Interacting quantum plasmons in metal-dielectric structures

Tigran V. Shahbazyan

Department of Physics, Jackson State University, Jackson, MS 39217 USA

Abstract

We develop a consistent quantum description of surface plasmons interacting with quantum emitters and external electromagnetic field. Within the framework of macroscopic electrodynamics in dispersive and absorptive medium, we derive, in the Markov approximation, the canonical Hamiltonian, commutation relations, and coupling parameters for the plasmon modes in metal-dielectric structures of arbitrary shape and composition. We then develop a quantum description of interacting plasmons in terms of bosonic modes with linear dispersion whose interactions with quantum emitters and electromagnetic field are mediated by classical plasmons. Such a description, which bridges between the macroscopic and canonical schemes, fully accounts for the optical dispersion and losses in metals and can serve as a framework for studying non-Markovian effects in plasmonics.
Over the past decade, quantum plasmonics [1] underwent a rapid development fueled by a host of recently discovered phenomena such as strong exciton-plasmon coupling effects [2–7], plasmon-assisted hot carrier generation [8–10], plasmonic laser (spaser) [11–15], plasmon tunneling [16–19] and more, along with a growing number of applications. Surface plasmons are collective electron excitations living at the metal-dielectric interfaces which can interact strongly with light and localized electron excitations such as excitons in molecules or semiconductors, referred hereafter as quantum emitters (QEs) [20]. Although classical description of many experiments in terms of local field enhancement has largely been successful, a growing number of topics and applications require a rigorous quantum approach [21–26]. In nanoscale systems, the local fields can change strongly over the length scale well below the diffraction limit, and so the plasmon interactions with the electromagnetic (EM) field and QEs depend sensitively on the system parameters such as geometry or the QE position. While the coupling parameters, characterizing these interactions, have been suggested in several forms by analogy with the cavity modes [27–29], they should emerge from a consistent quantization procedure for interacting plasmons. Another challenge for quantum plasmons is to account for strong optical dispersion and losses in metals that give rise to non-Markovian dynamics in plasmonic systems [30–34].

Within canonical quantization scheme, localized plasmon modes with discrete frequency spectrum $\omega_m$ are described by the Hamiltonian

$$\hat{H}_{pl} = \sum_m \hbar \omega_m \hat{a}_m^\dagger \hat{a}_m,$$

(1)

where $\hat{a}_m^\dagger$ and $\hat{a}_m$ are, respectively, the plasmon creation and annihilation operators obeying the canonical commutation relations $[\hat{a}_m, \hat{a}_n^\dagger] = \delta_{mn}$. Plasmon interactions with the QEs are usually described, similar to cavity modes, by Jaynes-Cummings interaction Hamiltonian

$$\hat{H}_{pl-qe} = \sum_{im} \hbar g_{im} (\hat{\sigma}_i^\dagger \hat{a}_m + \hat{a}_m^\dagger \hat{\sigma}_i),$$

(2)

where $\hat{\sigma}_i^\dagger$ and $\hat{\sigma}_i$ are, respectively, the raising and lowering operators for $i$th QE and $g_{im}$ is the QE-plasmon coupling, which, in this approach, is an ad hoc parameter. Although widely employed, the canonical scheme has significant limitations when used in metal-dielectric structures characterized by a complex dielectric function $\varepsilon(\omega, \mathbf{r}) = \varepsilon'(\omega, \mathbf{r}) + i\varepsilon''(\omega, \mathbf{r})$, as it ignores the medium optical dispersion and, hence, is unsuitable for describing non-Markovian effects in plasmonics.
On the other hand, the material dispersion effects are inherent in the macroscopic approach based upon the fluctuation-dissipation (FD) theorem [35–37]. Here, the EM fields in inhomogeneous and dispersive medium are quantized in terms of reservoir noise operators \( \hat{f}(\omega, \mathbf{r}) \) driven by the Hamiltonian \( \hat{H}_N = \int_0^\infty d\omega \int dV \hbar \omega \hat{f}^\dagger(\omega, \mathbf{r}) \cdot \hat{f}(\omega, \mathbf{r}) \) and obeying commutation relations \([\hat{f}(\omega, \mathbf{r}), \hat{f}^\dagger(\omega', \mathbf{r}')] = I \delta(\omega - \omega') \delta(\mathbf{r} - \mathbf{r}')\), where \( I \) is the unit tensor.

Interactions with QEs are described by the Hamiltonian term \( \hat{H}_{\text{int}} = - \sum_i \hat{p}_i \cdot \hat{E}(\mathbf{r}_i) \), where \( \hat{p}_i \) and \( \hat{E}(\mathbf{r}_i) \) are, respectively, the QE dipole moment and electric field operators. The latter is given by

\[
\hat{E}(\mathbf{r}) = \int_0^\infty d\omega \int dV' D(\omega; \mathbf{r}, \mathbf{r}') \hat{P}_N(\omega, \mathbf{r}') + \text{H.c.},
\]

where \( \hat{P}_N(\omega, \mathbf{r}) = (i/2\pi) \sqrt{\hbar \varepsilon''(\omega, \mathbf{r})} \hat{f}(\omega, \mathbf{r}) \) is the noise polarization vector and \( D(\omega; \mathbf{r}, \mathbf{r}') \) is EM dyadic Green function defined as \( \nabla \times \nabla \times D - (\omega^2/c^2) \varepsilon = (4\pi\omega^2/c^2) I \).

