Non-Markovian theory of collective plasmon-molecule excitations in nanojunctions combined with classical electrodynamic simulations

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ABSTRACT

We present a pseudoparticle nonequilibrium Green function formalism as a tool to study the coupling between plasmons and excitons in nonequilibrium molecular junctions. The formalism treats plasmon-exciton couplings and intra-molecular interactions exactly, and is shown to be especially convenient for exploration of plasmonic absorption spectrum of plexitonic systems, where combined electron and energy transfers play an important role. We demonstrate the sensitivity of the molecule-plasmon Fano resonance to junction bias and intra-molecular interactions (Coulomb repulsion and intra-molecular exciton coupling). The electromagnetic theory is used in order to derive self-consistent field-induced coupling terms between the molecular and the plasmon excitations. Our study opens a way to deal with strongly interacting plasmon-exciton systems in nonequilibrium molecular devices.

Keywords: Nanojunctions, Plasmon-exciton coupling, Plasmonics, Collective excitations

1. INTRODUCTION

Recent progress in nanofabrication techniques and advances in laser technologies open new directions in research of plasmonic materials at nanoscale.[1,2] Nanoplasmonics finds its application in optical devices,[3–6] photovoltaics,[7–9] and biology.[10–13] In particular, field enhancement by SPs at nanoscale allows the detection of optical response in current carrying molecular junctions.[14] Plasmon coupling to molecular excitations[15] is studied by a field of research named plexcitonics.[16] Such couplings yield a possibility for coherent control of molecular systems[17,18] and are utilized in molecular photodevices.[19–21] Advances in experimental techniques has caused a surge of theoretical research in the areas of nanoplasmonics and plexcitonics. Usually plasmon excitations are studied utilizing the laws of classical electrodynamics,[22–26] while the molecular system is treated quantum-mechanically.[27–32] We used a similar scheme to study transport in molecular junctions driven by surface plasmons (SP).[33,34] Recently, quantum descriptions of plasmonic excitatitons started to appear. For example, time-dependent density functional theory was employed to simulate plasmon excitations in relatively small metallic clusters in Refs.[35–38] while Ref.[39] utilized a quantum master equation to study the effect of plasmonic excitations on the current.

The observation of Fano resonances[40] in plasmonic nanostructures[41] gave impetus to a quantum description of excitations. Such considerations have been done for quantum dot (QD)-metal nanoparticle (MNP) system, where the MNP was studied classically while oscillations of the QD were treated within a density matrix approach.[42–44] Both influence of plasmon system on semiconductor dipole and vice versa were taken into account, and nonlinear Fano effects and bistabiluty were discussed within a mean-field approximation. Recently a fully quantum description of the model was reported in Ref.[45] Finally, a mean-field quantum study of the dips in the absorption spectrum of a molecule between a pair of metallic spheres was presented in Ref.,[46] within an equilibrium Green function formalism. It relies on the factorization of the collective excitations into separated plasmonic and molecular contributions. In this respect, it is well to bear in mind that the dips discussed in Ref.[46]

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can arise from both Fano-like interference and hybridization of a molecule dipole and the plasmon resonances.[47] This hybridization gives rise to a new quasiparticle - polariton.[48–50] Thus, the mean-field type factorization of the molecular and plasmon excitations is not safe in the case of strong plasmon-exciton coupling. Note that in junctions with molecules often chemisorbed on metal surfaces the molecule-plasmon interaction is rather strong, which prohibits perturbative treatment or even usual separation into pure plasmonic and molecular degrees of freedom. Note also that at short ranges of junction gaps pure classical electrodynamics usually employed for study of plasmon excitations, becomes inadequate.

Mixed, non separable, excitations of the molecule-plasmon system bring into play fascinating physics related to the interplay between charge and energy transport through molecular junctions. Especially intriguing is the effect of strong exciton-plasmon coupling on charge transport (current) through the junction. The formulation of microscopic conditions (chemical composition, contact to leads, electrodes structure) for similar plasmon induced coherent optical response in molecular junctions, and its effect on the charge transport is an open challenging task. Along with the potential for new physical phenomena affecting the controllability of transport through molecular junctions, comes the challenge to develop appropriate and reliable theoretical tools to study this strong coupling regime. Mixed coherent excitations of the excitons-plasmons system exclude the validity of Markovian and perturbative approaches, and necessitate an increase in the junction Hilbert space to account for plasmonic degrees of freedom. The generalization of the molecular Hilbert space depends on the physics involved. When a fully quantum mechanical treatment of the plasmonic degrees of freedom becomes essential, a pseudoparticle (PP) approach may be used, where standard methods of the quantum field theory are applicable to the PP operators (see below).

Recently, research efforts of Galperin et al. were focused on the on application of the PP non-equilibrium Green function (NEGF) technique to inelastic transport.[51] The technique is a useful tool for description of open nonequilibrium systems in the language of many-body states (see discussion below). Later we applied the methodology to formulate a fully quantum desctription of strongly correlated plexcitonic systems.[52] Our approach not only generalizes previous considerations[46] bounded to zero-temperature equilibrium (linear response) conditions, but is technically much more convenient in considerations of molecule-plasmon interactions in junctions, where combined coherent electron/energy transfer mechanisms play an important role in the observed physics. Note that a similar but approximate description within the standard NEGF formalism would require a fourth-order perturbation theory to take the effects into account. In other cases, a semi-classical description of the interaction between the molecule with the SPs and the radiation field is sufficient. Then the relatively strong coupling to molecular excitations necessitates a self consistent treatment of plasmonic and molecular excitations. In this case excitations of plasmonic and molecular degrees of freedom can be accounted for implicitly, as time-dependent interactions.

Our goal in this work is to develop a non-Markovian quantum theory of the collective plasmon-molecule excitations in nanojunctions combined with consistent electrodynamical calculations. In other words, we are going to extend model based methodology of Ref.[52] to develop practical implementations for realistic systems based on combination of quantum description of the plexcitonic subsystem with classical electrodynamic simulations. This includes calculation of frequency dependent interactions in a molecular bridge dressed by plasmons due to the presence of metallic contacts.

2. QUANTUM THEORY OF COLLECTIVE PLASMON-MOLECULE EXCITATIONS IN NANOJUNCTIONS BASED ON PP NEGF APPROACH

In the case of strong molecule-plasmon interaction, relevant for the case of molecular junctions when molecules are chemisorbed on at least one of the contacts, separation of molecule and plasmon degrees of freedom is questionable. Thus description in the basis of the whole system (in this case polariton states) becomes important. Extension of molecular spectroscopy, conveniently formulated for isolated molecule systems in the language of molecular states, to molecular junctions also requires a technique which utilizes many-body states as a basis. Such methodology is invaluable tool also in studies of combined charge and energy transfer at surfaces and interfaces. The latter is important in particular for basic energy research. One of methodologies is the PP NEGF (the auxiliary operator representation in the NEGF). Originally the method was developed to describe strongly correlated systems (e.g. the Kondo effect). However, it can also be applied to a simpler problem of

describing transport in the molecular states language all the way down to the Kondo temperature, T_K. The PP NEGF has several advantages: 1. The method is conceptually simple; 2. Its practical implementations rely on a set of controlled approximations (standard diagrammatic perturbation theory techniques can be applied); 3. Already in its simplest implementation, the non-crossing approximation (NCA), the PP NEGF goes beyond standard quantum master equation 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 the on-the-molecule interactions.

