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# Photonics and Spectroscopy in Nanojunctions: A Theoretical Insight

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## Abstract

Progress of experimental techniques at nanoscale in the last decade made optical measurements in current-carrying nanojunctions a reality thus indicating emergence of a new field of research coined as optoelectronics. Optical spectroscopy of open nonequilibrium systems is a natural meeting point for (at least) two research areas: nonlinear optical spectroscopy and quantum transport, each with its own theoretical toolbox. We review recent progress in the field comparing theoretical treatments of optical response in nanojunctions as is accepted in nonlinear spectroscopy and quantum transport communities. A unified theoretical description of spectroscopy in nanojunctions is presented. We argue that theoretical approaches of the quantum transport community (and in particular, the Green function based considerations) yield a convenient tool for optoelectronics when radiation field is treated classically, and that differences between the toolboxes may become critical when studying quantum radiation field in junctions.

## 1 Introduction

Optical spectroscopy is an important diagnostic tool routinely applied to study molecules (either in gas, or condensed phases, or adsorbed on surfaces). In nanojunctions spectroscopic applications range from characterization of molecular structures and junction interfaces, to introducing nanoscale thermometry, to inducing and controlling molecular dynamics and chemistry. Wide range of spectroscopic techniques is utilized in the studies including (to name a few) infrared,<sup>1-4</sup> X-ray,<sup>5,6</sup> sum frequency generation (SFG),<sup>7-10</sup> as well as surface (SERS)<sup>11-15</sup> and tip-enhanced (TERS)<sup>16-22</sup> Raman spectroscopies.

In recent years optical experiments in current-carrying single-molecule junctions became a reality.<sup>23-30</sup> Combination of the fields of optical spectroscopy and molecular electronics indicates emergence of a new field of research, coined

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molecular optoelectronics.<sup>31</sup> In particular, multiple experiments reported detection of current-induced photon emission (electroluminescence).<sup>32–51</sup> Among them vibrationally<sup>39,50</sup> and spatially<sup>42</sup> resolved photo-emission, electroluminescence as a measure of multi-electron processes<sup>41,43,46,49</sup> and noise<sup>44–46</sup> in junctions, as well as indicator of vibronic motion<sup>48</sup> and real space energy transfer<sup>51</sup> were reported. Alternatively, external illumination was utilized as means to control electron transfer and transport.<sup>52–62</sup> Measurements of light induced magnetization in chiral molecules were also reported in the literature.<sup>63–68</sup>

For molecules chemisorbed on metallic surfaces or encapsulated in nanocavities molecular excitations are coupled with plasmons. This interaction leads to enhancement of molecular signal,<sup>69–72</sup> which yields possibility to measure optical response of single molecule.<sup>73–76</sup> Thus engineering effective plasmonic structures is crucially important, and nanoplasmonics becomes an inherent part in construction and operation of any molecular optoelectronic device.<sup>3,40,43,45,57,58,77–86</sup> Note that while usually construction of nanometer scale gaps is the way to form areas of high electromagnetic field (hot spots),<sup>77</sup> possibility of surface enhanced spectroscopy without nanogaps was also reported.<sup>82</sup>

As already mentioned surface enhanced Raman (SERS)<sup>87–90</sup> and tip-enhanced Raman (TERS)<sup>91,92</sup> spectroscopies are utilized as indicators of structural changes and dynamics in junctions. Simultaneous measurements of SERS and conductivity<sup>93–101</sup> provide information on dynamical correlations between the two signals<sup>95,102</sup> and current-induced heating,<sup>94,96</sup> and characterize charging states of molecules in junctions.<sup>99,101,103</sup>

While initially most of optical experiments in junctions were focused on steady-state response, lately time-dependent and transient characteristics started to attract attention. Optical pump-probe type measurements in junctions were realized in the form of time-dependent voltage induced plasmonic luminescence.<sup>47</sup> Laser pulse induced transport measurements as a tool to assess the intramolecular dynamics on a sub-picosecond time scale was also suggested.<sup>104,105</sup> Recently multidimensional spectroscopy measurements in presence of current (although not yet in junctions) were reported in the literature.<sup>106–108</sup>

Quantum effects in light-matter interactions is another recent development. For example, quantum effects in nanoplasmonics (such as transition of entanglement between photons and plasmons) recently started to attract attention indicating emergence of quantum plasmonics as new field of research.<sup>109–121</sup> Similarly, strong light-molecule coupling in nanocavities,<sup>122–126</sup> when states of light and matter cannot be separately distinguished and a hybrid state (polariton) is formed, reveals quantum nature of external electromagnetic field. Finally, very recently ultra-strong coupling regime (the regime where the coupling between light and matter becomes the largest energy scale in the system) was achieved experimentally.<sup>127</sup>

Experimental advancements in nanojunction spectroscopy posed a challenge for adequate theoretical description.<sup>31,128,129</sup> In particular, these advancements resulted in necessity to combine theoretical tools of optical spectroscopy with those of quantum transport. Corresponding formulations were developed and applied to description of absorption and current-induced light emission,<sup>51,130–143</sup>

as well as light-induced current in junctions.<sup>60,104,105,130,144–150</sup> In these studies light-matter interaction mostly was treated combining classical electrodynamics of radiation field with quantum mechanical description of the molecule.<sup>129,150–162</sup> Similarly, theoretical approaches to (yet to be measured in junctions) multidimensional spectroscopy were proposed.<sup>108,163–166</sup>

Significant theoretical efforts were devoted to development of theory of Raman spectroscopy in current-carrying junctions<sup>167–172</sup> and its application to modeling of current induced heating,<sup>103,167,168,173,174</sup> dynamics and conformational changes,<sup>84,175,176</sup> chemistry,<sup>177</sup> control of charging states of the molecule,<sup>99,101,103,178</sup> study of time-dependent correlations between conductance and Raman,<sup>179–181</sup> and elucidation of chemical enhancement in SERS.<sup>102,179,180,182–186</sup> Here radiation field was mostly treated quantum mechanically. Also strong light-matter (plasmon-molecule) couplings were treated theoretically with radiation field described quantum mechanically.<sup>165,187–199</sup> Finally, quantum treatment of the field was required to describe optically measured noise characteristics of junctions.<sup>200,201</sup> Quantum effects in photonics and optical spectroscopy were discussed in recent reviews.<sup>202,203</sup>

From theoretical perspective optical spectroscopy in nanojunctions (optoelectronics) is a field where theoretical approaches of nonlinear optical spectroscopy meet those of quantum transport theory. Theoretical toolboxes of the two research communities are slightly different and sometimes also utilize a bit different language. For example, traditionally optical spectroscopy relies on bare perturbation theory (PT) in the Liouville space for classification of optical response of isolated molecular systems. Transitions in the latter are considered in the basis of many-body states of the molecule. This type of treatment became standard in the spectroscopy community. Naturally, this same approach is sometimes applied to open systems and/or when radiation field is treated quantum mechanically. Theoretical methods of quantum transport community are numerous. The common (and probably most developed) is the nonequilibrium Green's functions (NEGF) approach. It is formulated in the Hilbert space and in its canonical form utilizes quasiparticles (or elementary excitations, or molecular orbitals) as a basis.

This review compares theoretical approaches of the two communities in their treatment of spectroscopy in nanojunctions. We discuss their strong and weak sides and indicate limitations in applicability of the approaches. Structure of the review is the following. Section 2 discusses theoretical approaches to optical spectroscopy. To make the review self-contained in Section 2.1 we give a short introduction to theoretical methodology standard in the nonlinear optical spectroscopy community. Section 2.2 discusses photonics in nanojunctions from perspective of Green function methods. We first shortly introduce canonical NEGF in Section 2.2.1 and then follow with its two many-body flavors: the pseudoparticle NEGF (PP-NEGF) in Section 2.2.2 and Hubbard NEGF in Section 2.2.3. We compare the theoretical approaches and argue that the latter two formulations can be a convenient choice for optoelectronics. Theoretical considerations of spectroscopy in junctions with radiation field treated classically are presented in Section 3. Quantum treatment of radiation field in junctions is

discussed in Section 4. Section 5 concludes.

## 2 Theoretical methodology

A distinct feature of junction spectroscopy is mixing between optical and electronic characteristics of an optoelectronic device. Indeed, optical spectroscopy of isolated systems is focused on photon flux; this flux is the only channel of communication between the system and environments (measuring devices). On the contrary, in nanojunctions, where electron participating in optical scattering process is free to leave contributing to electron and energy fluxes, combined theoretical consideration of all the constituents is crucial. In this case one does not have optical signal independent of electric current, rather one has to deal with a comprehensive description.

Let consider junction under external illumination.<sup>1</sup> Hamiltonian of the total system is

$$\hat{H} = \hat{H}_M + \hat{H}_K + \hat{H}_p + \hat{V}_{MK} + \hat{V}_{MP} \quad (1)$$

Here  $\hat{H}_M$ ,  $\hat{H}_K$ , and  $\hat{H}_p$  are, respectively, matter (e.g., molecular), contacts, and radiation field Hamiltonians.  $\hat{V}_{MK}$  and  $\hat{V}_{MP}$  describe coupling to contacts and light-matter interaction. In general part or all of the contributions can be time-dependent due to external driving. Contacts and radiation field Hamiltonians are assumed to be reservoirs of free carriers (electrons and photons, respectively):  $\hat{H}_K = \sum_{k \in K} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k$  and  $\hat{H}_p = \sum_{\alpha} \hbar \omega_{\alpha} \hat{a}_{\alpha}^\dagger \hat{a}_{\alpha}$ , where  $\hat{a}_{\alpha}^\dagger$  ( $\hat{a}_{\alpha}$ ) and  $\hat{c}_k^\dagger$  ( $\hat{c}_k$ ) are creation (annihilation) operators for photon in mode  $\alpha$  and electron in state  $k$  of contact  $K$ . For simplicity below we specialize to bilinear coupling coupling to contacts and rotating wave approximation in light-matter interaction<sup>2</sup>

$$\hat{V}_{MP} = \sum_{m \in M} \sum_{\alpha} (U_{m\alpha} \hat{X}_m^\dagger \hat{a}_{\alpha} + H.c.) \quad (2)$$

$$\hat{V}_{MK} = \sum_{m \in M} \sum_{k \in K} (V_{mk} \hat{X}_m^\dagger \hat{c}_k + H.c.), \quad (3)$$

where  $\hat{X}_m^\dagger$  are matter excitation operators due to electron transfer from state  $k$  in contacts or optical excitation by radiation field.

Most theoretical studies in optical spectroscopy and quantum transport are focused on evaluation of fluxes (photon,  $p$ , and electron,  $e$ , respectively), which are defined as rates of change of carriers populations in baths (respectively, photon population of radiation field modes and electron density in contacts)<sup>204,205</sup>

$$I_p(t) = - \frac{d}{dt} \sum_{\alpha} \langle \hat{a}_{\alpha}^\dagger(t) \hat{a}_{\alpha}(t) \rangle = 2 \text{Im} \sum_{m \in M} \sum_{\alpha} U_{m\alpha} \langle \hat{X}_m^\dagger(t) \hat{a}_{\alpha}(t) \rangle \quad (4)$$

$$I_e^K(t) = - \frac{d}{dt} \sum_{k \in K} \langle \hat{c}_k^\dagger(t) \hat{c}_k(t) \rangle = 2 \text{Im} \sum_{m \in M} \sum_{k \in K} V_{mk} \langle \hat{X}_m^\dagger(t) \hat{c}_k(t) \rangle \quad (5)$$

<sup>1</sup>For future reference we write down a quantized radiation field.

<sup>2</sup>Note that more general couplings can be considered as well.<sup>130,146</sup>

Here, the operators are in Heisenberg picture and  $\langle \dots \rangle = \text{Tr}[\dots \hat{\rho}(t_0)]$  is quantum mechanical and statistical averaging with respect to initial density operator (usually assumed to be direct product of radiation field and electronic components  $\hat{\rho}(t_0) = \hat{\rho}_p(t_0) \otimes \hat{\rho}_e(t_0)$ ). Energy fluxes,  $J_p(t)$  and  $J_e^K(t)$ , are defined in a similar way as rates of change of energy in the baths.<sup>3</sup> The fluxes can be expressed in terms of single-particle Green functions (two time correlation functions; see below). Note that index  $m$  in Eqs. (2) and (4) has a meaning of *optical transfer* in the system, that is total number of electrons in  $M$  does not change. On the contrary,  $m$  in Eqs. (3) and (5) indicates *electron transfer* between  $M$  and  $K$ ; such transfer results in change of electron population in the system.

Other quantities of interest are related to statistics of photon<sup>208–211</sup> and electron<sup>212–214</sup> transport as well as cross-correlations between the two. Measurements of fluctuations of particle fluxes were reported in junction studies for photon<sup>215,216</sup> and electron transport.<sup>49,217–219</sup> Number of experiments demonstrated cross-correlation effects.<sup>41,46,220</sup> Theoretically fluctuations are characterized within the full counting statistics (for time-local cumulants of transfer distribution)<sup>221</sup> or via two-particle Green function, (e.g.,  $g(2)$ )<sup>222,223</sup> or current-current<sup>224–227</sup> correlation functions). Higher order correlation functions were also considered in the literature.<sup>228</sup>

Evaluation of the correlation functions is performed within either Liouville or Hilbert spaces with the former being standard choice in the nonlinear spectroscopy community. While the two representations are differ only in the way correlation function is evaluated, and ideally one expects the same result from both considerations, approximations involved in real-life calculations are quite different, so that results depend on the way (and level) of treatment. Below we give a short pedagogical introduction to different approaches and indicate their strong and weak sides.

## 2.1 Liouville space formulation

We start from a very short introduction to the Liouville space formulation - an accepted standard approach in the field of nonlinear optical spectroscopy. A comprehensive formulation can be found in Ref.<sup>204</sup>, which became a standard reference for classification and interpretation of optical experiments.

Expressing photon flux, Eq.(4), in interaction picture with respect to the light-matter coupling (2) yields  $I_p(t) = 2 \text{Im} \sum_{m,\alpha} U_{m\alpha} \text{Tr}[\hat{X}_{I,m}^\dagger(t) \hat{a}_{I,\alpha}(t) \hat{\rho}_I(t)]$ , where subscript  $I$  indicates interaction picture. Integral form of the Liouville-

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<sup>3</sup>However, note recent discussion on inconsistency of this definition with thermodynamic laws.<sup>206,207</sup>

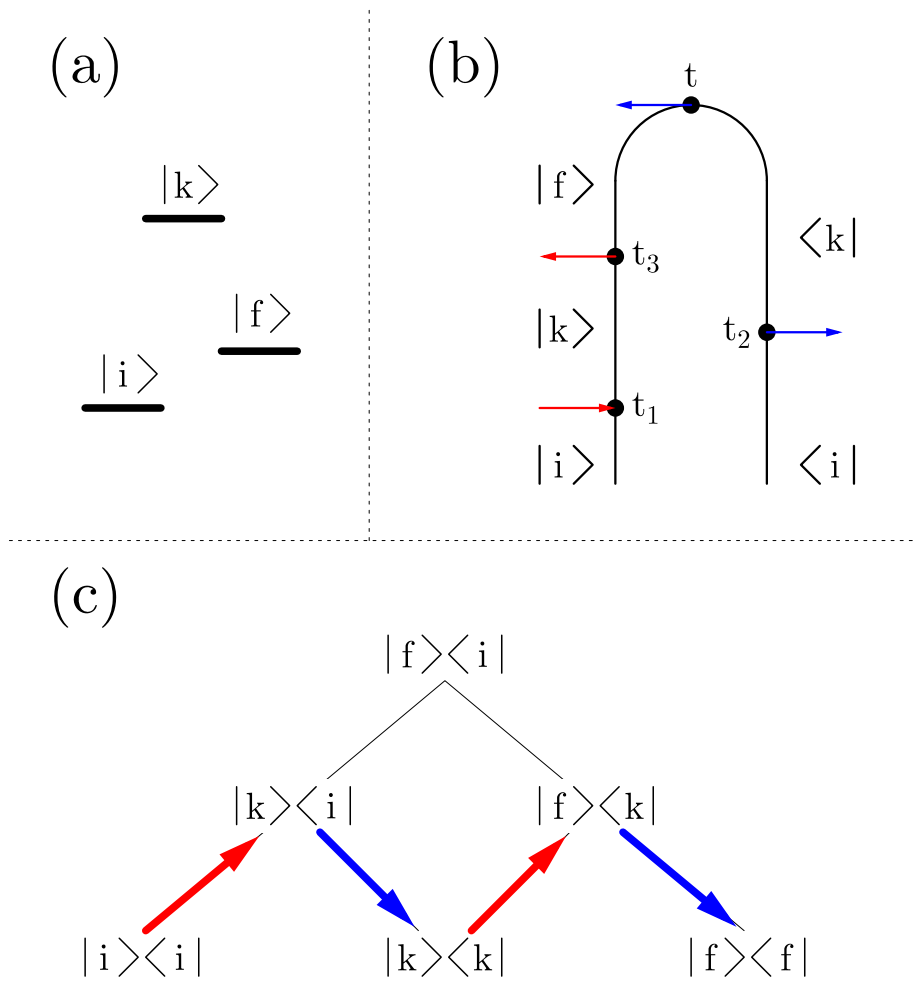


Figure 1: Liouville space formulation of an optical spectroscopy. Shown are (a) three level system  $\hat{H}_M$ , (b) double-sided Feynman diagram representing a spontaneous light emission process, and (c) corresponding Liouville space pathway.