The FD approach has been extensively used to model spontaneous emission, strong coupling effects and non-Markovian dynamics in metal-dielectric structures [30–34, 38–45]. Its major drawback in relation to plasmonics is that, while surface plasmons reside primarily at the metal-dielectric interfaces, the eigenstates of \( \hat{H}_N \) extend over the entire system reservoir, i.e., the Hilbert space, spanned by the operators \( \hat{f}(\omega, \mathbf{r}) \), is excessively large. Furthermore, the plasmons only appear as resonances in the classical EM Green function \( D \), so that, in practical terms, the FD approach is limited to relatively simple systems (e.g., planar or spherical).

In principle, the Hamiltonians (1) and (2), along with the canonical commutations relations and QE-plasmon coupling, should emerge within the FD framework starting with a suitable mode expansion for the EM Green function in Eq. (3) to define the plasmon operators [46–48]. To the best of our knowledge, this has not yet been accomplished for general shape structures. In general, an expansion of \( D \) over a discrete set of EM modes leads to the dissipation coupling between the modes, mediated by \( \varepsilon''(\omega, \mathbf{r}) \), which violate the canonical commutations relations [48], unless such a coupling vanishes due to the system symmetry (e.g., in spherical systems) [47]. However, as we demonstrate in this Letter, for surface plasmons treated as collective electron excitations interacting with the EM field and QEs, a consistent quantum description can be developed in metal-dielectric structures of arbitrary shape and composition.

Specifically, starting within the FD framework, we derive, in the Markov approximation,
the plasmon Hamiltonian, the canonical commutations relations, and the plasmon coupling to the EM field and QEs. We then present an approach describing quantum plasmons in terms of a discrete set of bosonic modes with linear dispersion whose interactions with the EM field and QEs are mediated by the classical plasmons. This approach, which fully accounts for the medium optical dispersion and losses, bridges between the FD and canonical schemes and is suitable for studying non-Markovian effects in quantum plasmonics.

We consider a metal-dielectric structure characterized by dielectric function of the form
\[ \varepsilon(\omega, \mathbf{r}) = \sum_i \theta_i(\mathbf{r}) \varepsilon_i(\omega), \]
where \( \theta_i(\mathbf{r}) \) is unit step function that vanishes outside the connected region, metal or dielectric, of volume \( V_i \) that is characterised by a uniform dielectric function \( \varepsilon_i(\omega) \). For unretarded electron motion, the potentials \( \Phi_m(\mathbf{r}) \) and frequencies \( \omega_m \) of plasmon modes are determined by the quasistatic Gauss law as
\[ \nabla \cdot [\varepsilon'(\omega_m, \mathbf{r}) \nabla \Phi_m(\mathbf{r})] = 0, \]
and the mode fields, which we choose to be real, are \( \mathbf{E}_m(\mathbf{r}) = -\nabla \Phi_m(\mathbf{r}) \). Importantly, the different mode fields are orthogonal in each connected region,
\[ \int dV_i \mathbf{E}_m(\mathbf{r}) \cdot \mathbf{E}_n(\mathbf{r}) = \delta_{mn} \int dV_i \mathbf{E}_m^2(\mathbf{r}), \]
implying the absence of dissipation coupling between the modes: \( \int dV \varepsilon''(\omega, \mathbf{r}) \mathbf{E}_m(\mathbf{r}) \mathbf{E}_n(\mathbf{r}) = 0 \) for \( m \neq n \).

The near-field Green function that defines the field operator can be split into free-space and plasmon parts,
\[ D = D_0 + D_{pl}. \]
The first term, when inserted into Eq. (3), yields the electric field due to noise fluctuations, while the second term defines the normal mode expansion of the plasmon field operator. In the following, we focus only on the plasmonic sector of the Hilbert space. In the absence of dissipation coupling, the plasmon Green function can be derived exactly in the following form:
\[ D_{pl}(\omega; \mathbf{r}, \mathbf{r'}) = \sum_m D_m(\omega) \mathbf{E}_m(\mathbf{r}) \mathbf{E}_m(\mathbf{r'}), \]
where
\[ D_m(\omega) = \frac{4\pi}{\int dV \mathbf{E}_m^2(\mathbf{r})} - \frac{4\pi}{\int dV \varepsilon(\omega, \mathbf{r}) \mathbf{E}_m^2(\mathbf{r})}. \]
The first term ensures that \( D_{pl} = 0 \) for \( \varepsilon = 1 \) (or, in the limit \( \omega \to \infty \)). Since \( \int dV \varepsilon'(\omega_m, \mathbf{r}) \mathbf{E}_m^2(\mathbf{r}) = 0 \) due to the Gauss law, the plasmon Green function exhibits plasmon poles in the lower half of complex frequency plane. In the frequency domain \( \varepsilon''(\omega)/\varepsilon'(\omega) \ll 1, \)
expanding $\varepsilon'(\omega, \mathbf{r})$ in Eq. (6) near $\omega_m$, we obtain [49, 51]

$$D_{pl}(\omega; \mathbf{r}, \mathbf{r}') = \sum_m \frac{\omega_m}{4U_m} \frac{E_m(\mathbf{r})E_m(\mathbf{r}')}{\omega_m - \omega - \frac{i}{2}\gamma_m(\omega)},$$