The method is based on considerations of spectral decomposition of second quantized operators $\hat{c}^\dagger_\nu$ in terms of many-body states $|m\rangle$ of the system. Extension of the usual Hilbert space to higher dimensions allows representation of the many-body states in terms of creation (and annihilitaion) *PP* operators $\hat{d}^\dagger_m$ ($\hat{d}_m$), which follow the usual Fermi or Bose statistics depending on the nature of the state they represent $\hat{c}^\dagger_\nu \equiv \sum_{m_1,m_2} \xi^\nu_{m_1 m_2} \hat{d}^\dagger_{m_1} \hat{d}_{m_2}$ where $\xi^\nu_{m_1 m_2} \equiv \langle m_1|\hat{c}^\dagger_\nu|m_2\rangle$ is the phase factor of the expansion. The physical subspace of the total PP Hilbert space is defined by the constraint $\hat{Q} = \sum_m \hat{d}^\dagger_m \hat{d}_m = 1$. This constraint can be implemented *e.g.* by introducing a Lagrange multiplier[53,54] or an operator delta function leading to the appearance of a complex chemical potential.[55,56] Note that representation in terms of many-body states $|m\rangle$ allows to take into account all the correlations within the system exactly.

In the extended Hilbert space standard methods of the quantum field theory are applicable to the PP operators. In particular, single particle Green function on the Keldysh contour

$$G_{m_1 m_2}(\tau_1,\tau_2) = -i\langle T_c\, \hat{d}_{m_1}(\tau_1)\, \hat{d}^\dagger_{m_2}(\tau_2)\rangle \tag{1}$$

satisfies the usual Dyson equation $\mathbf{G} = \mathbf{g} + \mathbf{g}\boldsymbol{\Sigma}\mathbf{G}$ where $\mathbf{g}$ is the bare GF, i.e. the GF in the absence of molecule-baths couplings, and $\boldsymbol{\Sigma}$ is the PPs self-energy due to coupling to the baths. Projecting the Dyson equation on the contour and to the physical subspace results in a set of matrix (in the molecular many-body states basis) equations for the lesser and retarded PP Green functions (see Appendices in Ref.[51] for details)

$$\mathbf{G}^r(E) = [E\mathbf{I} - \mathbf{H}_M - \boldsymbol{\Sigma}^r(E)]^{-1} \tag{2}$$

$$\mathbf{G}^<(E) = \mathbf{G}^r(E)\, \boldsymbol{\Sigma}^<(E)\, \mathbf{G}^a(E) \tag{3}$$

Here $\boldsymbol{\Sigma}^r(E)$ and $\boldsymbol{\Sigma}^<(E)$ are retarded and lesser projections of the self-energy. The solution is self-consistent, since self-energies in Eqs. (2)-(3) depend on the Green functions. When system of equations (2)-(3) has been solved, molecular junctions responses to external perturbations (current, optical absorption and emission spectrum, non-equilibrium Raman signal, etc.) can be calculated utilizing the PP Green functions (see Refs.[51,52] for details).

Model. The Hamiltonian of the junction is

$$\hat{H} = \hat{H}_M + \sum_{K=L,R,P} \left(\hat{H}_K + \hat{V}_K\right) \tag{4}$$

Here $\hat{H}_M$ is molecular Hamiltonian

$$\hat{H}_M = \sum_{c=1}^{D} \left[\sum_{s=g,e} \varepsilon_s \hat{c}^\dagger_{cs}\hat{c}_{cs} + \frac{U}{2}\hat{N}_c(\hat{N}_c - 1)\right] + \sum_{c=1}^{D-1}\left[-\sum_{s=g,e} t_s \hat{c}^\dagger_{cs}\hat{c}_{(c+1)s} + J\hbar\hat{b}^\dagger_c\hat{b}_{c+1} + H.c.\right], \tag{5}$$

$\hat{H}_K$ ($K = L, R$) is Hamiltonian of the contacts, and $\hat{V}_K$ describes electron transfer between the molecule and contacts.

$$\hat{H}_K = \sum_{\kappa\in K} \varepsilon_\kappa \hat{c}^\dagger_\kappa \hat{c}_\kappa \tag{6}$$

$$\hat{V}_K = \sum_{\substack{\kappa\in K \\ s=g,e}} \left(V_{\kappa s}\, \hat{c}^\dagger_\kappa \hat{c}_{c_K s} + H.c.\right) \tag{7}$$

where $c_K = 1$ (D) for $K = L$ (R). In Eqs (5)-(6) $\hat{c}^\dagger_{cs}$ $(\hat{c}_{cs})$ and $\hat{c}^\dagger_\kappa$ $(\hat{c}_\kappa)$ are creation (annihilation) operators for electron in the molecular orbital s at the site c of the chain and contact state κ, respectively. $\hat{b}^\dagger_K(\hat{b}_K)$ creates (destroys) plasmon in a nanoparticle $(K = L, R)$ or excitons at a site c of the molecule $(K = c \in M$, $\hat{b}^\dagger_c \equiv \hat{c}^\dagger_{ce}\hat{c}_{cg})$. $\hat{N}_c \equiv \sum_{s=g,e} \hat{c}^\dagger_{cs}\hat{c}_{cs}$ is the total charge of the site c.

The Hamiltonian of the SPs $\hat{H}_P$ has the form

$$\hat{H}_P = \sum_n \hbar\omega_n \hat{a}^\dagger_n \hat{a}_n \tag{8}$$

where n is the mode number, $\hat{a}^\dagger_n$ and $\hat{a}_n$ are the plasmonic creation and annihilation operators, and $\hat{V}_{MP}$ describes coupling between molecular dipoles $\mathbf{D}_c$ and plasmons

$$\hat{V}_P = -\sum_{c=1}^{D} \mathbf{D}_c \cdot \mathbf{E}(\mathbf{r}_c) \tag{9}$$

Here $\mathbf{E}(\mathbf{r}_c)$ is the electric field at a point $\mathbf{r}_c$ of the position of dipole $c \in \{1, \ldots, D\}$.

