

Nonlinear spectroscopy of cavity polaritons

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Confinement of molecules within a cavity leads to a strong coupling between light and matter degrees of freedom, merging the two into a quasiparticle known as a polariton. Theoretical treatments of molecular polaritons generally utilize either exact diagonalization of the interacting molecule-cavity system Hamiltonian or perturbation theory to analyze intracavity light-matter interactions. The former is constrained in its capacity to account for the open nature of the molecular cavity system, while the treatment of strong interactions within perturbation theory represents a weakness of the latter. Here, we introduce a pseudoparticle nonequilibrium Green's function (PP-NEGF) formulation for molecular polariton spectroscopy. This formulation addresses the limitations of currently available approaches by accounting for all intrasystem interactions exactly and treating system-bath couplings within diagrammatic expansion and extends a recent NEGF-based formulation for nonlinear optical spectroscopy [J. Chem. Phys. **162**, 074108 (2025)] to strongly interacting molecular systems. Theoretical derivations are demonstrated through numerical simulations, where we examine the impact of strong light-matter interaction on fluxes and multidimensional optical spectroscopy of cavity polaritons.

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I. INTRODUCTION

Recent experimental advances in cavity spectroscopy have given rise to the field of molecular polaritonics [1–12]. Confinement within the cavity leads to strong coupling between molecular and photon degrees of freedom. The enhanced interaction strength enables control over electron and energy transfer, nuclear dynamics, and chemistry in cavity molecular systems [2,7–9,13–19]. Since coupling to a single molecule remains weak, most cavity experiments are performed with samples containing many molecules, whose collective response (bright state) proportionally enhances the coupling strength to the square root of the number of molecules in the sample. Nevertheless, initial experiments on single-molecule spectroscopy in plasmonic nanocavities have been documented in the literature [20,21].

Theoretically, the strength of light-matter coupling necessitates a precise accounting of the interaction. Typically, the Jaynes-Cummings (or, more generally, Tavis-Cummings) Hamiltonian is employed to describe an ensemble of molecular excitations coupled to a Bose cavity mode. In the presence of vibrations, the Holstein-Tavis-Cummings model is utilized. Exact diagonalization is applied to ascertain the eigenvalues of the Hamiltonian, which yield the energies of lower and upper polaritons, as well as dark molecular states (which do not interact with the cavity mode). The open

character of the system is considered in an *ad hoc* manner, using either single-particle scattering or the closely related input-output methodology [22,23]. More advanced treatments employ non-Hermitian quantum mechanics [24,25] to account for the open character at the level of the system Hamiltonian. Exceptional points (degeneracies of the non-Hermitian Hamiltonian) [26–28] indicate significant changes in system responses [29–34]. Recently, we demonstrated that such approaches have limitations in their applicability, suggesting that more accurate formulations may be required [35]. Other theoretical considerations utilize diagrammatic perturbation theory [36,37] or mean field treatment [9,38] to address strong light-matter interactions. Although the results from these formulations may provide qualitatively correct behavior, the theoretical level employed is insufficient for studying strong interactions.

Almost all experimental measurements to date have concentrated exclusively on the optical response of molecular cavity systems. However, the scanning tunneling microscopy (STM) setup utilized in single-molecule nanocavity experiments indicates that measurements in current-carrying cavity systems are imminent [20,21]. It is noteworthy that the initial measurements of conductivity in organic semiconductor cavities have been reported in the literature [13]. Consequently, the majority of theoretical considerations focus on the optical response of molecular cavity systems. In particular, the multidimensional spectroscopy of polaritons has been theoretically examined [39–41]. Such studies utilize standard tools of nonlinear optical spectroscopy [42]. The cavity enhancement of electron transport has been theoretically analyzed in Ref. [37] using a diagrammatic perturbation theory approach, which is not fully adequate in the presence of strong light-matter interaction.

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Recently, we employed standard nonequilibrium Green's function (NEGF) methodology to develop a theory of nonlinear optical spectroscopy for open quantum systems [43,44]. We compared this formulation with the traditional approach to nonlinear optical spectroscopy and argued that the applicability of the latter to open systems is limited. In particular, the predictions of the traditional formulation become especially unreliable when photon and electron fluxes are strongly interdependent, which is the situation encountered in polaritonic systems. Subsequently, we applied the newly developed NEGF-based approach to discuss multidimensional spectroscopy in Ref. [45]. For simplicity, the analysis was conducted for noninteracting molecular systems. While incorporating interactions is straightforward, the corresponding NEGF treatment would require the use of diagrammatic perturbation theory, which is not the optimal method for describing strong light-matter interactions.

Here, we present a theoretical approach to nonlinear optical spectroscopy of open quantum systems that addresses the limitations of standard spectroscopy theory and accurately treats strong light-matter interactions. This approach is founded on a non-self-consistent diagrammatic expansion within the pseudoparticle (PP-) NEGF, which is the many-body variant of the NEGF. We utilize this formulation to explore transport and multidimensional optical spectroscopy in molecular cavity junctions.

The structure of the paper is organized as follows. In Sec. II, we introduce the model of a molecular cavity system and discuss the treatment of its responses within the bare diagrammatic expansion of the PP-NEGF. Numerical examples and discussions are provided in Sec. III. Section IV summarizes our findings and outlines future research directions.

II. NONLINEAR OPTICAL SPECTROSCOPY

A. Model

We consider molecule M to be strongly interacting with cavity mode C . The molecule is coupled to two metallic contacts: the left contact L and the right contact R . The cavity mode is connected to a thermal bath (th) and is driven by an external radiation field (rad). A sketch of the model is presented in Fig. 1. Hamiltonian of the model is

$$\hat{H} = \hat{H}_M + \hat{H}_C + \hat{V}_{MC} + \sum_{K=L,R} (\hat{H}_K + \hat{V}_{MK}) + \sum_{B=\text{rad,th}} (\hat{H}_B + \hat{V}_{CB}). \quad (1)$$

Molecule is represented by its set of many-body states $\{|m\rangle\}$, while the cavity mode is described by a set of states of a harmonic oscillator $\{|c\rangle\}$. The coupling occurs between molecular optical transitions and cavity mode excitations.

$$\begin{aligned} \hat{H}_M &= \sum_{m \in M} E_m |m\rangle \langle m|, & \hat{H}_C &= \sum_{c \in C} \omega_C n_c |c\rangle \langle c|, \\ \hat{V}_{MC} &= \sum_{\substack{m_1, m_2 \in M \\ c_1, c_2 \in C}} g_{m_1 m_2, c_1 c_2} |m_2\rangle \langle m_1| \otimes |c_1\rangle \langle c_2|. \end{aligned} \quad (2)$$

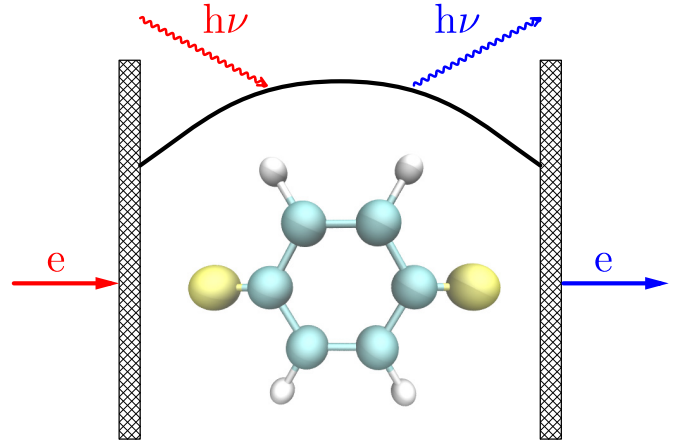


FIG. 1. Nonlinear spectroscopy of a molecular cavity junction.