(7)

where $U_m$ is the plasmon mode energy [52],

$$U_m = \frac{1}{16\pi} \int dV \frac{\partial[\omega_m \varepsilon'(\omega_m, \mathbf{r})]}{\partial \omega_m} E_m^2(\mathbf{r}),$$

(8)

and $\gamma_m(\omega)$ is the frequency-dependent decay rate [49, 51],

$$\gamma_m(\omega) = \frac{2\int dV \varepsilon''(\omega, \mathbf{r}) E_m^2(\mathbf{r})}{\int dV \frac{\partial\varepsilon'(\omega_m, \mathbf{r})}{\partial \omega_m} E_m^2(\mathbf{r})}.$$

(9)

If only in the metallic regions is the dielectric function dispersive and complex, the plasmon decay rate takes the standard form [20] $\gamma_m(\omega) = \varepsilon''(\omega)/[\partial\varepsilon'(\omega_m)/\partial \omega_m]$. Using Eqs. (5) and (9), it is easy to check that $D_{pl}$ satisfies the relation

$$\int dV \varepsilon''(\omega, \mathbf{r}) D_{pl}^{\ast}(\omega; \mathbf{r}, \mathbf{r}') D_{pl}(\omega; \mathbf{r}, \mathbf{r}'') = 4\pi \text{Im} D_{pl}(\omega; \mathbf{r}', \mathbf{r}''),$$

which ensures consistency with the FD theorem [35–37].

Inserting the plasmon Green function (7) into Eq. (3), we obtain the normal mode expansion for the plasmon field operator: $\hat{E}_{pl}(\mathbf{r}) = \sum_m \hat{E}_m(\mathbf{r})$, where

$$\hat{E}_m(\mathbf{r}) = \sqrt{\frac{\hbar \omega_m}{4U_m}} E_m(\mathbf{r})(\hat{a}_m + \hat{a}_m^\dagger),$$

(10)

is the individual mode operator. Here, we defined the plasmon annihilation operator $\hat{a}_m$ as

$$\hat{a}_m = -i \int_0^\infty \frac{d\omega}{\sqrt{2\pi}} \frac{\hat{f}_m(\omega)}{\omega_m - \omega - \frac{i}{2}\gamma_m(\omega)},$$

(11)

where $\hat{f}_m$ is noise operator projected on a plasmon mode:

$$\hat{f}_m(\omega) = -\sqrt{\frac{\omega_m}{8\pi U_m}} \int d\mathbf{r} \sqrt{\varepsilon''(\omega, \mathbf{r})} E_m(\mathbf{r}) \cdot \hat{f}(\omega, \mathbf{r}).$$

(12)

Commutation relations for $\hat{f}_m$ follow from those for $\hat{f}$ and from Eqs. (11) and (9),

$$[\hat{f}_m(\omega), \hat{f}_n^\dagger(\omega')] = \delta_{mn} \delta(\omega - \omega') \gamma_m(\omega).$$

(13)

Now, using Eqs. (11) and (13), we obtain commutation relations for the plasmon operators:

$$[\hat{a}_m, \hat{a}_n^\dagger] = \delta_{mn} \int_0^\infty \frac{d\omega}{2\pi} \frac{\gamma_m(\omega)}{(\omega_m - \omega)^2 + \gamma_m^2(\omega)/4}.$$  

(14)

In the Markov approximation, replacing $\gamma_m(\omega)$ with $\gamma_m = \gamma_m(\omega_m)$ and extending the integral to negative frequencies, we obtain the canonical commutation relations $[\hat{a}_m, \hat{a}_n^\dagger] = \delta_{mn}$. The
plasmon Hamiltonian (1) follows from the normal mode expansion (10) by checking that, for each mode, the normal-ordered Hamiltonian is

\[ \hat{H}_m = \frac{1}{8\pi} \int dV \frac{\partial (\omega_m \varepsilon')}{\partial \omega_m} \hat{E}_m^2 = \hbar \omega_m \hat{a}_m \hat{a}_m, \]

(15)

where we dropped the terms \( \hat{a}_m \hat{a}_m \) and \( \hat{a}^\dagger_m \hat{a}^\dagger_m \). The factor \( \frac{1}{2} \) difference between Eqs. (8) and (15) reflects the presence of both positive and negative frequency terms in \( \hat{E}_m(r) \) [52].

We stress that, with help of the plasmon Green function (7), both the canonical Hamiltonian (1) and commutation relations are explicitly obtained for any plasmonic structure.

Turning to the plasmon dynamics, the time-evolution of projected noise operators (12) is determined by the Heisenberg equations,

\[ \dot{\hat{f}}_m(\omega) = -(i/\hbar)[\hat{f}_m(\omega), \hat{H}_N] = -i\omega \hat{f}_m(\omega), \]

(16)

where the dot stands for time derivative. From this relation and Eq. (11), the Heisenberg equations for the plasmon operators readily follow:

\[ \dot{\hat{a}}_m(t) = -\left(\gamma_m/2 + i\omega_m\right)\hat{a}_m(t) + \hat{f}_m(t), \]

(17)

where \( \hat{f}_m(t) = (2\pi)^{-1/2} \int_0^\infty d\omega \hat{f}_m(\omega)e^{-i\omega t} \) is time-domain projected noise operator. The commutation relations for \( \hat{f}_m(t) \) are obtained from Eq. (13) as

\[ [\hat{f}_m(t), \hat{f}^\dagger_n(t')] = \delta_{mn} \gamma_m \delta(t - t'), \]

(18)

where the Markov approximation was used again. Thus, the Markovian dynamics of plasmon operators \( \hat{a}_m(t) \) is described by quantum Langevin equation (17) with the white-noise source \( \hat{f}_m(t) \), which guarantees [53] the equal-time commutation relations: \( [\hat{a}_m(t), \hat{a}^\dagger_n(t)] = \delta_{mn} \).