The electric field operator of the quantized SPs is[57]

$$\mathbf{E}(\mathbf{r}) = -\sum_n A_n \nabla\varphi_n(\mathbf{r})(\hat{a}_n + \hat{a}^\dagger_n), \qquad A_n = \sqrt{\frac{4\pi\hbar s_n}{\varepsilon_h s'_n}} \tag{10}$$

where the SP eigenmodes $\varphi_n(\mathbf{r})$ are described by a wave equation (with homogeneous boundary conditions)

$$\nabla\Theta(\mathbf{r})\nabla\varphi_n(\mathbf{r}) = s_n\nabla^2\varphi_n(\mathbf{r}), \tag{11}$$

s_n is an eigenvalue corresponding to mode n, and $\Theta(\mathbf{r})$ is the characteristic function equal to 1 for $\mathbf{r}$ in the metal component and 0 for $\mathbf{r}$ in the dielectric. Note that the eigenvalues s_n are all real and contained in the range $1 > s_n > 0$. The eigenmodes are normalized by an integral over the volume V of the system, $\int_V |\nabla\varphi_n(\mathbf{r})|^2 = 1$. The physical frequency ω_n of the SPs is defined by an equation $\mathrm{Re}[s(\omega_n)] = s_n$, and $s'_n \equiv \mathrm{Re}[ds(\omega_n)/d\omega_n]$.

Below we shall treat the SPs also quasiclassically, considering $\hat{a}_n$ as a classical quantity (c-number) a_n with time dependence given by $a_n = a_{0n}\exp(-i\omega t)$, where a_{0n} is a slowly varying amplitude. The number of coherent SPs per mode is then given by $N_1 = |a_{0n}|^2$. This approximation neglects the quantum fluctuations of the SP amplitudes.

2.1 Preliminary Results

In Ref.[52] we applied the PP NEGF methodology to predict form of Fano resonances in the absorption spectrum of molecular junctions. Our considerations generalizes previously proposed quantum considerations[46] to non-equilibrium realm of a junction and non-zero temperature, and goes beyond linear response in treating the absorption spectrum. We demonstrated the sensitivity of the molecule-plasmon Fano resonance to junction bias and intra-molecular interactions, and showed importance of calculating the spectra in nonequilibrium systems beyond the linear response. This study opens a way to deal with strongly interacting plasmon-exciton systems in nonequilibrium molecular devices. The goal of our research is to extend the methodology to realistic systems and combine simulations of plasmon excitations by external electromagnetic field with the quantum response of the junction.

3. DRESSED INTERACTION

SIn this part we describe a self-consistent procedure of calculating plasmon-induced effective interactions. Results of these calculations will be utilized in the transport simulations within the PP NEGF approach outlined above. Consider a system of charged particles (electrons) situated in the vicinity of a plasmonic metal nanosystem. When an electron undergoes a transition with some frequency ω, this transition is accompanied by local electric

fields oscillating with the same frequency. These fields excite SP modes with the corresponding frequencies whose fields overlap in space with the transition fields. The local optical fields of the SPs can excite a resonant transition of another electron. This process, which in the quantum mechanical language is the electron-electron interaction by the exchange of an SP quantum, renormalizes ('dresses') the direct interaction between these two charges. As a result, the direct ('bare') Coulomb interaction between the electrons, $V(\mathbf{r}-\mathbf{r}') = 1/(\varepsilon_h |\mathbf{r}-\mathbf{r}'|)$, where ε_h is the dielectric constant of the embedding medium, is replaced by the dressed interaction $W(\mathbf{r},\mathbf{r}';\omega)$. By definition,[58] $W(\mathbf{r},\mathbf{r}';\omega)$ is the potential created at a point $\mathbf{r}$ by a charge positioned at another point $\mathbf{r}'$ and oscillating with frequency ω. Therefore, the potential in the presence of an external charge of density $\rho(\mathbf{r}')$ can be written as (see also[59])

$$\Phi(\mathbf{r},\omega) = \int d\mathbf{r}' W(\mathbf{r},\mathbf{r}';\omega)\rho(\mathbf{r}') \tag{12}$$

In the quasistatic approximation, $W(\mathbf{r},\mathbf{r}';\omega)$ satisfies the continuity equation[58]

$$\nabla_{\mathbf{r}}\left[\varepsilon(\mathbf{r},\omega)\nabla_{\mathbf{r}} W(\mathbf{r},\mathbf{r}';\omega)\right] = -4\pi\delta(\mathbf{r}-\mathbf{r}') \tag{13}$$

where dielectric function of the system $\varepsilon(\mathbf{r},\omega)$ is expressed as $\varepsilon(\mathbf{r},\omega) = \varepsilon_m(\omega)\Theta(\mathbf{r}) + \varepsilon_h[1-\Theta(\mathbf{r})]$. Here, $\Theta(\mathbf{r})$ is the characteristic function equal to 1 when $\mathbf{r}$ belongs to the metal and 0 otherwise, and $\varepsilon_m(\omega)$ is the dielectric function of the uniform metal.

A general solution to this equation can be written in terms of the retarded Green's function of the system G^r, which can be presented as a spectral expansion over SP eigenmodes $\varphi_n(\mathbf{r})$ and the corresponding eigenvalues s_n as

$$G^r(\mathbf{r},\mathbf{r}';\omega) = \sum_n \frac{s_n}{s(\omega)-s_n}\varphi_n(\mathbf{r})\varphi_n(\mathbf{r}') \tag{14}$$

where $s(\omega) = 1/[1-\varepsilon_m(\omega)/\varepsilon_h]$ is the spectral parameter. If the system is in an infinite space (or the boundaries are remote enough), then the solution to Eq.(13) is simplified to $W(\mathbf{r},\mathbf{r}';\omega) = V(\mathbf{r}-\mathbf{r}') + W^{ind}(\mathbf{r},\mathbf{r}';\omega)$ where the induced part of the dressed interaction is equal to

$$W^{ind}(\mathbf{r},\mathbf{r}';\omega) \equiv \frac{4\pi}{\varepsilon_h} G^r(\mathbf{r},\mathbf{r}';\omega) \tag{15}$$

Below we consider molecular chains of one ($D=1$) and two ($D=2$) dimers. The first model was used to extend consideration of Ref.[46] to nonequilibrium and beyond mean-field type of treatment. The second allows us to consider influence of intramolecular energy exchange on absorption spectrum of the junction. In particular we examine features of exciton compensation of Coulomb blockade[60] in the plasmon spectrum.