Contacts are modeled as continua of electronic states $\{k\}$, with each contact assumed to be at its equilibrium. The coupling between contacts and molecules results in electronic transitions within the system, combined with electron transfer into or out of a contact:

$$\begin{aligned} \hat{H}_K &= \sum_{k \in K} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k, \\ \hat{V}_{MK} &= \sum_{m_1, m_2 \in M} \sum_{k \in K} (V_{m_1 m_2, k} |m_2\rangle \langle m_1| \hat{c}_k + \text{H.c.}). \end{aligned} \quad (3)$$

Here, $K = \{L, R\}$ and $\hat{c}_k^\dagger$ ($\hat{c}_k$) creates (annihilates) electron in state k of the contacts. Note that in Eq. (3) number of electrons in the state $|m_2\rangle$ is bigger than that in the state $|m_1\rangle$: $N_{m_2} = N_{m_1} + 1$. Finally, the radiation field and thermal bath are modeled as continua of modes α and β , respectively. They induce (de)excitations of the cavity mode:

$$\begin{aligned} \hat{H}_{\text{rad}} &= \sum_{\alpha \in \text{rad}} \omega_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha, & \hat{H}_{\text{th}} &= \sum_{\beta \in \text{th}} \omega_\beta \hat{b}_\beta^\dagger \hat{b}_\beta, \\ \hat{V}_{C, \text{rad}} &= \sum_{c_1, c_2 \in C} \sum_{\alpha \in \text{rad}} (U_{c_1 c_2, \alpha} |c_2\rangle \langle c_1| \hat{a}_\alpha + \text{H.c.}), \\ \hat{V}_{C, \text{th}} &= \sum_{c_1, c_2 \in C} \sum_{\beta \in \text{th}} (M_{c_1 c_2, \beta} |c_2\rangle \langle c_1| \hat{b}_\beta + \text{H.c.}). \end{aligned} \quad (4)$$

Here, $\hat{a}_\alpha^\dagger$ ($\hat{a}_\alpha$) and $\hat{b}_\beta^\dagger$ ($\hat{b}_\beta$) create (annihilate) a photon in mode α of the radiation field and a phonon in mode β of the thermal bath, respectively. Note that while the model (1)–(4) is general, couplings to the radiation and thermal baths are assumed to be weak and considered below within the rotating wave approximation (RWA).

B. The PP-NEGF formulation

The primary advantage of the PP-NEGF formulation lies in its capacity to access many-body states of the system $\{|S\rangle\}$. In this model, these states are considered as the direct product of many-body states of an isolated molecule and the states of the cavity mode:

$$|S\rangle = |m\rangle \otimes |c\rangle. \quad (5)$$

Similar to the NEGF, which utilizes standard (single-quasiparticle) second quantization, PP-NEGF employs second quantization within the realm of many-body states. Operators $\hat{p}_S^\dagger$ ($\hat{p}_S$) create (annihilate) the many-body state $|S\rangle$. These operators satisfy usual commutation or anticommutation relations for Bose (even number of electrons) or Fermi (odd number of electrons) state $|S\rangle$. Any optical or electronic transition in the system is represented as the destruction of one state and the creation of another. Naturally, the formulation extends beyond the physical Hilbert space. Its physically relevant part is enforced by the normalization condition

$$Q \equiv \sum_S \hat{p}_S^\dagger \hat{p}_S = 1. \quad (6)$$

Normalization (6) is incorporated into the standard NEGF theory, modifying the definition of a Green's function by introducing an integral over the complex chemical potential $i\lambda$,

$$\delta_{Q,1} = \frac{\beta}{2\pi} \int_{-\pi/\beta}^{+\pi/\beta} d\lambda e^{-i\beta\lambda(Q-1)} \left(\beta \equiv \frac{1}{k_B T} \right),$$

performing evaluations, and taking $\lim_{\lambda \rightarrow 0}$. This will keep only $Q = 1$ (i.e., physical subspace) contributions. The methodology was first developed as a way to solve the infinite- U Anderson model for equilibrium magnetic systems [46]. Its nonequilibrium variant was introduced in a celebrated paper by Wingreen and Meir as a slave-boson technique [51]. Renewed interest in strongly correlated materials out of equilibrium resulted in the application of the PP-NEGF as an impurity solver in the nonequilibrium dynamical mean field theory [47].

The central object in the PP-NEGF is the single-pseudoparticle Green's function of the open quantum system:

$$G_{S_1 S_2}(\tau_1, \tau_2) = -\langle T_c \hat{p}_{S_1}(\tau_1) \hat{p}_{S_2}^\dagger(\tau_2) \rangle, \quad (7)$$

where T_c is the Keldysh contour ordering operator and $\tau_{1,2}$ are the contour variables. Its dynamics is described by the Dyson

equation

$$\sum_{S_3} \left(\delta_{S_1, S_3} i \frac{\partial}{\partial \tau_1} - H_{S_1 S_3}^{\text{sys}} \right) G_{S_3 S_2}(\tau_1, \tau_2) = \delta_{S_1, S_2} \delta(\tau_1, \tau_2) + \sum_{S_3} \int_c d\tau_3 \Sigma_{S_1 S_3}(\tau_1, \tau_3) G_{S_3 S_2}(\tau_3, \tau_2), \quad (8)$$

projections of which must be modified to fulfill (6). Here, $\hat{H}^{\text{sys}} = \hat{H}_M + \hat{H}_C + \hat{V}_{MC}$ and Σ represents the self-energy that accounts for coupling to contacts, the thermal bath, and the radiation field.

Following standard nonlinear spectroscopy, which employs bare perturbation theory in radiation field-matter interaction to classify and characterize optical processes, the NEGF-based approach in Ref. [44] employs a non-self-consistent diagrammatic expansion in radiation field-matter interaction, while molecular coupling to metal contacts is considered exactly. A similar formulation for the PP-NEGF is more complicated because, within the pseudoparticle framework, molecule-cavity system couplings to contacts and the thermal bath are many-body interactions that must be accounted for in their diagrammatic expansions. Furthermore, the diagrammatic expansion for the system's couplings to the radiation field interconnects with processes representing coupling to the contacts and thermal bath: these are diagrams with the two couplings crossing each other [see Figs. 2(f) and 2(g)]. Strictly speaking, instead of optical, one must consider optoelectronic spectroscopy in molecular cavities.

Developing an expansion similar to standard spectroscopy theory requires considering the coupling of the radiation field to the cavity degrees of freedom in an order-by-order fashion. Moreover, for the resulting scheme to be meaningful, it must be conserving (upholding charge and energy conservation laws). It is crucial to highlight that the violation of conservation laws in standard optical spectroscopy methods [48,49], when applied to open systems, drives the development of

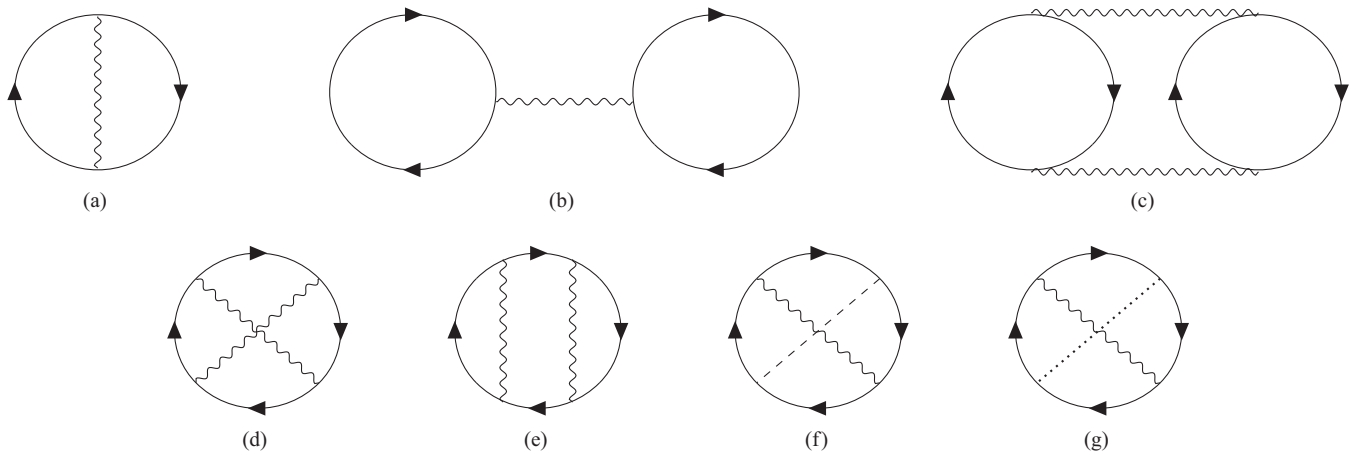


FIG. 2. The Luttinger-Ward functionals involving interaction of the cavity system with the radiation field. Shown are (a), (b) second- and (c)–(g) fourth-order contributions. Panel (e) shows reducible fourth-order contribution (contrary to standard diagrammatic rules, it must be taken into account in non-self-consistent formulation). Panels (f) and (g) show mixed (radiation field with metal contact and with thermal bath) contributions. Directed solid line represents electron propagator G_A . Wavy line represents free photon Green's function $f_\alpha(\tau, \tau')$. Dashed line represents free electron in the contacts $g_k(\tau, \tau')$. Dotted line represents free phonon in thermal bath $h_\beta(\tau, \tau')$. Both directions are possible for each wavy, dashed, and dotted lines.