In contrast to cavity modes, the plasmons are localized at the scale well below the diffraction limit and, therefore, interact with the EM field \( \mathbf{E}(t) \) similar to point dipoles. The interaction Hamiltonian is

\[ H_{\text{pl-em}} = -\sum_m \mu_m \cdot \mathbf{E}(t), \]

where \( \mu_m = \int dV \hat{P}_m(r) \) is the plasmon dipole moment operator and \( \hat{P}_m(r) \) is the polarization vector operator. To determine \( \hat{P}_m(r) \), we resort to the Gauss law (4) presented in the form \( \nabla \cdot \mathbf{E}_m(r) + 4\pi \nabla \cdot \mathbf{P}_m(r) = 0 \), where \( \mathbf{P}_m(r) = \chi'(\omega_m, \mathbf{r}) \mathbf{E}_m(r) \) is the mode polarization vector and \( \chi(\omega, \mathbf{r}) \) is the system susceptibility. In the Markov approximation, converting this relation to the operator form, \( \hat{P}_m(r) = \chi'(\omega_m, \mathbf{r}) \hat{E}_m(r) \), and using the mode expansion (11), for monochromatic external field \( \mathbf{E}(t) = \mathbf{E} e^{-i\omega_L t} + \mathbf{E}^* e^{i\omega_L t} \), we obtain in the rotating wave approximation (RWA)

\[ H_{\text{pl-em}} = -\sum_m (\mu_m \cdot \mathbf{E} e^{-i\omega_L t} \hat{a}_m^\dagger + \text{H.c.}), \]

(19)
where $\mu_m \equiv \mu_m(\omega_m)$, and we introduced frequency-dependent transition matrix element, to be used later:

$$
\mu_m(\omega) = \frac{1}{2} \sqrt{\frac{\hbar \omega_m}{U_m}} \int dV \chi'(\omega, r) E_m(r). 
$$  \hfill (20)

The scaling factor $\sqrt{\hbar \omega_m/U_m}$ in Eq. (20) converts the plasmon energy $U_m$ to $\hbar \omega_m$ in order to match the energy of the EM field. With matrix element (20), the plasmon spontaneous decay rate is given by the standard expression [53]

$$
\gamma_{\text{rad}} = \frac{W_{\text{rad}}}{U_m} = \frac{4 \omega_m^3 \mu_m^2}{3 \hbar c^3},
$$

where $W_{\text{rad}} = \frac{p_m^2 \omega_m^4}{3 c^3}$ is the power radiated by a dipole $p_m$.

Let us now turn to interactions between plasmons and QEs modeled, e.g., by two-level systems situated at $r_i$ with dipole moments $\hat{p}_i = \mu_i (\hat{\sigma}_i^+ + \hat{\sigma}_i)$, where $\mu_i = \mu n_i$ is the transition matrix element ($n_i$ is dipole orientation). Using the mode expansion (10) in the interaction Hamiltonian $\hat{H}_{\text{pl}-\text{qe}} = -\sum_i \hat{p}_i \cdot \hat{E}_{\text{pl}}(r)$, we obtain the interaction Hamiltonian (2) with coupling $g_{im}$ given by

$$
\hbar g_{im} = -\sqrt{\frac{\hbar \omega_m}{U_m}} \mu_i \cdot E_m(r_i). 
$$  \hfill (21)

Using Eq. (8), the QE-plasmon coupling can be recast in a cavity-like form

$$
g_{im}^2 = \frac{2 \pi \mu_i^2 \omega_m}{\hbar \gamma_m^{(i)}}, \quad \frac{1}{\gamma_m^{(i)}} = \frac{2 [\mu_i \cdot E_m(r_i)]^2}{\int dV \left| \frac{\partial (\omega_m \varepsilon')}{\partial \omega_m} \right| E_m^2},
$$

where $\gamma_m^{(i)}$ is the projected plasmon mode volume [51, 54], which characterizes the plasmon field confinement at a point $r_i$ in the direction $n_i$. Since the Gauss equation (14) is scale-invariant [20], the coupling parameters (20) and (21) are independent of the overall field normalization. By rescaling the fields as $\tilde{E}_m(r) = \sqrt{U_m/4 \hbar \omega_m} E_m(r)$, these parameters are brought to a more familiar form $g_{im} = -\mu_i \cdot \tilde{E}_m(r_i)/\hbar$ and $\mu_m = \int dV \chi'(\omega_m, r) \tilde{E}_m(r)$.

