{\sum_{j'=1}^j \Re[\Omega_{j'}] - i|\Im[\Omega_j]|}. \quad (\text{B8})$$

This form of $h_k^{(n)}$ therefore allows the incorporation of excited state lifetimes as in an effective Hamiltonian and only pure dephasing remains unaccounted for.

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