Green's function-based alternatives. Indeed, the NEGF-based formulation in Ref. [44] is conserving by design. Similarly, we aim to establish a conserving PP-NEGF scheme. The scheme we propose is based on the following approximations:

(1) As demonstrated in Ref. [50], conservation laws are upheld if, in the last term of Eq. (8), one substitutes $\Sigma[G]G$ with $\Sigma[G_A]G_A$, where G_A is any ansatz Green's function and $\Sigma[G_A]$ is the functional derivative of the corresponding Luttinger-Ward potential.

(2) As G_A , we propose utilizing the Green's function of the molecular system, focusing exclusively on the contributions from coupling to metallic contacts or solely to the thermal bath (excluding the radiation field). Additionally, in the simulations below, we apply the non-crossing approximation for the couplings, which is adequate for the molecule-in-a-cavity system.

(3) All diagrams, describing coupling to the radiation field (encompassing both pure radiation field contributions and diagrams involving crossings with other processes), will be

examined within a non-self-consistent expansion akin to that of Ref. [44]. The corresponding Luttinger-Ward functionals up to fourth order are illustrated in Fig. 2. It is worth noting that crossing diagrams arising from coupling with contacts and the thermal bath also exist; however, we disregard these as they are less pertinent for the purpose of developing spectroscopy. Indeed, processes of simultaneous exchange of electrons with metallic contacts and energy with the thermal bath are less critical for spectroscopy. Moreover, due to weak system-bath coupling, they are rare (i.e., do not have a significant contribution). Note that, in principle, one may keep those processes. This would lead to a treatment that is more involved technically (the cost of numerical effort would be greater), but would not make significant changes to the results.

Below, we will focus on the simulation of electron (e) and photon (p) fluxes, which can be approximately expressed in terms of projections of the Green's function (see Appendix A for derivation):

$$\begin{aligned}
 I_e^K(t) &= -2 \text{Im} \sum_{S_1, S_2, S_3, S_4} \zeta_{S_1} \int_{-\infty}^t dt' (\Sigma_{S_1 S_2, S_3 S_4}^K(t, t') G_{S_1 S_3}^<(t, t') G_{S_4 S_2}^>(t', t) \\
 &\quad - \Sigma_{S_1 S_2, S_3 S_4}^{K>}(t, t') G_{S_1 S_3}^>(t, t') G_{S_4 S_2}^<(t', t)), \\
 I_p(t) &= 2 \text{Im} \sum_{S_1, S_2, S_3, S_4} \zeta_{S_1} \int_{-\infty}^t dt' (\Sigma_{S_1 S_2, S_3 S_4}^{\text{rad}<}(t, t') G_{S_1 S_3}^<(t, t') G_{S_4 S_2}^>(t', t) \\
 &\quad - \Sigma_{S_1 S_2, S_3 S_4}^{\text{rad}>}(t, t') G_{S_1 S_3}^>(t, t') G_{S_4 S_2}^<(t', t)). \tag{9}
 \end{aligned}$$

Here, $\zeta_S = +1$ or -1 for Bose (even number of electrons) or Fermi (odd number of electrons) state $|S\rangle$, respectively,

$$\begin{aligned}
 \Sigma_{S_1 S_2, S_3 S_4}^K(\tau, \tau') &= \sum_{k \in K} V_{S_1 S_2, k} g_k(\tau, \tau') V_{k, S_3 S_4}, \\
 \Sigma_{S_1 S_2, S_3 S_4}^{\text{rad}}(\tau, \tau') &= \sum_{\alpha \in \text{rad}} U_{S_1 S_2, \alpha} f_\alpha(\tau, \tau') U_{\alpha, S_3 S_4} \tag{10}
 \end{aligned}$$

are the self-energies due to coupling to the contact K and the radiation field, and

$$\begin{aligned}
 g_k(\tau, \tau') &= -i \langle T_c \hat{c}_k(\tau) \hat{c}_k^\dagger(\tau') \rangle_0, \\
 f_\alpha(\tau, \tau') &= -i \langle T_c \hat{a}_\alpha(\tau) \hat{a}_\alpha^\dagger(\tau') \rangle_0 \tag{11}
 \end{aligned}$$

are, respectively, the Green's function of a free electron in state k of the contact and a free photon in mode α of the radiation field. Figure 3 shows diagrammatic representations for expressions in Eq. (9). Exchange of an electron (dashed line) or a photon (wavy line) between the system and the corresponding bath results in a change of the system state from $|S_1\rangle$ to $|S_2\rangle$ when the transfer is from the bath to the system or from $|S_4\rangle$ to $|S_3\rangle$ when the transfer is from the system to the bath. The sum over all states and integration over the contour variable τ' are implied.

For future reference, we also define self-energy due to coupling to the thermal bath and the corresponding Green's

function of the free phonon in mode β of the thermal bath:

$$\begin{aligned}
 \Sigma_{S_1 S_2, S_3 S_4}^{\text{th}}(\tau, \tau') &= \sum_{\beta \in \text{th}} M_{S_1 S_2, \beta} h_\beta(\tau, \tau') M_{\beta, S_3 S_4}, \\
 h_\beta(\tau, \tau') &= -i \langle T_c \hat{b}_\beta(\tau) \hat{b}_\beta^\dagger(\tau') \rangle_0. \tag{12}
 \end{aligned}$$

We note in passing that in expressions above, only $G^<$ belongs to the physical subspace of the extended Hilbert space

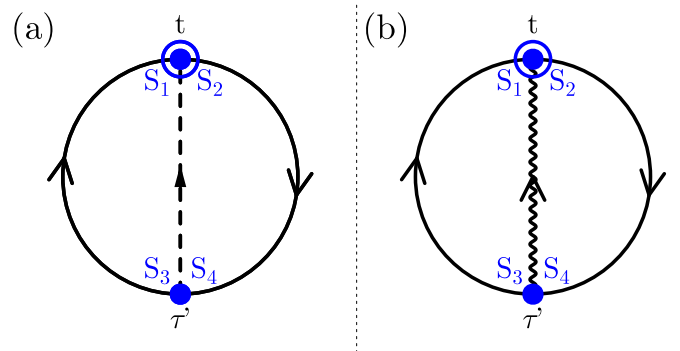


FIG. 3. Diagrams representing expressions for (a) electron and (b) photon fluxes [Eq. (9)]. The directed solid line represents the pseudoparticle Green's function (7). The dashed and wavy lines represent, respectively, self-energies due to coupling to contact K and radiation field [Eq. (10)]. t is the time of the flux. See text for additional explanations.

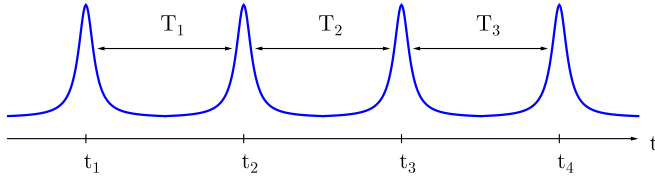


FIG. 4. Laser pulse sequence for the multidimensional spectroscopy.

(for more details see, e.g., Refs. [51,52]). Thus, in constructing diagrammatic expansions, one must evaluate both lesser and greater projections within the same order to get the result (flux) in the corresponding order of the expansion.