Summarizing this part, the canonical Hamiltonian for plasmons interacting with the EM field and QEs has the form $H = H_{\text{pl}} + H_{\text{pl}-\text{qe}} + H_{\text{pl-em}} + H_{\text{qe}} + H_{\text{qe-em}}$, where we added the standard Hamiltonian terms $H_{\text{qe}}$ and $H_{\text{qe-em}}$ for QEs and their interaction with the EM field, respectively. The plasmon-QE and plasmon-EM coupling parameters $g_{im}$ and $\mu_m$, respectively, are now explicitly obtained within the quantization procedure. For plasmons, the canonical scheme is valid only in the Markov approximation that ignores the dielectric function dispersion. However, in metal-dielectric structures, the effects of dispersion can be very significant, and so a quantum description that includes such effects is needed.

The Langevin equation (17) implies that each plasmon mode is driven only by the reservoir’s part its electric field overlaps with [see Eq. (12)]. These projected reservoir modes
(PRM) form a discrete subspace of the full reservoir Hilbert space spanned by the operators
\[ \hat{b}_m(\omega) = \hat{f}_m(\omega) / \sqrt{\gamma_m(\omega)}, \]
which obey the commutation relations
\[ [\hat{b}_m(\omega), \hat{b}_n^\dagger(\omega')] = \delta_{mn} \delta(\omega - \omega'). \tag{23} \]
The time-evolution of PRM operators is determined by the Heisenberg equations
\[ \dot{\hat{b}}_m(\omega) = -(i/\hbar) [\hat{b}_m(\omega), \hat{H}_b] = -i\omega \hat{b}_m(\omega) \]
[compare to Eq. (16)] with the Hamiltonian
\[ \hat{H}_b = \sum_m \int_0^\infty d\omega \ h \omega \ \hat{b}_m^\dagger(\omega) \hat{b}_m(\omega) \tag{24} \]
that acts in the PRM subspace. The PRMs and plasmons can be set as independent dynamical variables by adding the Hamiltonian term that couples them. Then, upon tracing the PRMs out, one would arrive, in the standard way, at the master equation for the density matrix [53]. Here we chose a different approach and instead describe the system directly in terms of PRMs.

The interaction Hamiltonian between PRMs and QEs is obtained from the QE-plasmon coupling term (2) by using the relation (11) between the plasmon and PRM operators, with
\[ \hat{f}_m(\omega) = \hat{b}_m(\omega) \sqrt{\gamma_m(\omega)}, \]
where \( g_{im} \) is given by Eq. (21). To elucidate the mechanism behind the QE-PRM interaction, we note that the rate of energy transfer (ET) from a QE to plasmons is [51]
\[ \Gamma_{im}(\omega) = 2 \hbar \ Im \ [\mu_i D_{pi}(\omega; r_i, r_i) \mu_i] = \sum_m \Gamma_{im}(\omega), \tag{27} \]
where \( \Gamma_{im}(\omega) \) is the ET rate for an individual plasmon mode. Then, with help of Eqs. (7) and (21), we obtain
\[ \Gamma_{im}(\omega) = \frac{g_{im}^2 \gamma_m(\omega)}{(\omega_m - \omega)^2 + \frac{1}{4} \gamma_m^2(\omega)} = 2 \pi |q_{im}(\omega)|^2, \tag{28} \]
implicating that the QE-PRM interactions are mediated by plasmons absorbing the QE energy. The same relation is obtained by evaluating the transition probability rate,
\[ \Gamma_{im}(\omega) = \frac{2 \pi}{\hbar} \int_0^\infty d\omega' |h q_{im}(\omega')|^2 \delta(h \omega' - h \omega), \tag{29} \]
where the frequency integral runs over all final states, indicating that the classical effect of resonance ET is derived from the Hamiltonian (25) in the lowest order.

The PRM coupling to the EM field $\mathbf{E}(t)$ is described by the Hamiltonian $H_{\text{int}} = -\text{Re} \int dV \hat{E}_{\text{pl}}(r) \cdot \mathbf{P}(t, r)$, where $\mathbf{P} = \chi \mathbf{E}$ is the induced polarization vector. For a monochromatic field, using Eqs. (10) and (11), we obtain

$$
\hat{H}_{b-\text{em}} = -\sum_m \int_0^\infty d\omega \left[ d_m^*(\omega) \mathbf{E} e^{-i\omega L t} \hat{b}_m^\dagger(\omega) + \text{H.c.} \right],
$$

(30)

where $d_m(\omega)$ is the transition matrix element,

$$
d_m(\omega) = \sqrt{\frac{\gamma_m(\omega)}{2\pi}} \frac{-i\mu_m(\omega_L)}{\omega_m - \omega - \frac{1}{2} \gamma_m(\omega)},
$$

(31)

and $\mu_m(\omega)$ is given by Eq.(20) [compare to Eq.(26)]. In the first order, the transition probability rate is

$$
\Gamma_m(\omega_L) = \frac{2\pi}{\hbar} \int_0^\infty d\omega |d_m(\omega) \cdot \mathbf{E}|^2 \delta(\hbar \omega - \hbar \omega_L),
$$

(32)

which, in fact, represents the rate of EM energy absorption by a plasmon mode [compare to Eqs. (27) and (28)]:

$$
\Gamma_m(\omega_L) = \frac{2\pi}{\hbar^2} |d_m(\omega_L) \cdot \mathbf{E}|^2 = \frac{2}{\hbar} \text{Im} \left[ \mathbf{E}^* \alpha_m(\omega_L) \mathbf{E} \right].
$$

(33)

Here, $\alpha_m(\omega)$ is optical polarizability tensor of a plasmon mode that defines its response to an external field [49, 51]:

$$
\alpha_m(\omega) = \frac{1}{\hbar \omega_m - \omega - \frac{1}{2} \gamma_m(\omega)},
$$

(34)

Thus, the PRM-EM transition matrix element $d_m(\omega)$ reproduces plasmon resonance in the absorption spectrum. Note that, in contrast to the canonical scheme, here the dielectric function dispersion is controlled by the external field. We stress that these results are valid for any metal-dielectric structure supporting localized plasmons.