von Neumann equation for the total density matrix is

$$\begin{aligned}
|\rho_I(t)\rangle\rangle &= T \exp \left[ -i \int_{t_0}^t ds \mathcal{V}_{I,MP}(s) \right] |\rho(t_0)\rangle\rangle \\
&\equiv \left[ 1 + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1} \dots \int_{t_0}^{t_2} dt_1 \right. \\
&\quad \left. \mathcal{V}_{I,MP}(t_n) \mathcal{V}_{I,MP}(t_{n-1}) \dots \mathcal{V}_{I,MP}(t_1) \right] |\rho(t_0)\rangle\rangle
\end{aligned} \tag{6}$$

Here  $T$  is the time ordering operator, expression is written in the Liouville space, and  $\mathcal{V}_{I,MP}$  is interaction picture form of the superoperator corresponding to the Hilbert space operator  $\hat{V}_{MP}$  of (2). Expansion of the evolution operator ( $T$  ordered exponent in first row of Eq.(6)) in Taylor series (second and third rows of (6)) yields bare perturbation theory (PT) in  $\hat{V}_{MP}$ , which presents evolution of the total density matrix as a sum of time-ordered ( $t \geq t_n \geq t_{n-1} \geq \dots \geq t_1 \geq t_0$ ) sets of light-matter interactions. Taking into account that any Liouville space superoperator is expressed in Hilbert space as a commutator of the corresponding operator, every  $\mathcal{V}_{I,MP}(t_i)$  in (6) acts on either bra or ket of the result of prior evolution,  $\int_{t_0}^{t_i} dt_{i-1} \dots \int_{t_0}^{t_2} dt_1 \mathcal{V}_{I,MP}(t_{i-1}) \dots \mathcal{V}_{I,MP}(t_1) |\rho(t_0)\rangle\rangle$ . Thus, Liouville space expression for photon flux (4),

$$I_p(t) = 2 \text{Im} \sum_{m \in M} \sum_{\alpha} \langle\langle a_{I,\alpha}^\dagger(t) X_{I,m}(t) |\rho_I(t)\rangle\rangle \equiv \sum_{n=0}^{\infty} I_p^{(n)}(t), \tag{7}$$

can be conveniently presented on the Schwinger-Keldysh contour<sup>229,230</sup> as sets of points representing interaction with radiation field at times  $t_1, \dots, t_n$  on forward (bra evolution) and backward (ket evolution) branches (see Fig. 1). Time of observation  $t$  naturally belongs to both branches. By convention arrows indicate creation ( $\hat{a}_\alpha^\dagger$ , pointing to left) or annihilation ( $\hat{a}_\alpha$ , pointing to right) photon operators for quantum radiation field, or corresponding negative and positive components when radiation field is treated classically. Graphical representations of the type shown in Fig. 1b, coined double-sided Feynman diagrams,<sup>4</sup> are widely utilized in the spectroscopy community to classify optical processes. Time ordered sequences of changes in the state of the system (changes in its bra and ket with time) are known as pathways in Liouville space (see Fig. 1c); they are instrumental in discussing propagation of coherences and populations in the system resulting from optical scattering processes. Similarly, one can expand electron flux  $I_e^K(t)$ , Eq. (5), in orders of light-matter interaction  $\hat{V}_{MP}$ , Eq.(2). Expansions in coupling to contacts  $\hat{V}_{MK}$ , Eq.(3), were also considered in the literature.<sup>139</sup>

Bare PT (6) in  $\hat{V}_{MP}$  decouples light and matter degrees of freedom, i.e. each contribution is a product of two correlation functions (electron and photon), which have to be evaluated independently. Often after completing the

<sup>4</sup>Note that the name is a bit misleading, because for quantum radiation field a diagram is characterized also by contractions (Green function) of corresponding field operators (see Fig. 3 below).



derivation incoming field is assumed to be in a coherent state, and transfer to classical representation is performed. Thus, optical response to classical field only requires evaluation of the electronic multi-time correlation function. Even contributions in the expansion (7) usually drop out because of the odd number of photon creation/annihilation operators in the correlation function (for classical field these terms drop out by symmetry in the case of isotropic medium<sup>204</sup>). Sometimes quantum description is used for a subset of modes, while the rest of the field is treated classically.<sup>231</sup> Note that application of bare PT to description of quantum fields (or to molecule-contacts coupling  $\hat{V}_{MP}$ ) may be problematic even when perturbation theory is applicable (e.g., when ratio of light-matter coupling is small compared with the system coupling to electronic bath). The reason is ability of photons to serve as an intermediates inducing effective non-Markov interactions within electron system. The latter enters theoretical description via electron self-energies, which cannot be properly described within bare PT (see discussion in Section 2.2.1).

Contrary to isolated systems, in junctions electron correlation is averaged over both system (molecule) and bath (contacts) degrees of freedom. As long as light-matter interaction is assumed to be confined to the system (molecule) only (i.e. electron operators in the correlation function are those of the system only), the multi-time correlation function can be evaluated by employing the regression formula. This procedure is often utilized and is exact when system evolution is Markovian.<sup>232</sup> Note that while formally time-local quantum master equation can always be derived, in practice evaluation of the time-convolutionless propagator is a complicated task.<sup>233</sup> Thus, most practical applications so far utilize effective Markovian propagators, which (when employed with the regression formula) may be problematic. In particular, within the approach every interaction with the optical field results in the destruction of the molecule-contacts coherence. The latter is an artifact of the formulation, which may lead to qualitative failures (see discussion in Section 3).

To summarize, the Liouville space superoperator formulation of nonlinear optical spectroscopy has several important advantages. First, the formulation follows evolution of the density matrix in real time, which allows for an intuitive graphical representation of optical processes in the form of double sided Feynman diagrams. Second, system's response can be described within the basis of its many-body states (eigenbasis of the Hamiltonian  $\hat{H}_M$ ), which allows to account for all the intra-system interactions exactly and paves a way to incorporate results of standard quantum-chemistry simulations (usually performed for isolated molecules) into numerical modelling of optoelectronic devices. These advantages were mentioned in many works on optical spectroscopy.<sup>132,139,164,165,169,204,234,235</sup> At the same time the bare PT and utilization of the regression formula may be problematic. The former fails to adequately describe open systems when radiation field is treated quantum mechanically. The latter leads to qualitative mistakes due to approximate nature of effective Markovian propagators employed in practical simulations. This is true for both classical and quantum radiation field treatments. Note that multi-time correlation functions in principle can be evaluated numerically exactly (i.e.

without employing the regression formula).<sup>236–239</sup> However, significant cost of such approaches so far limits their applicability to simple models. Also, standard approach (e.g., Redfield quantum master equation), which employs many-body states of the system as a basis, does not properly account for the system (molecule) - electronic baths (contacts) couplings.<sup>240,241</sup>

Below we show that Hilbert space Green function formulations are capable to yield (within similar level of theory) the same advantages while avoiding pitfalls of the Liouville space superoperator methods.

## 2.2 Hilbert space formulations

While theoretical treatments of quantum transport utilize both Hilbert and Liouville space formulations, the former is the choice of the nonequilibrium Green function (NEGF) technique. Below we focus on the NEGF (and its generalizations) and discuss application of the technique to description of optical spectroscopy in nanojunctions.

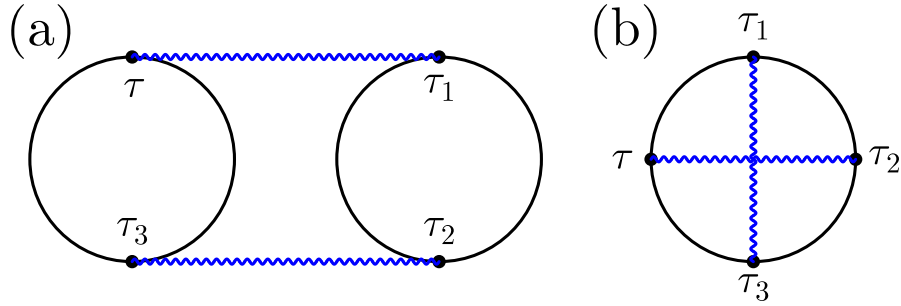


Figure 2: Feynman diagrams for (a) two-particle scattering and (b) virtual photon exchange. Solid (black) and wavy (blue) lines represent electron and photon Green function, respectively.

Evolution of a nonequilibrium system in the Hilbert space relies on contour (rather than real time as in Liouville space) ordering. A particular ordering of contour variables, which we will denote by Greek index  $\tau$  in contrast to  $t$  indicating real time, defines projection of a correlation function. These projections are equivalent to double sided Feynman diagrams of the Liouville space formulation, although number of contour projections is smaller (requirement of real time ordering in the Liouville space formulation results in bigger number of such projections, i.e. one contour projection includes several double sided Feynman diagrams). Note that projections and diagrams (in their original meaning) are different things. For example, Fig. 2 demonstrates two different fourth order Feynman diagrams representing two-particle scattering and virtual photon exchange processes, respectively; both diagrams will have the same set of projections.

Historically introduction of the contour is a consequence of an attempt to

build analog of Feynman diagrams for nonequilibrium systems. Feynman diagrammatic technique relies on the Gell-Mann and Low theorem<sup>242</sup> which (for equilibrium system at zero temperature) allows to establish connection between initial ( $t_0 \rightarrow -\infty$ ) and final ( $t_0 \rightarrow +\infty$ ) ground states of the system. Absence of such connection in nonequilibrium situation necessitates using bra and ket of the starting state as initial and final states of the process (i.e. starting state density matrix is utilized for quantum mechanical and statistical averaging).<sup>5</sup> Ref.<sup>244</sup> presents a beautiful and thorough discussion about relations between the Feynman (zero temperature equilibrium), Matsubara (finite temperature equilibrium), and Keldysh (nonequilibrium) theories.

Fluxes (4) and (5) can be *exactly* expressed in terms of Green functions as<sup>205,247–249</sup>

$$I_p(t) = -2 \operatorname{Re} \sum_{\alpha_1, \alpha_2} \int_{t_0}^t ds \left[ \Pi_{\alpha_1 \alpha_2}^<(t, s) F_{\alpha_2 \alpha_1}^>(s, t) - \Pi_{\alpha_1 \alpha_2}^>(t, s) F_{\alpha_2 \alpha_1}^<(s, t) \right] \quad (8)$$

$$I_e^K(t) = 2 \operatorname{Re} \sum_{m_1, m_2 \in M} \int_{t_0}^t ds \left[ \Sigma_{m_1 m_2}^{K, <}(t, s) G_{m_2 m_1}^>(s, t) - \Sigma_{m_1 m_2}^{K, >}(t, s) G_{m_2 m_1}^<(s, t) \right] \quad (9)$$

where  $< (>)$  are lesser (greater) projections of electron  $G$  and photon  $F$  Green functions as well as electronic self-energy due to coupling to contact  $K$ ,  $\Sigma^K$ , and photon self-energy due to coupling to electrons,  $\Pi$ . Their explicit on-the-contour definitions are

$$G_{m_1 m_2}(\tau_1, \tau_2) = -i \left\langle T_c \hat{X}_{m_1}(\tau_1) \hat{X}_{m_2}^\dagger(\tau_2) \right\rangle \quad (10)$$

$$F_{\alpha_1 \alpha_2}(\tau_1, \tau_2) = -i \left\langle T_c \hat{a}_{\alpha_1}(\tau_1) \hat{a}_{\alpha_2}^\dagger(\tau_2) \right\rangle \quad (11)$$

$$\Sigma_{m_1 m_2}^K(\tau_1, \tau_2) = \sum_{k \in K} V_{m_1 k} g_k(\tau_1, \tau_2) V_{k m_2} \quad (12)$$

Here  $T_c$  is the contour ordering operator,  $\tau_{1,2}$  are contour variables, and  $g_k(\tau_1, \tau_2) \equiv -i \langle T_c \hat{c}_k(\tau_1) \hat{c}_k^\dagger(\tau_2) \rangle$  is the Green function of free electron in state  $k$  of contact  $K$ . Explicit expression for the photon self-energy,  $\Pi_{\alpha_1, \alpha_2}(\tau_1, \tau_2)$ , depends on the level of treatment (e.g., order of diagrammatic perturbation theory employed - see below). While analytical forms of the self-energy  $\Sigma^K$  is known, other constituents of the fluxes expressions (8) and (9) have to be evaluated by solving a set of coupled equations.

Note that expression for photon flux, Eq.(8), is relevant only when radiation field is treated quantum mechanically. For classical field one either has to evaluate multi-time correlation functions as discussed in section 2.1, or solve time-dependent problem for a system (molecule) coupled to external classical

<sup>5</sup>Note that if initial correlations are to be taken into account one needs to consider a combination of the Keldysh and Matsubara contours. We do not discuss this possibility here, an interested reader is encouraged to consult Refs.<sup>243–246</sup>.

field. The latter situation was considered in many works,<sup>146,151–153,155–158</sup> where radiation field was treated classically propagating Maxwell equations along with quantum mechanical treatment of electron dynamics. Expression for electron flux, Eq.(9), is always correct. Note also that in junctions where formation of the local field is affected by both plasmon excitations in the contacts and molecular response bare perturbation theory (which for a particular optical process discards back action of the matter on the field) may be not enough. This was shown in studies considering radiation field both classically<sup>155,157</sup> and quantum mechanically.<sup>193</sup> Finally, the fact that, e.g., electron Green functions  $G$  enters expressions for both fluxes,<sup>6</sup> Eqs. (8) and (9), indicates inter-dependence of the fluxes and demonstrates a necessity of consistent (i.e. within the same level of theory) description of an optoelectronic device responses.

### 2.2.1 Nonequilibrium Green functions (NEGF)

NEGF utilizes language of quasiparticles (or elementary excitations, or orbitals):  $d_i^\dagger$  ( $\hat{d}_i$ ) are the usual operators of the second quantization which create (annihilate) electron in orbital  $i$  of the system  $M$ . The approach is most convenient when intra-system interactions are small compared with the coupling to electronic baths, so that the former can be treated within diagrammatic perturbation theory. In this case one can utilize, e.g., set of molecular (or Kohn-Sham) orbitals to represent electronic structure of the molecule. The latter are (de)populated by electron transfer between electronic reservoirs and molecule. Thus index  $m$  in Eq.(9) stands for such an orbital, so that electron flux is exactly expressed in terms of single particle Green functions

$$G_{ij}(\tau_1, \tau_2) = -i\langle T_c \hat{d}_i(\tau_1) \hat{d}_j^\dagger(\tau_2) \rangle \quad (13)$$

Green functions (11) and (13) are defined by solving Dyson equations

$$G_{ij}(\tau_1, \tau_2) = G_{ij}^0(\tau_1, \tau_2) \quad (14)$$

$$+ \sum_{k,m} \int_c d\tau_3 \int_c d\tau_4 G_{ik}^0(\tau_1, \tau_3) \Sigma_{km}^p(\tau_3, \tau_4) G_{mj}(\tau_4, \tau_2)$$

$$F_{\alpha_1, \alpha_2}(\tau_1, \tau_2) = F_{\alpha_1, \alpha_2}^0(\tau_1, \tau_2) \quad (15)$$

$$+ \sum_{\alpha_3, \alpha_4} \int_c d\tau_3 \int_c d\tau_4 F_{\alpha_1, \alpha_3}^0(\tau_1, \tau_3) \Pi_{\alpha_3 \alpha_4}(\tau_3, \tau_4) F_{\alpha_4, \alpha_2}(\tau_4, \tau_2)$$

Here  $G^0$  and  $F^0$  are the Green functions in the absence of the light-matter coupling  $\hat{V}_{MP}$ ,  $\Sigma^p$  is electronic self-energy due to coupling to radiation field, and  $\Pi$  is photon self-energy due to coupling to electrons. The two latter quantities can be derived only approximately; the approximations should satisfy conservation laws for physical quantities. A way to formulate conserving approximations was

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<sup>6</sup>Electron Green function enters expression for photon flux, Eq.(8), via photon self-energy  $\Pi$ .

formulated in the works by Kadanoff and Baym.<sup>250,251</sup> An interested reader is encouraged to consult book<sup>252</sup> for a detailed consideration of the issue.

Diagrammatic perturbation theory is built by constructing the Luttinger-Ward functional,  $\Phi$ . The latter is collection of all dressed connected skeleton diagrams (i.e., connected combinations of Green functions  $G$  and  $F$  that have no self-energy insertions).<sup>253,254</sup> Expressions for self-energies are obtained as functional derivatives<sup>252,255</sup>

$$\Sigma_{m_1 m_2}^p(\tau_1, \tau_2) = \frac{\delta\Phi[G, F]}{\delta G_{m_2 m_1}(\tau_2, \tau_1)} \quad (16)$$

$$\Pi_{\alpha_1, \alpha_2}(\tau_1, \tau_2) = - \frac{\delta\Phi[G, F]}{\delta F_{\alpha_2 \alpha_1}(\tau_2, \tau_1)} \quad (17)$$

An example of fourth order (in light-matter interaction) contribution to the functional  $\Phi$  is shown in Fig. 2b. Functional derivatives in Eqs. (16) and (17) corresponds to removal of one straight (Green function  $G$ ) or wavy (Green function  $F$ ) line, respectively.