Another signal we present in simulations is two-dimensional spectroscopy of photon flux. Here, the radiation field is treated classically, and the flux characterizes the response of the molecular cavity system to a sequence of four laser pulses with time delays between them, T_1 , T_2 , and T_3 (the pulses themselves are assumed to be instantaneous in time). The signal is

$$S_p(T_1, T_2, T_3) = - \int_{-\infty}^{+\infty} dt I_p(t), \quad (13)$$

where $I_p(t)$ is defined in Eq. (9) and T_i ($i = 1, 2, 3$) are time delays between driving field pulses (see Fig. 4). The Fourier transform in T_1 and T_3 yields the system response in the two-dimensional spectroscopy:

$$S_p(\Omega_1, T_2, \Omega_3) = \text{Re} \int_0^\infty dT_1 \int_0^\infty dT_3 S_p(T_1, T_2, T_3) \times e^{i\Omega_1 T_1 + i\Omega_3 T_3}. \quad (14)$$

Explicit expressions are derived in Appendix B. We note that the PP-NEGF formulation produces an *energy-resolved* version of the conventional density matrix-based approach (see discussion in Appendix B for details).

The four most important differences between the traditional and new (Green's function-based) formulations are as follows:

(1) Traditional spectroscopy formulation destroys system-bath coherences at the time of the system's interaction with the radiation field, while suggested Green's function approaches preserve those coherences.

(2) Traditional spectroscopy does not account for all radiation field-induced interactions, while all the interactions are accounted for in the NEGF formulations.

(3) Photon and other (electron and energy) fluxes are treated as independent within the traditional formulation. This does not represent the actual physics correctly because photons, electrons, and intramolecular excitations participate in interactions that are common to all of them. Moreover, this leads to a violation of charge and energy conservation in the system. NEGF formulations account for the interdependence of all the fluxes by invoking the Luttinger-Ward functional as a starting point for the treatment of all the processes.

(4) Traditional spectroscopy is based on bare perturbation theory expansion in the light-matter interaction, which accounts for all diagrams, including the decoupled virtual processes. The latter are not relevant for the physics of the system.

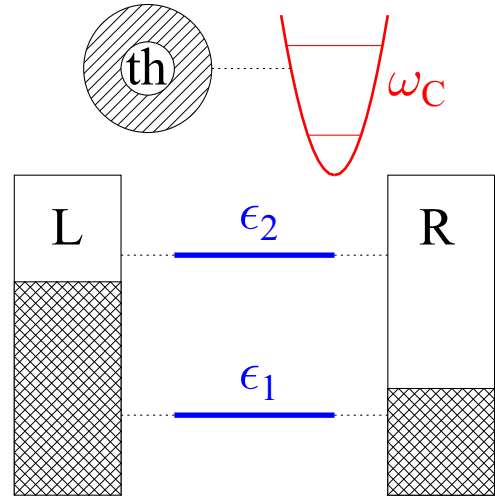


FIG. 5. Sketch of the molecular cavity model used in simulations of fluxes.

NEGF formulations disregard those irrelevant contributions (decoupled diagrams are dropped).

III. NUMERICAL EXAMPLES AND DISCUSSION

We now present two examples demonstrating the application of the PP-NEGF theory to the spectroscopy of molecular cavity systems. In the first example, we examine the impact of strong light-matter coupling on photon flux and electron current. The second example explores multidimensional optical spectroscopy.

A. Fluxes in molecular cavity system

For flux simulations, we utilize a HOMO-LUMO model to represent the molecule and a harmonic oscillator to depict the cavity mode (see Fig. 5). The second quantization forms of the Hamiltonians are

$$\hat{H}_M = \sum_{i=1,2} \varepsilon_i \hat{d}_i^\dagger \hat{d}_i, \quad \hat{H}_C = \omega_C \hat{c}^\dagger \hat{c}. \quad (15)$$

Connection to many-body state expressions of Eq. (2) is achieved through the spectral decomposition of the standard second quantization operators:

$$\begin{aligned} \hat{d}_i^\dagger &= \sum_{m_1, m_2} |m_2\rangle \langle m_2| \hat{d}_i^\dagger |m_1\rangle \langle m_1| \equiv \sum_{m_1, m_2} |m_2\rangle \xi_{m_2 m_1}^i \langle m_1|, \\ \hat{c}^\dagger &= \sum_{c_1, c_2} |c_2\rangle \langle c_2| \hat{c}^\dagger |c_1\rangle \langle c_1| \equiv \sum_{c_1, c_2} |c_2\rangle \eta_{c_2 c_1} \langle c_1|. \end{aligned} \quad (16)$$

The model introduces four electronic states $|m\rangle$:

$$\begin{aligned} |0\rangle &\equiv |0, 0\rangle, \quad |g\rangle \equiv |1, 0\rangle, \quad |e\rangle \equiv |0, 1\rangle, \quad \text{and} \\ |f\rangle &\equiv |1, 1\rangle, \end{aligned} \quad (17)$$

with energies 0, ε_1 , ε_2 , and $\varepsilon_1 + \varepsilon_2$, respectively.

Parameters of the simulations are (energies are in eV) $\varepsilon_1 = -1$, $\varepsilon_2 = 1$, and $\omega_C = 2$. Molecular coupling to the

cavity is

$$g_{m_1 m_2, c_1 c_2} = g_0 (\delta_{m_1, g} \delta_{m_2, x} + \delta_{m_1, x} \delta_{m_2, g}) \times (\sqrt{n_{c_1}} \delta_{n_{c_1}, n_{c_2}+1} + \sqrt{n_{c_2}} \delta_{n_{c_1}, n_{c_2}-1}), \quad (18)$$

with $g_0 = 1$. Interaction with the baths (contacts, thermal bath, and electromagnetic field) is characterized by corresponding escape rates (dissipation matrices):

$$\begin{aligned} \Gamma_{S_1 S_2, S_3 S_4}^K(E) &\equiv 2\pi \sum_{k \in K} V_{S_1 S_2, k} V_{k, S_3 S_4} \delta(E - \varepsilon_k), \\ \gamma_{c_1 c_2, c_3 c_4}^{\text{th}}(\omega) &\equiv 2\pi \sum_{\beta \in \text{th}} M_{c_1 c_2, \beta} M_{\beta, c_3 c_4} \delta(\omega - \omega_\beta), \\ \gamma_{c_1 c_2, c_3 c_4}^{\text{rad}}(\omega) &\equiv 2\pi \sum_{\alpha \in \text{rad}} U_{c_1 c_2, \alpha} U_{\alpha, c_3 c_4} \delta(\omega - \omega_\alpha). \end{aligned} \quad (19)$$

For electronic levels, we assume the wide band approximation and take escape rates from levels 1 and 2 to be the same and equal into both contacts, $\Gamma = 0.005$. Cavity escape rates into thermal and radiation baths are assumed to be

$$\gamma(\omega) = \gamma_0 (\omega/\omega_0)^2 e^{-\omega/\omega_0}, \quad (20)$$

with $\gamma_0 = 0.02$ and $\omega_0 = 2$. For parameter values considered, the photon number basis up to five photons is enough to describe the cavity mode. Contacts and the thermal bath are in thermal equilibrium: Fermi-Dirac and Bose-Einstein distributions, respectively. The electromagnetic field is assumed to be an empty continuum of modes. The Fermi energy is taken as the origin, $E_F = 0$, and bias V_{sd} is applied to the left contact (STM-type situation), resulting in $\mu_L = E_F + eV_{sd}$ and $\mu_R = E_F$. Calculations are carried out at room temperature, $T = 300$ K, and in a steady-state regime. They are performed on energy grid spanning the range from -10 to 10 with step 10^{-4} .