The Hamiltonian $\hat{H} = \hat{H}_b + \hat{H}_{b-\text{qe}} + \hat{H}_{b-\text{em}} + \hat{H}_{\text{qe}} + \hat{H}_{\text{qe-em}}$ provides a starting point for studying quantum correlations and non-Markovian dynamics in hybrid plasmonic systems. Within this framework, classical plasmons mediate the interactions of PRMs with the EM field and QEs to induce resonant coupling between the system components. Namely, the classical enhancement effects such as resonance ET between QEs and plasmons and resonant plasmon excitation by the EM field, which underpin most of the plasmon-enhanced
spectroscopy phenomena, are now encoded in the coupling parameters (26) and (31), respectively, and emerge in the lowest order of perturbation theory. In higher orders, these classical effects will modulate quantum correlations and non-Markovian dynamics in hybrid plasmonic systems.

In summary, we have derived, in the Markov approximation, the canonical Hamiltonian and commutation relations within the FD framework and provided explicit expressions for coupling parameters characterizing plasmon interactions with quantum emitters and the electromagnetic field. Beyond the Markov approximation, we developed a quantum approach in terms of a discrete set of bosonic modes with linear dispersion, whose interactions with quantum emitters and the electromagnetic field are mediated by classical plasmons.

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SUPPLEMENTAL MATERIAL

Plasmon modes

We consider a metal-dielectric structure supporting surface plasmons that are localized at the length scale much smaller than the radiation wavelength. In the absence of retardation effects, each connected volume $V_i$ of the structure, metallic or dielectric, is characterized by a uniform dielectric function $\varepsilon_i(\omega)$ so that the full dielectric function has the form 

$$\varepsilon(\omega, \mathbf{r}) = \sum_i \theta_i(\mathbf{r})\varepsilon_i(\omega),$$

where $\theta_i(\mathbf{r})$ is unit step function that vanishes outside $V_i$. The system eigenmodes are determined by the quasistatic Gauss law

$$\nabla \cdot \left[ \varepsilon'(\omega_m, \mathbf{r}) \nabla \Phi_m(\mathbf{r}) \right] = 0,$$

where $\Phi_m(\mathbf{r})$ and $\omega_m$ are the mode potentials and frequencies, respectively, and the mode electric fields, which can be chosen real, are defined as $E_m(\mathbf{r}) = -\nabla \Phi_m(\mathbf{r})$. In the plasmon frequency region, where $\varepsilon''(\omega)/\varepsilon'(\omega) \ll 1$, the mode frequencies are defined by the real part of dielectric function, while its imaginary part defines the mode decay rates.

Let us show that the eigenmodes of Eq. (35) are orthogonal in each connected volume $V_i$:

$$\int dV_i E_m(\mathbf{r}) \cdot E_n(\mathbf{r}) = \delta_{mn} \int dV_i E_m^2(\mathbf{r}).$$

Using $\varepsilon(\omega, \mathbf{r}) = 1 + 4\pi \chi(\omega, \mathbf{r}) = 1 + 4\pi \sum_i \chi_i(\omega)\theta_i(\mathbf{r})$, where $\chi$ is the susceptibility, we multiply Eq. (35) by $\Phi_n(\mathbf{r})$ and integrate over the system volume to obtain

$$\int dV E_m \cdot E_n + 4\pi \sum_i \chi'_i(\omega_m) \int dV_i E_m \cdot E_n = 0$$

(37)

Making a replacement $m \leftrightarrow n$ in Eq. (37) and subtracting the result from Eq. (37), we arrive at the overcomplete system

$$\sum_i [\chi'_i(\omega_m) - \chi'_i(\omega_n)] \int dV_i E_m \cdot E_n = 0,$$

(38)

and the orthogonality relation Eq. (36) readily follows. An important consequence of Eq. (36) is the absence of dissipation coupling between the modes, i.e., for $m \neq n$,

$$\int dV \varepsilon''(\omega, \mathbf{r}) E_m(\mathbf{r}) E_n(\mathbf{r}) = \sum_i \varepsilon''_i \int dV_i E_m E_n = 0,$$

(39)

which allows one to obtain the exact plasmon Green function in the presence of losses.
Plasmon Green function

The EM dyadic Green function for Maxwell equations in the presence of inhomogeneous medium satisfies

\[
\left[ \nabla \times \nabla \times - \frac{\omega^2}{c^2} \varepsilon(\omega, \mathbf{r}) \right] D(\omega; \mathbf{r}, \mathbf{r}') = \frac{4\pi \omega^2}{c^2} I \delta(\mathbf{r} - \mathbf{r}')
\]

where we adopted normalization convenient in the near field limit. Applying \( \nabla \) to both sides, one finds equation for the longitudinal part of the Green function

\[
\nabla \left[ \varepsilon(\omega, \mathbf{r}) D(\omega; \mathbf{r}, \mathbf{r}') \right] = -4\pi \nabla I \delta(\mathbf{r} - \mathbf{r}').
\]

