

# Multidimensional optical spectroscopy of a single molecule in a current-carrying state

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The nonlinear optical signals from an open system consisting of a molecule connected to metallic leads, in response to a sequence of impulsive pulses, are calculated using a superoperator formalism. Two detection schemes are considered: coherent stimulated emission and incoherent fluorescence. The two provide similar but not identical information. The necessary superoperator correlation functions are evaluated either by converting them to ordinary (Hilbert space) operators which are then expanded in many-body states, or by using Wick's theorem for superoperators to factorize them into nonequilibrium two point Green's functions. As an example we discuss a stimulated Raman process that shows resonances involving two different charge states of the molecule in the same signal.

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## I. INTRODUCTION

Single molecule spectroscopy provides most valuable information about distributions (rather than averages) of molecular parameters but is typically limited to slow ( $>ms$ ) processes.<sup>1-4</sup> Ultrafast (subpicosecond) dynamics can be probed by subjecting the molecule to a sequence of short pulses and detecting nonlinear signals and their variation with the controlled delay periods.<sup>5-9</sup> Coherent wave mixing spectroscopies in bulk detect a macroscopic electric field generated by a collection of molecules driven in phase by the external laser pulses.<sup>5,6</sup> Heterodyne detection provides both the amplitude and the phase of the signal field.<sup>10</sup> Various groups of Liouville space pathways of the density matrix can then be separated by looking at signals generated in different phase-matching directions. Single molecule signals, in contrast, may not be dissected in this way since they are isotropic. Nevertheless, the various groups of pathways may be separated by their dependence on the phases of the pulses. This is known in NMR as *phase cycling*.<sup>11-14</sup> An alternative, incoherent fluorescence detection, is the method of choice for single molecule spectroscopy. The optical electric field is not observed in this case but photons are counted instead. Phase cycling has been used for bulk fluorescence<sup>15-19</sup> and has most recently been demonstrated at the single molecule level<sup>20</sup> and interpreted as wave packet interferometry.<sup>18</sup>

Molecules in a current-carrying state<sup>21-29</sup> constitute an interesting example of an open quantum system<sup>30,31</sup> which is of fundamental interest, with numerous applications to molecular electronics devices. They have been extensively studied both experimentally, either in scanning tunneling microscopy (STM) or when connected to two leads, and theoretically.<sup>22,29,32</sup> Historically, most measurements focused on either the average current or its higher moments (noise).<sup>33-36</sup> The dependence of the current on parameters such as the bias voltage reveals useful information on the system, e.g., orbital energies and carrier mobilities. Molecular vibrational information can be obtained from inelastic electron

tunneling spectra which show resonances in the currents as vibrational channels open up by tuning the external bias. Optical measurements in junctions provide additional information. Both fluorescence<sup>37</sup> and Raman signals<sup>38,39</sup> have been measured. This has motivated theoretical investigations.<sup>40-44</sup>

It is possible to create and manipulate optical fields on femtosecond time scales which are much shorter compared to the time it takes to vary the bias across a junction. Thus, in principle, time resolved nonlinear optical signals may reveal information which is inaccessible from current measurements. Nonlinear optical methods are routinely used for bulk samples. Recently, phase dependent nonlinear fluorescence measurement was reported for single molecules.<sup>20</sup> It should be possible to apply the same technique to molecular junctions.

In this paper we develop a response formalism for describing nonlinear optical signals in junctions which are generated by sequences of phase controlled excitation pulses. Two detection modes are considered: coherent (stimulated emission) and incoherent (fluorescence). We use a density matrix approach to derive compact formal expressions for the possible signals in terms of time ordered products of superoperators. Two methods for evaluating these expressions for open many-electron system are then employed. In the first approach we convert the superoperator expressions into sums of ordinary (Hilbert space) correlation functions. The latter are then expanded in many-electron eigenstates involving various numbers of electrons. The time evolution between successive light-matter interactions may involve processes which change the total charge of the molecule. These give rise to new resonances which are not possible in a closed system. This will be demonstrated in Sec. III.

The second approach avoids the calculation of many-electron states by neglecting electron correlations. Instead, it employs Wick's theorem to factorize the multipoint superoperator correlation function into products of two-point Green's functions. These may be evaluated using a broad arsenal of well-developed approximations. In Sec. IV we write

the signal as a time-ordered correlation function of Fermi creation and annihilation superoperators. Using the superoperator Wick's theorem we recast each time-ordered correlation function as a sum over various combinations of products of Liouville space Green's functions. The latter are equivalent to the nonequilibrium Green functions appearing in the Keldysh formalism.<sup>45,46</sup> In contrast to the first approach, here the Green's functions include the coupling to the leads through self-energies. Superoperator time ordering is essential for the application of Wick's theorem. This theorem does not generally apply when electron–electron interactions and coupling to phonons are included. However, these can be treated perturbatively.

## II. FOUR-WAVE-MIXING SIGNALS

We consider a junction, where a molecule is coupled to two conducting electrodes and subjected to a voltage bias and is further driven by a sequence of several laser pulses. The system is described by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_{\text{tun}} + \mathcal{H}_f + \mathcal{H}_{\text{int}}. \quad (1)$$

Here  $\mathcal{H}_S$  is the molecular Hamiltonian. At this point there is no need to specify it, except that its electronic degrees of freedom can be described using a basis set of orbitals  $i \in S$ , with creation (annihilation) Fermi operators  $\hat{c}_i^\dagger$  ( $\hat{c}_i$ ).  $\mathcal{H}_S$  may include electron–electron or electron–phonon interactions, but such details do not affect the formal derivation of the optical signal presented in this section.  $\mathcal{H}_A$  and  $\mathcal{H}_B$  represent the two electrodes, which are described by noninteracting electrons with Fermi energies  $\varepsilon_{F,A}$  and  $\varepsilon_{F,B}$

$$\mathcal{H}_{A,B} = \sum_{\alpha \in A,B} \varepsilon_{\alpha} \hat{b}_{\alpha}^{\dagger} \hat{b}_{\alpha}, \quad (2)$$

while the tunneling is given by

$$\mathcal{H}_{\text{tun}} = \sum_{x=A,B} \sum_{\substack{\alpha \in x \\ i \in S}} h_{\alpha i} \hat{b}_{\alpha}^{\dagger} \hat{c}_i + \text{h.c.} \equiv \hat{T} + \hat{T}^{\dagger}, \quad (3)$$

where  $\hat{T} = \sum_{x=A,B} \sum_{\substack{\alpha \in x \\ i \in S}} h_{\alpha i} \hat{b}_{\alpha}^{\dagger} \hat{c}_i$ . The indices  $i$  ( $\alpha$ ) denote system (electrode) orbitals.  $\mathcal{H}_{\text{tun}}$  describes the system–electrodes coupling, and  $h_{\alpha i}$  is the tunneling matrix element between the orbitals in the electrodes and molecule.

We shall adopt a quantum description of the radiation field.<sup>48</sup> This is convenient but is not essential since classical fields will yield the same signal. The field Hamiltonian takes the form

$$\mathcal{H}_f = \sum_k \hbar \omega_k \hat{a}_k^{\dagger} \hat{a}_k, \quad (4)$$

where  $\hat{a}_k$  annihilates a photon from field mode  $k$ . The field–molecule coupling is

$$\mathcal{H}_{\text{int}} = -[\hat{\mathcal{E}}(\mathbf{r}, t) + \hat{\mathcal{E}}^{\dagger}(\mathbf{r}, t)](\hat{V}^{\dagger} + \hat{V}), \quad (5)$$

where  $\hat{V} = \sum_i \sum_{j>i} \mu_{ij} \hat{c}_i^{\dagger} \hat{c}_j$  is the part of the dipole operator describing de-excitation processes of the molecule and  $\hat{\mathcal{E}}(\mathbf{r}, t) \equiv \sum_l (2\pi \hbar \omega_l / \Omega)^{1/2} \hat{a}_l e^{i\mathbf{k}_l \mathbf{r} - i\omega_l t}$  is the positive frequency component of the field. We assume that the field is only coupled to the molecule and not to the leads, which is expected when the field is resonant with the molecule but not

with the leads. We also ignore other possible processes, such as ones where the field creates an electron hole pair in the molecule and electrode through a coupling of the form  $\hat{c}_i^{\dagger} \hat{b}_{\alpha} \hat{a}_l$ .

The optical signal, defined as the rate of change of the photon occupation number in some field modes selected for detection, is

$$S(t) \equiv \text{Tr} \sum_{k \in S} \frac{d}{dt} (\hat{a}_k^{\dagger} \hat{a}_k \hat{\rho}_{\text{full}}(t)), \quad (6)$$

where  $\hat{\rho}_{\text{full}}$  is the density matrix of all matter and field degrees of freedom. It should be distinguished from the density matrix of the matter, which we denote by  $\hat{\rho}$ . Using the Heisenberg equation of motion and Eq. (5) we get

$$S(t) = \frac{i}{\hbar} \text{Tr} \sum_{k \in S} [\mathcal{H}_{\text{int}}(t), \hat{a}_k^{\dagger} \hat{a}_k] \hat{\rho}_{\text{full}}(t). \quad (7)$$

In the derivation of Eq. (7) we have used the fact that the field–molecule coupling  $\mathcal{H}_{\text{int}}$  is the only part of the Hamiltonian which does not commute with  $\hat{a}_k^{\dagger} \hat{a}_k$ . The commutation relation in Eq. (7) can be evaluated easily, resulting in

$$S(t) = -\frac{2}{\hbar} \Im \text{Tr} \hat{\mathcal{E}}_s^{\dagger}(\mathbf{r}, t) (\hat{V}^{\dagger} + \hat{V}) \hat{\rho}_{\text{full}}(t). \quad (8)$$

Here, the operator  $\hat{\mathcal{E}}_s^{\dagger}$  refer to the detected field modes. In the following we assume that a single field mode is detected. The generalization to multiple modes is straightforward. The average in Eq. (8) is taken over a density matrix whose evolution depends on the interaction with all field modes, and the signal includes contributions to all orders in the field.