3.1 Calculation of Dressed Interactions for the First Model

Consider a point dipole positioned at point $\mathbf{r}_1$ and oscillating with frequency ω. The external charge density $\rho_1(\mathbf{r}')$ due to the presence of this dipole can be written as[61]

$\rho_1(\mathbf{r}') = -\mathbf{D}_1 \cdot \nabla_{\mathbf{r}'}\delta(\mathbf{r}'-\mathbf{r}_1)$. Both the plasmonic metal nanosystem and the dipole are found in a external uniform electric field $\mathbf{E}_0$ directed along z axis. A uniform field can be thought of as being produced by appropriate positive and negative charges at infinity.[62] For example, if there are two charges $\pm Q$, located at positions $z = \mp R$, then in a region near the origin whose dimensions are very small compared to R there is an approximately constant electric field $E_0 \simeq 2Q/R^2$ parallel to the z axis. In the limit as $R, Q \to \infty$, with Q/R^2 constant, this approximation becomes exact. The external charge density $\rho_2(\mathbf{r}')$ due to the presence of this dipole can be written as

$$\rho_2(\mathbf{r}') = Q\delta(\mathbf{r}'-\mathbf{r}_a) - Q\delta(\mathbf{r}'-\mathbf{r}_b) \tag{16}$$

where $r_{a,b} = R$, $\theta_a = \pi$, $\theta_b = 0$. The dipole and the two charges create potential $\Phi(\mathbf{r},\omega) = \Phi_1(\mathbf{r},\omega) + \Phi_2(\mathbf{r},\omega)$ where $\Phi_1(\mathbf{r},\omega)$ is the potential created by the dipole

$$\Phi_1(\mathbf{r},\omega) = -\mathbf{D}_1 \int d\mathbf{r}' W(\mathbf{r},\mathbf{r}';\omega)\nabla_{\mathbf{r}'}\delta(\mathbf{r}'-\mathbf{r}_1) = \mathbf{D}_1 \nabla_{\mathbf{r}'} W(\mathbf{r},\mathbf{r}';\omega)|_{\mathbf{r}'=\mathbf{r}_1}, \tag{17}$$

and $\Phi_2(\mathbf{r},\omega)$ is the potential created by two charges $\pm Q$

$$\Phi_2(\mathbf{r},\omega) = Q[W(\mathbf{r},\mathbf{r}_a;\omega) - W(\mathbf{r},\mathbf{r}_b;\omega)] \tag{18}$$

and we used Eq.(12). The dipole interaction energy can be written as $U = -\mathbf{D}_1 \cdot \mathbf{E}(\mathbf{r}_1,\omega)$ where $\mathbf{E}(\mathbf{r}_1,\omega)$ is the electric field at a point $\mathbf{r}_1$, the position of the dipole. Electric field $\mathbf{E}(\mathbf{r}_1,\omega)$ consists of two contributions $\mathbf{E}(\mathbf{r}_1,\omega) = \mathbf{E}_1(\mathbf{r}_1,\omega) + \mathbf{E}_2(\mathbf{r}_1,\omega)$ where $\mathbf{E}_1(\mathbf{r}_{1k},\omega) \sim \mathbf{D}_1$ is the electric field at a point $\mathbf{r}_1$ induced by the dipole itself, and $\mathbf{E}_2(\mathbf{r}_k,\omega)$ is the electric field at a point $\mathbf{r}_1$ induced by the two charges. Then $U = U_1 + U_2$ where energy U_1 describing non-radiative decay of the dipole into the metal, $\gamma_{m1}(\omega)$ ($\frac{1}{2}\operatorname{Im} U_1 = -\hbar\gamma_{m1}(\omega)$, Ref.[61]), and the shift of the transition frequency of the dipole due to interaction with metal ($\sim \operatorname{Re} U_1$) is defined by

$$U_1 \;\; = -\mathbf{D}_1 \cdot \mathbf{E}_1(\mathbf{r}_1,\omega) \tag{19}$$

Energy U_2 describing the interaction of the dipole with the external field in the vicinity of a plasmonic metal nanosystem is given by

$$U_2 \;\; = -\mathbf{D}_1 \cdot \mathbf{E}_2(\mathbf{r}_1,\omega) \tag{20}$$

Field $\mathbf{E}_1(\mathbf{r},\omega)$ may be calculated by potential $\Phi_1(\mathbf{r},\omega)$

$$\mathbf{E}_1(\mathbf{r},\omega) = -\nabla_{\mathbf{r}}\Phi_1(\mathbf{r},\omega) = -\nabla_{\mathbf{r}}\mathbf{D}_1\nabla_{\mathbf{r}'}W(\mathbf{r},\mathbf{r}';\omega)|_{\mathbf{r}'=\mathbf{r}_1} \tag{21}$$

where we used Eq.(17). Field $\mathbf{E}_2(\mathbf{r},\omega)$ may be calculated by potential $\Phi_2(\mathbf{r},\omega)$

$$\mathbf{E}_2(\mathbf{r},\omega) = -\nabla_{\mathbf{r}}\Phi_2(\mathbf{r},\omega) = -Q\nabla_{\mathbf{r}}[W(\mathbf{r},\mathbf{r}_a;\omega) - W(\mathbf{r},\mathbf{r}_b;\omega)] \tag{22}$$

Substituting Eqs.(21) and (22) into Eqs.(19) and (20), respectively, one gets

$$U_1 \;\; = (\mathbf{D}_1 \cdot \nabla_{\mathbf{r}})(\mathbf{D}_1 \cdot \nabla_{\mathbf{r}'})W(\mathbf{r},\mathbf{r}';\omega)|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_1} \tag{23}$$

and

$$U_2 \;\; = Q(\mathbf{D}_1 \cdot \nabla_{\mathbf{r}})[W(\mathbf{r},\mathbf{r}_a;\omega) - W(\mathbf{r},\mathbf{r}_b;\omega)]|_{\mathbf{r}=\mathbf{r}_1} \tag{24}$$

3.2 Calculation of Dressed Interactions for the Second Model

Consider two point dipoles positioned at points $\mathbf{r}_1$ and $\mathbf{r}_D$, respectively, and oscillating with frequency ω. The external charge densities $\rho_{1,D}(\mathbf{r}')$ due to the presence of these dipoles can be written as[61] $\rho_{1,D}(\mathbf{r}') = -\mathbf{D}_{1,D} \cdot \nabla_{\mathbf{r}'}\delta(\mathbf{r}'-\mathbf{r}_{1,D})$. Both the plasmonic metal nanosystem and the dipoles are found in a external uniform electric field $\mathbf{E}_0$ directed along z axis. A uniform field can be thought of as being produced by appropriate positive and negative charges at infinity (see above). The external charge density $\rho_2(\mathbf{r}')$ due to the presence of this dipole can be written like before, Eq.(16). The dipoles and the two charges create potential $\Phi(\mathbf{r},\omega) = \Phi_1(\mathbf{r},\omega) + \Phi_2(\mathbf{r},\omega) + \Phi_D(\mathbf{r},\omega)$ where $\Phi_{1,D}(\mathbf{r},\omega)$ are the potentials created by the dipoles

$$\Phi_{1,D}(\mathbf{r},\omega) = -\mathbf{D}_{1,D}\int d\mathbf{r}' W(\mathbf{r},\mathbf{r}';\omega)\nabla_{\mathbf{r}'}\delta(\mathbf{r}'-\mathbf{r}_{1,D}) = \mathbf{D}_{1,D}\nabla_{\mathbf{r}'}W(\mathbf{r},\mathbf{r}';\omega)|_{\mathbf{r}'=\mathbf{r}_{1,D}}, \tag{25}$$