In the near field, it is convenient to switch to the Green function for the potentials \( D(\omega; \mathbf{r}, \mathbf{r}') \), defined as

\[
D(\omega; \mathbf{r}, \mathbf{r}') = \nabla \nabla' D(\omega; \mathbf{r}, \mathbf{r}'),
\]

which satisfies

\[
\nabla \cdot [\varepsilon(\omega, \mathbf{r}) \nabla D(\omega; \mathbf{r}, \mathbf{r}')] = 4\pi \delta(\mathbf{r} - \mathbf{r}').
\]

In free space (\( \varepsilon = 1 \)), the near-field Green’s function has the form

\[
D_0(\mathbf{r} - \mathbf{r}') = -\frac{1}{|\mathbf{r} - \mathbf{r}'|}.
\]

For arbitrary \( \varepsilon(\omega, \mathbf{r}) \), we separate out the free-space and plasmon parts as \( D = D_0 + D_{pl} \) to obtain the equation for \( D_{pl} \):

\[
\nabla \cdot \left[ \varepsilon(\omega, \mathbf{r}) \nabla D_{pl}(\omega; \mathbf{r}, \mathbf{r}') \right] = -\nabla \cdot \left[ [\varepsilon(\omega, \mathbf{r}) - 1] \nabla D_0(\omega; \mathbf{r}, \mathbf{r}') \right].
\]

Assume, for a moment, that the dielectric function \( \varepsilon(\omega, \mathbf{r}) \) is real (\( \varepsilon'' = 0 \)) and expand the plasmon Green’s function in terms of eigenmodes of Eq. (35) as

\[
D_{pl}(\omega; \mathbf{r}, \mathbf{r}') = \sum_m D_m(\omega) \Phi_m(\mathbf{r}) \Phi_m(\mathbf{r}'),
\]

with real coefficients \( D_m(\omega) \). Let us apply to both sides of Eq. (43) the integral operator \( \int dV' \Phi_m(\mathbf{r}') \Delta' \). Using the mode orthogonality, it is easy to prove the relation

\[
\int dV' \Phi_m(\mathbf{r}') \Delta' D_{pl}(\omega; \mathbf{r}, \mathbf{r}') = -D_m(\omega) \int dV E_m^2(\mathbf{r})
\]

to use in the left-hand side, and the relation

\[
\int dV' \Phi_m(\mathbf{r}') \Delta' D_0(\omega; \mathbf{r}, \mathbf{r}') = 4\pi \Phi_m(\mathbf{r})
\]

to use in the right-hand side. Then, we obtain

\[
D_m \nabla \cdot \left[ \varepsilon(\omega, \mathbf{r}) \nabla \Phi_m(\mathbf{r}) \right] = 4\pi \frac{\nabla \cdot \left[ [\varepsilon(\omega, \mathbf{r}) - 1] \nabla \Phi_m(\mathbf{r}) \right]}{\int dV E_m^2(\mathbf{r})}.
\]
Finally, multiplying Eq. (47) by $\Phi_m(r)$ and integrating the result over the system volume, we obtain [51]

$$D_m(\omega) = \frac{4\pi}{\int dV E_m^2(r)} - \frac{4\pi}{\int dV \varepsilon(\omega, r) E_m^2(r)},$$

and the plasmon Green function takes the form

$$D(\omega; r, r') = \sum_mD_m(\omega)E_m(r)E_m(r').$$

The first term in Eq. (48) ensures that $D_m = 0$ in the limit $\omega \to \infty$ (or, in free space with $\varepsilon = 1$).

To incorporate the losses, we note that in Eq. (48) with complex dielectric function $\varepsilon(\omega, r) = \varepsilon'(\omega, r) + i\varepsilon''(\omega, r)$, the imaginary part can be considered as perturbation. In the first order, according to the standard perturbation theory, the diagonal matrix element $\int dV \varepsilon''(\omega, r) E_m^2(r)$ affects only the spectrum but leaves the eigenmodes unchanged, which is equivalent to having full complex dielectric function $\varepsilon(\omega, r)$ in Eq. (48). In higher orders, both the spectrum and the eigenmodes should change as the perturbation causes transitions between the basis states via non-diagonal terms $\int dV \varepsilon''(\omega, r) E_m(r)E_n(r)$ with $m \neq n$. However, for quasistatic modes, all non-diagonal matrix elements vanish [see Eq. (39)], implying that the plasmon Green function Eq. (49) with complex coefficients (48) is exact in all orders.