Typically one considers signals to a given order in specific field modes, treating the coupling to the molecule as a perturbation, and expanding the total field + matter density matrix to the desired order. This can be conveniently done using a Liouville space (superoperator) representation. The time evolution of the density matrix is naturally described in Liouville space. Superoperators provide a compact bookkeeping device for the ordering of products of operators in Hilbert space. Given a Hilbert space operator  $\hat{A}$ , one defines a “right” (R) and a “left” (L) superoperator via

$$\begin{aligned} \hat{A}_L \hat{X} &\equiv \hat{A} \hat{X}, \\ \hat{A}_R \hat{X} &\equiv \hat{X} \hat{A}, \end{aligned} \quad (9)$$

where  $\hat{X}$  is an arbitrary Hilbert space operator. We further introduce the following linear combinations:

$$\hat{A}_{\pm} \equiv \frac{1}{\sqrt{2}} (\hat{A}_L \pm \hat{A}_R). \quad (10)$$

Finally we define the time-ordering operator in Liouville space  $\mathcal{T}$  which reorders products of superoperators so that their time arguments increase from right to left.

With these tools, Eq. (8) can be written in the interaction picture, as

$$S(t) = -\frac{2}{\hbar} \Im \text{Tr} \hat{\mathcal{E}}_{sL}^{\dagger}(\mathbf{r}, t) [\hat{V}_L^{\dagger}(t) + \hat{V}_L(t)] \hat{\rho}_{\text{full}}(t), \quad (11)$$

where

$$\hat{\rho}_{\text{full}}(t) = \mathcal{T} \exp \left\{ -\frac{i}{\hbar} \int_{-\infty}^t d\tau \sqrt{2} \mathcal{H}_{\text{int}}(-\tau) \right\} \hat{\rho}_{\text{full}}(-\infty), \quad (12)$$

while interaction picture superoperators are given by

$$X_\nu(t) \equiv (e^{i(\mathcal{H}-\mathcal{H}_{\text{int}})t} X e^{-i(\mathcal{H}-\mathcal{H}_{\text{int}})t})_\nu \quad \nu = L, R. \quad (13)$$

Equation (11) is general and allows to calculate any type of signal. To proceed further we employ the semiclassical approximation by assuming that the external fields are in a coherent state,<sup>47</sup> and that the field–matter interaction does not result in a major change the state of the field. In this case one can eliminate the field degrees of freedom by bringing them into a normal order and then replacing the field operators with their expectation values. We can then identify two types of signals, stimulated emission and fluorescence. These signals were derived by Marx *et al.*<sup>48</sup> for an isolated molecule, but the derivation is equally valid for a molecule connected to leads.

The stimulated signal is given by

$$S^{\text{stim}}(t) = -\frac{2}{\hbar} \Im \text{Tr} \mathcal{E}_s^*(\mathbf{r}, t) [\hat{V}_L^\dagger(t) + \hat{V}_L(t)] \hat{\rho}(t), \quad (14)$$

where

$$\hat{\rho}(t) = \mathcal{T} \exp \left\{ -\frac{i}{\hbar} \int_{-\infty}^t d\tau \sqrt{2} \mathcal{H}_{\text{int}}(\tau) \right\} \hat{\rho}(-\infty). \quad (15)$$

$\hat{\rho}$  is the material density matrix, while the field is taken to be in a coherent state. This semiclassical approximation should be applied also for the field–matter interaction appearing in Eq. (15). Equation (14) describes stimulated emission or absorption of the detected modes.

The fluorescence signal originates from two interactions with the same field mode which is initially in the vacuum state. In that case, the ordering of field creation and annihilation operators is important. This signal is given by<sup>48</sup>

$$S^{\text{fl}}(\omega_s, t) = \frac{4\pi}{\Omega} \omega_s \Re \int_{-\infty}^t \text{Tr} \mathcal{T} \hat{V}_L(t) \hat{V}_R^\dagger(\tau) e^{i\omega_s(t-\tau)} \hat{\rho}(t), \quad (16)$$

where  $\hat{\rho}(t)$  is given by Eq. (15). Equation (16) describes spontaneous emission into the detected mode. More generally, the signal is obtained by convoluting Eq. (16) with a gating spectrogram which represents the spectral and temporal resolution of the detector, see Refs. 49 and 50.

Hereafter we focus on processes where the signals (14) and (16) are generated by driving the molecule using four temporally well separated pulses. This setup was implemented recently.<sup>19</sup> The emission pattern from a single molecule is markedly different from the directional beam obtained in four-wave mixing for bulk samples. The small size of the molecule allows emission in all directions. We therefore suppress the field momentum and molecular position variables. However, various components of the signal can be selected by using phase cycling.<sup>12–14,51–53</sup> We write

$$\mathcal{H}_{\text{int}} = -\sum_{j=1}^4 [\mathcal{E}_j(t) e^{i\varphi_j} + \mathcal{E}_j^*(t) e^{-i\varphi_j}] (\hat{V}^\dagger(t) + \hat{V}(t)). \quad (17)$$

The four fields can be distinguished by the externally controlled phases  $\varphi_j$  as well as by time they are applied (for impulsive pulses) or, alternatively, by their frequency (for a CW setup).

Various contributions to the signal can be measured by varying all phases and selecting the part which has the desired functional dependence on all phases  $\pm\varphi_1 \pm \varphi_2 \pm \varphi_3 \pm \varphi_4$ . Such *phase cycling* from a single molecule is possible by current laser technology, as demonstrated in a recent experiment.<sup>20</sup> This requires repeated independent measurements with different choices of phases.<sup>18</sup>

To derive the stimulated signal, we single out the detected mode (hereby denoted 4). Then the time ordered exponential in Eq. (15) is expanded to third order in the field–matter interaction, keeping all contributions involving one interaction with each of the pulses. This leads to

$$\begin{aligned} S_{\pm\varphi_1 \pm \varphi_2 \pm \varphi_3 \pm \varphi_4}^{\text{stim}}(t) &= -\frac{4\sqrt{2}}{\hbar^4} \Re \int \int \int_{-\infty}^t d\tau_1 d\tau_2 d\tau_3 \\ &\times \left\langle \mathcal{T} \mathcal{E}_s^*(t) e^{-i\varphi_4} [\hat{V}_L^\dagger(t) + \hat{V}_L(t)] \right. \\ &\times \left. \prod_{j=1}^3 (\mathcal{E}_j(t) e^{i\varphi_j} + \mathcal{E}_j^*(t) e^{-i\varphi_j}) [\hat{V}_-^\dagger(t) + \hat{V}_-(t)] \right\rangle. \quad (18) \end{aligned}$$

The component with a desired phase (e.g.,  $\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4$ ) can be selected by keeping the corresponding terms in the product of field amplitudes in Eq. (18). Other processes, such as pump–probe can be calculated in a similar fashion, by considering two pulses and two interactions with each pulse.

The fluorescence signal generated by the four pulses is obtained from Eq. (16) by expanding  $\hat{\rho}$  to fourth order in the interaction and keeping the terms with one interaction with each of the pulses. This gives

$$\begin{aligned} S_{\pm\varphi_1 \pm \varphi_2 \pm \varphi_3 \pm \varphi_4}^{\text{fl}}(\omega_s, t) &= \frac{16\pi}{\Omega \hbar^4} \omega_s \Re \int_{-\infty}^t d\tau e^{i\omega_s(t-\tau)} \\ &\times \int \int \int \int_{-\infty}^t d\tau_1 d\tau_2 d\tau_3 d\tau_4 \left\langle \mathcal{T} \hat{V}_L(t) \hat{V}_R^\dagger(\tau) \right. \\ &\times \left. \prod_{j=1}^4 (\mathcal{E}_j(t) e^{i\varphi_j} + \mathcal{E}_j^*(t) e^{-i\varphi_j}) [\hat{V}_-^\dagger(t) + \hat{V}_-(t)] \right\rangle, \quad (19) \end{aligned}$$

where  $\langle \cdot \cdot \cdot \rangle$  denotes an average over the initial density matrix of the matter. The desired signal is characterized by a specific dependence on phases and can be selected as was done in Eq. (18).

Equations (18) and (19) constitute a very compact formal representation for the signal in terms of time-ordered correlation functions of superoperators. In the following two sections we illustrate two methods for evaluating these expressions, either in term of molecular many-body states or in terms of two-point Green's functions.

### III. STIMULATED-RAMAN SIGNALS EXPANDED IN MANY-BODY EIGENSTATES

In this section we evaluate the correlation functions of Sec. II in terms of the many-body states and energies of the

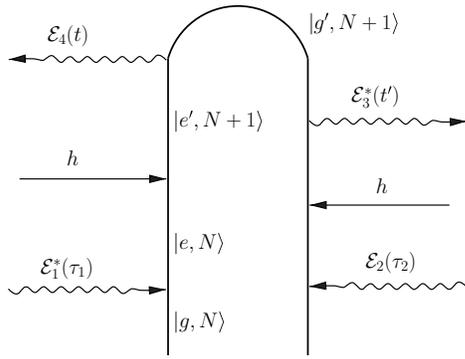


FIG. 1. Stimulated Raman process involving a change of the molecular charge state.

free molecule (in the absence of the lasers and the radiation field). We focus on a specific stimulated process during which the molecular charge varies. The signal then includes resonances involving two different charge states. Such resonances are not possible for an isolated molecule. The superoperator correlation functions are first rewritten as Hilbert space correlation functions, transforming products of terms to Hilbert space, and using the cyclic property of the trace. Then a resolution of the identity in terms of the molecular many-body states is employed.