Figure 6 shows photon, $A_C(E)$, and electron, $A_i(E)$ ($i = 1, 2$), spectral functions inside and outside of the cavity. Their expressions are given by:

$$\begin{aligned} A_C(E) &= \sum_{S_1, S_2, S_3, S_4} \zeta_{S_1} \eta_{S_2 S_1} \eta_{S_4 S_3}^* \int \frac{d\epsilon}{2\pi} \\ &\times [G_{S_1 S_3}^>(\epsilon) G_{S_4 S_2}^<(E + \epsilon) - G_{S_1 S_3}^<(\epsilon) G_{S_4 S_2}^>(E + \epsilon)], \\ A_i(E) &= \sum_{S_1, S_2, S_3, S_4} \zeta_{S_1} \xi_{S_2 S_1}^i [\xi_{S_4 S_3}^i]^* \int \frac{d\epsilon}{2\pi} \\ &\times [G_{S_1 S_3}^>(\epsilon) G_{S_4 S_2}^<(E + \epsilon) - G_{S_1 S_3}^<(\epsilon) G_{S_4 S_2}^>(E + \epsilon)]. \end{aligned} \quad (21)$$

Strong interaction between molecular excitation and the cavity creates mixed light-matter states known as polaritons. The formation of these states is characterized by an experimentally measurable cavity spectral function (photon spectrum), as shown in Fig. 6(a). Intracavity interaction modifies the single peak in the photon spectrum at the cavity mode frequency into a more complex structure. It is important to note that the simple picture of a two-level system representing the cavity mode [see inset in Fig. 6(a)], which predicts two polaritons (lower and upper), breaks down due to the presence of multiple cavity mode states and various charging states of the molecule. Note that the asymmetry of the polariton peaks

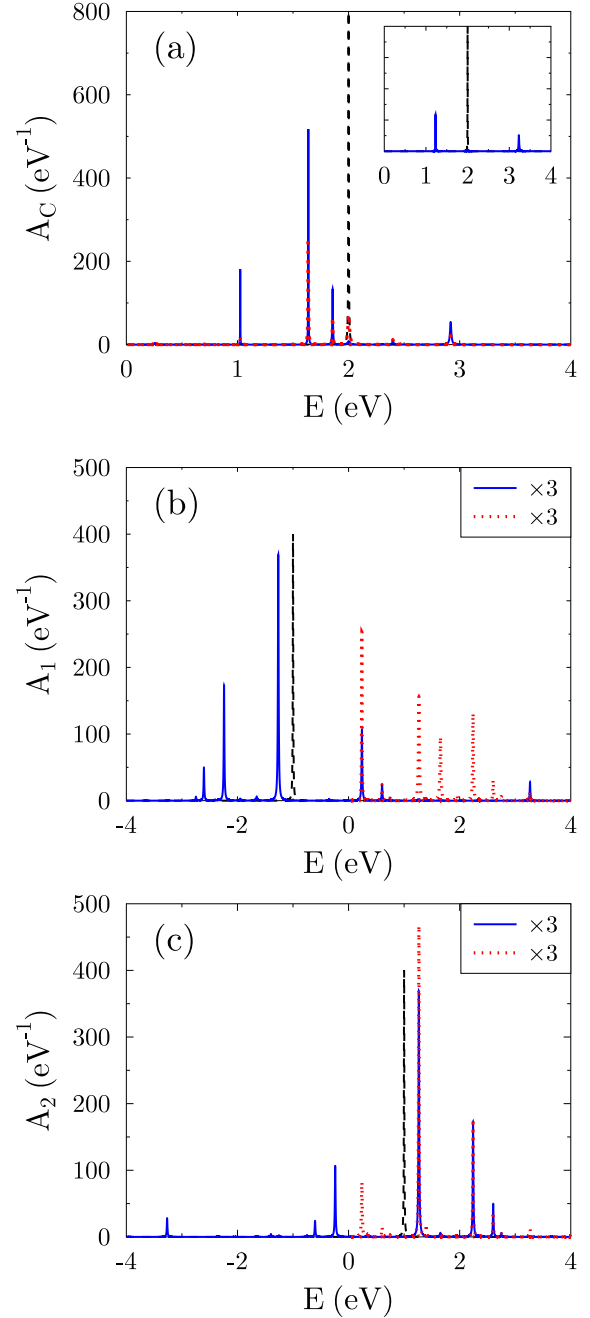


FIG. 6. Spectral functions inside (solid line, blue and dotted line, red) and outside (dashed line, black) of the cavity at $V_{sd} = 0$ (solid line, blue) and $V_{sd} = 1.5$ (dotted line, red). Shown are (a) cavity A_C , (b) electron HOMO A_1 , and (c) electron LUMO A_2 level spectral functions. In panels (b) and (c), density of states is scaled by factor of 3. Inset in panel (a) shows results of calculation performed with only two lowest states of the oscillator representing the cavity mode.

relative to the cavity mode frequency shown in the inset is due to ultrastrong molecule-cavity coupling treated beyond the RWA. This interaction also induced changes in spectral functions of electronic levels [measurable as conductances—see Figs. 6(b) and 6(c)]. The emergence of additional peaks signifies the opening of new channels that influence electron current through the junction. The effect of bias (dotted red line) manifests in the population of excited states and the

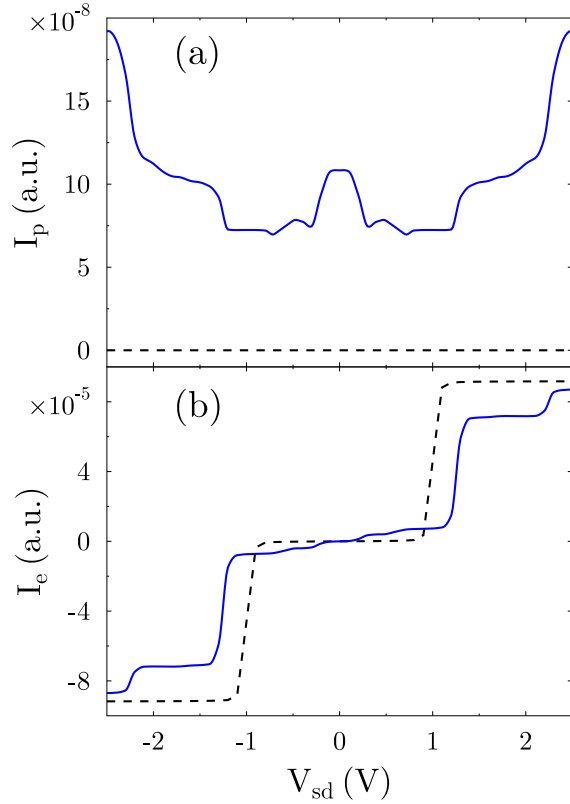


FIG. 7. Fluxes inside (solid line, blue) and outside (dashed line, black) of the cavity. Shown are (a) photon I_p and (b) electron $I_e \equiv I_e^L = -I_e^R$ fluxes.

depletion of the ground state due to coupling with contacts, resulting in a redistribution of intensity among the channels and the opening of new channels.

Figure 7 illustrates photon and electron fluxes. Intracavity interaction induces a photon flux that is negligible in the case of a decoupled cavity mode, when the only cause of the flux is excitations in the thermal bath [see 7(a)], and modifies the electric current [see 7(b)]. It is important to note that the latter may either increase or decrease as compared to the situation in the absence of the coupling to the cavity mode, depending on the position and strength of additional peaks in the spectral function, interference between tunneling channels, and the bias profile in the junction. The value of intracavity coupling used in the simulation is representative of many-molecule junctions. The effect on the electronic spectral function in a single-molecule junction will be much weaker. Therefore, for a single molecule in a cavity, the impact of strong coupling on the flux is likely to be measurable only when new resonances play a critical role in transport. For instance, this is relevant in semiconductor leads where a cutoff (band gap) in allowed transmission channels exists in the system.

B. Multidimensional optical spectroscopy

Multidimensional optical spectroscopy describes how a system responds to a sequence of laser pulses, with the radiation field treated classically. Under the rotating wave

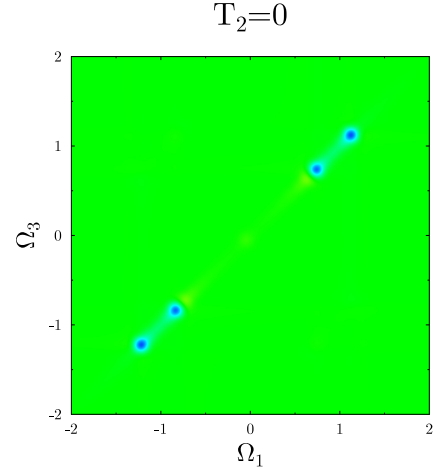


FIG. 8. Multidimensional signal $S_p(\Omega_1, T_2, \Omega_3)$ [Eq. (14)] for the two-level model employed in obtaining inset in Fig. 6(a). The calculation is performed for $T_2 = 0$ and $V_{sd} = 0$.

approximation, the interaction with the radiation field is

$$\hat{V}_{C,\text{rad}}(t) = \sum_{c_1, c_2} (\mathcal{V}_{c_1 c_2} \mathcal{E}^*(t) |c_1\rangle \langle c_2| + \mathcal{V}_{c_1 c_2}^* \mathcal{E}(t) |c_2\rangle \langle c_1|), \quad (22)$$

where $E_{c_1} < E_{c_2}$ and $\mathcal{E}$ ($\mathcal{E}^*$) is the positive (negative) frequency component of the radiation field. An explicit expression of the signal is derived in Appendix B, Eq. (B9).