and $\Phi_2(\mathbf{r},\omega)$ is the potential created by two charges $\pm Q$, $\Phi_2(\mathbf{r},\omega) = Q[W(\mathbf{r},\mathbf{r}_a;\omega) - W(\mathbf{r},\mathbf{r}_b;\omega)]$, and we used Eq.(12). The interaction energy of dipoles $i = 1, D$ can be written as $U_i = -\mathbf{D}_i \cdot \mathbf{E}(\mathbf{r}_i,\omega)$ where the electric field at a point $\mathbf{r}_i$, the position of dipole i, $\mathbf{E}(\mathbf{r}_i,\omega)$, consists of three contributions: $\mathbf{E}(\mathbf{r}_i,\omega) = \mathbf{E}_1(\mathbf{r}_i,\omega) + \mathbf{E}_2(\mathbf{r}_i,\omega) + \mathbf{E}_D(\mathbf{r}_i,\omega)$. Here $\mathbf{E}_1(\mathbf{r}_i,\omega) \sim \mathbf{D}_1$ is the electric field at a point $\mathbf{r}_1$ induced by the dipole itself, $\mathbf{E}_2(\mathbf{r}_i,\omega)$ is the electric field at a point $\mathbf{r}_i$ induced by the two charges, and $\mathbf{E}_D(\mathbf{r}_i,\omega) \sim \mathbf{D}_D$ is the electric field at a point $\mathbf{r}_1$ induced by the dipole $\mathbf{D}_D$. The interaction energy of dipoles 1 and D can be written in a symmetrized form as $U = U_1 + U_D = U_{1D} + U_{D1} + U_{11} + U_{DD} + U_2$ where

$$U_{1D} = -\frac{1}{2}\mathbf{D}_1 \cdot \mathbf{E}_D(\mathbf{r}_1,\omega) \tag{26}$$

$$U_{D1} = -\frac{1}{2}\mathbf{D}_D \cdot \mathbf{E}_1(\mathbf{r}_D,\omega) \tag{27}$$

describe the ("dressed") dipole-dipole interaction. Energy $U_{11(DD)}$ describing non-radiative decay of dipole $1(D)$ into the metal, $\gamma_{m1(D)}(\omega)$ ($\mathrm{Im}\, U_{11(DD)} = -\hbar\gamma_{m1(D)}(\omega)$, Ref.[61]) and the shift of the transition frequency of the dipole due to interaction with metal ($\mathrm{Re}\, U_{11(DD)}$) is defined by

$$U_{11(DD)} = -\frac{1}{2}\mathbf{D}_{1(D)} \cdot \mathbf{E}_{1(D)}(\mathbf{r}_{1(D)}, \omega) \tag{28}$$

Energy U_2 describing the interaction of dipole i with the external field in the vicinity of a plasmonic metal nanosystem is given by

$$U_2 \;\; = -\sum_{i=1,D} \mathbf{D}_i \cdot \mathbf{E}_2(\mathbf{r}_i, \omega) \equiv \sum_{i=1,D} U_{2i} \tag{29}$$

where $\mathbf{E}_2(\mathbf{r}_i, \omega) = -Q\nabla_{\mathbf{r}}[W(\mathbf{r}, \mathbf{r}_a; \omega) - W(\mathbf{r}, \mathbf{r}_b; \omega)]|_{\mathbf{r}=\mathbf{r}_i}$. Field $\mathbf{E}_{1,D}(\mathbf{r}, \omega)$ may be calculated by potential $\Phi_{1,D}(\mathbf{r}, \omega)$

$$\mathbf{E}_{1,D}(\mathbf{r}, \omega) = -\nabla_{\mathbf{r}}\Phi_{1,D}(\mathbf{r}, \omega) = -\nabla_{\mathbf{r}}\mathbf{D}_{1,D}\nabla_{\mathbf{r}'}W(\mathbf{r}, \mathbf{r}'; \omega)|_{\mathbf{r}'=\mathbf{r}_{1,D}} \tag{30}$$

where we used Eq.(17). Using Eqs.(26), (27), (28) and (30), we get

$$U_{1D} = \frac{1}{2}(\mathbf{D}_1 \cdot \nabla_{\mathbf{r}})(\mathbf{D}_D \cdot \nabla_{\mathbf{r}'})W(\mathbf{r}, \mathbf{r}'; \omega)|_{\mathbf{r}=\mathbf{r}_1, \mathbf{r}'=\mathbf{r}_D} \equiv \frac{1}{2}\hbar J(\omega), \tag{31}$$

$$U_{D1} = \frac{1}{2}(\mathbf{D}_D \cdot \nabla_{\mathbf{r}})(\mathbf{D}_1 \cdot \nabla_{\mathbf{r}'})W(\mathbf{r}, \mathbf{r}'; \omega)|_{\mathbf{r}=\mathbf{r}_D, \mathbf{r}'=\mathbf{r}_1} \equiv \frac{1}{2}\hbar J(\omega), \tag{32}$$

and

$$U_{ii} = \frac{1}{2}(\mathbf{D}_i \cdot \nabla_{\mathbf{r}})(\mathbf{D}_i \cdot \nabla_{\mathbf{r}'})W(\mathbf{r}, \mathbf{r}'; \omega)|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_i} \tag{33}$$

where $i = 1, D$ and $\mathbf{D}_1$ and $\mathbf{D}_2$ are considered real quantities. One can see from Eqs.(31) and (32) that $U_{1D} = U_{D1}$. This can be expected from the reciprocity theorem,[63] according to which the fields of two dipoles $\mathbf{D}_1$ and $\mathbf{D}_D$ at positions $\mathbf{r}_1$ and $\mathbf{r}_D$ and oscillating with the same frequency ω are related as $\mathbf{D}_1 \cdot \mathbf{E}_D(\mathbf{r}_1, \omega) = \mathbf{D}_2 \cdot \mathbf{E}_1(\mathbf{r}_2, \omega)$ (see Eqs.(26) and (27)). In that case the sum $U_{1D} + U_{D1}$, Eqs.(31) and (32), converts to Eq.(5) of Ref.[58]

The sum $U_{1D} + U_{D1}$ may be used in the "excitonic" part of Hamiltonian (5) describing the "dressed" exciton-exciton interaction

$$H_{exc-exc} = \hbar[J(\omega)b_1^+ b_D + J^*(\omega)b_D^+ b_1] \tag{34}$$

In case of usual ("undressed") interaction (J does not depend on frequency) between dipoles, Hamiltonian (34) also coincides with the usual exciton Hamiltonian written in the Heitler-London approximation.[64] Quantities U_{1D}, U_{D1} and U_{ii} strongly depend on frequency near plasmonic resonances due to the strong dependence of dressed interactions $W(\mathbf{r}, \mathbf{r}'; \omega)|_{\mathbf{r}=\mathbf{r}_1, \mathbf{r}'=\mathbf{r}_D}$ and $W(\mathbf{r}, \mathbf{r}'; \omega)|_{\mathbf{r}=\mathbf{r}'=\mathbf{r}_i}$, Eqs.(31), (32) and (33). This results in essentially non-Markovian dynamics of the system under consideration that necessitates corresponding non-Markovian description (see below).