It is important to note that contrary to bare PT (an expansion to a particular order), diagrammatic PT sums a particular type of diagrams (the type corresponding to a particular order) to infinity. Indeed, Luttinger-Ward functional  $\Phi$  is expressed in terms of full Green functions  $G$  and  $F$  rather than their zero order analogs  $G^0$  and  $F^0$ .<sup>7</sup> This summation is central for conserving character of an approximation. Note also that necessity (for quantum radiation field) to solve simultaneously two coupled (via their self-energies) Dyson equations (14) and (15) corresponds to formation of the local field due to both external source and system response. The situation is relevant for, e.g., molecules in nanocavities or in vicinity of metal surfaces. However, even if one can assume independence of the radiation field on molecular response<sup>8</sup>, still for an approximation to be conserving one has to sum a subset of diagrams to infinity - via dependence of electron self-energy  $\Sigma^p$  on full Green function  $G$  and structure of the Dyson equation (14). Bare PT does not take into account these resummations and thus will violate conservation laws. As a result traditional classification of optical processes (and utilization of the double sided Feynman diagrams as is standard in optical spectroscopy community) becomes questionable in comprehensive treatments of open systems.

To summarize, an important advantage of the NEGF is existence of established set of rules (the nonequilibrium diagrammatic technique) to treat interactions in the system (in particular, light-matter interaction) in an organized perturbative way preserving physical conservation laws. The approach is capable to exactly account for system (molecule) coupling to electronic baths (contacts). It is also instrumental in studying counting statistics of transport both in steady-state<sup>256</sup> and transient<sup>257,258</sup> regimes. NEGF is direct successor to original (Feynman and Matsubara) Green function formulations<sup>244</sup> and as such

<sup>7</sup>Note that also structure of the Dyson equations, Eqs. (14) and (15), implies resumming which accounts for reducible diagrams.

<sup>8</sup>One has to use  $F^0$  everywhere in this case and disregard Eq.(15).

allows physically motivated choice of relevant diagrams in the same way as does the Feynman diagrammatic technique. The main drawback of the method with respect to optoelectronic problems is its quasiparticle formulation. This significantly complicates treatment of strong intra-system interactions and makes (TD)DFT (also formulated in the basis of effective single particle orbitals) a method of choice for electronic structure simulations.<sup>259–261</sup> The latter does not connect well with traditional optical spectroscopy language and has some limitations related to both foundations of (TD)DFT (e.g., utilization of Kohn-Sham orbitals as physical objects) and in terms of its applications to transport.<sup>262</sup>

We now turn to many-body flavors of the NEGF which to some extent are capable of overcoming these limitations.

### 2.2.2 Pseudoparticle NEGF

Contrary to creation (annihilation) of quasiparticles in orbitals in the usual second quantization, pseudoparticle operators create (annihilate) many-body states of a system (molecule). For example, pseudoparticle  $S$  (corresponding to eigenstate  $|S\rangle$  of the Hamiltonian  $\hat{H}_M$ ) is constructed by applying creation operator  $\hat{p}_S^\dagger$  to unphysical vacuum  $|vac\rangle$ . Pseudoparticle operators satisfy the usual commutation or anticommutation relations depending on the Bose (e.g., even number of electrons) or Fermi (e.g., odd number of electrons) character of the corresponding many-body state. Any full set of many-body states should fulfill normalization condition (sum over many-body states probabilities should be one). This condition is not automatically satisfied by the second quantization in the space of many-body states of the system, and should be imposed to restrict the so called extended Hilbert space to its physical subspace

$$\hat{Q} \equiv \sum_S \hat{p}_S^\dagger \hat{p}_S = 1 \quad (18)$$

Naturally, pseudoparticle representation diagonalizes the system Hamiltonian,  $\hat{H}_M = \sum_S E_S \hat{p}_S^\dagger \hat{p}_S$ . However, it makes  $\hat{V}_{MK}$  non-quadratic: index  $m$  in Eq. (3) indicates transition ( $S_1, S_2$ ) between pair of states which differ by single electron, so the interaction becomes  $\hat{V}_{MK} = \sum_{S_1, S_2 \in M} \sum_{k \in K} \left( V_{(S_1 S_2), k} \hat{p}_{S_2}^\dagger \hat{p}_{S_1} \hat{c}_k + H.c. \right)$ . Similarly, index  $m$  in Eq. (2) stands for a transition between pair of states with the same number of electrons. A simplified version of the pseudoparticle methodology is well known already long time as slave-boson technique (see, e.g., Refs.<sup>263,264</sup> - classics of quantum transport in junctions). Recently, development of the dynamical mean field theory renewed interest in the methodology.<sup>265</sup>

In PP-NEGF central object of interest is single pseudoparticle Green function

$$G_{S_1 S_2}(\tau_1, \tau_2) = -i \left\langle T_c \hat{p}_{S_1}(\tau_1) \hat{p}_{S_2}^\dagger(\tau_2) \right\rangle \quad (19)$$

Contrary to the NEGF where intra-system interactions are treated by the diagrammatic perturbation series, PP-NEGF is perturbative in system-baths couplings. However, all the standard diagrammatic machinery (including methodology to build conserving approximations) of the NEGF is applicable also to

pseudo-particle Green functions. The PP-NEGF is defined by solving the Dyson equation of the same structure as in Eq.(14) with the difference that self-energy (perturbatively) accounts for system-baths couplings. Green function (19) can be considered as a generalization of the reduced (system) density matrix  $\sigma_{S_1 S_2}(t)$ . Indeed, while the latter provides information on populations and coherences at a particular (local) time, PP-NEGF gives also temporal correlations; its lesser projection taken at equal times is the system density matrix:  $i\zeta_{S_1} G_{S_1 S_2}^<(t, t) = \sigma_{S_1 S_2}(t)$  (here  $\zeta_S = +1$  ( $-1$ ) for Bose (Fermi) state  $|S\rangle$ ).

The main technical difference between NEGF and PP-NEGF comes from the necessity to impose restriction (18). This results in several unusual properties of pseudoparticle Green functions. For example, NEGF fluctuation-dissipation relation,  $G_{ij}^>(t_1, t_2) - G_{ij}^<(t_1, t_2) = G_{ij}^r(t_1, t_2) - G_{ij}^a(t_1, t_2)$ , becomes for the PP-NEGF in the  $\hat{Q} = 0$  subspace  $G_{S_1 S_2}^>(t_1, t_2) = G_{S_1 S_2}^r(t_1, t_2) - G_{S_1 S_2}^a(t_1, t_2)$  because  $G_{S_1 S_2}^<(t_1, t_2)$  does not have contributions in  $\hat{Q} = 0$ ; Dyson equations for retarded ( $\hat{Q} = 0$  subspace) and lesser ( $\hat{Q} = 1$  subspace) projections are decoupled in the PP-NEGF; to reflect physical reality any projection in the diagrammatic expansion should contain only one lesser Green function (sum of charges  $\hat{Q}$  from different contributions in any diagram should be 1 - this is contribution from any lesser Green function, then the diagram as a whole belongs to physical subspace of the extended Hilbert space); etc. An interested reader is encouraged to consult Refs.<sup>265-268</sup>. In particular, Ref.<sup>266</sup> is a beautiful introduction to the methodology, Ref.<sup>268</sup> contains explicit expressions for self-energies due to coupling to fermionic (e.g., contacts) and bosonic (e.g., radiation field or thermal environment) baths.

To summarize, PP-NEGF has several important advantages: 1. The method is conceptually simple; 2. Standard diagrammatic perturbation theory can be applied (in particular, this means that physical conservation laws are preserved within the methodology); 3. Already in its lowest (second) order in system-baths interactions, the non-crossing approximation (NCA), the pseudoparticle NEGF goes beyond standard QME approaches by accounting for both non-Markovian effects and hybridization of molecular states; 4. The method is capable of treating transport in the language of many-body states of the isolated molecule, exactly accounting for all intra-molecular interactions. We stress that while (similar to the Liouville space formulation) PP-NEGF describes a system utilizing its many-body states (eigenstates of  $\hat{H}_M$ ) and accounts (albeit perturbatively) for hybridization between states of the system and baths, it avoids the two main problems of the Liouville space superoperator method (as discussed at the end of Section 2.1). As any approximate scheme the pseudoparticle NEGF has its own limitations,<sup>269</sup> however those are important mostly at low temperatures (below Kondo temperature). Also, lowest order of the method (NCA) was recently shown to be sensitive to details of accompanying approximations.<sup>270</sup> Finally, an important deficiency of the methodology is related to its inability to yield information on full counting statistics. Presumably, the problem comes from its formulation within extended (unphysical) Hilbert space. We now turn to a methodology which allows to overcome the difficulty.

### 2.2.3 Hubbard NEGF

Hubbard Green functions were originally introduced as a tool to develop perturbative expansion about the atomic limit in interaction between atoms with the goal to describe electron correlations in narrow energy bands.<sup>271</sup> The methodology was further developed and applied to study magnetically ordered systems.<sup>272-274</sup> These considerations were focused on equilibrium strongly correlated lattice models. Recently we utilized the approach to consider nonequilibrium atomic limit, thus introducing diagrammatic technique for nonequilibrium Hubbard Green functions.<sup>275</sup>

The Hubbard NEGF is capable of describing physics of open current carrying nanojunctions starting from atomic limit (system and baths are decoupled) with all intra-system interactions taken into account exactly; system-baths couplings are used as small parameters in perturbative expansion. In this sense it is similar to PP-NEGF discussed above with important difference that the methodology is formulated solely in physical Hilbert space. Contrary to PP-NEGF, which studies temporal correlations between pairs of many-body states of the system, Eq.(19), Hubbard NEGF focuses on similar correlations between transitions from one many-body state to another. The latter are described by Hubbard (or projection) operators

$$\hat{X}_{S_1 S_2} = |S_1\rangle\langle S_2| \quad (20)$$

The correlation function (nonequilibrium Hubbard Green function) is defined on the contour as

$$G_{(S_1 S_2), (S_3 S_4)}(\tau_1, \tau_2) = -i \left\langle T_c \hat{X}_{S_1 S_2}(\tau_1) \hat{X}_{S_3 S_4}^\dagger(\tau_2) \right\rangle \quad (21)$$

This definition is similar in spirit to the NEGF. Indeed, spectral decomposition of a quasiparticle annihilation operator,  $\hat{d}_i = \sum_{S_1, S_2} \langle S_1 | \hat{d}_i | S_2 \rangle \hat{X}_{S_1 S_2}$ , immediately shows connection between (13) and (21). Indices  $m$  in Eqs. (2)-(5) are such transitions between many-body states,  $m = (S_1 S_2)$ : Bose type transitions in Eqs. (2) and (4) and Fermi - in Eqs. (3) and (5).

Cornerstone for both NEGF and PP-NEGF diagrammatic techniques is the Wick's theorem<sup>242,243</sup> which relies on (anti)commutation relations for creation and annihilation (Fermi) Bose operators:  $[\hat{d}_i; \hat{d}_j^\dagger]_{\pm} = \delta_{i,j}$  and  $[\hat{p}_{S_1}; \hat{p}_{S_2}^\dagger]_{\pm} = \delta_{S_1, S_2}$ , respectively. It is crucial that result of (anti)commutation is a number. This is not so for Hubbard operators (20):  $[\hat{X}_{S_1 S_2}; \hat{X}_{S_3 S_4}^\dagger]_{\pm} = \delta_{S_2, S_4} \hat{X}_{S_1 S_3} \pm \delta_{S_1, S_3} \hat{X}_{S_4 S_2}$ . Nevertheless, a variant of Wick's theorem for Hubbard operators was developed for equilibrium systems.<sup>272-274</sup> The consideration was based on commutation properties of equilibrium density matrix with Hubbard operators. In junctions one has to deal with a mixture of quasiparticle excitations in the baths and Hubbard operators describing eigenstates of the system Hamiltonian  $\hat{H}_M$ . Moreover, the system is in a nonequilibrium state. To build nonequilibrium diagrammatic technique for Hubbard Green functions we made two assumptions: 1. originally (at  $t_0 \rightarrow -\infty$ ) system and baths were decoupled and the system (molecule) was in thermal equilibrium and 2. after coupling was established the system reached steady-state defined solely by bath induced



boundary conditions (i.e. memory of the initial state was lost). The latter is a usual assumption within the NEGF, and thus the former is unimportant for long time behavior of the system. Choice of thermal equilibrium as the initial condition allows to employ the Wick's theorem of Refs.<sup>272-274</sup> for Hubbard operators, while the standard Wick's theorem<sup>242,243</sup> is utilized to decouple quasiparticle correlation functions in perturbative expansion. The latter introduce boundary conditions imposed by baths on the system. After expansion to desired order in the coupling is finished, the diagrams are dressed in complete analogy with the standard diagrammatic technique. This results in a modified version of the Dyson type equation

$$G_{m_1 m_2}(\tau_1, \tau_2) = \sum_{m_3} \int_c d\tau_3 g_{m_1 m_3}(\tau_1, \tau_3) P_{m_3 m_2}(\tau_3, \tau_2) \quad (22)$$

$$g_{m_1 m_2}(\tau_1, \tau_2) = g_{m_1 m_2}^0(\tau_1, \tau_2) \quad (23)$$

$$+ \sum_{m_3, m_4} \int_c d\tau_3 \int_c d\tau_4 g_{m_1 m_3}^0(\tau_1, \tau_3) \Sigma_{m_3 m_4}(\tau_3, \tau_4) g_{m_4 m_2}(\tau_4, \tau_2)$$

Here  $m_i$  stands for transition between a pair of many-body states,  $G_{m_1 m_2}(\tau_1, \tau_2)$  is the Hubbard Green function (21),  $g_{m_1 m_2}(\tau_1, \tau_2)$  is the locator,  $g_{m_1 m_2}^0(\tau_1, \tau_2)$  is the locator in the absence of coupling to the baths, and  $P_{m_1 m_2}(\tau_1, \tau_2)$  is the strength operator. Eqs. (22)-(23) are exact in the same sense as the usual Dyson equation. For details of derivation and rules of the nonequilibrium diagrammatic technique interested reader is encouraged to consult Ref.<sup>275</sup> and references therein.

It is important to note that the nonequilibrium diagrammatic technique for Hubbard Green functions is a generalization of the Liouville superoperator formulation described in Section 2.1. On-the-contour diagrams are directly related to NEGF Feynman diagrams and account for both projections (as is the case in the double sided Feynman diagrams) and contractions between Hubbard operators of the system, quasiparticle operators representing electrons in contacts, and radiation field operators - respectively, Green functions (21), (12), and (11) (compare Fig. 3 with Fig. 1b). Note that the Hubbard NEGF can also be considered as a Green function generalization of the real-time perturbation theory developed for density matrices<sup>276-279</sup> and as an extension of auxiliary fields Hubbard Green function approach<sup>280-285</sup> (as it yields an organized diagrammatic procedure to account for the system-baths couplings and allows evaluation of multi-time correlation functions). Contrary to the PP-NEGF, the Hubbard NEGF is formulated solely in the physical Hilbert space. As a result it can be utilized to study full counting statistics of transport (see preliminary data in Section 4 below). However, the approach (at current level of development) has an important formal limitation: no clear way of constructing the Luttinger-Ward functional  $\Phi$  has been proposed so far. Thus, while model simulations which we performed in Ref.<sup>275</sup> show close correspondence with exact results, at the moment one cannot formally guarantee conserving character of the Hubbard NEGF diagrammatic expansions. A way to overcome the difficulty may

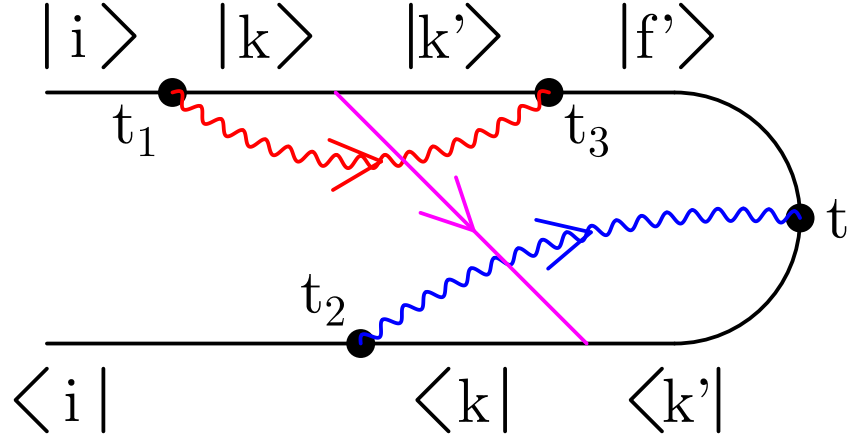


Figure 3: An example of optical scattering process in junction.  $|i\rangle$  and  $|k\rangle$  are eigenstates of a neutral molecule,  $|k'\rangle$  and  $|f'\rangle$  are eigenstates of a cation. Wavy lines (red and blue) represent photon Green functions (11), straight line (magenta) indicates electron self-energy due to coupling to contacts (12).

be in constructing path integral formulation for the Hubbard NEGF utilizing generalized coherent states.<sup>286</sup> This direction requires further research.