A full calculation of the signal is complicated by the sheer number of contributions. All of them can be calculated using the formalism presented below. To see why this is the case let us consider the pump-probe signal from an isolated molecule.<sup>48,54</sup> Figure 5 in Ref. 54 depicts eight possible processes, four of which correspond to stimulated Raman processes. These are the only possible processes provided that the molecule is isolated and is initially in its electronic ground state. These conditions do not apply for a molecule coupled to leads for two reasons. First, the molecule may be initially in an electronic excited state or in a coherent superposition of states. Furthermore, the molecule's evolution between optical interactions is more complex since hopping to and from the leads can change the oxidation state of the molecule. On top of that, one may wish to describe the coupling to the leads as a perturbation, keeping contributions only up to a desired order. Consideration of all processes involving a certain number of hopping events in addition to the four couplings to the leads resulting in a proliferation of pathways.

As an illustration we shall focus on the process depicted in Fig. 1. The molecule is initially in the ground state  $|g\rangle$  with  $N$  electrons. Absorption of a photon from the pump pulse brings it to an excited state,  $|e, N\rangle$ . An electron then hops from one of the leads onto the molecule (denoted by a straight arrow), creating an  $N + 1$  electron state,  $|e', N + 1\rangle$ . Finally, the negatively charged molecule emits a photon into the probe mode in a stimulated process.

This is only one of the many possible sixth order processes, with four interactions with the optical field, and two tunneling interactions with the leads. In addition, there are processes where the electron jumps from the molecule to the leads, which will involve positively charged ( $N - 1$  electrons)

molecular states, and more. The various processes may be controlled by the lead configurations and bias. The process depicted in Fig. 1 will exhibit resonance at the transition frequencies of the molecule with  $N$  as well as  $N + 1$  electrons. These are distinguishable from transitions with other charge states and provide an interesting example of a nonlinear process involving two different charge states.

The signal corresponding to the process depicted in Fig. 1 can be obtained from Eq. (18) by switching to the interaction picture with respect to the molecule-field coupling, expanding to second order in the tunneling element, and selecting the contribution which matches the diagram. This leads to

$$S(t) = \frac{2}{\hbar^6} \Re e^{i(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)} \int^t dt' \int^t d\tau'_1 \int^{\tau'_1} d\tau_1 \times \int^{\tau'_1} d\tau'_2 \int^{\tau'_2} d\tau_2 \mathcal{E}_4^*(t) \mathcal{E}_3(t') \mathcal{E}_2^*(\tau_2) \mathcal{E}_1(\tau_1) \times \langle \mathcal{T} \hat{V}_L(t) \hat{V}_R^\dagger(t') \hat{T}_L^\dagger(\tau'_1) \hat{V}_L^\dagger(\tau_1) \hat{T}_R(\tau_2) \hat{V}_R(\tau_2) \rangle. \quad (20)$$

At this point, the superoperator correlation function in Eq. (20) will be converted to Hilbert space by keeping track of the time ordering, using the definition of right and left superoperators, and the cyclic property of traces of products of operators. This results in

$$S(t) = \frac{2}{\hbar^6} \Re e^{i(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)} \int^t dt' \int^t d\tau'_1 \int^{\tau'_1} d\tau_1 \times \int^{\tau'_1} d\tau'_2 \int^{\tau'_2} d\tau_2 \mathcal{E}_4^*(t) \mathcal{E}_3(t') \mathcal{E}_2^*(\tau_2) \mathcal{E}_1(\tau_1) \times \langle \hat{V}(\tau_2) \hat{T}(\tau_2) \hat{V}^\dagger(t') \hat{V}(t) \hat{T}^\dagger(\tau'_1) \hat{V}^\dagger(\tau_1) \rangle. \quad (21)$$

Substitution of  $\hat{T}$  in Eq. (21) allows us to factorize the molecular and lead contributions

$$S(t) = \frac{2}{\hbar^6} \Re \int^t dt' \int^t d\tau'_1 \int^{\tau'_1} d\tau_1 \int^{\tau'_1} d\tau'_2 \times \int^{\tau'_2} d\tau_2 \mathcal{E}_4^*(t) \mathcal{E}_3(t') \mathcal{E}_2^*(\tau_2) \mathcal{E}_1(\tau_1) e^{i(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)} \times \sum_{\substack{k \in A, B \\ i \in S}} \sum_{\substack{l \in A, B \\ j \in S}} h_{ki}^* h_{lj} \langle \hat{b}_k^\dagger(\tau'_2) \hat{b}_l(\tau'_1) \rangle_{\text{leads}} \times \langle \hat{V}(\tau_2) \hat{c}_j(\tau_2) \hat{V}^\dagger(t') \hat{V}(t) \hat{c}_i^\dagger(\tau'_1) \hat{V}^\dagger(\tau_1) \rangle_{\text{molecule}}. \quad (22)$$

We shall assume a zero temperature free Fermion gas model for the leads,

$$\langle \hat{b}_k^\dagger(t) \hat{b}_l(t') \rangle = \delta_{kl} f_k(\varepsilon_k) e^{(i/\hbar)\varepsilon_k(t-t')}, \quad (23)$$

where  $f_k$  is the Fermi function of the lead containing state  $k$ . We assume that the tunneling matrix elements depend on the lead states only through their energy  $h_{ki} \simeq h_i(\varepsilon_k)$ . With these assumptions the sums over lead states are replaced by

an integral up to the Fermi energy,

$$S(t) = \frac{2}{\hbar^6} \Re \sum_{i,j \in S} \sum_{x=A,B} \int^t dt' \int^t d\tau'_1 \int^{\tau'_1} d\tau_1 \int^{\tau'_1} d\tau'_2 \\ \times \int^{\tau'_2} d\tau_2 \int^{\varepsilon_{F,x}} d\varepsilon \rho_x(\varepsilon) \mathcal{E}_4^*(t) \mathcal{E}_3(t') \mathcal{E}_2^*(\tau_2) \\ \times \mathcal{E}_1(\tau_1) e^{i(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)} h_i^*(\varepsilon) h_j(\varepsilon) e^{-(i/\hbar)\varepsilon(\tau'_1 - \tau'_2)} \\ \times \langle \hat{V}(\tau_2) \hat{c}_j(\tau'_2) \hat{V}^\dagger(t') \hat{V}(t) \hat{c}_i^\dagger(\tau'_1) \hat{V}^\dagger(\tau_1) \rangle_{\text{molecule}}, \quad (24)$$

where  $\rho_x(\varepsilon)$  is the density of states in lead  $x$ .

The molecular correlation function may be now evaluated by expanding in its many-body eigenstates. Since the molecule is initially in its ground state, which belongs to the  $N$ -electrons Hilbert space  $\mathcal{D}_N$ , only states with  $N + 1$  electrons would lead to a nonvanishing contribution when inserted between  $\hat{c}_i^\dagger(\tau'_1)$  and  $\hat{c}_j(\tau'_2)$ . All time integrations can be performed by substituting

$$\mathcal{E}(t) = \frac{1}{2\pi} \int d\omega e^{-i\omega t} \mathcal{E}(\omega)$$

for the field envelopes. We shall calculate the time-integrated signal

$$S \equiv \int dt S(t). \quad (25)$$

A straightforward, but tedious calculation results in

$$S = \frac{1}{4\hbar^6 \pi^3} \Im \sum_{x=A,B} \sum_{f \in \mathcal{D}_{N+1}} \int^{\varepsilon_{F,x}} d\varepsilon \rho_x(\varepsilon) \\ \times \int d\omega_1 d\omega_2 d\omega_3 d\omega_4 T_{fg}^{(4,1)}(-\omega_4, \omega_1; \varepsilon) \\ \times T_{fg}^{(3,2)*}(-\omega_3, \omega_2; \varepsilon) \frac{1}{\omega_2 - \omega_3 - (E_f - E_g - \varepsilon)/\hbar - i\eta} \\ \times \delta(\omega_1 - \omega_2 + \omega_3 - \omega_4). \quad (26)$$

Here

$$T_{fg}^{(a,b)}(-\omega_a, \omega_b; \varepsilon) = \sum_{i \in S} \sum_{\substack{\alpha \in \mathcal{D}_N \\ \alpha > g}} \sum_{\substack{\beta \in \mathcal{D}_{N+1} \\ \beta > f}} \mu_{f\beta} \mu_{\alpha g} h_i^*(\varepsilon) \\ \times \langle \psi_\beta^{(N+1)} | \hat{c}_i^\dagger | \psi_\alpha^{(N)} \rangle \mathcal{E}_b(\omega_b) \mathcal{E}_a^*(\omega_a) \\ \times \frac{1}{\omega_a - (E_\alpha - E_g)/\hbar + i\eta} \\ \times \frac{1}{\omega_a - (E_\beta - \varepsilon - E_g)/\hbar + i\eta}, \quad (27)$$

is a *transition amplitude* describing the process taking the molecule from its initial state  $g$  to a final state  $f$  with an additional electron, while interacting with pulses  $b$  and  $a$ . The signal shows resonances from states with  $N$  and  $N + 1$  electrons on the molecule. The many-body energies appearing in Eq. (26) can include electronic and vibrational states, as well as effects of Coulomb interactions.