We start by presenting results for a simplified model with only the two lowest states of the oscillator representing the cavity mode. This model was employed in spectral function simulations shown in the inset of Fig. 6(a). Figure 8 shows

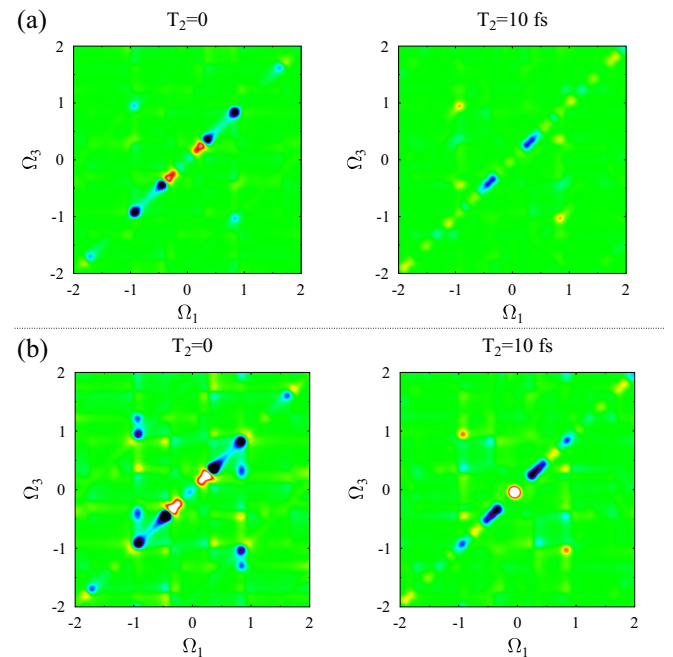


FIG. 9. Multidimensional signal $S_p(\Omega_1, T_2, \Omega_3)$ [Eq. (14)] for $T_2 = 0$ and 10 fs. Shown are results for (a) $V_{sd} = 0$ and (b) $V_{sd} = 1.5$ eV.

a two-dimensional signal for the model. As expected, on the diagonal (i.e., $\Omega_1 = \Omega_3$) we see peaks corresponding to the lower and upper polaritons. Contrary to a more complicated (more realistic—see discussion below) modeling, there are no coherences (off-diagonal peaks) in this simple model.

Figure 9 presents the multidimensional optical spectroscopy signal for a molecular cavity in an unbiased [Fig. 9(a)] and a biased [Fig. 9(b)] junction. The primary distinction between the two scenarios lies in the population of many-body states. When bias is applied, the excited states of the system become populated, leading to an increase in number of optical transitions probed by the laser excitations. Consequently, a greater number of coherences between the transitions are observed. The delay T_2 between the pump and probe reveals the evolution of the system's excitations, allowing us to estimate the coherence lifetime. The latter is defined by dephasing rate γ , Eq. (20), taken at the frequency of the transition. Note that symmetry to diagonal in Fig. 9 is due to equality $S(\Omega_1, T_2, \Omega_3) = S(-\Omega_1, T_2, -\Omega_3)$ [see Eq. (14)].

IV. CONCLUSIONS

Experimental advances in cavity spectroscopy have led to the emergence of the field of molecular polaritonics. Cavity confinement enhances the strength of light-matter interaction, which influences electron and energy transfers, nuclear dynamics, and chemistry, thereby providing a means to control the response of the molecular system. To further increase the coupling strength between molecular excitations and the cavity mode, the vast majority of experiments conducted thus far have focused on many-molecule samples, although the initial results on single-molecule spectroscopy in plasmonic nanocavities have been documented in the literature. Almost all experimental measurements to date have concentrated exclusively on the optical response (photon flux) of molecular cavity systems. However, the STM setup used in single-molecule nanocavity experiments indicates that simultaneous measurement of the optical signal (photon flux) and current (electron flux) in such systems is the next logical step.

We consider an open molecular cavity system with strong coupling between molecular excitations and the cavity mode. Photon flux (the signal typically measured in experiments) and electron (the signal yet to be measured in molecular cavity systems) are treated within the PP-NEGF approach. This extends our recent NEGF formulation for nonlinear optical spectroscopy [44] to the case of strongly interacting systems. The theoretical formulation is illustrated with numerical simulations using a molecular cavity model. Within this model, we simulate electron and photon fluxes and demonstrate that even ultrastrong coupling (experimentally realized in many-molecule samples) leads to relatively small changes in electron flux. Thus, the observation of the coupling's effect on current in single-molecule nanocavity systems may only be measurable when new (interaction-induced) spectral density resonances play a critical role in transport, opening tunneling channels that would otherwise be blocked by, for example, the band gap in semiconductor leads. We show that the simple picture of upper and lower polaritons, frequently used in

theoretical considerations (e.g., within the Jaynes-Cummings model), breaks down in the more general case of an open molecular nanocavity system due to the presence of multiple optical transitions and several charging states of the molecule. In addition to the fluxes, we also simulated a two-dimensional optical spectroscopy signal. We show that in the presence of bias, the signal provides a richer picture of excitations and coherences due to the bias-induced population of molecular excited states.

Our study extends the theory of nonlinear optical spectroscopy to strongly interacting open nonequilibrium molecular systems. It provides a theoretical tool for the analysis of what we hope will be, similar to electroluminescence and Raman spectroscopy studies, soon-to-be-available experimental measurements in current-carrying molecular polaritonic systems.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are openly available [53].

APPENDIX A: PP-NEGF EXPRESSIONS FOR PHOTON AND ELECTRON FLUXES

Derivation of expressions for fluxes within the PP-NEGF closely follows the derivation of electron flux within the standard NEGF [54]. Electron and photon fluxes are defined as rates of change of populations in corresponding baths:

$$\begin{aligned} I_e^K(t) &\equiv -\sum_{k \in K} \frac{d}{dt} \langle \hat{c}_k^\dagger(t) \hat{c}_k(t) \rangle, \\ I_p(t) &\equiv -\sum_{\alpha \in \text{rad}} \frac{d}{dt} \langle \hat{a}_\alpha^\dagger(t) \hat{a}_\alpha(t) \rangle, \end{aligned} \quad (\text{A1})$$

where, by agreement, positive flux corresponds to flow into the system. For Hamiltonian (1)–(4), this leads to

$$\begin{aligned} I_e^K(t) &= -2 \text{Re} \sum_{k \in K} \sum_{m_1, m_2 \in M} V_{m_1 m_2, k} G_{k, m_1 m_2}^<(t, t), \\ I_p(t) &= 2 \text{Re} \sum_{\alpha \in \text{rad}} \sum_{c_1, c_2} U_{c_1 c_2, \alpha} G_{\alpha, c_1 c_2}^<(t, t). \end{aligned} \quad (\text{A2})$$

To find lesser projections of Green's functions on the right-hand sides of the expressions, we consider their definitions on the Keldysh contour:

$$\begin{aligned} G_{k, m_1 m_2}(\tau_1, \tau_2) &\equiv -i \langle T_c \hat{c}_k(\tau_1) \hat{p}_{m_1}^\dagger(\tau_2) \hat{p}_{m_2}(\tau_2) \rangle, \\ G_{\alpha, c_1 c_2}(\tau_1, \tau_2) &\equiv -i \langle T_c \hat{a}_\alpha(\tau_1) \hat{p}_{c_1}^\dagger(\tau_2) \hat{p}_{c_2}(\tau_2) \rangle, \end{aligned} \quad (\text{A3})$$

and use equations of motion to derive

$$G_{k,m_1m_2}(\tau_1, \tau_2) = \sum_{m_3m_4} \int d\tau' g_k(\tau_1, \tau') V_{k,m_3m_4} G_{m_3m_4,m_1m_2}(\tau', \tau_2),$$

$$G_{\alpha,c_1c_2}(\tau_1, \tau_2) = \sum_{c_3,c_4} \int d\tau' f_\alpha(\tau_1, \tau') U_{\alpha,c_3c_4} G_{c_3c_4,c_1c_2}(\tau', \tau_2), \quad (\text{A4})$$

where g_k and f_α are defined in Eq. (11) and

$$G_{m_3m_4,m_1m_2}(\tau', \tau_2) \equiv -i \langle T_c \hat{p}_{m_3}^\dagger(\tau') \hat{p}_{m_4}(\tau') \hat{p}_{m_2}^\dagger(\tau_2) \hat{p}_{m_1}(\tau_2) \rangle,$$

$$G_{c_3c_4,c_1c_2}(\tau', \tau_2) \equiv -i \langle T_c \hat{p}_{c_3}^\dagger(\tau') \hat{p}_{c_4}(\tau') \hat{p}_{c_2}^\dagger(\tau_2) \hat{p}_{c_1}(\tau_2) \rangle. \quad (\text{A5})$$