### 3 Classical light

Until recently most simulations of optical properties in junctions were performed utilizing classical radiation fields. Roughly one can separate these studies into two groups: steady-state and time-dependent considerations. In the latter group (and for harmonic driving) either transition to Floquet space,<sup>149,287–289</sup> or transformation into the rotating frame of the field allow to formulate effective time-independent problem.<sup>147,249</sup>

If light-matter coupling is relatively weak so that perturbative expansion in the interaction can be performed, bare PT expansion (as discussed in Section 2.1) is justified, and standard tools of nonlinear optical spectroscopy can be used in studies of junctions. These studies are often performed for steady-state regime (in the frequency domain). For example, Refs.<sup>132,139</sup> utilized the Liouville space formulation to discuss current induced fluorescence in molecular junctions. Ref.<sup>169</sup> studied stimulated and spontaneous light emission. Multidimensional optical spectroscopy in junctions was considered in Refs.<sup>163,164</sup>. Evaluation of the resulting multi-time electronic correlation functions, Eq.(6), was performed either employing quasiparticle language and utilizing the standard Wick's theorem,<sup>132,163</sup> or relying on the quantum regression formula.<sup>139,164,169</sup>

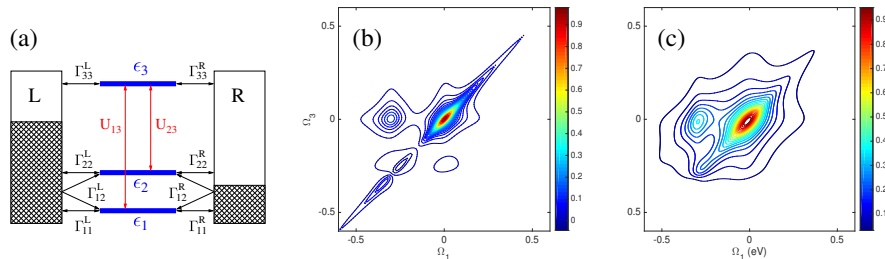


Figure 4: An example of 2D optical signal in a nanojunction. Shown are (a) junction model, (b) NEGF (exact for the model) and (c) PP-NEG results. Lindblad/Redfield Liouville space formulation yields zero signal. Reprinted from [Y. Gao and M. Galperin, *J. Chem. Phys.*, 2016, **144**, 244106], with the permission of AIP Publishing.

The former way is exact; the price to pay is necessity to work in the quasi-particle (orbital) basis assuming noninteracting (quadratic) character of the molecular Hamiltonian. Such assumptions are quite common in DFT based simulations, however one has to be cautious when taking Kohn-Sham orbitals as proper representations for molecular orbitals. In particular, in junctions the approach may lead to qualitative failures in predicting junction responses to external perturbations.<sup>262</sup> Possible pitfalls of the regression formula were discussed in Section 2.1. For example, in Ref.<sup>290</sup> we used a three level model to demonstrate that the regression formula (when quantum master equation utilizes second order to account for system-baths couplings) fails to reproduce coherent 2D optical response of a junction. At the same time the PP-NEG methodology (within the same, second order, level of treatment of system-baths couplings) yields qualitatively correct signal (see Fig. 4).

Explicit time-dependent simulations with respect to spectroscopy in nanojunctions are often employed to simulate plasmon excitations induced in metallic contacts by external time-dependent radiation field. A numerical scheme propagates Maxwell equations (e.g., the finite-difference time domain approach<sup>291</sup> is a popular choice) with the quantum system response entering the calculation via polarization current density.<sup>157</sup> Junction dynamics is usually simulated within quantum master equation or Green function approaches. A clear advantage of the former is time-locality of the density matrix; however, low order treatments of system-contacts couplings may result in qualitative failures.<sup>241,292</sup> An easy heuristic workaround is introduction of buffer zones, which while being part of the dynamical calculation provide smooth connection between nonequilibrium system and equilibrium baths.<sup>293,294</sup> More rigorous (yet still not too heavy to remain practical) methodology is the hierarchical equation of motion approach;<sup>295–297</sup> its main limitation is restriction to high temperatures. Dynamical simulations employing Green functions are naturally more demanding,<sup>245,246,248,266</sup> and usually (when going beyond adiabatic regime) approxima-

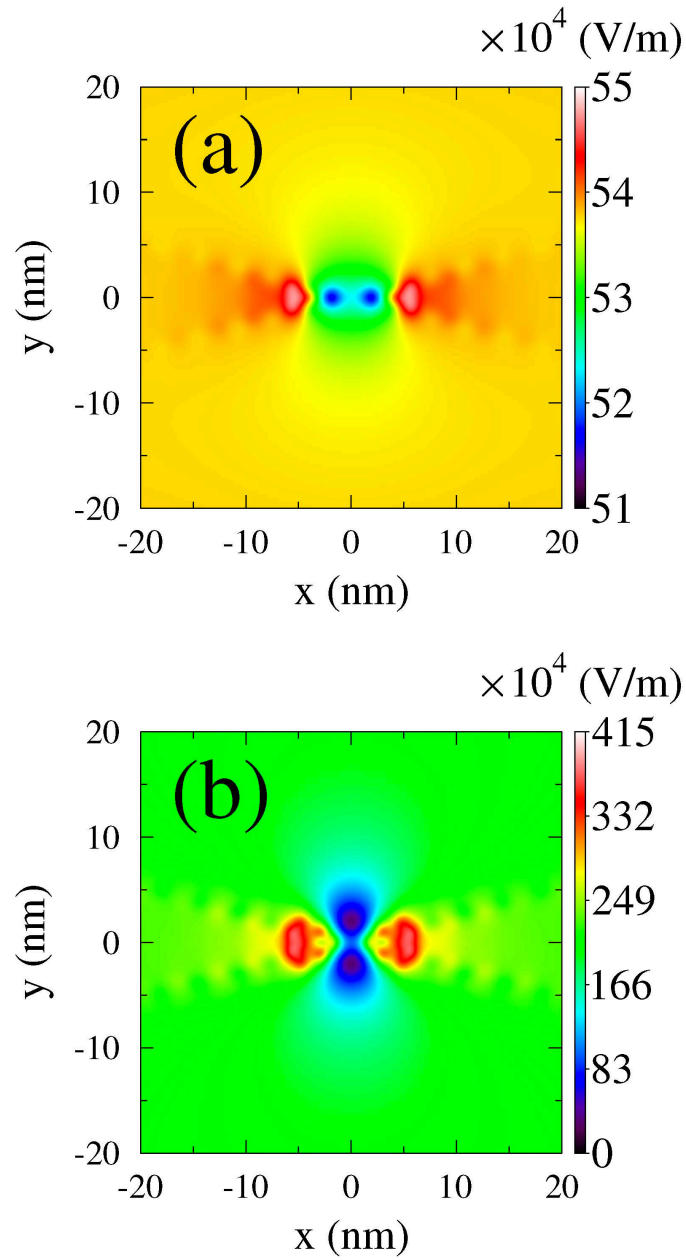


Figure 5: Instantaneous near field strength in a junction calculated (a) without and (b) with the molecular response. Reprinted (figure) with permission from [A. J. White, M. Sukharev, and M. Galperin, *Phys. Rev. B* **86**, 205324, 2012.] Copyright (2012) by the American Physical Society. <http://dx.doi.org/10.1103/PhysRevB.86.205324>

tions are required to make the approach practical.<sup>298</sup> An interesting development is a representation which maps time-nonlocal interacting Dyson equation onto a noninteracting auxiliary Hamiltonian with additional bath degrees of freedom; the latter problem can be efficiently solved.<sup>299</sup> We employed NEGF within the wide-band approximation to simulate transport and optical response of molecular junctions driven by time-dependent plasmonic field.<sup>146,153,157</sup> Among other things we demonstrated importance of molecular response in formation of the local field (see Fig 5) and hence also in junction responses. The latter indicates that due to the crucial role of plasmonic enhancement in junction spectroscopies one has to be careful when applying bare PT treatments to study optics in nanojunctions even with classical fields.

Another case where working in time-domain may be preferable is pump-probe type spectroscopy. Quantitative mapping of fast voltage pulse by plasmonic luminescence (probe) was demonstrated in STM junction measurements.<sup>47</sup> An opposite proposal of pumping by light (laser pulse pairs sequences) and probing dc current<sup>104</sup> and noise<sup>105</sup> was put forward as a way to access intramolecular dynamics on the sub-picosecond time scale.<sup>9</sup> Theoretical simulations were performed utilizing quantum master equation<sup>104</sup> and NEGF<sup>105</sup> (see Fig. 6); experimental verification of the proposed approach is an ongoing research in the group of Prof. Yoram Selzer.

Finally, a distinct feature of spectroscopy in open systems (nanojunctions) is the fact that photons and electrons participate in the same scattering process but contribute to different separately measured signals (e.g., photon flux and electron current). This simple idea is behind all the suggestions of measuring transport characteristics of one agent to describe properties of the other. In terms of theoretical treatment this is an indication of necessity to treat both photon and electron fluxes, Eqs. (4) and (5), at the same level of theory. Technically this is seen from the fact that both fluxes can be expressed in terms of the same correlation (Green) functions, which has to be evaluated at the same level of theory in both cases. For example, Refs.<sup>179,180</sup> consider temporal correlations between Raman signal and conductance for a model of junction driven by time-dependent classical field (see Fig. 7). Electron Green function, which enters expressions for both fluxes, was evaluated exactly with respect to light-matter coupling.

## 4 Quantum light

Quantum treatment of radiation field is required when purely quantum effects are pronounced in the light-matter interaction. These effects include photons in entangled and squeezed states, measurements of counting statistics of photon flux, interactions induced by quantum light in electron subsystem, etc. Note that the latter are present even in the absence of an external field.<sup>300</sup>

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<sup>9</sup>DC transport measurements are an important part of the suggestion, because electronic components are too slow to directly measure dynamics with picosecond resolution.

Turning to theoretical treatment of Raman spectroscopy in nanojunctions, it is worth mentioning that any spontaneous light emission (SLE) has to be considered quantum mechanically.<sup>204</sup> Thus, corresponding theoretical derivations always start from quantum treatment of the field, Eq.(4). After the derivation is completed, one can switch to classical description. Then bare PT and corresponding multi-time correlation functions, Eq.(6), become a safe way for description of optical response in junctions. Alternatively one may decide to stay with quantum treatment of the field. This is what was done in our NEGF and PP-NEGF theoretical studies of Raman spectroscopy in junctions.<sup>103,167,168,171–174,183</sup> Following the standard nonlinear optical spectroscopy formulation, they rely on bare PT expansion in the light-matter interaction. Resulting treatment is to some extent similar to that of Refs.<sup>132,163</sup> for NEGF treatments and is better than state-based formulations of Refs.<sup>139,164,169</sup> in treating molecule-contacts coupling for PP-NEGF treatments; the only difference is that Green function approaches make it easier to separate specifically Raman diagrams from other SLE contributions.<sup>170</sup> The central point is that these are bare PT (in light-matter coupling) considerations, and as such they describe light scattering from broadened (due to molecule-contacts hybridization) nonequilibrium current-carrying states (or levels) of the molecule. This is not a comprehensive treatment of responses of an optoelectronic device. Nevertheless, such approaches are still useful for qualitative understanding of Raman scattering in nanojunctions.

We now give a short overview of recent theoretical studies of Raman scattering in current carrying junctions. After first simultaneous measurements of Raman and conductance in molecular junctions were reported,<sup>94,95</sup> a theory of Raman scattering from current carrying molecular states was developed (along the lines discussed above) in Refs.<sup>167,168</sup> and utilized to discuss estimation of a ‘nonequilibrium temperature’ of molecular vibrations (extent of heating of the vibrations by electron flux) from ratio of Stokes and anti-Stokes peak intensities. Refs.<sup>173,174</sup> extended the latter analysis to electronic heating in molecular junctions in an attempt to interpret measurements presented in Ref.<sup>96</sup>. It was found that contrary to vibrational heating in junctions, data on electronic heating is much less reliable except at very low biases. In particular, modeling showed that the main contribution observed in the experiments as electronic heating may result from non-equilibrium electronic distribution in the molecule, while contribution from actual electronic heating in the contacts is negligible.

Charge transfer (chemical) contribution to surface enhanced Raman was discussed in Ref.<sup>183</sup>. Here quantum bare PT treatment of light-matter interaction was compared with quasi-classical approach. The latter was shown to be inadequate at biases beyond threshold defined by characteristic frequencies of molecular vibrations (i.e. when inelastic effects become pronounced).

Experimentally observed bending of Stokes lines under bias in an OPV3 junction<sup>27</sup> was explained by dependence of molecular vibrational normal modes on charging state of the molecule in Ref.<sup>301</sup>. Charging induced frequency renormalization was studied in Ref.<sup>301</sup> using a model where molecule-phonon coupling was taken into account up to quadratic term in shift from equilibrium (this

quadratic term yields anharmonic effects in the model). Estimating model parameters from first principle simulations resulted in shift of vibrational frequency similar to experimental data on Stokes line bending (see Fig. 8). Utilization of state-based approach (the PP-NEGF) in first principles simulation<sup>103</sup> provided an easy way to simulate the Raman spectrum. Studies of charge-induced renormalization of vibrational frequencies were later reported also in Refs.<sup>99,101</sup>.

Besides Raman shift and intensity of Stokes and anti-Stokes lines, widths and shapes of Raman peaks may also be a source of information on junction structure. Width of Stokes line and its dependence on junction characteristics (relaxation rates, proximity of electronic level to Fermi energy, and bias) were discussed within a generic HOMO-LUMO model in Ref.<sup>171</sup>. Experimental observation and theoretical analysis of Fano-like lineshapes in the Raman spectra was presented in Ref.<sup>172</sup> (see Fig 9). The study found that observed Fano-like features in principle can be given by interference between vibrational and electronic Raman scattering amplitudes (the Fano resonance); however model calculations suggested that the observed lineshape asymmetry was dominated by purely electronic scattering sidebands that dress vibrational Stokes peaks.

As stated above a comprehensive treatment of an optoelectronic device should account for all the fluxes (photon and electron) at the same level of theory. When considering quantum field such comprehensive consideration requires especial care. In particular (as was discussed in Section 2.2.1), for the consideration to satisfy physical conservation laws one is forced to abandon the bare PT approach. The latter is well known to be a non-conserving approximation which may fail qualitatively when vertical flow (redistribution of electronic population in energy) is present.<sup>250-252,255,303</sup> For example, in the theory of inelastic transport, which is technically equivalent to electron-photon interaction, second order bare PT (Born approximation) is non-conserving, and one has to employ the self-consistent Born approximation to get meaningful results.<sup>304</sup> The same situation holds for any other interaction which causes vertical flow in the system (see, e.g., Ref.<sup>305</sup>). Thus, e.g., it is not surprising that any consideration of current-induced fluorescence with radiation field being treated quantum mechanically leads to a self-consistent treatment.<sup>130,131</sup>

The main difference between classical and quantum fields (with respect to conserving character of approximation) is ability of the latter to mediate photon supported effective electron-electron interaction. Technically this interaction comes in the form of electronic self-energy due to coupling to radiation field, which being approximated in an inappropriate way (e.g., within bare PT) leads to violation of charge and energy conservation laws. A proper way to derive conserving approximations was discussed in Section 2.2.1 (see Eqs. (16) and (17) there). We note that the restrictions on application of standard tools of nonlinear optical spectroscopy to nanojunctions are relevant only for radiation fields treated quantum mechanically, because classical fields do not induce time-nonlocal interactions in electronic subsystem (i.e. technically they do not produce self-energies). To illustrate the point in Ref.<sup>249</sup> we utilized NEGF to consider optical and electronic responses (fluxes) of a nanojunction within the bare PT (as accepted in nonlinear spectroscopy community) and diagrammatic

PT (as is usual in quantum transport considerations) approaches (see Fig. 10).

Quantum treatment of radiation field is also required for strong light-matter interaction. Here light and matter degrees of freedom cannot be separately distinguished, and thus theoretical treatment should be performed in the basis of eigenstates of the Hamiltonian  $\hat{H}_M + \hat{H}_p + \hat{V}_{MP}$ , Eq.(1), accounting for the matter, the light, and interaction between them. We note that Green function methods presented in Sections 2.2.2 and 2.2.3 are ideally suited for the task. Note that also here conserving character of resulting approximation should be satisfied; however this time it is self-energy due to coupling to other baths (e.g., contacts or thermal environment, etc.) rather than self-energies coming from accounting for the light-matter interaction, are to be build properly. In Ref.<sup>193</sup> we utilized the PP-NEGF to study strong molecule-plasmon interaction in nanojunctions. Fig. 11 shows sensitivity of a molecule-plasmon Fano resonance to junction bias and intra-molecular interactions.

Finally, theoretical treatments related to statistics of photon flux also require quantum description of the radiation field. Note that an accurate (conserving, as discussed above) treatment in this case is even more important: while in Ref.<sup>249</sup> we demonstrated sensitivity of flux (first cumulant of the full counting statistics, FCS) higher order cumulants of the FCS are much more sensitive to details of theoretical modeling.<sup>207,292</sup> Participation of photons and electrons in the same process reveals itself in inter-dependence of optical and transport characteristics of an optoelectronic device. For example, ability of the plasmon emission spectrum to characterize finite frequency quantum noise of electron transport was demonstrated experimentally<sup>46</sup> and discussed theoretically<sup>201</sup> (see Eqs. (10) and (12) in Ref.<sup>201</sup> for formal connection between plasmonic light emission and the quantum noise). Similarly, optical spectra as a source of information on multielectron processes in junctions was measured<sup>40</sup> and studied theoretically<sup>200</sup> (see Fig. 12). Refs.<sup>306,307</sup> considered noise of photon and electron fluxes as well as cross-correlation counting statistics. The consideration utilized quantum master equation within the Born-Markov approximation, which is known to be problematic for description of relatively strong (compared to  $k_B T$ ) system-bath couplings  $\Gamma$ .<sup>240,241,292</sup> For a molecule chemisorbed on metallic surface  $\Gamma \sim 0.01 - 0.5$  eV<sup>308,309</sup> while room temperature is  $k_B T \sim 0.03$  eV. Thus Green function approaches, which are not limited by high temperature restriction, are preferable for treatment of counting statistics in molecular junctions. From the two state-based Green function methodologies introduced above (Sections 2.2.2 and 2.2.3) only the Hubbard NEGF provides possibility to simulate FCS (see Fig. 13). Application of the Hubbard NEGF to description of optoelectronic devices is a direction for future research.