The signal given in Eqs. (26) and (27) can be simplified when the four pulses are very short (impulsive). We consider four temporally well separated pulses, which act on

the system at times  $\tilde{\tau}_i$ ,  $i = 1, 2, 3, 4$ , so that the time delays  $t_i = \tilde{\tau}_{i+1} - \tilde{\tau}_i$  are much larger than the pulse durations. We focus on the same process depicted in Fig. 1. We can now disregard the limits of integrations over the time variables  $t$ ,  $\tau_1$ ,  $\tau_2$  since the correct ordering is ensured by the pulse envelopes. In addition, the short duration of the pulses allows to replace the limit of integrations over  $\tau'_j$ , namely the electron hopping events, with the time of the pulses, while making only a small error. With the help of Eqs. (24) and (25), the signal assumes the form

$$S \simeq \frac{2}{\hbar^6} \Re \sum_{i,j \in S} \sum_{x=A,B} \int dt dt' d\tau_1 d\tau_2 \int_{\tilde{\tau}_1}^{\tilde{\tau}_4} d\tau'_1 \int_{\tilde{\tau}_2}^{\tilde{\tau}_3} d\tau'_2 \\ \times \int^{\varepsilon_{F,x}} d\varepsilon \rho_x(\varepsilon) \mathcal{E}_4^*(t) \mathcal{E}_3(t') \mathcal{E}_2^*(\tau_2) \mathcal{E}_1(\tau_1) \\ \times e^{i(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)} h_i^*(\varepsilon) h_j(\varepsilon) e^{-(i/\hbar)\varepsilon(\tau'_1 - \tau'_2)} \\ \times \langle \hat{V}(\tau_2) \hat{c}_j(\tau'_2) \hat{V}^\dagger(t') \hat{V}(t) \hat{c}_i^\dagger(\tau'_1) \hat{V}^\dagger(\tau_1) \rangle_{\text{molecule}}. \quad (28)$$

The dependence of this signal on the times,  $\tilde{\tau}_j$ , where the pulses act on the system can be made explicit by introducing the modified Fourier transform

$$\tilde{\mathcal{E}}_j(\omega) e^{i\omega \tilde{\tau}_j} \equiv \int dt \mathcal{E}_j(t) e^{i\omega t}, \quad (29)$$

$$\mathcal{E}_j(t) = \frac{1}{2\pi} \int d\omega \tilde{\mathcal{E}}_j(\omega) e^{i\omega(\tilde{\tau}_j - t)}, \quad (30)$$

where  $\tilde{\mathcal{E}}(\omega)$  is the Fourier transform of a pulse centered at  $t = 0$ .

An evaluation of the correlation function in Eq. (28) in term of the many body states of the isolated molecule results in time integrals which are easy to perform. In fact, all the integrals over variables of field amplitudes are simple Fourier transforms, leading to

$$S(\tilde{\tau}_1, \tilde{\tau}_2, \tilde{\tau}_3, \tilde{\tau}_4) \\ = \frac{2}{\hbar^4} \Re \sum_{x=A,B} \sum_{f \in \mathcal{D}_{N+1}} \int^{\varepsilon_{F,x}} d\varepsilon \rho_x(\varepsilon) e^{i(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)} \\ \times T_{fg}^{(4,1)}(\tilde{\tau}_4, \tilde{\tau}_1; \varepsilon) T_{fg}^{(3,2)*}(\tilde{\tau}_3, \tilde{\tau}_2; \varepsilon), \quad (31)$$

with the transition amplitudes

$$T_{fg}^{(a,b)}(\tilde{\tau}_a, \tilde{\tau}_b; \varepsilon) \equiv \sum_{i \in S} \sum_{\substack{\alpha \in \mathcal{D}_N \\ \alpha > g}} \sum_{\substack{\beta \in \mathcal{D}_{N+1} \\ \beta > f}} \mu_{f\beta} \mu_{\alpha g} h_i^*(\varepsilon) \\ \times \langle \psi_\beta^{(N+1)} | \hat{c}_i^\dagger | \psi_\alpha^{(N)} \rangle \tilde{\mathcal{E}}_b[(E_\alpha - E_g)/\hbar] \\ \times \tilde{\mathcal{E}}_a^*[(E_\beta - E_f)/\hbar] \\ \times \frac{e^{i(E_\alpha - E_g)\tilde{\tau}_b/\hbar - i(E_\beta - E_f)\tilde{\tau}_a/\hbar}}{(E_\beta - E_\alpha - \varepsilon)} \\ \times (e^{i(E_\beta - E_\alpha - \varepsilon)\tilde{\tau}_a/\hbar} - e^{i(E_\beta - E_\alpha - \varepsilon)\tilde{\tau}_b/\hbar}). \quad (32)$$

The transition frequencies between the many body states are revealed by varying the delay intervals between pulses.

#### IV. STIMULATED FOUR-WAVE-MIXING SIGNALS EXPANDED IN MANY-BODY GREEN'S FUNCTIONS

Equations (9) and (18) hold for operators  $\hat{V}$  that conserve the number of particles; the fact that such operators are composed of a product of creation and annihilation operators is immaterial. One may wonder whether it is possible to consistently define “left” and “right” Fermi superoperators, with the goal of making Wick’s theorem applicable. Such a formalism was introduced by Schmutz,<sup>55</sup> see also Refs. 40 and 46. The definition of Fermi superoperators requires a nontrivial choice of signs. In fact, the definition allows us to convert any physical operator, which conserves the number of particles, to an effectively non-Fermionic superoperator which is decomposed into products of Fermi superoperators.

The details of the formalism are somewhat involved and are given in Appendix A. However, all that is required in order to apply these results is that the Fermi superoperators satisfy the same commutation relations of ordinary Fermionic operators,

$$\{\hat{c}_{i\alpha}, \hat{c}_{j\beta}^\dagger\} = \delta_{ij}\delta_{\alpha\beta}, \quad (33)$$

$$\{\hat{c}_{i\alpha}^\dagger, \hat{c}_{j\beta}^\dagger\} = 0, \quad (34)$$

$$\{\hat{c}_{i\alpha}, \hat{c}_{j\beta}\} = 0, \quad (35)$$

where  $\{.,.\}$  is the anticommutator and  $\alpha, \beta = R, L$  or  $+, -$ .

The signal (18) can be written as a correlation function of creation and annihilation superoperators by substituting the expressions for  $\hat{V}$  and  $\hat{V}^\dagger$ . In order to move the Fermi operators around within a product we need a prescription for converting a superoperator of a product to products of superoperators. In the  $\pm$  representation we use the relations

$$(\hat{c}_i^\dagger \hat{c}_j)_- = \frac{1}{\sqrt{2}}[\hat{c}_{i+}^\dagger \hat{c}_{j+} - \hat{c}_{j-} \hat{c}_{i-}^\dagger], \quad (36)$$

$$(\hat{c}_i^\dagger \hat{c}_j)_+ = \frac{1}{\sqrt{2}}[\hat{c}_{i+}^\dagger \hat{c}_{j-} + \hat{c}_{i-}^\dagger \hat{c}_{j+} + \delta_{ij}], \quad (37)$$

which can be verified from the definitions of the fermionic superoperators.  $\hat{V}_L$  in Eq. (18) is replaced by  $\hat{V}_+$  using  $\hat{V}_L = (\hat{V}_+ + \hat{V}_-)/\sqrt{2}$ , noting that the  $\hat{V}_-$  part do not contribute, since any trace with  $\hat{X}_-$  as the left most (non-Fermionic) operator vanishes. The factor of  $\hat{V}_L^\dagger$  is treated in the same manner. Substitution of Eqs. (36) and (37) in Eq. (18) gives

$$\begin{aligned} S_{\pm\varphi_1\pm\varphi_2\pm\varphi_3-\varphi_4}^{\text{stim}}(t) &= \frac{1}{\hbar^4} \Re \int^t d\tau_1 d\tau_2 d\tau_3 \mathcal{E}_s(t) e^{-i\varphi_4} \\ &\times \prod_{m=1}^3 [\mathcal{E}_m(\tau_m) e^{i\varphi_m} + \mathcal{E}_m^*(\tau_m) e^{-i\varphi_m}] \\ &\times \left\langle \mathcal{T} \sum_{ij} \mu_{ij} (\hat{c}_{i+}^\dagger(t) \hat{c}_{j-}(t) + \hat{c}_{i-}^\dagger(t) \hat{c}_{j+}(t)) \right. \\ &\times \left. \prod_{l=1}^3 \left[ \sum_{i_l, j_l} \mu_{i_l j_l} (\hat{c}_{i_l+}^\dagger(\tau_l) \hat{c}_{j_l+}(\tau_l) - \hat{c}_{j_l-}(\tau_l) \hat{c}_{i_l-}^\dagger(\tau_l)) \right] \right\rangle. \end{aligned} \quad (38)$$

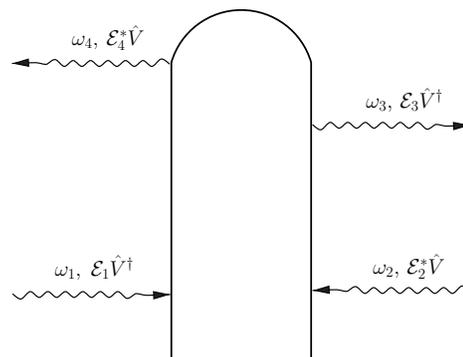


FIG. 2. Heterodyne-detected process where the molecule interacts with four field modes. [This is one out of the eight possible contributions  $\propto e^{i(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)}$ , since modes 1, 2, 3, can act on either the ket or the bra.]

In the derivation of Eq. (38) we have omitted the  $\delta_{ij}$  from Eq. (37) as the terms in which it appears would have a trace with  $\hat{V}_-$  (or  $\hat{V}_L^\dagger$ ) as the leftmost term, which vanishes identically (since it represents the trace of a commutator).

We now briefly discuss the merits of using superoperators. Superoperators allow us to derive compact expressions for the optical signals, making it easy to select the paths contributing to a specific signal. But this is not the whole story. Superoperators are required if Wick’s theorem is to be used, since its validity depends on the existence of a suitable time-ordering prescription. *Physical observables are given by time ordered products of superoperators, which translate into non time ordered products of ordinary operators.*

We now revisit the stimulated Raman process that was expanded in many-body states in Sec. III. The process considered here, depicted in Fig. 2 is more general than the one of Fig. 1, since it includes the same field–matter interaction together with all orders of the molecule–leads coupling, since the latter are naturally taken care of. In the following we assume a CW setup where the driving fields do not vary in time,  $\mathcal{E}_i(t) = \mathcal{E}_i e^{-i\omega_i t}$ . We also make the rotating wave approximation (RWA). These two approximations are not strictly needed for the application of the Green’s function approach and may be easily relaxed.