3.3 Relations between Real and Imaginary Parts of Induced Dipole Interactions

Consider the induced part of the dressed interaction $W^{ind}(\mathbf{r}, \mathbf{r}'; \omega) \equiv \frac{4\pi}{\varepsilon_h}G^r(\mathbf{r}, \mathbf{r}'; \omega)$, Eq.(15). The real and imaginary parts of the retarded Green's function $G^r(\mathbf{r}, \mathbf{r}'; \omega)$ obey the dispersion relation,[65] according to which

$$\mathrm{Im}\, W^{ind}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{\pi}P\int_{-\infty}^{\infty} \frac{\mathrm{Re}\, W^{ind}(\mathbf{r}, \mathbf{r}'; \omega')}{\omega - \omega'}d\omega', \tag{35}$$

and

$$\mathrm{Im}\, U_{1(2)}^{ind}(\omega) = \frac{1}{\pi}P\int_{-\infty}^{\infty} \frac{\mathrm{Re}\, U_{1(2)}^{ind}(\omega')}{\omega - \omega'}d\omega' \tag{36}$$

for the first model, where the induced parts of U_1 and U_2 are defined by the same formulas (23) and (24), respectively, where the dressed interaction $W(\mathbf{r}, \mathbf{r}'; \omega)$ should be substituted by its induced part $W^{ind}(\mathbf{r}, \mathbf{r}'; \omega')$. The last formula may be used for checking numerical results. Similar relations may be obtained also for the second model.

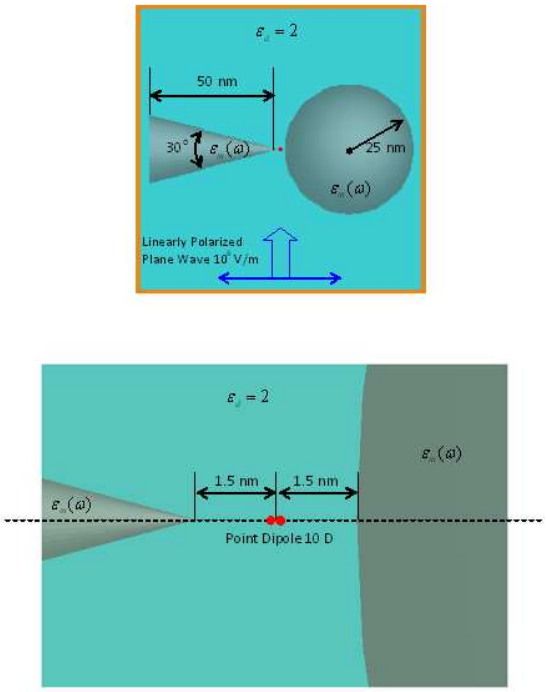

Figure 1. Geometry for the first model. The dimensions are given in the figure.

3.4 Simulations beyond Quasistatic Approximation

Eqs.(19), (20), (26), (27), (28) are rather general and may be used beyond the quasistatic approximation. Here we calculate fields $\mathbf{E}(\mathbf{r}_i, \omega)$ on the right-hand side of these equations for more realistic geometries of the contacts like the bowtie antenna,[66] a conical metal tip, as one contact, and a metal sphere, as another contact[67] etc., using the finite-difference time-domain (FDTD) method.[68] We used commercially available FDTD Solutions software by Lumerical.[69]

Consider the first model: one point dipole ($D_1 = 10D$) positioned between a silver cone and a sphere as shown in Fig.1. The structure is illuminated by linearly polarized plane wave with the amplitude of electric field of $10^8 V/m$. The metal cone and the sphere are described using a Drude dielectric model, $\varepsilon_m(\omega) = \varepsilon_0 - \omega_p^2/[\omega(\omega + i\gamma)]$, with parameters $\varepsilon_0 = 3.57$, $\omega_p = 9.1eV$, and $\gamma = 0.052eV$ corresponding to silver. Fig.2 shows the real (describing the shift of the transition frequency of the dipole due to interaction with metal) and imaginary (describing non-radiative decay of the dipole into the metal) parts of energy U_1, Eq.(19), as functions of frequency. Fig.3 shows the real and imaginary parts of energy U_2 describing the interaction of the dipole with the external field in the vicinity of a plasmonic metal nanosystem, Eq.(20), as functions of frequency.

Now consider the second model: two point dipoles ($D_1 = D_2 = 10D$) positioned between a silver cone and a sphere as shown in Fig.4. Fig.5 shows the "dressed" dipole-dipole interaction U_{1D}, Eq.(26), as a function of frequency.

Figs.6 and 7 show the real (describing the shift of the transition frequency of the dipole due to interaction with metal) and imaginary (describing non-radiative decay of the dipole into the metal) parts of energies U_{DD} and U_{11} , respectively, Eq.(28), as functions of frequency. Fig.8 shows the real and imaginary parts of energy U_2 for the second model, Eq.(29), describing the interaction of the dipoles with external field in the vicinity of a plasmonic metal nanosystem, as functions of frequency.

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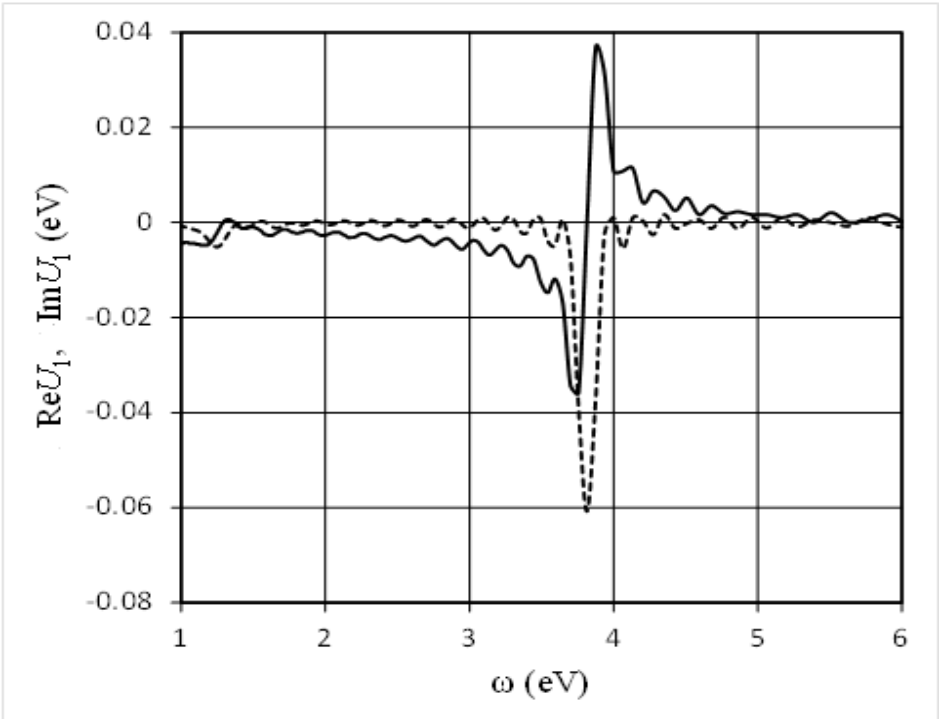

Figure 2. First model. Real (solid line) and imaginary (dashed line) parts of energy U_1 , Eq.(19), as functions of frequency.