## 5 Conclusions

In recent years optical experiments in current-carrying nanojunctions became a reality indicating emergence of a new field of research coined optoelectronics. Experimental advances challenged theory to develop adequate approaches



to characterize responses of open nonequilibrium systems to external drivings. The field of optoelectronics is a natural meeting point of (at least) two research communities: nonlinear optical spectroscopy and quantum transport. Each of the communities has its own theoretical toolbox. We reviewed recent progress in the field comparing theoretical treatments of optical spectroscopy in nanojunctions. In particular, bare perturbation theory usually performed in the Liouville space and formulated in the language of superoperators (a standard theoretical tool in spectroscopic studies of isolated systems) was compared with theoretical approaches accepted in quantum transport community. With respect to the latter we focus on the Hilbert space Green function based considerations. Standard nonequilibrium Green function (NEGF) was discussed together with its state-based flavors: pseudoparticle and Hubbard NEGF. We argued that the Green function considerations yield a convenient tool for optoelectronics when radiation field is treated either classically or quantum mechanically. We showed that bare perturbation theory becomes inapplicable, when a comprehensive treatment of nanojunction responses to bias and quantized radiation field is the goal of the study. We conclude that the Hubbard NEGF is a promising methodology which generalizes the standard tools of nonlinear optical spectroscopy, which is capable of comprehensive studies of optoelectronic devices. Further development of the methodology and its applications to nanojunctions spectroscopy are directions for future research.

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## References

- [1] Y. Jun and X.-Y. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 13224–13225.
- [2] V. Burtman, A. Ndobé and Z. Vardeny, *Solid State Commun.*, 2005, **135**, 563 – 573.
- [3] L. Bernard, Y. Kamdzhilov, M. Calame, S. J. van der Molen, J. Liao and C. Schönenberger, *J. Phys. Chem. C*, 2007, **111**, 18445–18450.
- [4] A. Scott, C. A. Hacker and D. B. Janes, *J. Phys. Chem. C*, 2008, **112**, 14021–14026.
- [5] M. Lefenfeld, J. Baumert, E. Sloutskin, I. Kuzmenko, P. Pershan, M. Deutsch, C. Nuckolls and B. M. Ocko, *Proc. Natl. Acad. Sci.*, 2006, **103**, 2541–2545.
- [6] S. Conoci, S. Petralia, P. Samorí, F. Raymo, S. Di Bella and S. Sortino, *Adv. Funct. Mater.*, 2006, **16**, 1425–1432.

- [7] Z. Wang, J. A. Carter, A. Lagutchev, Y. K. Koh, N.-H. Seong, D. G. Cahill and D. D. Dlott, *Science*, 2007, **317**, 787–790.
- [8] J. A. Carter, Z. Wang and D. D. Dlott, *Acc. Chem. Res.*, 2009, **42**, 1343–1351.
- [9] H. Asanuma, H. Noguchi, Y. Huang, K. Uosaki and H.-Z. Yu, *J. Phys. Chem. C*, 2009, **113**, 21139–21146.
- [10] P. J. N. Kett, M. T. L. Casford and P. B. Davies, *J. Phys. Chem. Lett.*, 2012, **3**, 3276–3280.
- [11] A. Nitzan, *Science*, 2007, **317**, 759–760.
- [12] G.-K. Liu, J. Hu, P.-C. Zheng, G.-L. Shen, J.-H. Jiang, R.-Q. Yu, Y. Cui and B. Ren, *J. Phys. Chem. C*, 2008, **112**, 6499–6508.
- [13] B. Liu, A. Blaszczyk, M. Mayor and T. Wandlowski, *ACS Nano*, 2011, **5**, 5662–5672.
- [14] S. L. Kleinman, R. R. Frontiera, A.-I. Henry, J. A. Dieringer and R. P. Van Duyne, *Phys. Chem. Chem. Phys.*, 2013, **15**, 21–36.
- [15] E. A. Pozzi, A. B. Zrimsek, C. M. Lethiec, G. C. Schatz, M. C. Hersam and R. P. Van Duyne, *J. Phys. Chem. C*, 2015, **119**, 21116–21124.
- [16] N. Jiang, E. T. Foley, J. M. Klingsporn, M. D. Sonntag, N. A. Valley, J. A. Dieringer, T. Seideman, G. C. Schatz, M. C. Hersam and R. P. Van Duyne, *Nano Lett.*, 2012, **12**, 5061–5067.
- [17] M. D. Sonntag, J. M. Klingsporn, L. K. Garibay, J. M. Roberts, J. A. Dieringer, T. Seideman, K. A. Scheidt, L. Jensen, G. C. Schatz and R. P. Van Duyne, *J. Phys. Chem. C*, 2012, **116**, 478–483.
- [18] J. M. Klingsporn, M. D. Sonntag, T. Seideman and R. P. Van Duyne, *J. Phys. Chem. Lett.*, 2014, **5**, 106–110.
- [19] J. M. Klingsporn, N. Jiang, E. A. Pozzi, M. D. Sonntag, D. Chulhai, T. Seideman, L. Jensen, M. C. Hersam and R. P. V. Duyne, *J. Am. Chem. Soc.*, 2014, **136**, 3881–3887.
- [20] N. Chiang, N. Jiang, D. V. Chulhai, E. A. Pozzi, M. C. Hersam, L. Jensen, T. Seideman and R. P. Van Duyne, *Nano Lett.*, 2015, **15**, 4114–4120.
- [21] X. Wang, J.-H. Zhong, M. Zhang, Z. Liu, D.-Y. Wu and B. Ren, *Anal. Chem.*, 2016, **88**, 915–921.
- [22] C. Toccafondi, G. Picardi and R. Ossikovski, *J. Phys. Chem. C*, 2016, **120**, 18209–18219.
- [23] J.-H. Tian, B. Liu, X. Li, Z.-L. Yang, B. Ren, S.-T. Wu, N. Tao and Z.-Q. Tian, *J. Am. Chem. Soc.*, 2006, **128**, 14748–14749.

- [24] D. R. Ward, G. D. Scott, Z. K. Keane, N. J. Halas and D. Natelson, *J. Phys.: Condens. Matter*, 2008, **20**, 374118.
- [25] F. Rossel, M. Pivetta and W.-D. Schneider, *Surf. Sci. Rep.*, 2010, **65**, 129 – 144.
- [26] T. Shamai and Y. Selzer, *Chem. Soc. Rev.*, 2011, **40**, 2293–2305.
- [27] D. Natelson, Y. Li and J. B. Herzog, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5262–5275.
- [28] S. V. Aradhya and L. Venkataraman, *Nature Nanotech.*, 2013, **8**, 399–410.
- [29] Z. H. Kim, *Front. Phys.*, 2014, **9**, 25–30.
- [30] R. Matsushita and M. Kiguchi, *Phys. Chem. Chem. Phys.*, 2015, **17**, 21254–21260.
- [31] M. Galperin and A. Nitzan, *Phys. Chem. Chem. Phys.*, 2012, **14**, 9421–9438.
- [32] F. Touhari, E. J. A. J. Stoffels, J. W. Gerritsen, H. van Kempen and P. Callant, *Appl. Phys. Lett.*, 2001, **79**, 527–529.
- [33] G. Hoffmann, L. Libioulle and R. Berndt, *Phys. Rev. B*, 2002, **65**, 212107.
- [34] G. Hoffmann, R. Berndt and P. Johansson, *Phys. Rev. Lett.*, 2003, **90**, 046803.
- [35] E. Cavar, M.-C. Blüm, M. Pivetta, F. m. c. Patthey, M. Chergui and W.-D. Schneider, *Phys. Rev. Lett.*, 2005, **95**, 196102.
- [36] H. Yanagi, H. Mukai and M. Nair, *Thin Solid Films*, 2006, **499**, 123 – 128.
- [37] W.-J. Li, K. L. Kavanagh, A. A. Talin, W. M. Clift, C. M. Matzke and J. W. P. Hsu, *J. Appl. Phys.*, 2007, **102**, 013703.
- [38] P. Brodard, *CHIMIA*, 2007, **61**, 613–616.
- [39] S. W. Wu, G. V. Nazin and W. Ho, *Phys. Rev. B*, 2008, 205430.
- [40] G. Schull, N. Neel, P. Johansson and R. Berndt, *Phys. Rev. Lett.*, 2009, **102**, 057401.
- [41] N. L. Schneider, G. Schull and R. Berndt, *Phys. Rev. Lett.*, 2010, **105**, 026601.
- [42] C. Chen, P. Chu, C. A. Bobisch, D. L. Mills and W. Ho, *Phys. Rev. Lett.*, 2010, **105**, 217402.

- [43] Z. C. Dong, X. L. Zhang, H. Y. Gao, Y. Luo, C. Zhang, L. G. Chen, R. Zhang, X. Tao, Y. Zhang, J. L. Yang and J. G. Hou, *Nat. Photon.*, 2010, **4**, 50–54.
- [44] N. L. Schneider, F. Matino, G. Schull, S. Gabutti, M. Mayor and R. Berndt, *Phys. Rev. B*, 2011, **84**, 153403.
- [45] N. L. Schneider and R. Berndt, *Phys. Rev. B*, 2012, **86**, 035445.
- [46] N. L. Schneider, J. T. Lü, M. Brandbyge and R. Berndt, *Phys. Rev. Lett.*, 2012, **109**, 186601.
- [47] C. Grosse, M. Etzkorn, K. Kuhnke, S. Loth and K. Kern, *Appl. Phys. Lett.*, 2013, **103**, 183108.
- [48] J. Lee, S. M. Perdue, A. R. Perez and V. A. Apkarian, *ACS Nano*, 2014, **8**, 54–63.
- [49] A. Burtzloff, N. L. Schneider, A. Weismann and R. Berndt, *Surf. Sci.*, 2016, **643**, 10 – 12.
- [50] A. Yu, S. Li, B. Dhital, H. P. Lu and W. Ho, *J. Phys. Chem. C*, 2016, **120**, 21099–21103.
- [51] H. Imada, K. Miwa, M. Imai-Imada, S. Kawahara, K. Kimura and Y. Kim, *Nature*, 2016, **538**, 364–367.
- [52] S. J. van der Molen, J. Liao, T. Kudernac, J. S. Agustsson, L. Bernard, M. Calame, B. J. van Wees, B. L. Feringa and C. Schönenberger, *Nano Lett.*, 2009, **9**, 76–80.
- [53] G. Noy, A. Ophir and Y. Selzer, *Angew. Chem. Int. Ed.*, 2010, **49**, 5734–5736.
- [54] E. S. Tam, J. J. Parks, W. W. Shum, Y.-W. Zhong, M. B. Santiago-Berrios, X. Zheng, W. Yang, G. K.-L. Chan, H. D. Abruña and D. C. Ralph, *ACS Nano*, 2011, **5**, 5115–5123.
- [55] S. Battacharyya, A. Kibel, G. Kodis, P. A. Liddell, M. Gervaldo, D. Gust and S. Lindsay, *Nano Lett.*, 2011, **11**, 2709–2714.
- [56] I. Rattalino, V. Cauda, P. Motto, T. Limongi, G. Das, L. Razzari, F. Parenti, E. Di Fabrizio, A. Mucci, L. Schenetti, G. Piccinini and D. Demarchi, *RSC Adv.*, 2012, **2**, 10985–10993.
- [57] M. Vadai, N. Nachman, M. Ben-Zion, M. Bürkle, F. Pauly, J. C. Cuevas and Y. Selzer, *J. Phys. Chem. Lett.*, 2013, **4**, 2811–2816.
- [58] P. P. Pal, N. Jiang, M. D. Sonntag, N. Chiang, E. T. Foley, M. C. Hersam, R. P. Van Duyne and T. Seideman, *J. Phys. Chem. Lett.*, 2015, **6**, 4210–4218.

- [59] T. Sendler, K. Luka-Guth, M. Wieser, Lokamani, J. Wolf, M. Helm, S. Gemming, J. Kerbusch, E. Scheer, T. Huhn and A. Erbe, *Adv. Sci.*, 2015, **2**, 1500017.
- [60] D. Cvetko, G. Fratesi, G. Kladnik, A. Cossaro, G. P. Brivio, L. Venkataraman and A. Morgante, *Phys. Chem. Chem. Phys.*, 2016, **18**, 22140–22145.
- [61] D. Taherinia and C. D. Frisbie, *J. Phys. Chem. C*, 2016, **120**, 6442–6449.
- [62] H. Y. He, S. T. Pi, Z. Q. Bai, M. Banik, V. A. Apkarian and R. Q. Wu, *J. Phys. Chem. C*, 2016, **120**, 20914–20921.
- [63] Y. Paltiel, G. Jung, T. Aqua, D. Mocatta, U. Banin and R. Naaman, *Phys. Rev. Lett.*, 2010, **104**, 016804.
- [64] B. Göhler, V. Hamelbeck, T. Z. Markus, M. Kettner, G. F. Hanne, Z. Vager, R. Naaman and H. Zacharias, *Science*, 2011, **331**, 894–897.
- [65] R. Naaman and D. H. Waldeck, *J. Phys. Chem. Lett.*, 2012, **3**, 2178–2187.
- [66] O. Ben Dor, N. Morali, S. Yochelis, L. T. Baczewski and Y. Paltiel, *Nano Lett.*, 2014, **14**, 6042–6049.
- [67] H. Einati, D. Mishra, N. Friedman, M. Sheves and R. Naaman, *Nano Lett.*, 2015, **15**, 1052–1056.
- [68] P. C. Mondal, P. Roy, D. Kim, E. E. Fullerton, H. Cohen and R. Naaman, *Nano Lett.*, 2016, **16**, 2806–2811.
- [69] D. L. Jeanmaire and R. P. Van Duyne, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 1977, **84**, 1–20.
- [70] S. Nie and S. R. Emory, *Science*, 1997, **275**, 1102–1106.
- [71] K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari and M. S. Feld, *Phys. Rev. Lett.*, 1997, **78**, 1667–1670.
- [72] J.-F. Li, S.-Y. Ding, Z.-L. Yang, M.-L. Bai, J. R. Anema, X. Wang, A. Wang, D.-Y. Wu, B. Ren, S.-M. Hou, T. Wandlowski and Z.-Q. Tian, *J. Am. Chem. Soc.*, 2011, **133**, 15922–15925.
- [73] J. I. Gersten, R. L. Birke and J. R. Lombardi, *Phys. Rev. Lett.*, 1979, **43**, 147–150.
- [74] J. Gersten and A. Nitzan, *The Journal of Chemical Physics*, 1980, **73**, 3023–3037.
- [75] B. N. J. Persson, *Chem. Phys. Lett.*, 1981, **82**, 561–565.
- [76] K. A. Willets and R. P. Van Duyne, *Ann. Rev. Phys. Chem.*, 2007, **58**, 267–297.

- [77] D. R. Ward, N. K. Grady, C. S. Levin, N. J. Halas, Y. Wu, P. Nordlander and D. Natelson, *Nano Lett.*, 2007, **7**, 1396–1400.
- [78] J. B. Lassiter, J. Aizpurua, L. I. Hernandez, D. W. Brandl, I. Romero, S. Lal, J. H. Hafner, P. Nordlander and N. J. Halas, *Nano Lett.*, 2008, **8**, 1212–1218.
- [79] O. Pérez-González, N. Zabala, A. G. Borisov, N. J. Halas, P. Nordlander and J. Aizpurua, *Nano Lett.*, 2010, **10**, 3090–3095.
- [80] R. Arielly, A. Ofarim, G. Noy and Y. Selzer, *Nano Lett.*, 2011, **11**, 2968–2972.
- [81] J. B. Herzog, M. W. Knight, Y. Li, K. M. Evans, N. J. Halas and D. Natelson, *Nano Lett.*, 2013, **13**, 1359–1364.
- [82] A. B. Zrimsek, A.-I. Henry and R. P. Van Duyne, *J. Phys. Chem. Lett.*, 2013, **4**, 3206–3210.
- [83] Y. Zhang, Y.-R. Zhen, O. Neumann, J. K. Day, P. Nordlander and N. J. Halas, *Nat. Commun.*, 2014, **5**, 4424.
- [84] F. Benz, C. Tserkezis, L. O. Herrmann, B. de Nijs, A. Sanders, D. O. Sigle, L. Pukenas, S. D. Evans, J. Aizpurua and J. J. Baumberg, *Nano Lett.*, 2015, **15**, 669–674.
- [85] Y. Li, M. L. Simeral and D. Natelson, *J. Phys. Chem. C*, 2016, **120**, 22558–22564.
- [86] K. T. Crampton, A. Zeytunyan, A. S. Fast, F. T. Ladani, A. Alfonso-Garcia, M. Banik, S. Yampolsky, D. A. Fishman, E. O. Potma and V. A. Apkarian, *J. Phys. Chem. C*, 2016, **120**, 20943–20953.
- [87] B. Vlčková, M. Moskovits, I. Pavel, K. Šišková, M. Sládková and M. Šlouf, *Chem. Phys. Lett.*, 2008, **455**, 131 – 134.
- [88] J.-F. Li, Y.-F. Huang, S. Duan, R. Pang, D.-Y. Wu, B. Ren, X. Xu and Z.-Q. Tian, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2493–2502.
- [89] J. F. Li, Y. F. Huang, Y. Ding, Z. L. Yang, S. B. Li, X. S. Zhou, F. R. Fan, W. Zhang, Z. Y. Zhou, W. Yin, B. Ren, Z. L. Wang and Z. Q. Tian, *Nature*, 2010, **464**, 392–395.
- [90] M. Moskovits, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5301–5311.
- [91] M. D. Sonntag, E. A. Pozzi, N. Jiang, M. C. Hersam and R. P. V. Duyne, *J. Phys. Chem. Lett.*, 2014, **5**, 3125–3130.
- [92] S.-Y. Ding, J. Yi, J.-F. Li, B. Ren, D.-Y. Wu, R. Panneerselvam and Z.-Q. Tian, *Nat. Rev. Mater.*, 2016, **1**, 16021.