The signal corresponding to the process depicted in Fig. 2 is given by

$$\begin{aligned} S_{\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4}(t) &= \frac{2}{\hbar^4} \Re \mathcal{E}_1 \mathcal{E}_2^* \mathcal{E}_3 \mathcal{E}_4^* e^{i(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)} \\ &\times \int^t dt' d\tau_1 \int^{\tau_1} d\tau_2 e^{i\omega_4 t - i\omega_3 \tau_1} e^{i\omega_2 \tau_2 - i\omega_1 \tau_1} \\ &\times \langle \mathcal{T} \hat{V}_L(t) \hat{V}_R^\dagger(\tau_1) \hat{V}_L^\dagger(\tau_1) \hat{V}_R(\tau_2) \rangle. \end{aligned} \quad (39)$$

This signal is most naturally described in the  $R, L$  representation, since transforming to the  $\pm$  representation would result in several correlation functions instead of the single one in Eq. (39).

In order to apply Wick’s theorem, the correlation function in Eq. (39) should be recast in terms of the elementary Fermi creation and annihilation superoperators. Using the definition of the Fermi superoperators, we can write the operators  $\hat{V}$  and

$\hat{V}^\dagger$ , which were introduced in Sec. II, as

$$\hat{V}_L(t) = \sum_{\substack{i,j \\ j>i}} \mu_{ij} \hat{c}_{iL}^\dagger(t) \hat{c}_{jL}(t), \quad (40)$$

$$\hat{V}_R(t) = \sum_{\substack{i,j \\ j>i}} \mu_{ij} \hat{c}_{jR}(t) \hat{c}_{iR}^\dagger(t), \quad (41)$$

$$\hat{V}_L^\dagger(t) = \sum_{\substack{i,j \\ j<i}} \mu_{ij} \hat{c}_{iL}^\dagger(t) \hat{c}_{jL}(t), \quad (42)$$

$$\hat{V}_R^\dagger(t) = \sum_{\substack{i,j \\ j<i}} \mu_{ij} \hat{c}_{jR}(t) \hat{c}_{iR}^\dagger(t). \quad (43)$$

Substitution of Eqs. (40)–(43) in Eq. (39) gives

$$S = 2\Re \mathcal{E}_1 \mathcal{E}_2^* \mathcal{E}_3 \mathcal{E}_4^* e^{i(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)} \int dt' d\tau_1 \\ \times \int d\tau_2 e^{i\omega_4 t - i\omega_3 t'} e^{i\omega_2 \tau_2 - i\omega_1 \tau_1} \mathcal{C}(t, t', \tau_1, \tau_2), \quad (44)$$

where

$$\mathcal{C}(t, t', \tau_1, \tau_2) = \hbar^{-4} \sum_{\substack{i_1, j_1 \\ j_1 > i_1}} \sum_{\substack{i_2, j_2 \\ j_2 < i_2}} \sum_{\substack{i_3, j_3 \\ j_3 < i_3}} \sum_{\substack{i_4, j_4 \\ j_4 > i_4}} \mu_{i_1 j_1} \mu_{i_2 j_2} \mu_{i_3 j_3} \mu_{i_4 j_4} \\ \times \langle \mathcal{T} \hat{c}_{i_1 L}^\dagger(t^+) \hat{c}_{j_1 L}(t) \hat{c}_{j_2 R}(t') \hat{c}_{i_2 R}^\dagger(t') \\ \times \hat{c}_{i_3 L}^\dagger(\tau_1^+) \hat{c}_{j_3 L}(\tau_1) \hat{c}_{j_4 R}(\tau_2^+) \hat{c}_{i_4 R}^\dagger(\tau_2) \rangle \quad (45)$$

where  $t^+$  denotes a time which is infinitesimally larger than  $t$ . These infinitesimal time shifts are introduced to ensure that the time ordering is well defined and corresponds to the order

of operators in Eqs. (40)–(43). We have omitted the time argument  $t$  on the right-hand side of Eq. (44) since in the CW setup the signal does not depend on it.

Making use of Wick's theorem, the correlation function in Eq. (45) can be factorized into two-point correlation functions

$$G_{mn}^{\alpha\beta}(t, t') \equiv -\frac{i}{\hbar} \langle \mathcal{T} \hat{c}_{m\alpha}(t) \hat{c}_{n\beta}^\dagger(t') \rangle, \quad (46)$$

where  $\alpha, \beta = R, L$  or  $\pm$ .

The Liouville space two-point functions are connected to the non-equilibrium Green functions appearing in the Keldish technique. In the  $R, L$  representation, we have<sup>41</sup>

$$G_{mn}^{LL}(t, t') = -\frac{i}{\hbar} \langle \mathcal{T} \hat{c}_m(t) \hat{c}_n^\dagger(t') \rangle \equiv G_{mn}^T(t, t'), \quad (47)$$

$$G_{mn}^{RR}(t, t') = +\frac{i}{\hbar} \langle \tilde{\mathcal{T}} \hat{c}_m(t) \hat{c}_n^\dagger(t') \rangle \equiv -G_{mn}^{\tilde{T}}(t, t'), \quad (48)$$

$$G_{mn}^{LR}(t, t') = -\frac{i}{\hbar} \langle \hat{c}_m(t) \hat{c}_n^\dagger(t') \rangle \equiv G_{mn}^<(t, t'), \quad (49)$$

$$G_{mn}^{RL}(t, t') = \frac{i}{\hbar} \langle \hat{c}_n^\dagger(t') \hat{c}_m(t) \rangle \equiv -G_{mn}^>(t, t'), \quad (50)$$

where  $T$  ( $\tilde{T}$ ) is the time ordering (anti-time ordering) in Hilbert space.  $G^>$  ( $G^<$ ) is known as the greater (lesser) Green's function while  $G^T$  and  $G^{\tilde{T}}$  and the time-ordered and anti-time-ordered Green functions respectively. The corresponding relations in the  $\pm$  representation are given in Appendix B for completeness.

We can now employ Wick's theorem to factorize the correlation function in Eq. (45) into two-point functions. This is straightforward but tedious, due to the number of terms, and yields

$$\mathcal{C}(t, t', \tau_1, \tau_2) = \sum_{\substack{i_1, j_1 \\ j_1 > i_1}} \sum_{\substack{i_2, j_2 \\ j_2 < i_2}} \sum_{\substack{i_3, j_3 \\ j_3 < i_3}} \sum_{\substack{i_4, j_4 \\ j_4 > i_4}} \mu_{i_1 j_1} \mu_{i_2 j_2} \mu_{i_3 j_3} \mu_{i_4 j_4} \\ \times \{ G_{j_1 i_1}^{LL}(t, t^+) G_{j_2 i_2}^{RR}(t', t') [G_{j_3 i_3}^{LL}(\tau_1, \tau_1^+) G_{j_4 i_4}^{RR}(\tau_2^+, \tau_2) - G_{j_4 i_3}^{RL}(\tau_2, \tau_1) G_{j_3 i_4}^{LR}(\tau_1, \tau_2)] \\ - G_{j_1 i_1}^{LL}(t, t^+) G_{j_2 i_3}^{RL}(t', \tau_1) [G_{j_3 i_2}^{LR}(\tau_1, t') G_{j_4 i_4}^{RR}(\tau_2^+, \tau_2) - G_{j_4 i_2}^{RR}(\tau_2, t') G_{j_3 i_4}^{LR}(\tau_1, \tau_2)] \\ + G_{j_1 i_1}^{LL}(t, t^+) G_{j_2 i_4}^{RR}(t', \tau_2) [G_{j_3 i_2}^{LR}(\tau_1, t') G_{j_4 i_3}^{RL}(\tau_2, \tau_1) - G_{j_4 i_2}^{RR}(\tau_2, t') G_{j_3 i_3}^{LL}(\tau_1, \tau_1^+)] \\ - G_{j_2 i_1}^{RL}(t', t) G_{j_1 i_2}^{LR}(t, t') [G_{j_3 i_3}^{LL}(\tau_1, \tau_1^+) G_{j_4 i_4}^{RR}(\tau_2^+, \tau_2) - G_{j_4 i_3}^{RL}(\tau_2, \tau_1) G_{j_3 i_4}^{LR}(\tau_1, \tau_2)] \\ + G_{j_2 i_1}^{RL}(t', t) G_{j_1 i_3}^{LL}(t, \tau_1) [G_{j_3 i_2}^{LR}(\tau_1, t') G_{j_4 i_4}^{RR}(\tau_2^+, \tau_2) - G_{j_4 i_2}^{RR}(\tau_2, t') G_{j_3 i_4}^{LR}(\tau_1, \tau_2)] \\ - G_{j_2 i_1}^{RL}(t', t) G_{j_1 i_4}^{LR}(t, \tau_2) [G_{j_3 i_2}^{LR}(\tau_1, t') G_{j_4 i_3}^{RL}(\tau_2, \tau_1) - G_{j_4 i_2}^{RR}(\tau_2, t') G_{j_3 i_3}^{LL}(\tau_1, \tau_1^+)] \\ + G_{j_3 i_1}^{LL}(\tau_1, t) G_{j_1 i_2}^{LR}(t, t') [G_{j_2 i_3}^{RL}(t', \tau_1) G_{j_4 i_4}^{RR}(\tau_2^+, \tau_2) - G_{j_2 i_4}^{RR}(t', \tau_2) G_{j_3 i_3}^{RL}(\tau_2, \tau_1)] \\ - G_{j_3 i_1}^{LL}(\tau_1, t) G_{j_1 i_3}^{LL}(t, \tau_1) [G_{j_2 i_2}^{RR}(t', t') G_{j_4 i_4}^{RR}(\tau_2^+, \tau_2) - G_{j_2 i_4}^{RR}(t', \tau_2) G_{j_3 i_2}^{RR}(\tau_2, t')] \\ + G_{j_3 i_1}^{LL}(\tau_1, t) G_{j_1 i_4}^{LR}(t, \tau_2) [G_{j_2 i_2}^{RR}(t', t') G_{j_4 i_3}^{RL}(\tau_2, \tau_1) - G_{j_2 i_3}^{RL}(t', \tau_1) G_{j_4 i_2}^{RR}(\tau_2, t')] \\ - G_{j_4 i_1}^{RL}(\tau_2, t) G_{j_1 i_2}^{LR}(t, t') [G_{j_3 i_3}^{RL}(t', \tau_1) G_{j_4 i_4}^{LR}(\tau_1, \tau_2) - G_{j_2 i_4}^{RR}(t', \tau_2) G_{j_3 i_3}^{LL}(\tau_1, \tau_1^+)] \\ + G_{j_4 i_1}^{RL}(\tau_2, t) G_{j_1 i_3}^{LL}(t, \tau_1) [G_{j_2 i_2}^{RR}(t', t') G_{j_3 i_4}^{LR}(\tau_1, \tau_2) - G_{j_2 i_4}^{RR}(t', \tau_2) G_{j_3 i_2}^{LR}(\tau_1, t')] \\ - G_{j_4 i_1}^{RL}(\tau_2, t) G_{j_1 i_4}^{LR}(t, \tau_2) [G_{j_2 i_2}^{RR}(t', t') G_{j_3 i_3}^{LL}(\tau_1, \tau_1^+) - G_{j_2 i_3}^{RL}(t', \tau_1) G_{j_3 i_2}^{LR}(\tau_1, t')] \}. \quad (51)$$

The Green's functions, given in Eq. (46), describe the molecule without the fields (interacting with the electrodes). Since the junction is assumed to be at steady state, these Green's functions depend on their time arguments only through their difference. This symmetry could be used to rewrite the expression for the signal in terms of integrals over frequency domain Green's functions. An example is presented in Appendix C.