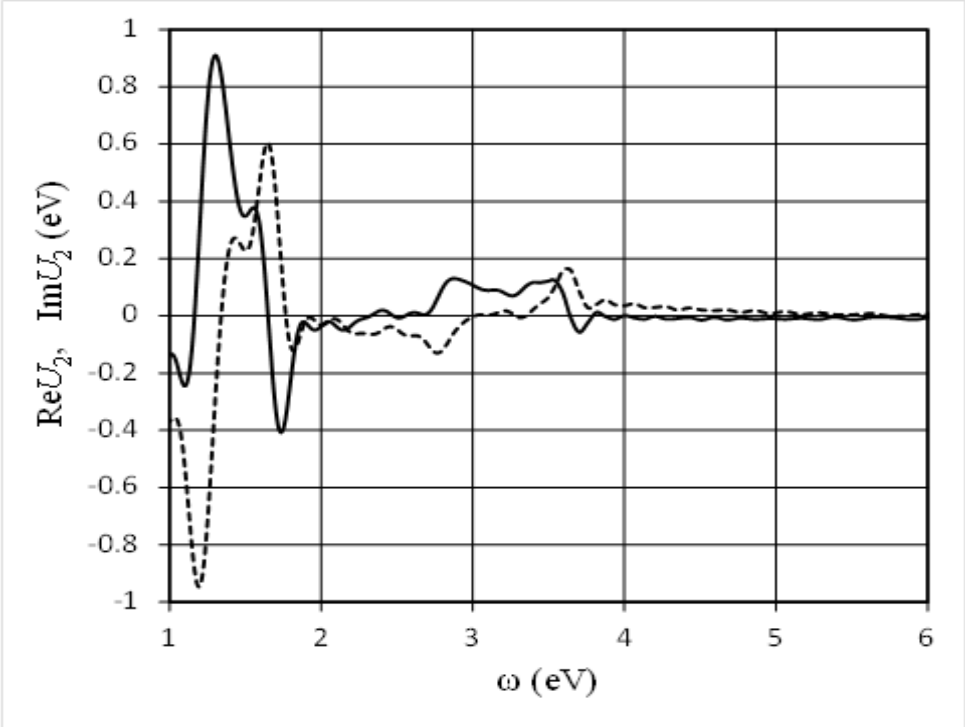

Figure 3. First model. Real (solid line) and imaginary (dashed line) parts of energy U_2 describing the interaction of the dipole with the external field in the vicinity of a plasmonic metal nanosystem, Eq.(20), as functions of frequency.

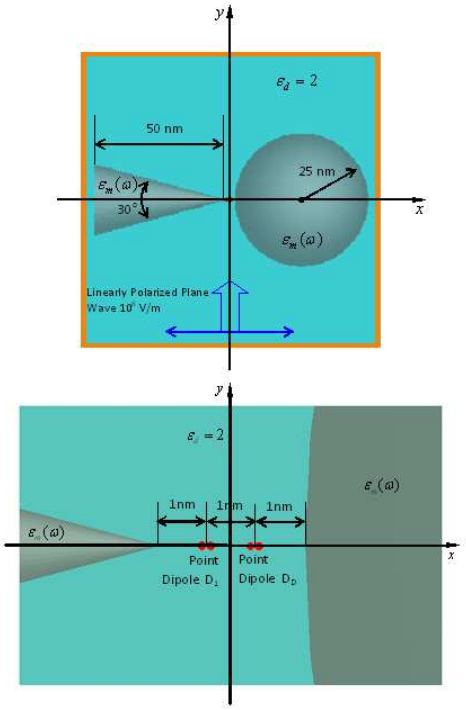

Figure 4. The second model: two point dipoles positioned at a distance of 1 nm from each of other between a silver cone and a sphere. The dimensions are given in the figure.

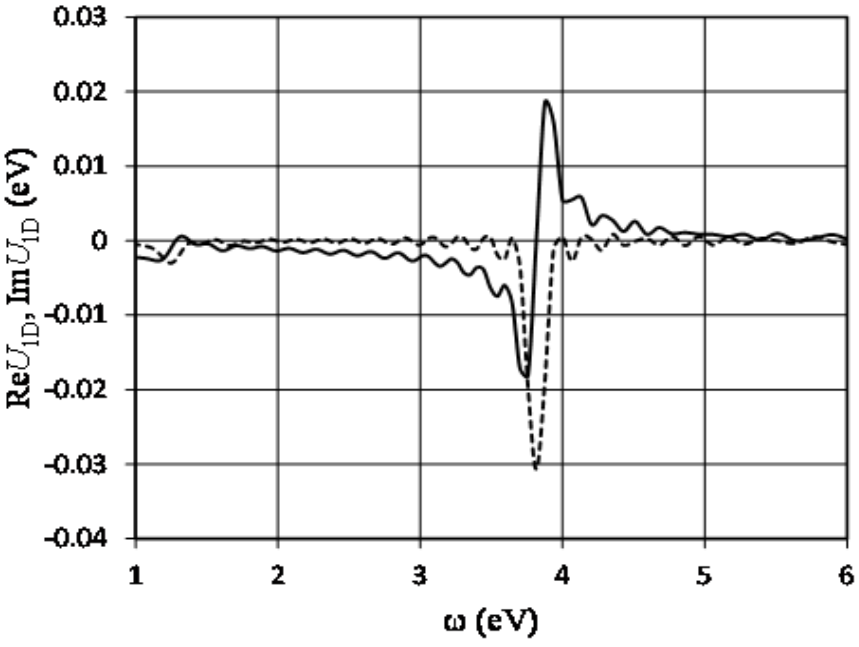

Figure 5. Second model. "Dressed" dipole-dipole interaction U_{1D}, Eq.(26), as a function of frequency. $\mathrm{Re}\, U_{1D}$ - solid line, $\mathrm{Im}\, U_{1D}$ - dashed line.