- [93] A. Jaiswal, K. G. Tavakoli and S. Zou, *Anal. Chem.*, 2006, **78**, 120–124.
- [94] Z. Ioffe, T. Shamai, A. Ophir, G. Noy, I. Yutsis, K. Kfir, O. Cheshnovsky and Y. Selzer, *Nature Nanotech.*, 2008, **3**, 727–732.
- [95] D. R. Ward, N. J. Halas, J. W. Ciszek, J. M. Tour, Y. Wu, P. Nordlander and D. Natelson, *Nano Lett.*, 2008, **8**, 919–924.
- [96] D. R. Ward, D. A. Corley, J. M. Tour and D. Natelson, *Nature Nanotech.*, 2011, **6**, 33–38.
- [97] A. L. Schmucker, G. Barin, K. A. Brown, M. Rycenga, A. Coskun, O. Buyukcakir, K. D. Osberg, J. F. Stoddart and C. A. Mirkin, *Small*, 2013, **9**, 1900–1903.
- [98] R. Matsuhita, M. Horikawa, Y. Naitoh, H. Nakamura and M. Kiguchi, *J. Phys. Chem. C*, 2013, **117**, 1791–1795.
- [99] Y. Li, P. Doak, L. Kronik, J. B. Neaton and D. Natelson, *Proc. Natl. Acad. Sci.*, 2014, **111**, 1282–1287.
- [100] S. Kaneko, D. Murai, S. Fujii and M. Kiguchi, *Int. J. Mod. Phys. B*, 2016, **30**, 1642010.
- [101] Y. Li, P. Zolotavin, P. Doak, L. Kronik, J. B. Neaton and D. Natelson, *Nano Lett.*, 2016, **16**, 1104–1109.
- [102] M. Banik, V. A. Apkarian, T.-H. Park and M. Galperin, *J. Phys. Chem. Lett.*, 2013, **4**, 88–92.
- [103] A. J. White, S. Tretiak and M. Galperin, *Nano Lett.*, 2014, **14**, 699–703.
- [104] Y. Selzer and U. Peskin, *J. Phys. Chem. C*, 2013, **117**, 22369–22376.
- [105] M. A. Ochoa, Y. Selzer, U. Peskin and M. Galperin, *J. Phys. Chem. Lett.*, 2015, **6**, 470–476.
- [106] G. Nardin, T. M. Autry, K. L. Silverman and S. T. Cundiff, *Opt. Express*, 2013, **21**, 28617–28627.
- [107] K. J. Karki, J. R. Widom, J. Seibt, I. Moody, M. C. Lonergan, T. Pullerits and A. H. Marcus, *Nat. Commun.*, 2014, **5**, 5869.
- [108] E. Vella, H. Li, P. Grégoire, S. M. Tuladhar, M. S. Vezie, S. Few, C. M. Bazán, J. Nelson, C. Silva-Acuña and E. R. Bittner, *Sci. Rep.*, 2016, **6**, 29437–.
- [109] M. I. Stockman, *Opt. Express*, 2011, **19**, 22029–22106.
- [110] M. S. Tame, K. R. McEnery, S. K. Ozdemir, J. Lee, S. A. Maier and M. S. Kim, *Nature Phys.*, 2013, **9**, 329–340.

- [111] B. Luk'yanchuk, N. I. Zheludev, S. A. Maier, N. J. Halas, P. Nordlander, H. Giessen and C. T. Chong, *Nature Mater.*, 2010, **9**, 707–715.
- [112] F. J. G. de Abajo, *Nature*, 2012, **483**, 417–418.
- [113] J. A. Scholl, A. L. Koh and J. A. Dionne, *Nature*, 2012, **483**, 421–427.
- [114] K. J. Savage, M. M. Hawkeye, R. Esteban, A. G. Borisov, J. Aizpurua and J. J. Baumberg, *Nature*, 2012, **491**, 574–577.
- [115] P. Nordlander, *Science*, 2014, **343**, 1444–1445.
- [116] P. Z. El-Khoury and W. P. Hess, *Nano Lett.*, 2014, **14**, 4114–4118.
- [117] S. F. Tan, L. Wu, J. K. Yang, P. Bai, M. Bosman and C. A. Nijhuis, *Science*, 2014, **343**, 1496–1499.
- [118] W. Zhu, R. Esteban, A. G. Borisov, J. J. Baumberg, P. Nordlander, H. J. Lezec, J. Aizpurua and K. B. Crozier, *Nat. Commun.*, 2016, **7**, 11495.
- [119] F. Benz, M. K. Schmidt, A. Dreismann, R. Chikkaraddy, Y. Zhang, A. Demetriadou, C. Carnegie, H. Ohadi, B. de Nijs, R. Esteban, J. Aizpurua and J. J. Baumberg, *Science*, 2016, **354**, 726–729.
- [120] S. Lerch and B. M. Reinhard, *Adv. Mater.*, 2016, **28**, 2030–2036.
- [121] T. Wang and C. A. Nijhuis, *Appl. Mater. Today*, 2016, **3**, 73–86.
- [122] T. Schwartz, J. A. Hutchison, C. Genet and T. W. Ebbesen, *Phys. Rev. Lett.*, 2011, **106**, 196405.
- [123] J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux and T. W. Ebbesen, *Angew. Chem. Int. Ed.*, 2012, **51**, 1592–1596.
- [124] J. A. Hutchison, A. Liscio, T. Schwartz, A. Canaguier-Durand, C. Genet, V. Palermo, P. Samorí and T. W. Ebbesen, *Adv. Mater.*, 2013, **25**, 2481–2485.
- [125] T. Schwartz, J. A. Hutchison, J. Léonard, C. Genet, S. Haacke and T. W. Ebbesen, *ChemPhysChem*, 2013, **14**, 125–131.
- [126] A. Canaguier-Durand, E. Devaux, J. George, Y. Pang, J. A. Hutchison, T. Schwartz, C. Genet, N. Wilhelms, J.-M. Lehn and T. W. Ebbesen, *Angew. Chem. Int. Ed.*, 2013, **52**, 10533–10536.
- [127] K. Murch, *Nature Phys.*, 2017, **13**, 11–12.
- [128] C. R. Kagan and M. A. Ratner, *MRS Bulletin*, 2004, **29**, 376–384.
- [129] H. Chen, G. C. Schatz and M. A. Ratner, *Rep. Prog. Phys.*, 2012, **75**, 096402.



- [130] M. Galperin and A. Nitzan, *Phys. Rev. Lett.*, 2005, **95**, 206802.
- [131] M. Galperin and A. Nitzan, *J. Chem. Phys.*, 2006, **124**, 234709.
- [132] U. Harbola, J. B. Maddox and S. Mukamel, *Phys. Rev. B*, 2006, **73**, 075211.
- [133] M. Galperin and S. Tretiak, *J. Chem. Phys.*, 2008, **128**, 124705.
- [134] K. Miwa, M. Sakaue and H. Kasai, *J. Phys. Soc. Jpn.*, 2013, **82**, 063715.
- [135] K. Miwa, M. Sakaue and H. Kasai, *J. Phys. Soc. Jpn.*, 2013, **82**, 124707.
- [136] K. Miwa, M. Sakaue and H. Kasai, *Nanoscale Res. Lett.*, 2013, **8**, 204.
- [137] K. Miwa, H. Imada, M. Sakaue, H. Kasai and Y. Kim, *e-J. Surf. Sci. Nanotech.*, 2015, **13**, 385–390.
- [138] S. Ajisaka, B. Žunkovič and Y. Dubi, *Sci. Rep.*, 2015, **5**, 8312.
- [139] H. P. Goswami, W. Hua, Y. Zhang, S. Mukamel and U. Harbola, *J. Chem. Theory Comput.*, 2015, **11**, 4304–4315.
- [140] G. Chenkn, X.-g. Li and Z.-c. Dong, *Chin. J. Chem. Phys.*, 2015, **28**, 552–556.
- [141] T. A. Niehaus, T. Frauenheim and B. Korff, *J. Phys. Chem. C*, 2016, **120**, 3699–3704.
- [142] R. Wang, Y. Zhang, F. Bi, T. Frauenheim, G. Chen and C. Yam, *Nanoscale*, 2016, **8**, 13168–13173.
- [143] A. Dasgupta, D. Singh, R. P. N. Tripathi and G. V. P. Kumar, *J. Phys. Chem. C*, 2016, **120**, 17692–17698.
- [144] B. D. Fainberg, M. Jouravlev and A. Nitzan, *Phys. Rev. B*, 2007, **76**, 245329.
- [145] G. Li, S. Welack, M. Schreiber and U. Kleinekathöfer, *Phys. Rev. B*, 2008, **77**, 075321.
- [146] B. D. Fainberg, M. Sukharev, T.-H. Park and M. Galperin, *Phys. Rev. B*, 2011, **83**, 205425.
- [147] U. Peskin and M. Galperin, *J. Chem. Phys.*, 2012, **136**, 044107.
- [148] A. J. White, U. Peskin and M. Galperin, *Phys. Rev. B*, 2013, **88**, 205424.
- [149] L.-Y. Hsu, D. Xie and H. Rabitz, *J. Chem. Phys.*, 2014, **141**, 124703.
- [150] Z. Hu, M. A. Ratner and T. Seideman, *J. Chem. Phys.*, 2014, **141**, 224104.
- [151] K. Lopata and D. Neuhauser, *J. Chem. Phys.*, 2009, **131**, 014701.

- [152] K. Lopata and D. Neuhauser, *J. Chem. Phys.*, 2009, **130**, 104707.
- [153] M. Sukharev and M. Galperin, *Phys. Rev. B*, 2010, **81**, 165307.
- [154] H. Chen, J. M. McMahon, M. A. Ratner and G. C. Schatz, *J. Phys. Chem. C*, 2010, **114**, 14384–14392.
- [155] C. Arntsen, K. Lopata, M. R. Wall, L. Bartell and D. Neuhauser, *J. Chem. Phys.*, 2011, **134**, 084101.
- [156] M. Sukharev and A. Nitzan, *Phys. Rev. A*, 2011, **84**, 043802.
- [157] A. J. White, M. Sukharev and M. Galperin, *Phys. Rev. B*, 2012, **86**, 205324.
- [158] Y. Gao and D. Neuhauser, *J. Chem. Phys.*, 2012, **137**, 074113.
- [159] J. Mullin and G. C. Schatz, *J. Phys. Chem. A*, 2012, **116**, 1931–1938.
- [160] M. Kornbluth, A. Nitzan and T. Seideman, *J. Chem. Phys.*, 2013, **138**, 174707.
- [161] S. M. Parker, M. Smeu, I. Franco, M. A. Ratner and T. Seideman, *Nano Lett.*, 2014, **14**, 4587–4591.
- [162] G. Chen, X.-G. Li, Z.-Y. Zhang and Z.-C. Dong, *Nanoscale*, 2015, **7**, 2442–2449.
- [163] S. Rahav and S. Mukamel, *J. Chem. Phys.*, 2010, **133**, 244106.
- [164] B. K. Agarwalla, U. Harbola, W. Hua, Y. Zhang and S. Mukamel, *J. Chem. Phys.*, 2015, **142**, 212445.
- [165] P. Saurabh and S. Mukamel, *J. Chem. Phys.*, 2016, **144**, 124115.
- [166] H. Li, A. Gauthier-Houle, P. Grégoire, E. Vella, C. Silva-Acuña and E. R. Bittner, *Chem. Phys.*, 2016, **481**, 281 – 286.
- [167] M. Galperin, M. A. Ratner and A. Nitzan, *Nano Lett.*, 2009, **9**, 758–762.
- [168] M. Galperin, M. A. Ratner and A. Nitzan, *J. Chem. Phys.*, 2009, **130**, 144109.
- [169] U. Harbola, B. K. Agarwalla and S. Mukamel, *J. Chem. Phys.*, 2014, **141**, 074107.
- [170] M. Galperin, M. A. Ratner and A. Nitzan, *J. Chem. Phys.*, 2015, **142**, 137101.
- [171] Y. Gao, M. Galperin and A. Nitzan, *J. Chem. Phys.*, 2016, **144**, 244114.
- [172] S. Dey, M. Banik, E. Hulkko, K. Rodriguez, V. A. Apkarian, M. Galperin and A. Nitzan, *Phys. Rev. B*, 2016, **93**, 035411.

- [173] M. Galperin and A. Nitzan, *J. Phys. Chem. Lett.*, 2011, **2**, 2110–2113.
- [174] M. Galperin and A. Nitzan, *Phys. Rev. B*, 2011, **84**, 195325.
- [175] J.-T. Lü, M. Brandbyge, P. Hedegård, T. N. Todorov and D. Dundas, *Phys. Rev. B*, 2012, **85**, 245444.
- [176] X.-F. Lang, P.-G. Yin, E.-Z. Tan, T.-T. You and L. Guo, *J. Raman Spectrosc.*, 2013, **44**, 425–432.
- [177] D.-Y. Wu, L.-B. Zhao, X.-M. Liu, R. Huang, Y.-F. Huang, B. Ren and Z.-Q. Tian, *Chem. Commun.*, 2011, **47**, 2520–2522.
- [178] F. Mirjani, J. M. Thijssen and M. A. Ratner, *J. Phys. Chem. C*, 2012, **116**, 23120–23129.
- [179] T.-H. Park and M. Galperin, *Europhys. Lett.*, 2011, **95**, 27001.
- [180] T.-H. Park and M. Galperin, *Phys. Rev. B*, 2011, **84**, 075447.
- [181] T.-H. Park and M. Galperin, *Phys. Scripta T*, 2012, **151**, 014038.
- [182] L. L. Zhao, L. Jensen and G. C. Schatz, *Nano Lett.*, 2006, **6**, 1229–1234.
- [183] M. Oren, M. Galperin and A. Nitzan, *Phys. Rev. B*, 2012, **85**, 115435.
- [184] M. Banik, A. Nag, P. Z. El-Khoury, A. Rodriguez Perez, N. Guarrotxena, G. C. Bazan and V. A. Apkarian, *J. Phys. Chem. C*, 2012, **116**, 10415–10423.
- [185] N. Valley, N. Greeneltch, R. P. Van Duyne and G. C. Schatz, *J. Phys. Chem. Lett.*, 2013, **4**, 2599–2604.
- [186] P. Tarakeshwar, J. L. Palma, D. Finkelstein-Shapiro, A. Keller, I. Urdaneta, M. Calatayud, O. Atabek and V. Mujica, *J. Phys. Chem. C*, 2014, **118**, 3774–3782.
- [187] J. Zuloaga, E. Prodan and P. Nordlander, *Nano Lett.*, 2009, **9**, 887–891.
- [188] A. Ridolfo, O. Di Stefano, N. Fina, R. Saija and S. Savasta, *Phys. Rev. Lett.*, 2010, **105**, 263601.
- [189] A. Manjavacas, F. J. G. d. Abajo and P. Nordlander, *Nano Lett.*, 2011, **11**, 2318–2323.
- [190] P. Song, P. Nordlander and S. Gao, *J. Chem. Phys.*, 2011, **134**, 074701.
- [191] R. Esteban, A. G. Borisov, P. Nordlander and J. Aizpurua, *Nat. Commun.*, 2012, **3**, 825.
- [192] D. Marinica, A. Kazansky, P. Nordlander, J. Aizpurua and A. G. Borisov, *Nano Lett.*, 2012, **12**, 1333–1339.