Taking lesser projection of Eq. (A4) at $t_1 = t_2 \equiv t$ and substituting it into Eq. (A2) leads to

$$I_e^K(t) = 2 \text{Re} \int_{-\infty}^t dt' \sum_{m_1,m_2,m_3,m_4} (\Sigma_{m_1m_2,m_3m_4}^{K<}(t, t') G_{m_3m_4,m_1m_2}^>(t', t) - \Sigma_{m_1m_2,m_3m_4}^{K>}(t, t') G_{m_3m_4,m_1m_2}^{<}(t', t)),$$

$$I_p(t) = -2 \text{Re} \int_{-\infty}^t dt' \sum_{c_1,c_2,c_3,c_4} (\Sigma_{c_1c_2,c_3c_4}^{\text{rad}<}(t, t') G_{c_3c_4,c_1c_2}^>(t', t) - \Sigma_{c_1c_2,c_3c_4}^{\text{rad}>}(t, t') G_{c_3c_4,c_1c_2}^{<}(t', t)), \quad (\text{A6})$$

where self-energies are defined in Eq. (10).

Finally, taking into account that Green's functions are evaluated within the noncrossing approximation, we can express two-particle correlation functions (A5) in terms of single-particle Green's functions

$$G_{m_3m_4,m_1m_2}(\tau', \tau) = i\zeta_{m_1} G_{m_1m_3}(\tau, \tau') G_{m_2m_4}(\tau', \tau),$$

$$G_{c_3c_4,c_1c_2}(\tau', \tau) = i\zeta_{c_1} G_{c_1c_3}(\tau, \tau') G_{c_2c_4}(\tau', \tau). \quad (\text{A7})$$

Note that in the case of Eq. (A6), $\zeta_{m_1} = -1$ and $\zeta_{c_1} = +1$, because transitions describing electron flux are of Fermi type, while those describing photon flux are of Bose type. Substituting Eq. (A7) into Eq. (A6) leads to Eq. (9).

APPENDIX B: EXPRESSION FOR MULTIDIMENSIONAL SIGNAL

Derivation of the multidimensional signal is based on fourth order in light-matter interaction expression for photon flux. For simplicity, we exclude crossing diagrams similar to those shown in panels (f) and (g) of Fig. 2. Note that in multidimensional spectroscopy, radiation field is treated classically; thus, diagrams shown in panels (d) and (e) of Fig. 2 are not distinguishable.

Fourth order in light-matter interaction contribution to photon flux $I_p(t)$, Eq. (9), requires evaluation of Green's function (7) taking into account only second-order self-energy diagram provided by the functional shown in panel (a) of Fig. 2, because two orders of light-matter interaction are already taken into account in self-energies entering the expression for the flux. On the contour, diagrammatic expansion yields

$$I_p^{(4)}(t_4) = -\text{Re} \sum_{\{S_i^j\}} \int_c d\tau_1 \int_c d\tau_2 \int_c d\tau_3$$

$$\times \mathcal{E}^*(t_4) \mathcal{E}(t_3) \mathcal{E}^*(t_2) \mathcal{E}(t_1) \mathcal{V}_{S_1^4 S_2^4} \mathcal{V}_{S_3^4 S_2^4}^* \mathcal{V}_{S_1^2 S_2^2}^* \mathcal{V}_{S_1^1 S_2^1}^*$$

$$\times \langle T_c \hat{p}_{S_1^4}^\dagger(t_4) \hat{p}_{S_2^4}(t_4) \hat{p}_{S_2^2}^\dagger(\tau_3) \hat{p}_{S_1^2}(\tau_3)$$

$$\times \hat{p}_{S_2^1}^\dagger(\tau_2) \hat{p}_{S_2^1}(\tau_2) \hat{p}_{S_1^1}^\dagger(\tau_1) \hat{p}_{S_1^1}(\tau_1) \rangle, \quad (\text{B1})$$

where lesser and greater contributions in Eq. (9) were written as contour integration, S_i^j indicates state $|S_i\rangle$ at time t_j , t was substituted with t_4 , and t' was substituted with τ_3 . In addition, Green's function was replaced by explicit multitime correlation expression of the pseudoparticle operators and self-energy was rewritten for a classical radiation field using

$$\Sigma_{S_1 S_2, S_3 S_4}^{\text{rad} \geq}(t, t') \rightarrow -i \mathcal{E}(t) \mathcal{E}^*(t') \mathcal{V}_{S_1 S_2}^* \mathcal{V}_{S_3 S_4}. \quad (\text{B2})$$

Deriving an expression for the signal, we must keep in mind the ordered sequence of four pulses:

$$t_4 > t_3 > t_2 > t_1. \quad (\text{B3})$$

This restricts consideration to projections shown in Fig. 10. In the expressions below we use lesser, retarded, and advanced projections of the Green's function (7) employing the following relations specific for the PP-NEGF:

$$G_{S_1 S_2}^r(t_1, t_2) = \theta(t_1 - t_2) G_{S_1 S_2}^>(t_1, t_2),$$

$$G_{S_1 S_2}^a(t_1, t_2) = -\theta(t_2 - t_1) G_{S_1 S_2}^>(t_1, t_2), \quad (\text{B4})$$

where $\theta(x)$ is the Heaviside step function. In addition, for the lesser projection, we distinguish positive and negative time contributions

$$G_{S_1 S_2}^{<}(t_1, t_2) = \theta(t_1 - t_2) G_{S_1 S_2}^{<+}(t_1, t_2) + \theta(t_2 - t_1) G_{S_1 S_2}^{<-}(t_1, t_2)$$

$$\equiv G_{S_1 S_2}^{<+}(t_1, t_2) + G_{S_1 S_2}^{<-}(t_1, t_2). \quad (\text{B5})$$

For simplicity, we assume infinitely narrow pulses (pulse acts at a particular time only), then

$$\mathcal{E}(t) = \mathcal{E}_i e^{-i\omega_i t_i} \delta(t - t_i), \quad (\text{B6})$$

and the integral over the corresponding time can be disregarded.

Derivation of the photon signal S_p starts from identification of correspondence between contour variables τ_i and times of pulses t_i . Note that we have freedom in identification only in correspondence between τ_1 , τ_3 and t_1 , t_3 , because t_4 is fixed

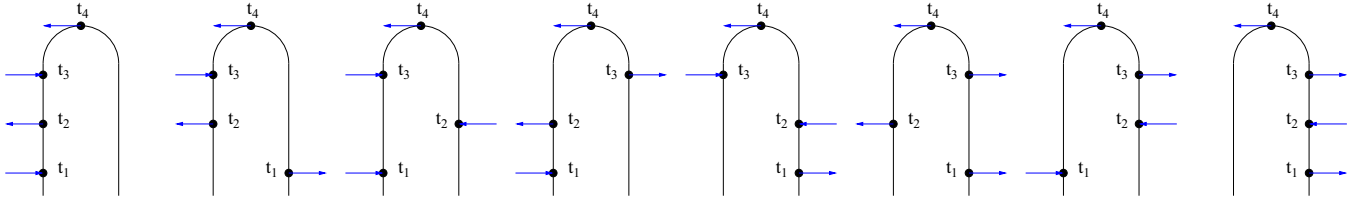


FIG. 10. Projections on the Keldysh contour contributing to S_p signal. Times t_1 , t_2 , t_3 , and t_4 correspond to times of four pulses. In addition, t_4 indicates the time of the photon flux.