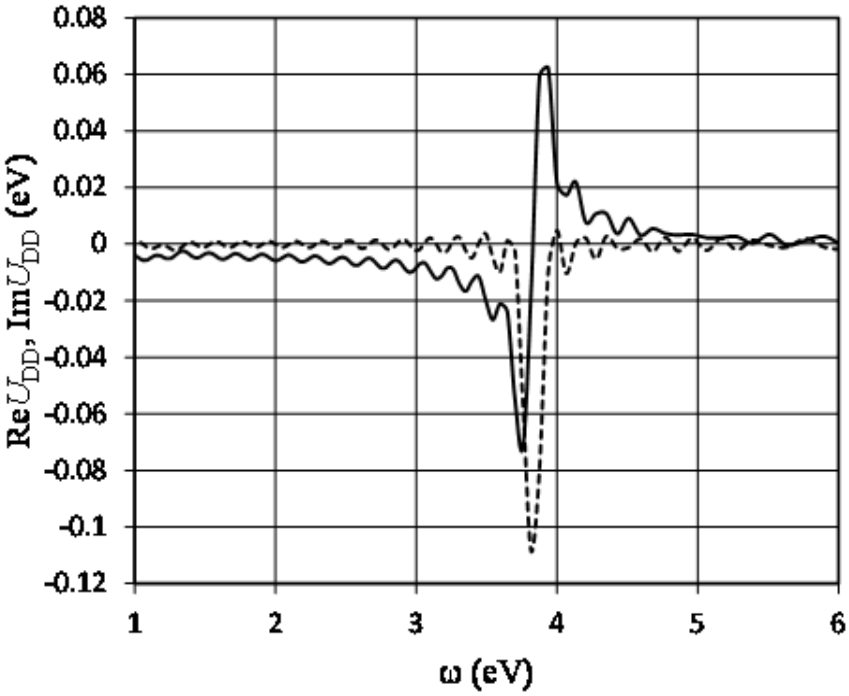

Figure 6. Second model. Imaginary (dashed line) and real (solid line) parts of U_{DD}, Eq.(28), as functions of frequency.

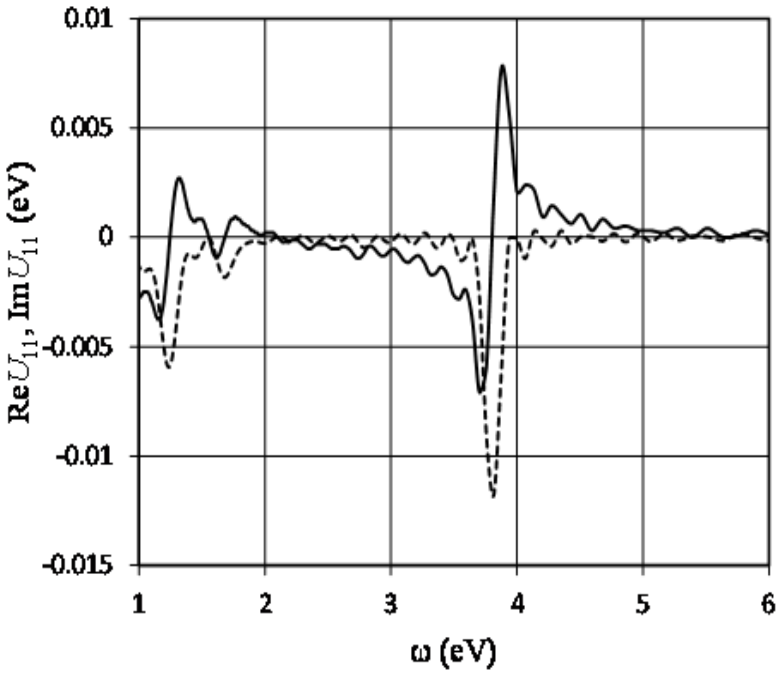

Figure 7. Second model. Imaginary (dashed line) and real (solid line) parts of U_{11}, Eq.(28), as functions of frequency.

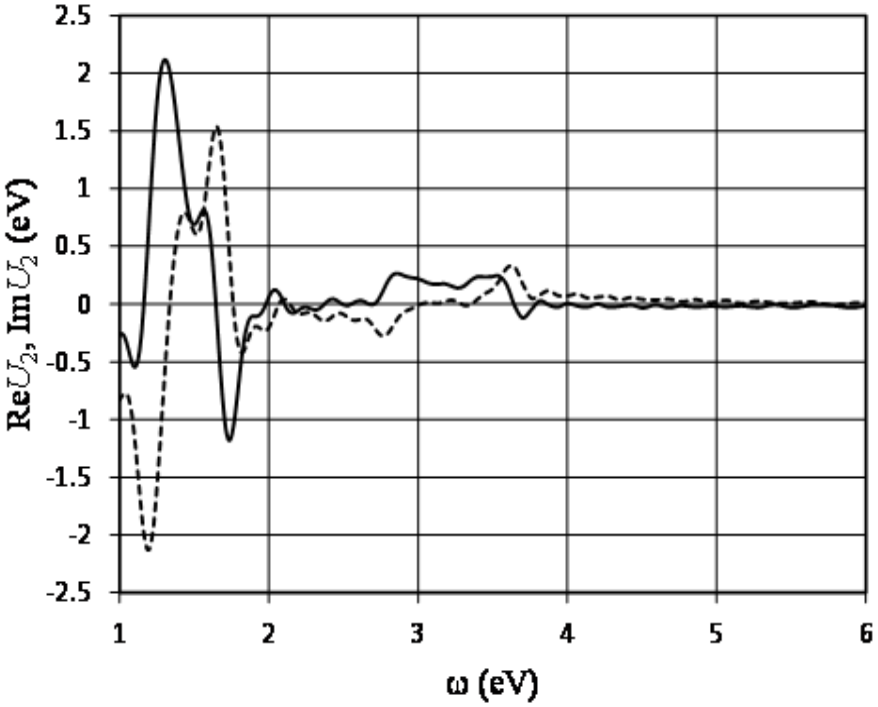

Figure 8. Second model. Imaginary (dashed line) and real (solid line) parts of U_2, Eq.(29), describing the interaction of the dipoles with external field in the vicinity of a plasmonic metal nanosystem, as functions of frequency.

4. CONCLUSION AND OUTLOOK

In this work we have developed the fundamentals of a non-Markovian quantum theory of the collective plasmon-molecule excitations in nanojunctions combined with classical electrodynamic simulations. Our preliminary results[70] and the figures of section 3.4 show that the values of the plasmon dressed exciton interactions and losses strongly change near plasmonic resonances. Specifically, the maximal value of $\gamma_{mi}(\omega)$ is of the same order of magnitude ~ 0.1 eV as its spectral width (see Fig.6 of Ref.[70]). This means essentially non-Markovian dynamics of the system that will be studied by the PP NEGF based theory with self-energies given by calculated above $J(\omega)$ and $\gamma_{mi}(\omega)$, and U_2^{ind} that may be expressed by the retarded Green's function in the quasistatic approximation (see above). The self-energies can be expressed also by the Green dyadic beyond the quasistatic approximation.[71,72] We also intend in devepoling our FDTD calculations to carry out self-consistent electrodynamical calculations taking into account the influence of a molecular bridge on the plasmonic system. These issues will be studied elsewhere.

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