- [193] A. J. White, B. D. Fainberg and M. Galperin, *J. Phys. Chem. Lett.*, 2012, **3**, 2738–2743.
- [194] P. Song, S. Meng, P. Nordlander and S. Gao, *Phys. Rev. B*, 2012, **86**, 121410.
- [195] O. Pérez-González, J. Aizpurua and N. Zabala, *Opt. Express*, 2013, **21**, 15847–15858.
- [196] F. Schlawin, K. E. Dorfman, B. P. Fingerhut and S. Mukamel, *Nat. Commun.*, 2013, **4**, 1782.
- [197] J. C. L. Carreño and F. P. Laussy, *Phys. Rev. A*, 2016, **94**, 063825.
- [198] J. C. L. Carreño, C. Sánchez Muñoz, E. del Valle and F. P. Laussy, *Phys. Rev. A*, 2016, **94**, 063826.
- [199] M. Kowalewski, K. Bennett and S. Mukamel, *J. Chem. Phys.*, 2016, **144**, 054309.
- [200] F. Xu, C. Holmqvist and W. Belzig, *Phys. Rev. Lett.*, 2014, **113**, 066801.
- [201] K. Kaasbjerg and A. Nitzan, *Phys. Rev. Lett.*, 2015, **114**, 126803.
- [202] P. Lodahl, S. Mahmoodian and S. Stobbe, *Rev. Mod. Phys.*, 2015, **87**, 347–400.
- [203] K. E. Dorfman, F. Schlawin and S. Mukamel, *Rev. Mod. Phys.*, 2016, **88**, 045008.
- [204] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, Oxford University Press, 1995, vol. 6.
- [205] H. Haug and A.-P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors*, Springer, Berlin Heidelberg, Second, Substantially Revised Edition edn., 2008.
- [206] M. Esposito, M. A. Ochoa and M. Galperin, *Phys. Rev. B*, 2015, **92**, 235440.
- [207] M. A. Ochoa, A. Bruch and A. Nitzan, *Phys. Rev. B*, 2016, **94**, 035420.
- [208] R. J. Glauber, *Phys. Rev. Lett.*, 1963, **10**, 84–86.
- [209] R. J. Glauber, *Phys. Rev.*, 1963, **131**, 2766–2788.
- [210] P. L. Kelley and W. H. Kleiner, *Phys. Rev.*, 1964, **136**, A316–A334.
- [211] M. O. Scully and W. E. Lamb, *Phys. Rev.*, 1969, **179**, 368–374.
- [212] L. S. Levitov and G. B. Lesovik, *JETP Lett.*, 1993, **58**, 230–235.

- [213] L. S. Levitov, H. Lee and G. B. Lesovik, *J. Math. Phys.*, 1996, **37**, 4845–4866.
- [214] Y. M. Blanter and M. Buttiker, *Phys. Rep.*, 2000, **336**, 1–166.
- [215] J. Kim, O. Benson, H. Kan and Y. Yamamoto, *Nature*, 1999, **397**, 500–503.
- [216] E. Zakka-Bajjani, J. Dufouleur, N. Coulombel, P. Roche, D. C. Glattli and F. Portier, *Phys. Rev. Lett.*, 2010, **104**, 206802.
- [217] D. Djukic and J. M. van Ruitenbeek, *Nano Lett.*, 2006, **6**, 789–793.
- [218] O. Tal, M. Krieger, B. Leerink and J. M. van Ruitenbeek, *Phys. Rev. Lett.*, 2008, **100**, 196804.
- [219] J.-C. Forgues, F. B. Sane, S. Blanchard, L. Spietz, C. Lupien and B. Reulet, *Sci. Rep.*, 2013, **3**, 2869.
- [220] T. Fujisawa, T. Hayashi, R. Tomita and Y. Hirayama, *Science*, 2006, **312**, 1634.
- [221] M. Esposito, U. Harbola and S. Mukamel, *Rev. Mod. Phys.*, 2009, **81**, 1665–1702.
- [222] C. Emary, C. Pörtl, A. Carmele, J. Kabuss, A. Knorr and T. Brandes, *Phys. Rev. B*, 2012, **85**, 165417.
- [223] S. Dambach, B. Kubala, V. Gramich and J. Ankerhold, *Phys. Rev. B*, 2015, **92**, 054508.
- [224] O. L. Bo and Y. Galperin, *J. Phys.: Condens. Matter*, 1996, **8**, 3033–3045.
- [225] U. Gavish, Y. Levinson and Y. Imry, *Phys. Rev. B*, 2000, **62**, R10637–R10640.
- [226] U. Gavish, Y. Imry and Y. Levinson, *Quantum noise, detailed balance and Kubo formula in nonequilibrium quantum systems*, arXiv: 0211681, 2002.
- [227] F. M. Souza, A. P. Jauho and J. C. Egues, *Phys. Rev. B*, 2008, **78**, 155303.
- [228] K. E. Dorfman and S. Mukamel, *Physica Scripta*, 2016, **91**, 083004.
- [229] J. Schwinger, *J. Math. Phys.*, 1961, **2**, 407–432.
- [230] L. V. Keldysh, *Sov. Phys. JETP*, 1965, **20**, 1018–1026.
- [231] K. E. Dorfman, F. Schlawin and S. Mukamel, *J. Phys. Chem. Lett.*, 2014, **5**, 2843–2849.
- [232] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems*, Oxford University Press, 2003.

- [233] L. Kidon, E. Y. Wilner and E. Rabani, *J. Chem. Phys.*, 2015, **143**, 234110.
- [234] S. Mukamel, *Phys. Rev. E*, 2003, **68**, 021111.
- [235] U. Harbola and S. Mukamel, *Phys. Rep.*, 2008, **465**, 191 – 222.
- [236] L. Mühlbacher and E. Rabani, *Phys. Rev. Lett.*, 2008, **100**, 176403.
- [237] R. B. Saptsov and M. R. Wegewijs, *Phys. Rev. B*, 2012, **86**, 235432.
- [238] R. B. Saptsov and M. R. Wegewijs, *Phys. Rev. B*, 2014, **90**, 045407.
- [239] G. Cohen, E. Gull, D. R. Reichman and A. J. Millis, *Phys. Rev. Lett.*, 2015, **115**, 266802.
- [240] M. Esposito and M. Galperin, *Phys. Rev. B*, 2009, **79**, 205303.
- [241] M. Esposito and M. Galperin, *J. Phys. Chem. C*, 2010, **114**, 20362–20369.
- [242] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems*, McGraw-Hill Book Company, 1971.
- [243] P. Danielewicz, *Ann. Phys.*, 1984, **152**, 239–304.
- [244] M. Wagner, *Phys. Rev. B*, 1991, **44**, 6104–6117.
- [245] A. Stan, N. E. Dahlen and R. van Leeuwen, *J. Chem. Phys.*, 2009, **130**, 224101.
- [246] P. Myöhänen, A. Stan, G. Stefanucci and R. van Leeuwen, *J. Phys.: Conf. Ser.*, 2010, **220**, 012017.
- [247] Y. Meir and N. S. Wingreen, *Phys. Rev. Lett.*, 1992, **68**, 2512–2515.
- [248] A.-P. Jauho, N. S. Wingreen and Y. Meir, *Phys. Rev. B*, 1994, **50**, 5528–5544.
- [249] Y. Gao and M. Galperin, *J. Chem. Phys.*, 2016, **144**, 174113.
- [250] G. Baym and L. P. Kadanoff, *Phys. Rev.*, 1961, **124**, 287–299.
- [251] G. Baym, *Phys. Rev.*, 1962, **127**, 1391–1401.
- [252] G. Stefanucci and R. van Leeuwen, *Nonequilibrium Many-Body Theory of Quantum Systems. A Modern Introduction.*, Cambridge University Press, 2013.
- [253] J. M. Luttinger and J. C. Ward, *Phys. Rev.*, 1960, **118**, 1417–1427.
- [254] C. De Dominicis and P. C. Martin, *J. Math. Phys.*, 1964, **5**, 14–30.
- [255] R. Haussmann, *Self-consistent Quantum-Field Theory and Bosonization for Strongly Correlated Electron Systems*, Springer-Verlag, Berlin Heidelberg, 1999.

- [256] A. O. Gogolin and A. Komnik, *Phys. Rev. B*, 2006, **73**, 195301.
- [257] G.-M. Tang and J. Wang, *Phys. Rev. B*, 2014, **90**, 195422.
- [258] Z. Yu, G.-M. Tang and J. Wang, *Phys. Rev. B*, 2016, **93**, 195419.
- [259] P. Damle, A. W. Ghosh and S. Datta, *Chem. Phys.*, 2002, **281**, 171–187.
- [260] Y. Xue, S. Datta and M. A. Ratner, *Chem. Phys.*, 2002, **281**, 151–170.
- [261] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor and K. Stokbro, *Phys. Rev. B*, 2002, **65**, 165401.
- [262] A. Baratz, M. Galperin and R. Baer, *J. Phys. Chem. C*, 2013, **117**, 10257–10263.
- [263] N. S. Wingreen and Y. Meir, *Phys. Rev. B*, 1994, **49**, 11040–11052.
- [264] N. Sivan and N. S. Wingreen, *Phys. Rev. B*, 1996, **54**, 11622–11629.
- [265] H. Aoki, N. Tsuji, M. Eckstein, M. Kollar, T. Oka and P. Werner, *Rev. Mod. Phys.*, 2014, **86**, 779–837.
- [266] M. Eckstein and P. Werner, *Phys. Rev. B*, 2010, **82**, 115115.
- [267] J. H. Oh, D. Ahn and V. Bubanja, *Phys. Rev. B*, 2011, **83**, 205302.
- [268] A. J. White and M. Galperin, *Phys. Chem. Chem. Phys.*, 2012, **14**, 13809–13819.
- [269] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet and C. A. Marianetti, *Rev. Mod. Phys.*, 2006, **78**, 865–951.
- [270] H.-T. Chen, G. Cohen, A. J. Millis and D. R. Reichman, *Phys. Rev. B*, 2016, **93**, 174309.
- [271] J. Hubbard, *Proc. R. Soc. Lond. A*, 1967, **296**, 82–99.
- [272] Y. A. Izyumov and Y. N. Skryabin, *Statistical Mechanics of Magentically Ordered Systems*, Consultants Bureau, New York and London, 1988.
- [273] Y. A. Izyumov, M. I. Katsnelson and Y. N. Skryabin, *Itinerant Electron Magnetism (in Russian)*, Nauka, Moscow, 1994.
- [274] S. G. Ovchinnikov and V. V. Val'kov, *Systems Operators in the Theory of Strongly Correlated Electrons*, Imperial College Press, 2004.
- [275] F. Chen, M. A. Ochoa and M. Galperin, *J. Chem. Phys.*, 2017, **146**, 092301.
- [276] H. Schoeller and G. Schön, *Phys. Rev. B*, 1994, **50**, 18436–18452.
- [277] J. König, J. Schmid, H. Schoeller and G. Schön, *Phys. Rev. B*, 1996, **54**, 16820–16837.

- [278] H. Schoeller, *Lect. Notes Phys.*, 2000, **544**, 137–166.
- [279] M. Leijnse and M. R. Wegewijs, *Phys. Rev. B*, 2008, **78**, 235424.
- [280] I. Sandalov, B. Johansson and O. Eriksson, *Int. J. Quant. Chem.*, 2003, **94**, 113–143.
- [281] J. Fransson, *Phys. Rev. B*, 2005, **72**, 075314.
- [282] I. Sandalov and R. G. Nazmitdinov, *J. Phys.: Condens. Matter*, 2006, **18**, L55–L61.
- [283] I. Sandalov and R. G. Nazmitdinov, *Phys. Rev. B*, 2007, **75**, 075315.
- [284] M. Galperin, A. Nitzan and M. A. Ratner, *Phys. Rev. B*, 2008, **78**, 125320.
- [285] J. Fransson, *Non-Equilibrium Nano-Physics. A Many-Body Approach.*, Springer, 2010.
- [286] A. Perelomov, *Generalized Coherent States and Their Applications*, Springer, 1986.
- [287] T.-S. Ho, K. Wang and S.-I. Chu, *Phys. Rev. A*, 1986, **33**, 1798–1816.
- [288] G. Stefanucci, S. Kurth, A. Rubio and E. K. U. Gross, *Phys. Rev. B*, 2008, **77**, 075339.
- [289] D. Rai and M. Galperin, *J. Phys. Chem. C*, 2013, **117**, 13730–13737.
- [290] Y. Gao and M. Galperin, *J. Chem. Phys.*, 2016, **144**, 244106.
- [291] S. D. Gedney, *Introduction to the finite-difference time-domain (FDTD) method for electromagnetics*, Morgan & Claypool, 2011.
- [292] M. Esposito, M. A. Ochoa and M. Galperin, *Phys. Rev. B*, 2015, **91**, 115417.
- [293] T. Zelovich, L. Kronik and O. Hod, *J. Chem. Theory Comput.*, 2014, **10**, 2927–2941.
- [294] L. Chen, T. Hansen and I. Franco, *J. Phys. Chem. C*, 2014, **118**, 20009–20017.
- [295] J. Jin, X. Zheng and Y. Yan, *J. Chem. Phys.*, 2008, **128**, 234703.
- [296] R. Härtle, G. Cohen, D. R. Reichman and A. J. Millis, *Phys. Rev. B*, 2013, **88**, 235426.
- [297] Y. Yan, *J. Chem. Phys.*, 2014, **140**, 054105.
- [298] S. Latini, E. Perfetto, A.-M. Uimonen, R. van Leeuwen and G. Stefanucci, *Phys. Rev. B*, 2014, **89**, 075306.



- [299] K. Balzer and M. Eckstein, *Phys. Rev. B*, 2014, **89**, 035148.
- [300] A. Baratz, A. J. White, M. Galperin and R. Baer, *J. Phys. Chem. Lett.*, 2014, **5**, 3545–3550.
- [301] K. Kaasbjerg, T. Novotný and A. Nitzan, *Phys. Rev. B*, 2013, **88**, 201405.
- [302] F. Chen, K. Miwa and M. Galperin, *Scientific Reports*, 2017, **7**, 9735.
- [303] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics*, W. A. Benjamin, Inc., New York, 1962.
- [304] T.-H. Park and M. Galperin, *Phys. Rev. B*, 2011, **84**, 205450.
- [305] P. Myöhänen, A. Stan, G. Stefanucci and R. van Leeuwen, *Phys. Rev. B*, 2009, **80**, 115107.
- [306] R. Sánchez, G. Platero and T. Brandes, *Phys. Rev. Lett.*, 2007, **98**, 146805.
- [307] R. Sánchez, G. Platero and T. Brandes, *Phys. Rev. B*, 2008, **78**, 125308.
- [308] I. Kinoshita, A. Misu and T. Munakata, *The Journal of Chemical Physics*, 1995, **102**, 2970–2976.
- [309] W. Tian, S. Datta, S. Hong, R. Reifenberger, J. I. Henderson and C. P. Kubiak, *J. Chem. Phys.*, 1998, **109**, 2874–2882.

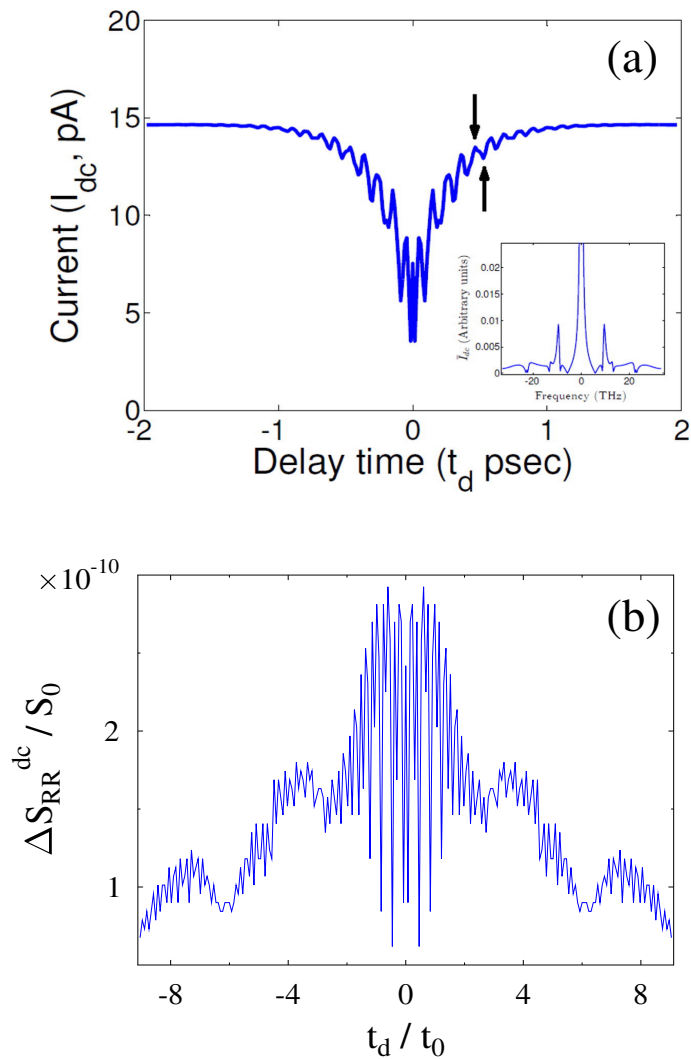


Figure 6: Pump-probe spectroscopy in nanojunctions. Laser pulse pair sequence induced (a) dc current and (b) dc noise plotted against delay time  $t_d$  reveal intramolecular dynamics on the sub-pico-second time scale. Fig. 6a reprinted with permission from Y. Selzer and U. Peskin, *J. Phys. Chem. C*, 2013, **117**, 22369-22376. Copyright (2013) American Chemical Society. Fig. 6b reprinted with permission from M. A. Ochoa, Y. Selzer, U. Peskin, and M. Galperin, *J. Phys. Chem. Lett.*, 2015, **6**, 470-476. Copyright (2013) American Chemical Society.