The signal given by Eqs. (44) and (51) is more general than that considered in Sec. III, since the Green's functions contain the lead-molecule interaction to all orders. In specific applications (with given level and coupling schemes) the signal will typically be dominated by few of the terms appearing in Eq. (51).

## V. FLUORESCENCE SIGNALS

Incoherent molecular optical spectroscopy<sup>5, 15, 16, 56</sup> may be interpreted as wave-function interferometry<sup>18, 53</sup> and provides similar (but not identical) information about Liouville space pathways than coherent heterodyne detected signals. Fluorescence signals can be treated using the same methods employed above for coherent signals. We demonstrate this using an example where the number of different contributions to the signal is small enough to be presented in terms of correlation functions. Each correlation functions can then be evaluated either by expanding it in many body eigenstates (Sec. III), or with the help of two-body Green's functions (see Sec. IV). We focus here on expressing the signal in terms of the correlation functions. In practical application to specific signals it may be possible to neglect some of the contributions.

In the spontaneous light emission process a photon is emitted into a vacant field mode. We examine processes where the system is excited by two pulses, but our treatment can be easily generalized to include more. [For instance, excitation with four pulses can be treated by following the steps below, but using Eq. (19) as a starting point instead of Eq. (52).] Following the excitation, the system spontaneously emits a photon.<sup>15, 16</sup> We further focus on processes where the molecule interacts with each pulse only once, leading to a signal which depends on the phases of both pulses. The superoperator correlation function corresponding to this signal was calculated by Marx *et al.* for an isolated molecule.<sup>48</sup> This expression is also valid for a molecule connected to electrodes as long as the unperturbed Hamiltonian, as well as the initial density matrix, are modified to include the electrodes. (See the discussion in Sec. II) The signal is given by

$$S^{\text{fl}}(\omega_s, t) = -\frac{4\pi}{\Omega\hbar^2}\omega_s\Re \int_{-\infty}^t d\tau \int^t d\tau_1 \int^t d\tau_2 e^{i\omega_s(t-\tau)} \times \langle \mathcal{T} \hat{V}_L(t) \hat{V}_R^\dagger(\tau) \mathcal{H}_{\text{int-}}(\tau_1) \mathcal{H}_{\text{int-}}(\tau_2) \rangle. \quad (52)$$

Equation (52) is obtained from Eq. (16) by expanding  $\hat{\rho}$  to second order in the field-matter interaction. The factors  $\hat{V}_L$  and  $\hat{V}_R^\dagger$  in Eq. (52) describe the emission into the unoccupied

mode while the two factors of  $\mathcal{H}_{\text{int}}$  describe interactions with the driving field.

Phase cycling can be used to select groups of pathways contributing to the signal. As an illustration we examine the part of the signal which scales as  $\sim e^{i\varphi_1 - i\varphi_2}$ . We note that the real part in Eq. (52) mixes the  $\sim e^{i\varphi_1 - i\varphi_2}$  and  $\sim e^{i\varphi_2 - i\varphi_1}$  components of the signal. The calculation of the latter is done in essentially the same way and is omitted for brevity. The  $\sim e^{i\varphi_1 - i\varphi_2}$  phase dependent part is obtained from Eq. (52) as follows. First, we take  $\mathcal{H}_{\text{int-}}(\tau_1)$  to interact with the first pulse and  $\mathcal{H}_{\text{int-}}(\tau_2)$  with the second. (Compensating for the other possibility by an overall factor of 2.) We then use  $\sqrt{2}\mathcal{H}_{\text{int-}}^{(j)}(\tau_j) = -\mathcal{E}_j(\tau_j) e^{i\varphi_j} \hat{V}_L^\dagger(\tau_j) - \mathcal{E}_j^*(\tau_j) e^{-i\varphi_j} \hat{V}_L(\tau_j) + \mathcal{E}_j(\tau_j) e^{i\varphi_j} \hat{V}_R^\dagger(\tau_j) + \mathcal{E}_j^*(\tau_j) e^{-i\varphi_j} \hat{V}_R(\tau_j)$  and only retain the terms with  $e^{i\varphi_1}$  in  $\mathcal{H}_{\text{int-}}^{(1)}$  and  $e^{-i\varphi_2}$  in  $\mathcal{H}_{\text{int-}}^{(2)}$ . We find

$$S_{\varphi_1 - \varphi_2}^{\text{fl}}(\omega_s, t) = -\frac{4\pi}{\Omega\hbar^2}\omega_s\Re e^{i\varphi_1 - i\varphi_2} \times \int^t d\tau d\tau_1 d\tau_2 e^{i\omega_s(t-\tau)} \mathcal{E}_1(\tau_1) \mathcal{E}_2^*(\tau_2) \times [\langle \mathcal{T} \hat{V}_L(t) \hat{V}_R^\dagger(\tau) \hat{V}_L(\tau_2) \hat{V}_L^\dagger(\tau_1) \rangle - \langle \mathcal{T} \hat{V}_L(t) \hat{V}_R^\dagger(\tau) \hat{V}_R(\tau_2) \hat{V}_L^\dagger(\tau_1) \rangle - \langle \mathcal{T} \hat{V}_L(t) \hat{V}_R^\dagger(\tau) \hat{V}_L(\tau_2) \hat{V}_R^\dagger(\tau_1) \rangle + \langle \mathcal{T} \hat{V}_L(t) \hat{V}_R^\dagger(\tau) \hat{V}_R(\tau_2) \hat{V}_R^\dagger(\tau_1) \rangle]. \quad (53)$$

Equation (53) is a convenient starting point for the application of Wick's theorem, following the prescription of Sec. IV. If one wishes to employ the approach presented in Sec. III instead, the various contributions should be split into the different possible time orderings and then rewritten as Hilbert space correlation functions.

Equation (53) may further be split according to the time ordering of interactions on the ket and bra. This can give rise to many contributions. We limit ourselves to a case where the pulses are temporally well separated and pulse 1 comes first, etc. This fixes the relative ordering between interactions with the pulses, thus leaving only the time ordering with the spontaneous emission on the bra to be determined. The terms in Eq. (53) are now split into the eight contributions presented diagrammatically in Fig. 3.

Diagram 3(i) represents the first term in Eq. (53). Similarly, 3(ii) and 3(iii) can be summed to give the second term in Eq. (53) while the sum of 3(iv) and 3(v) gives the third term in Eq. (53). Finally, 3(vi)–3(viii) correspond to the last term in Eq. (53). They differ only the time ordering between interactions.

Once the various time-orderings are separated, the superoperator correlation functions could be recast as Hilbert space correlation functions. For the eight contributions of Fig. 3, this gives

$$\begin{aligned}
S_{\varphi_1-\varphi_2}^{\text{fl}}(\omega_s, t) = & -\frac{4\pi}{\Omega\hbar^2}\omega_s\Re e^{i\varphi_1-i\varphi_2} \left\{ \int^t d\tau d\tau_1 d\tau_2 e^{i\omega_s(t-\tau)} \mathcal{E}_1(\tau_1)\mathcal{E}_2^*(\tau_2) \langle \hat{V}^\dagger(\tau)\hat{V}(t)\hat{V}(\tau_2)\hat{V}^\dagger(\tau_1) \rangle \right. \\
& - \int^t d\tau d\tau_1 \int^\tau d\tau_2 e^{i\omega_s(t-\tau)} \mathcal{E}_1(\tau_1)\mathcal{E}_2^*(\tau_2) \langle \hat{V}(\tau_2)\hat{V}^\dagger(\tau)\hat{V}(t)\hat{V}^\dagger(\tau_1) \rangle \\
& - \int^t d\tau_1 d\tau_1 \int^{\tau_2} d\tau e^{i\omega_s(t-\tau)} \mathcal{E}_1(\tau_1)\mathcal{E}_2^*(\tau_2) \langle \hat{V}^\dagger(\tau)\hat{V}(\tau_2)\hat{V}(t)\hat{V}^\dagger(\tau_1) \rangle \\
& - \int^t d\tau d\tau_2 \int^\tau d\tau_1 e^{i\omega_s(t-\tau)} \mathcal{E}_1(\tau_1)\mathcal{E}_2^*(\tau_2) \langle \hat{V}^\dagger(\tau_1)\hat{V}^\dagger(\tau)\hat{V}(t)\hat{V}(\tau_2) \rangle \\
& - \int^t d\tau_1 d\tau_1 \int^{\tau_1} d\tau e^{i\omega_s(t-\tau)} \mathcal{E}_1(\tau_1)\mathcal{E}_2^*(\tau_2) \langle \hat{V}^\dagger(\tau)\hat{V}^\dagger(\tau_1)\hat{V}(t)\hat{V}(\tau_2) \rangle \\
& + \int^t d\tau_1 d\tau_2 \mathcal{E}_1(\tau_1)\mathcal{E}_2^*(\tau_2) \left[ \int_{\tau_2}^t d\tau e^{i\omega_s(t-\tau)} \langle \hat{V}^\dagger(\tau_1)\hat{V}(\tau_2)\hat{V}^\dagger(\tau)\hat{V}(t) \rangle \right. \\
& \left. + \int_{\tau_1}^{\tau_2} d\tau e^{i\omega_s(t-\tau)} \langle \hat{V}^\dagger(\tau_1)\hat{V}^\dagger(\tau)\hat{V}(\tau_2)\hat{V}(t) \rangle + \int^{\tau_1} d\tau e^{i\omega_s(t-\tau)} \langle \hat{V}^\dagger(\tau)\hat{V}^\dagger(\tau_1)\hat{V}(\tau_2)\hat{V}(t) \rangle \right] \Big\} \quad (54)
\end{aligned}$$

which can serve as a starting point for an expansion in eigenstates, provided that one also expands perturbatively in the molecule–lead interaction as was done in Sec. III.