by time of the flux. Thus, we assign τ_1 to t_1 and τ_3 to t_3 and account for factor of 2 in the expression. Using projections shown in Fig. 10 in Eq. (B1) results in eight contributions to the multidimensional signal (13):

$$\begin{aligned}
 S_p(T_1, T_2, T_3) = & 2 \operatorname{Re}(\mathcal{E}_4^* \mathcal{E}_3 \mathcal{E}_2^* \mathcal{E}_1 e^{iT_1 \omega_1 + iT_2(\omega_1 - \omega_2) + iT_3 \omega_4} \operatorname{Tr}[\zeta G^{<-}(-T_1 - T_2 - T_3) \mathcal{V} G^r(T_3) \mathcal{V}^\dagger G^r(T_2) \mathcal{V} G^r(T_1) \mathcal{V}^\dagger \\
 & + \zeta G^{<+}(T_1 + T_2 + T_3) \mathcal{V}^\dagger G^a(-T_1) \mathcal{V} G^a(-T_2) \mathcal{V}^\dagger G^a(-T_3) \mathcal{V} + \zeta G^{<-}(-T_1) \mathcal{V} G^a(-T_2) \mathcal{V}^\dagger G^a(-T_3) \mathcal{V} G^r \\
 & \times (T_1 + T_2 + T_3) \mathcal{V}^\dagger + \zeta G^{<+}(T_1) \mathcal{V}^\dagger G^a(-T_1 - T_2 - T_3) \mathcal{V} G^r(T_3) \mathcal{V}^\dagger G^r(T_2) \mathcal{V} + \zeta G^{<-}(-T_1) \\
 & \times \mathcal{V} G^a(-T_2 - T_3) \mathcal{V} G^r(T_3) \mathcal{V}^\dagger G^r(T_1 + T_2) \mathcal{V}^\dagger + \zeta G^{<+}(T_1) \mathcal{V}^\dagger G^a(-T_1 - T_2) \mathcal{V}^\dagger G^a(-T_3) \mathcal{V} G^r(T_2 + T_3) \mathcal{V} \\
 & + \zeta G^{<-}(-T_1 - T_2) \mathcal{V}^\dagger G^a(-T_3) \mathcal{V} G^r(T_2 + T_3) \mathcal{V} G^r(T_1) \mathcal{V}^\dagger + \zeta G^{<+}(T_1 + T_2) \mathcal{V}^\dagger G^a(-T_1) \\
 & \times \mathcal{V} G^a(-T_2 - T_3) \mathcal{V} G^r(T_3) \mathcal{V}^\dagger]).
 \end{aligned} \quad (\text{B7})$$

Here,

$$T_3 = t_4 - t_3, \quad T_2 = t_3 - t_2, \quad T_1 = t_2 - t_1 \quad (\text{B8})$$

are time delays between the pulses. Substituting Eq. (B7) into Eq. (14) leads to

$$\begin{aligned}
 S_p(\Omega_1, T_2, \Omega_3) = & \int \frac{d\epsilon_1}{2\pi} \int \frac{d\epsilon_2}{2\pi} \\
 & (\mathcal{E}_4^* \mathcal{E}_3 \mathcal{E}_2^* \mathcal{E}_1 e^{iT_2(\omega_1 - \omega_2 + \epsilon_1 - \epsilon_2)} \\
 & \operatorname{Tr}[\zeta G^{<-}(\epsilon_1) \mathcal{V} G^r(\epsilon_1 + E_3) \mathcal{V}^\dagger G^r(\epsilon_2) \mathcal{V} G^r(\epsilon_1 + E_1) \mathcal{V}^\dagger + \zeta G^{<+}(\epsilon_2) \mathcal{V}^\dagger G^a(\epsilon_2 - E_1) \mathcal{V} G^a(\epsilon_1) \mathcal{V}^\dagger G^a(\epsilon_2 - E_3) \mathcal{V} \\
 & + \zeta G^{<-}(\epsilon_2 - E_1) \mathcal{V} G^a(\epsilon_1) \mathcal{V}^\dagger G^a(\epsilon_2 - E_3) \mathcal{V} G^r(\epsilon_2) \mathcal{V}^\dagger + \zeta G^{<+}(\epsilon_1 + E_1) \mathcal{V}^\dagger G^a(\epsilon_1) \mathcal{V} G^r(\epsilon_1 + E_3) \mathcal{V}^\dagger G^r(\epsilon_2) \mathcal{V} \\
 & + \zeta G^{<-}(\epsilon_2 - E_1) \mathcal{V} G^a(\epsilon_1) \mathcal{V} G^r(\epsilon_1 + E_3) \mathcal{V}^\dagger G^r(\epsilon_2) \mathcal{V}^\dagger + \zeta G^{<+}(\epsilon_1 + E_1) \mathcal{V}^\dagger G^a(\epsilon_1) \mathcal{V}^\dagger G^a(\epsilon_2 - E_3) \mathcal{V} G^r(\epsilon_2) \mathcal{V} \\
 & + \zeta G^{<-}(\epsilon_1) \mathcal{V}^\dagger G^a(\epsilon_2 - E_3) \mathcal{V} G^r(\epsilon_2) \mathcal{V} G^r(\epsilon_1 + E_1) \mathcal{V}^\dagger + \zeta G^{<+}(\epsilon_2) \mathcal{V}^\dagger G^a(\epsilon_2 - E_1) \mathcal{V} G^a(\epsilon_1) \mathcal{V} G^r(\epsilon_1 + E_3) \mathcal{V}^\dagger] \\
 & - \mathcal{E}_4 \mathcal{E}_3^* \mathcal{E}_2 \mathcal{E}_1^* e^{-iT_2(\omega_1 - \omega_2 + \epsilon_1 - \epsilon_2)} \\
 & \operatorname{Tr}[\mathcal{V} G^a(\epsilon_1 - W_1) \mathcal{V}^\dagger G^a(\epsilon_2) \mathcal{V} G^a(\epsilon_1 - W_3) \mathcal{V}^\dagger \zeta G^{<+}(\epsilon_1) + \mathcal{V}^\dagger G^r(\epsilon_2 + W_3) \mathcal{V} G^r(\epsilon_1) \mathcal{V}^\dagger G^r(\epsilon_2 + W_1) \mathcal{V} \zeta G^{<-}(\epsilon_2) \\
 & + \mathcal{V} G^a(\epsilon_2) \mathcal{V}^\dagger G^r(\epsilon_2 + W_3) \mathcal{V} G^r(\epsilon_1) \mathcal{V}^\dagger \zeta G^{<+}(\epsilon_2 + W_1) + \mathcal{V}^\dagger G^a(\epsilon_2) \mathcal{V} G^a(\epsilon_1 - W_3) \mathcal{V}^\dagger G^r(\epsilon_1) \mathcal{V} \zeta G^{<-}(\epsilon_1 - W_1) \\
 & + \mathcal{V} G^a(\epsilon_2) \mathcal{V} G^a(\epsilon_1 - W_3) \mathcal{V}^\dagger G^r(\epsilon_1) \mathcal{V}^\dagger \zeta G^{<+}(\epsilon_2 + W_1) + \mathcal{V}^\dagger G^a(\epsilon_2) \mathcal{V}^\dagger G^r(\epsilon_2 + W_3) \mathcal{V} G^r(\epsilon_1) \mathcal{V} \zeta G^{<-}(\epsilon_1 - W_1) \\
 & + \mathcal{V} G^a(\epsilon_1 - W_1) \mathcal{V}^\dagger G^a(\epsilon_2) \mathcal{V}^\dagger G^r(\epsilon_2 + W_3) \mathcal{V} \zeta G^{<+}(\epsilon_1) + \mathcal{V} G^a(\epsilon_1 - W_3) \mathcal{V}^\dagger G^r(\epsilon_1) \mathcal{V}^\dagger G^r(\epsilon_2 + W_1) \mathcal{V} \zeta G^{<-}(\epsilon_2)]).
 \end{aligned} \quad (\text{B10})$$

Here,

$$E_1 \equiv \Omega_1 + \omega_1, \quad E_3 \equiv \Omega_3 + \omega_4, \quad W_1 \equiv \Omega_1 - \omega_1, \quad W_3 \equiv \Omega_3 - \omega_4. \quad (\text{B11})$$

We note that the frequencies Ω_1 and Ω_3 in these expressions are given relative to the pulses' central frequencies.

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