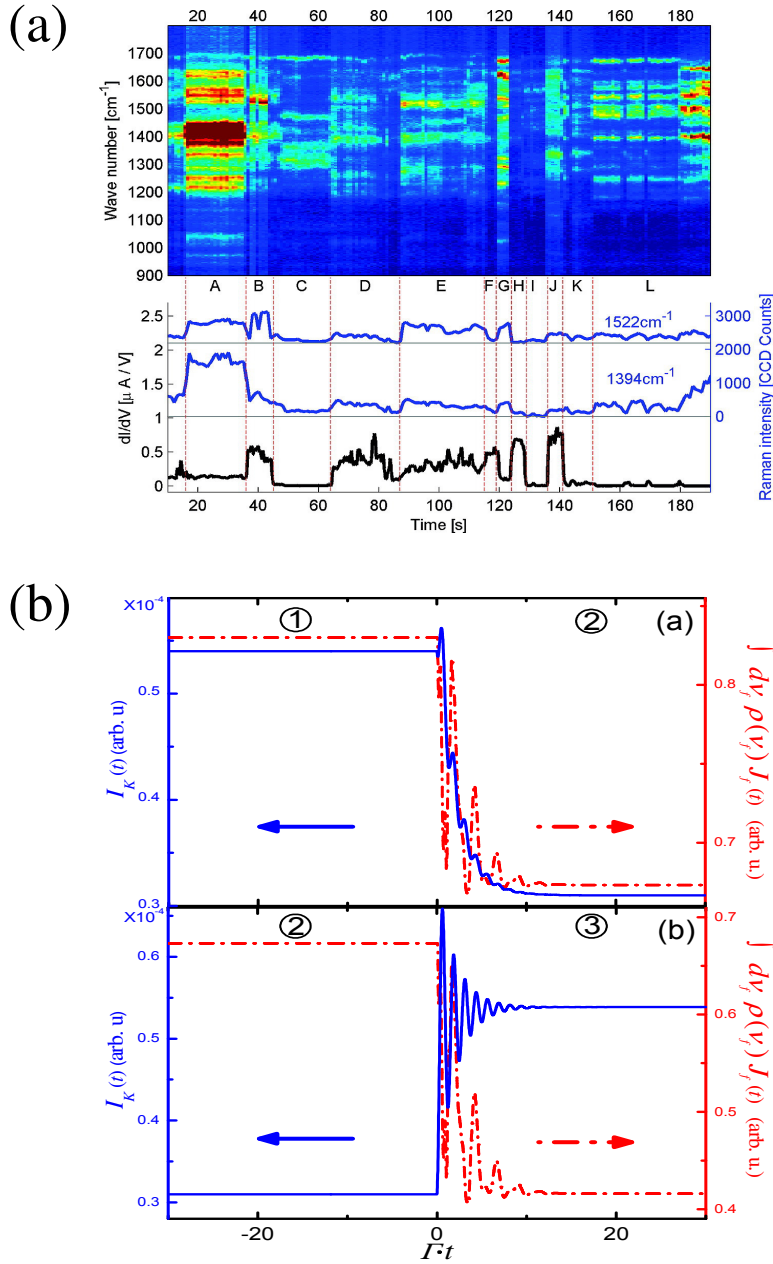


Figure 7: Time-dependent fluctuations in simultaneously measured electronic conductance and Raman response in molecular junctions. Shown are (a) experimental data and (b) a theoretical analysis. Fig.7a reprinted with permission from D. R. Ward, N. J. Halas, J. W. Ciszek, J. M. Tour, Y. Wu, P. Nordlander, D. Natelson, *Nano Lett.* 2008, **8**, 919-924. Copyright (2008) American Chemical Society. Fig. 7b reprinted with permission from [T.-H. Park and M. Galperin, *Phys. Rev. B*, **84**, 075447 (2011).] Copyright (2011) by the American Physical Society. <http://dx.doi.org/10.1103/PhysRevB.84.075447>

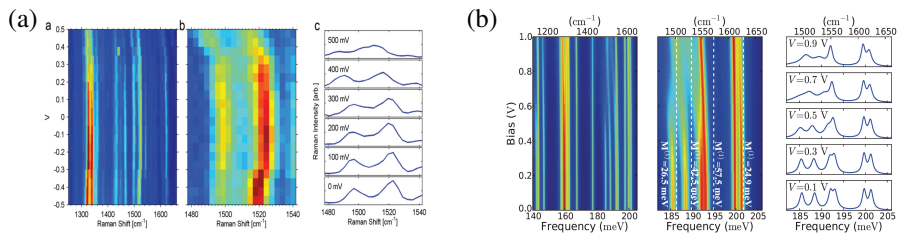


Figure 8: Bias dependence of Raman shift in OPV3 junction. Shown are (a) experimental data and (b) a theoretical analysis. Fig. 8a reprinted by permission from Macmillan Publishers Ltd: [Nature Nanotechnology] (Ref. <sup>96</sup>), copyright (2011). Fig. 8b reprinted with permission from [K. Kaasbjerg, T. Novotný, and A. Nitzan, Phys. Rev. B **88**, 201405 (2013).] Copyright (2013) by the American Physical Society. <http://dx.doi.org/10.1103/PhysRevB.88.201405>

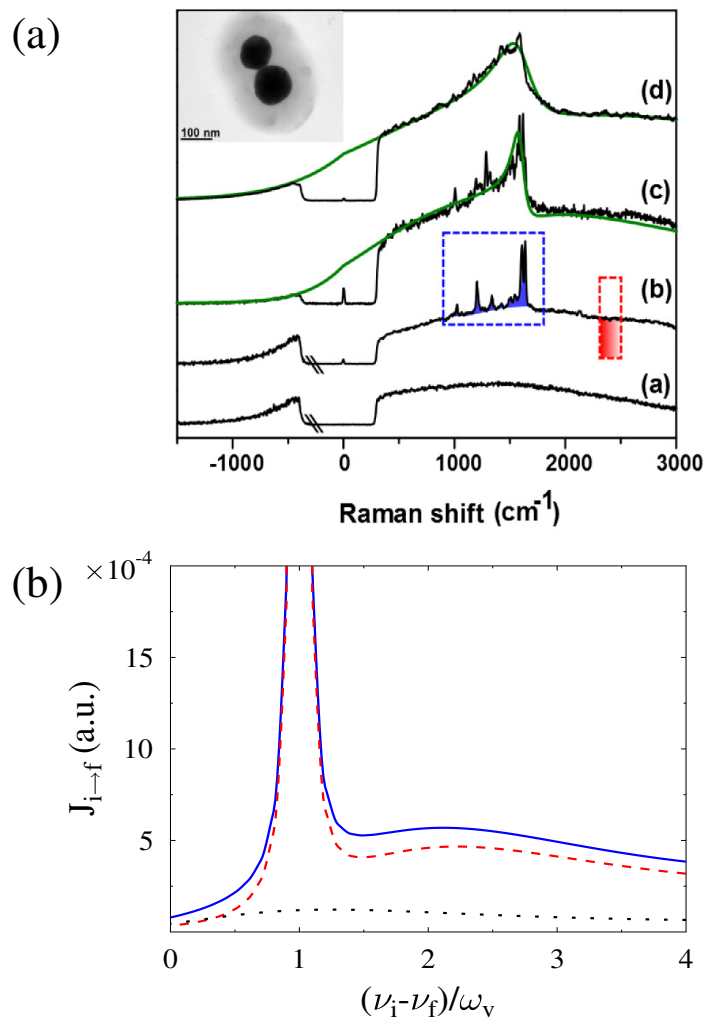


Figure 9: Fano-like lineshapes in the Raman spectra of molecules adsorbed at metal interfaces: (a) experimental data and (b) a theoretical analysis. Plotted in (b) are pure electronic (black dotted line), electronic-dressed vibrational Raman (red dashed line), and their sum (full blue line). Figure reprinted with permission from [S. Dey, M. Banik, E. Hulkko, K. Rodriguez, V. A. Apkarian, M. Galperin, and A. Nitzan, *Phys. Rev. B* **93**, 035411 (2016).] Copyright (2016) by the American Physical Society. <http://dx.doi.org/10.1103/PhysRevB.93.035411>

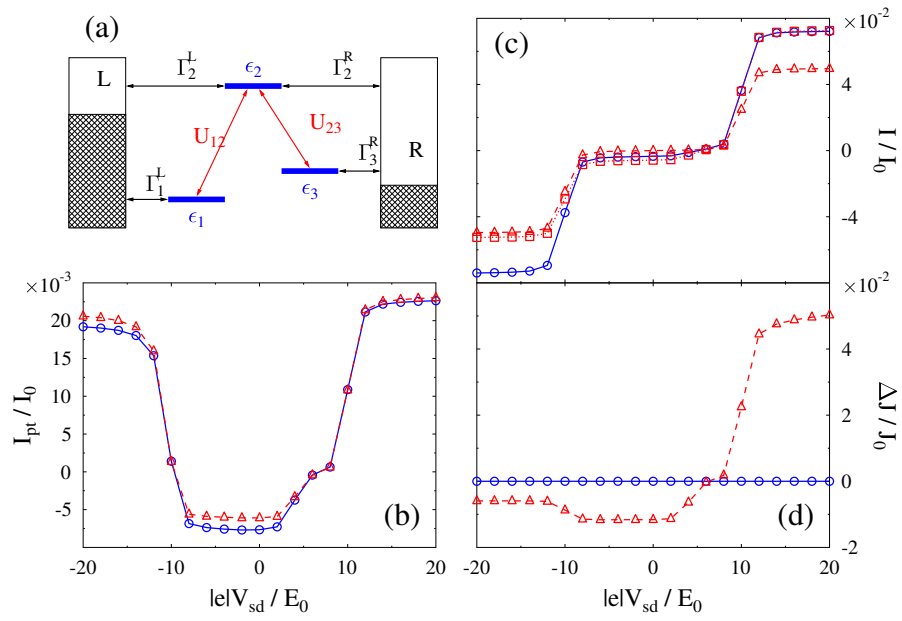


Figure 10: Physical conservation laws in junction spectroscopy. For a three-level model (a) calculations of photon (b) electron (c) and energy (d) fluxes within diagrammatic (solid blue line) and bare (dashed and dotted red lines) perturbation theories show violation of conservation laws by the latter. Reprinted from [Y. Gao and M. Galperin, *J. Chem. Phys.* 2016, **144**, 174113], with the permission of AIP Publishing.

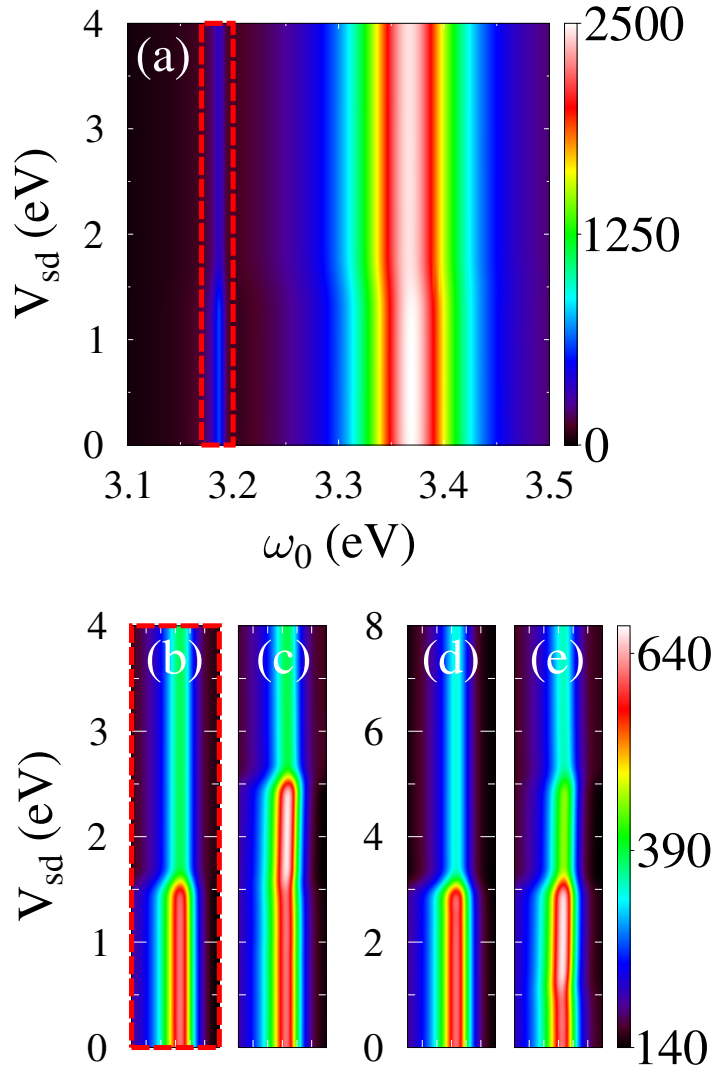


Figure 11: Strong exciton-plasmon coupling in junctions. PP-NEGF study of plasmon absorption spectrum as a function of bias (a) and close-up of Fano resonance (b-e) for different intra-system interactions and bias profiles. Reprinted with permission from (A. J. White, B. D. Fainberg, and M. Galperin, *J. Phys. Chem. Lett.* 2012, **3**, 2738-2743). Copyright (2012) American Chemical Society.

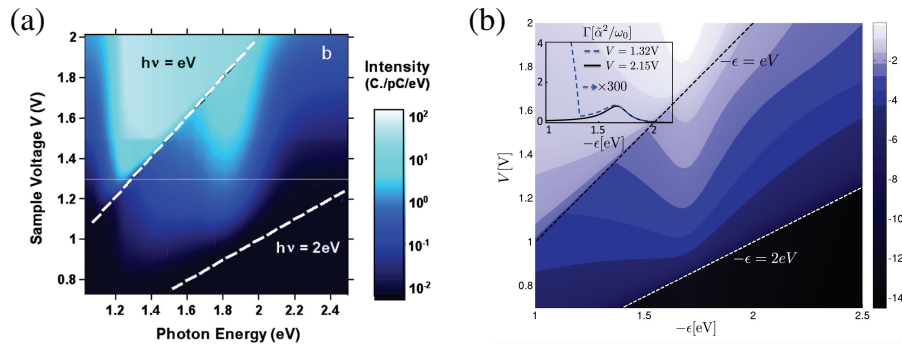


Figure 12: Bias induced light emission as a source of information on electron-electron and electron-plasmon interactions in junctions. Emission spectrum vs. applied bias: (a) experimental data and (b) a theoretical analysis. Fig. 12a reprinted with permission from [G. Schull, N. Neel, P. Johansson, and R. Berndt, Phys. Rev. Lett. **102**, 057401 (2009).] Copyright (2014) by the American Physical Society. <http://dx.doi.org/10.1103/PhysRevLett.102.057401> Fig. 12b reprinted with permission from [F. Xu, C. Holmqvist, and W. Belzig, Phys. Rev. Lett. **113**, 066801 (2014).] Copyright (2014) by the American Physical Society. <http://dx.doi.org/10.1103/PhysRevLett.113.066801>



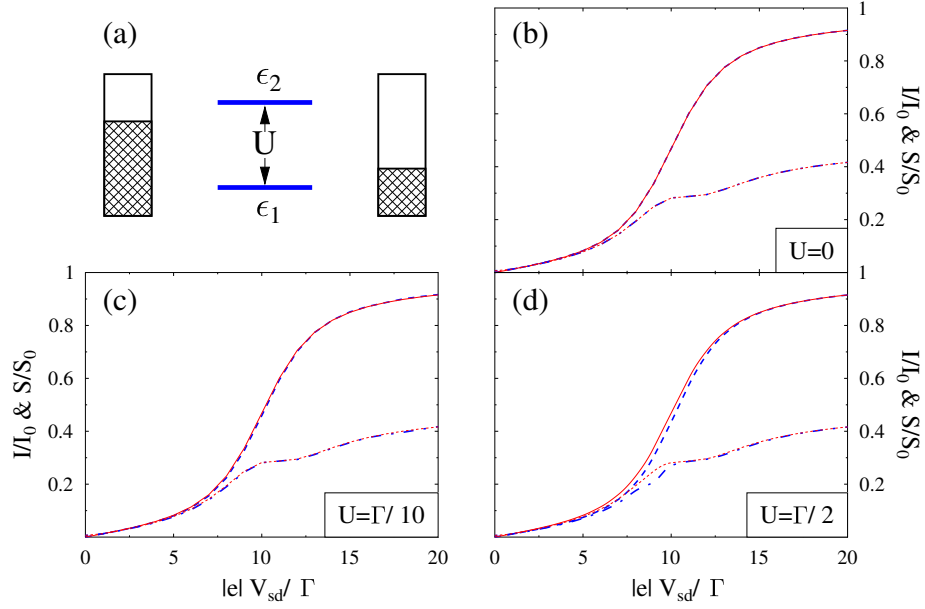


Figure 13: Full counting statistics of electron transport in junctions. Simulation is performed for Hubbard model (a),  $\hat{H}_M = \sum_{i=1,2} \epsilon_i \hat{n}_i + U \hat{n}_1 \hat{n}_2$ , with parameters  $\epsilon_2 = -\epsilon_1 = 5\Gamma$ . Shown are current ( $I_0 = e\Gamma/\hbar$ , solid red and dashed blue lines) and zero frequency noise ( $S_0 = e^2\Gamma/\hbar$ , dotted red and dash-dotted blue lines) calculated, respectively, within NEGF (red) and Hubbard NEGF (blue) methodologies for (b)  $U = 0$  (NEGF is exact here), (c)  $U = \Gamma/10$ , and (d)  $U = \Gamma/2$ . In (c) and (d) NEGF utilizes second order diagrammatic perturbation theory in  $U$ , Hubbard NEGF is second order in system-baths coupling (i.e. first order in  $\Gamma$ ).<sup>302</sup>