## VI. SUMMARY

In this paper we considered the nonlinear optical signals obtained from a molecule connected to conducting electrodes. The calculation naturally separates into two steps: the treatment of the interactions with the optical fields, and the calculation of the resulting correlation functions. These steps employ methods developed in different research fields. The interactions with the optical field is calculated using Liouville space approach commonly used in nonlinear spectroscopy. The evaluation of the correlation functions can be done using many body techniques employed to study transport in nano- and molecular-junctions. We have mainly focused on the first part, but also presented two recipes on how to approach the second.

The first recipe employed perturbation theory in the molecule-lead coupling. It is therefore most suitable for molecules which are weakly coupled to the leads. The molecule is described using the many-body states of an isolated molecule. These states can include electron–electron interactions and vibrational degrees of freedom. The second recipe is based on the application of Wick’s theorem. Here the coupling to the leads do not to be weak. However, electron–electron interactions must be treated perturbatively, followed by an application of Wick’s term to the resulting correlation function obtained at each order of perturbation theory.<sup>46</sup>

Coupling to the leads allows the molecular state to vary between successive interactions with the optical field. This greatly increases the complexity of the problem by allowing for processes which would be forbidden in an isolated molecule. The methods presented here allow us to calculate such signals, but the complexity forces us to focus on specific

examples instead of calculating the most general signal. Physical considerations should be used in order to reduce the number of contributing processes and simplify the signals. Such considerations may result from properties of the molecule, the lead-molecule coupling (i.e., almost isolated molecule), or the driving field configuration. Such considerations are also needed to distinguish between signals from molecules which are in- and out-of-equilibrium. For instance, the signals calculated in Sec. III can show charge-fluctuations, but these exist even when the junction is not biased.

The signals calculated in this paper are incoherent (i.e., scale linearly with the number of active molecules) and would also appear in bulk samples. However, molecular junctions are not bulk samples, and in that case the signal would originate from a single molecule. It is then not possible to use directionality to select different Liouville pathways. Phase cycling is an experimentally feasible alternative.

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## APPENDIX A: FERMIONIC CREATION AND ANNIHILATION SUPEROPERATORS

The fermionic superoperators are defined by the way they act on sectors of the many body density matrix. Let us denote by  $|M\rangle\langle N|$  the part of the density matrix whose ket is an  $M$  particle state while its bra is an  $N$  particle state. The left fermionic superoperators are defined as in Eq. (9)

$$\begin{aligned}
\hat{c}_{iL}|M\rangle\langle N| & \equiv \hat{c}_i|M\rangle\langle N|, \\
\hat{c}_{iL}^\dagger|M\rangle\langle N| & \equiv \hat{c}_i^\dagger|M\rangle\langle N|.
\end{aligned} \quad (A1)$$

However, moving a superoperator to the right of  $|M\rangle\langle N|$  could involve a sign depending on the number of particles in

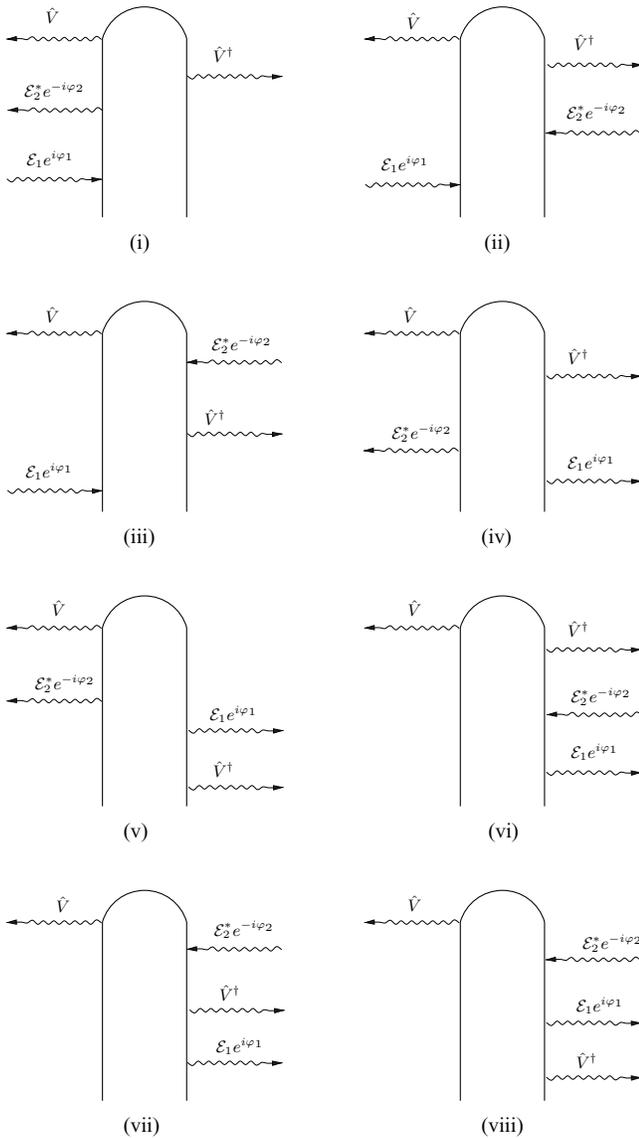


FIG. 3. All diagrams representing the various contributions to Eq. (52).

the wave functions

$$\begin{aligned}\hat{c}_{iR} |M\rangle \langle N| &\equiv (-1)^{M-N} |M\rangle \langle N| \hat{c}_i, \\ \hat{c}_{iR}^\dagger |M\rangle \langle N| &\equiv (-1)^{M-N+1} |M\rangle \langle N| \hat{c}_i^\dagger.\end{aligned}\quad (\text{A2})$$

Note that with this definition  $\hat{c}_R^\dagger$  not the Hermitian conjugate of  $\hat{c}_R$ .

A complication due to the sign convention in Eq. (A2) is that there is no simple way of defining a “right” superoperator composed of a general product of fermionic operators. One can immediately see that by inspecting Eq. (A2) and noting that (i) different parts of the density matrix are assigned different signs and (ii) creation and annihilation operators are treated differently. This drawback is not an issue for *physical operators*, which conserve the number of electrons and have equal number of creation and annihilation operators. As an example, let us examine the product  $\hat{c}_i^\dagger \hat{c}_j$ . It is not difficult to construct the associated left superoperator, which is given by

$$(\hat{c}_i^\dagger \hat{c}_j)_L = \hat{c}_{iL}^\dagger \hat{c}_{jL}. \quad (\text{A3})$$

Similarly, we find

$$(\hat{c}_i^\dagger \hat{c}_j)_R |M\rangle \langle N| = \hat{c}_{jR} \hat{c}_{iR}^\dagger |M\rangle \langle N| = |M\rangle \langle N| \hat{c}_i^\dagger \hat{c}_j. \quad (\text{A4})$$

Equation (A4) demonstrates that it is possible to consistently define a right superoperator of the product  $\hat{c}_i^\dagger \hat{c}_j$  as if it was a non-Fermionic operator, which is consistent with Eq. (9). As commented earlier, this is not possible for operators composed of odd products of creation annihilation operators. Similarly, a product of two creation operators would result in an additional sign. These complications never arise for physical, number conserving, operators, allowing us to use the formalism. These need to be added to describe superconductors or Josephson junctions which involve coherence between states with different numbers of electrons.

## APPENDIX B: NONEQUILIBRIUM GREEN'S FUNCTIONS IN THE $\pm$ REPRESENTATION

The Liouville Green functions in the  $\pm$  representation are given by<sup>41</sup>

$$G_{mn}^{--}(t, t') = -\frac{i}{\hbar} \theta(t - t') \{ \hat{c}_m(t), \hat{c}_n^\dagger(t') \} \equiv G_{mn}^r(t, t'), \quad (\text{B1})$$

$$G_{mn}^{++}(t, t') = \frac{i}{\hbar} \theta(t' - t) \{ \hat{c}_m(t), \hat{c}_n^\dagger(t') \} \equiv G_{mn}^a(t, t'), \quad (\text{B2})$$

$$G_{mn}^{-+}(t, t') = -\frac{i}{\hbar} \{ [ \hat{c}_m(t), \hat{c}_n^\dagger(t') ] \} \equiv G_{mn}^c(t, t'), \quad (\text{B3})$$

$$G_{mn}^{+-}(t, t') = 0. \quad (\text{B4})$$

Here  $G^r$  and  $G^a$  are the retarded and advanced Green functions.