**Plasmon pole expansion**

For real $\varepsilon(\omega, r)$, due to the Gauss law (35), the Green function (49) with coefficients (48) develops a pole as $|\omega|$ approaches $\omega_m$. For a complex dielectric function, the plasmon poles move to the lower half of the complex-frequency plane, and so the Green’s function, being analytic in the entire complex-frequency plane except those poles, can be presented as a sum over all plasmon poles. For $\omega$ approaching $\omega_m$, we expand $\varepsilon'(\omega, r)$ near $\omega_m$

$$\varepsilon'(\omega, r) \approx \varepsilon'(\omega_m, r) + \frac{\partial \varepsilon'(\omega_m, r)}{\partial \omega_m^2} (\omega^2 - \omega_m^2),$$

where we used $\varepsilon'(\omega, r) = \varepsilon'(-\omega, r)$, and so the coefficient (48), after omitting the non-resonant term, becomes

$$D_m(\omega) = \frac{\omega_m}{4U_m} \frac{2\omega_m}{\omega_m^2 - \omega^2 - i\omega_m\gamma_m(\omega)}.$$

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Here, we introduced the plasmon mode energy

$$U_m = \frac{1}{16\pi} \int dV \frac{\partial [\omega_m \varepsilon'(\omega_m, r)]}{\partial \omega_m} E_m^2(r),$$

(52)

and the frequency-dependent decay rate

$$\gamma_m(\omega) = \frac{2 \int dV \varepsilon''(\omega, r) E_m^2(r) \partial \varepsilon'(\omega_m, r)}{\int dV \partial \varepsilon'(\omega_m, r)/\partial \omega_m E_m^2(r)},$$

(53)

where $\gamma_m(\omega) = -\gamma_m(-\omega)$. Note that the representation of (51) is valid in the frequency region $\varepsilon''(\omega)/\varepsilon'(\omega) \ll 1$ or, equivalently, $\omega_m/\gamma_m \gg 1$.

The plasmon dyadic Green’s function is given by $D_{pl}(\omega; r, r') = \nabla' D_{pl}(\omega; r, r')$, where $D_{pl}(\omega; r, r')$ is defined by Eqs. (44) and (51),

$$D_{pl}(\omega; r, r') = \sum_m \frac{\omega_m^2}{2U_m \omega_m^2 - \omega^2 - i\omega_m \gamma_m(\omega)} E_m(r) E_m(r').$$

(54)

Using Eqs. (39) and (53), it is easy to check that the plasmon Green function (54) satisfies the relation

$$\int dV \varepsilon''(\omega, r) D_{pl}^*(\omega; r, r') D_{pl}(\omega; r, r'') = 4\pi \text{Im} D_{pl}(\omega; r', r''),$$

(55)

which is essential in the FD quantization approach.

For $\omega > 0$, non-resonant contributions to $D_{pl}$ can be disregarded and the Green function takes the form

$$D_{pl}(\omega; r, r') = \sum_m \frac{\omega_m}{4U_m \omega_m^2 - \omega - \frac{i}{2} \gamma_m(\omega)} E_m(r) E_m(r'),$$

(56)

which satisfies the relation (55) as well. In the Markov approximation, i.e., $\gamma_m(\omega) \to \gamma_m(\omega_m) \equiv \gamma_m$, the full Green functions (54) or (56) no longer satisfy the relation (55) but, near the resonance, their single-mode approximations do. Note, finally, that if only in the metallic regions is the dielectric function dispersive and complex, $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$, the plasmon decay rate takes the standard form $\gamma_m = 2\varepsilon''(\omega_m)/[\partial \varepsilon'(\omega_m)/\partial \omega_m]$.

**Optical polarizability**

Consider a plasmonic system subjected to an incident monochromatic field $E_i e^{-i\omega t}$ that is uniform on the system scale. The electric field generated by the plasmonic system in response to the incident has the form

$$E(\omega, r) = \int dV' \chi'(\omega, r') D_{pl}(\omega; r, r') E_i.$$  

(57)
Multiplying by Eq. (57) by $\chi'(\omega, r)$ and integrating over the system volume, we obtain the system induced dipole moment, $\mathcal{P} = \int dV \chi' \mathcal{E}$, as

$$\mathcal{P}(\omega) = \int dV dV' \chi'(\omega, r) \chi'(\omega, r') D_{\text{pl}}(\omega; r, r') \cdot \mathcal{E}. $$

(58)

Inserting the plasmon Green function Eq. (54) into Eq. (58), we obtain

$$\mathcal{P}(\omega) = \alpha_{\text{pl}}(\omega) \mathcal{E}_i$$

(59)

where $\alpha_{\text{pl}}(\omega) = \sum_m \alpha_m(\omega)$ is the plasmon polarizability tensor [51] and

$$\alpha_m(\omega) = \frac{1}{\hbar} \frac{2\omega_m \mu_m(\omega) \mu_m(\omega)}{\omega_m^2 - \omega^2 - i\omega_m \gamma_m(\omega)}.$$  

(60)

is the individual mode polarizability tensor, where

$$\mu_m(\omega) = \sqrt{\frac{\hbar \omega_m}{4 U_m}} \int dV' \chi'(\omega, r) E_m(r)$$

(61)

is the plasmon optical transition matrix element. Near the resonance, the mode polarizability simplifies to

$$\alpha_m(\omega) = \frac{1}{\hbar} \frac{\mu_m(\omega) \mu_m(\omega)}{\omega_m^2 - \omega - \frac{i}{2} \gamma_m(\omega)}.$$  

(62)

Note that, in order to satisfy the optical theorem that guarantees energy flux conservation, the plasmon decay rate $\gamma_m(\omega)$ should also include the radiative decay contribution [51]. The latter is given by a standard expression for a point-like dipole

$$\gamma_m^r(\omega) = \frac{4\mu_m^2 \omega^3}{3\hbar c^3}.$$  

(63)

where $\omega$-dependence of $\mu_m$ is implied. In the Markov approximation, one should set $\omega = \omega_m$ in $\mu_m$ and $\gamma_m$.

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