## APPENDIX C: REPRESENTATION OF THE SIGNALS IN TERMS OF FREQUENCY DOMAIN GREEN'S FUNCTIONS

In this appendix we demonstrate how to rewrite the many-body version of the optical signal given by Eqs. (44) and (51) in a frequency representation. This representation makes use of the fact that in absence of the fields the system is in a steady-state and therefore the various Green's functions depend only on the difference of its time variables. As a result, by substituting

$$G_{ij}^{\alpha\beta}(t, t') = \frac{1}{2\pi} \int dE e^{-(i/\hbar)E(t-t')} G_{ij}^{\alpha\beta}(E) \quad (\text{C1})$$

it is possible to perform all the time integrations explicitly. Combining this with the relations

$$G_{ij}^T(E) = -G_{ji}^{T*}(E), \quad (\text{C2})$$

$$G_{ij}^{>*}(E) = -G_{ji}^{>}(E), \quad (\text{C3})$$

$$G_{ij}^{<*}(E) = -G_{ji}^{<}(E), \quad (\text{C4})$$

allows us to simplify the expression for the signal. We focus here on a pump-probe signal, resulting from interaction with two field modes. In this case the phase-independent pump-probe signal can be simplified further, making use of the fact that the field amplitude dependent part turns out to be real. The calculation is very long, but straightforward. It results in

$$\begin{aligned}
S_{pp} = & 2 \frac{|\mathcal{E}_1|^2 |\mathcal{E}_2|^2}{\omega_1 \omega_2} \Re X^* \tilde{X} \int \frac{dE}{2\pi} \sum_{\substack{i_1, j_1 \\ j_1 > i_1}} \sum_{\substack{i_4, j_4 \\ j_4 > i_4}} \mu_{i_1 j_1} \mu_{i_4 j_4} G_{j_4 i_1}^>(E) G_{j_1 i_4}^<(E + \hbar(\omega_2 - \omega_1)) \\
& + \frac{|\mathcal{E}_1|^2 |\mathcal{E}_2|^2}{\omega_2^2} |X|^2 \int \frac{dE}{2\pi} \sum_{\substack{i_1, j_1 \\ j_1 > i_1}} \sum_{\substack{i_2, j_2 \\ j_2 < i_2}} \mu_{i_1 j_1} \mu_{i_2 j_2} G_{j_1 i_2}^>(E) G_{j_2 i_1}^<(E + \hbar(\omega_2 - \omega_1)) \\
& + \frac{|\mathcal{E}_1|^2 |\mathcal{E}_2|^2}{\omega_1^2} |\tilde{X}|^2 \int \frac{dE}{2\pi} \sum_{\substack{i_1, j_1 \\ j_1 > i_1}} \sum_{\substack{i_2, j_2 \\ j_2 < i_2}} \mu_{i_1 j_1} \mu_{i_2 j_2} G_{j_2 i_1}^>(E) G_{j_1 i_2}^<(E + \hbar(\omega_2 - \omega_1)) \\
& - 2 |\mathcal{E}_1|^2 |\mathcal{E}_2|^2 \int \frac{dE_2 dE_3}{(2\pi)^2} \sum_{\substack{i_1, j_1 \\ j_1 > i_1}} \sum_{\substack{i_2, j_2 \\ j_2 < i_2}} \sum_{\substack{i_4, j_4 \\ j_4 > i_4}} \Re \left[ X^* \mu_{i_1 j_1} \mu_{i_2 j_2} \mu_{i_4 j_4} \frac{1}{\omega_2 - i\eta} \frac{1}{\omega_2 + (E_2 - E_3)/\hbar + i\eta} \right. \\
& \times \left. \left\{ G_{j_4 i_1}^>(E_2) G_{j_1 i_2}^T(E_3) G_{j_2 i_4}^<(E_2 + \hbar(\omega_2 - \omega_1)) + G_{j_2 i_1}^T(E_2) G_{j_1 i_4}^<(E_3) G_{j_4 i_2}^>(E_3 + \hbar(\omega_1 - \omega_2)) \right\} \right] \\
& - 2 |\mathcal{E}_1|^2 |\mathcal{E}_2|^2 \int \frac{dE_1 dE_2}{(2\pi)^2} \sum_{\substack{i_1, j_1 \\ j_1 > i_1}} \sum_{\substack{i_2, j_2 \\ j_2 < i_2}} \sum_{\substack{i_3, j_3 \\ j_3 < i_3}} \Re \left[ \tilde{X}^* \mu_{i_1 j_1} \mu_{i_2 j_2} \mu_{i_3 j_3} \frac{1}{\omega_1 - i\eta} \frac{1}{\omega_2 + (E_1 - E_2)/\hbar + i\eta} \right. \\
& \times \left. \left\{ G_{j_2 i_1}^>(E_1) G_{j_1 i_3}^T(E_2) G_{j_3 i_2}^<(E_1 + \hbar(\omega_2 - \omega_1)) + G_{j_3 i_1}^T(E_1) G_{j_1 i_2}^<(E_2) G_{j_2 i_3}^>(E_2 + \hbar(\omega_1 - \omega_2)) \right\} \right] \\
& + 2\pi |\mathcal{E}_1|^2 |\mathcal{E}_2|^2 \Re \int \frac{dE_1 dE_2 dE_3 dE_4}{(2\pi)^4} \sum_{\substack{i_1, j_1 \\ j_1 > i_1}} \sum_{\substack{i_2, j_2 \\ j_2 < i_2}} \sum_{\substack{i_3, j_3 \\ j_3 < i_3}} \sum_{\substack{i_4, j_4 \\ j_4 > i_4}} \mu_{i_1 j_1} \mu_{i_2 j_2} \mu_{i_3 j_3} \mu_{i_4 j_4} \\
& \times \left[ \frac{1}{|\omega_1 + (E_4 - E_3)/\hbar + i\eta|^2} G_{j_2 i_1}^>(E_1) G_{j_1 i_2}^<(E_2) G_{j_4 i_3}^>(E_3) G_{j_3 i_4}^<(E_4) \right. \\
& + \frac{1}{\omega_1 + (E_2 - E_1)/\hbar - i\eta} \frac{1}{\omega_1 + (E_4 - E_3)/\hbar + i\eta} G_{j_4 i_1}^>(E_1) G_{j_1 i_4}^<(E_2) G_{j_2 i_3}^>(E_3) G_{j_3 i_2}^<(E_4) \left. \right] \\
& \times \delta[\omega_2 - \omega_1 + (E_1 - E_2 + E_3 - E_4)/\hbar] \\
& - 2\pi |\mathcal{E}_1|^2 |\mathcal{E}_2|^2 \Re \int \frac{dE_1 dE_2 dE_3 dE_4}{(2\pi)^4} \sum_{\substack{i_1, j_1 \\ j_1 > i_1}} \sum_{\substack{i_2, j_2 \\ j_2 < i_2}} \sum_{\substack{i_3, j_3 \\ j_3 < i_3}} \sum_{\substack{i_4, j_4 \\ j_4 > i_4}} \mu_{i_1 j_1} \mu_{i_2 j_2} \mu_{i_3 j_3} \mu_{i_4 j_4} \\
& \times \left\{ \frac{1}{\omega_1 + (E_2 - E_4)/\hbar - i\eta} \frac{1}{\omega_1 + (E_1 - E_3)/\hbar + i\eta} G_{j_3 i_1}^T(E_1) G_{j_1 i_4}^<(E_2) G_{j_2 i_3}^>(E_3) G_{j_4 i_2}^{\tilde{T}}(E_4) \right. \\
& \times 2\pi \delta[\omega_2 - \omega_1 + (E_3 - E_2)/\hbar] + \frac{1}{\omega_1 + (E_4 - E_3)/\hbar - i\eta} \frac{1}{\omega_1 + (E_4 - E_2) + i\eta} \\
& \times G_{j_2 i_1}^>(E_1) G_{j_1 i_3}^T(E_2) G_{j_4 i_2}^{\tilde{T}}(E_3) G_{j_3 i_4}^<(E_4) \pi \delta[\omega_2 - \omega_1 + (E_1 - E_4)/\hbar] \\
& + \frac{1}{\omega_1 + (E_3 - E_4)/\hbar - i\eta} \frac{1}{\omega_1 + (E_1 - E_4)/\hbar + i\eta} G_{j_3 i_1}^T(E_1) G_{j_1 i_2}^<(E_2) G_{j_2 i_4}^{\tilde{T}}(E_3) G_{j_4 i_3}^>(E_4) \\
& \times \pi \delta[\omega_2 - \omega_1 + (E_4 - E_2)/\hbar] + \frac{1}{\omega_1 + (E_2 - E_4)/\hbar - i\eta} \frac{1}{\omega_1 + (E_3 - E_4)/\hbar + i\eta} \\
& \times G_{j_2 i_1}^>(E_1) G_{j_1 i_4}^<(E_2) G_{j_3 i_2}^<(E_3) G_{j_4 i_3}^>(E_4) \pi \delta[\omega_2 - \omega_1 + (E_1 - E_2 - E_3 + E_4)/\hbar] \\
& + \frac{1}{\omega_1 + (E_4 - E_1)/\hbar - i\eta} \frac{1}{\omega_1 + (E_4 - E_3)/\hbar + i\eta} G_{j_4 i_1}^>(E_1) G_{j_1 i_2}^<(E_2) \\
& \times \left. G_{j_2 i_3}^>(E_3) G_{j_3 i_4}^<(E_4) \pi \delta[\omega_2 - \omega_1 + (E_1 - E_2 + E_3 - E_4)/\hbar] \right\}, \tag{C5}
\end{aligned}$$

where we have defined the auxiliary quantities

$$X \equiv \int \frac{dE}{2\pi} \sum_{\substack{i,j \\ j>i}} \mu_{ij} G_{ji}^T(E), \quad (\text{C6})$$

$$\tilde{X} \equiv \int \frac{dE}{2\pi} \sum_{\substack{i,j \\ j<i}} \mu_{ij} G_{ji}^T(E). \quad (\text{C7})$$

The expression (C5) for the signal looks cumbersome, but a closer inspection shows that the number of integrals in its terms is reduced compared to Eq. (44) due to the presence of  $\delta$ -functions. This rather complicated form appears since we have not made any assumptions on the coupling to the leads. It could be simplified for instance, by assuming that the Green's functions are diagonal in their indices.

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