Dipolar emitters at nanoscale proximity of metal surfaces: Giant enhancement of relaxation in microscopic theory

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We consider a nanoscale dipolar emitter (quantum dot, atom, fluorescent molecule, or rare-earth ion) in a nanometer proximity to a flat metal surface. There is strong interaction of this emitter with unscreened metal electrons in the surface nanolayer that causes enhanced relaxation due to surface plasmon excitation and Landau damping. To describe these phenomena, we developed analytical theory based on local random-phase approximation. For the system considered, conventional theory based on metal as continuous dielectric fails both qualitatively and quantitatively. Applications of the present theory and related phenomena are discussed.

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Recently, there has been explosive growth of nanoscience and nanotechnology. Nanosystems possess unique properties different from those of macroscopic materials when characteristic lengths governing their properties (e.g., electron mean-free path $l_{\text{ff}}$, the exciton Bohr radius, Debye radius $r_D$, etc.) become comparable to geometric sizes of the particles or distances between them. Then macroscopic description of nanostructured system may not be applicable even on the order of magnitude.

In this Rapid Communication, we consider a dipole emitter [semiconductor quantum dot (QD), dye molecule, atom, or rare-earth ion] at a nanometer-scale distance from the surface of a metal. We treat the metal microscopically in local random-phase approximation (LRPA). We found giant enhancement of the nonradiative decay of excitations in such emitters due to Coulomb interaction with electrons in the metal. In a nanometer-scale proximity to metal, this enhancement is an order of magnitude greater than in the existing theory, 1–3 that treats the metal as dielectric medium. We call such an approach, where the dielectric function possesses temporal but not spatial dispersion, as dielectric medium approximation (DMA).

Unique properties of QD’s make them attractive candidates for various optical applications from optical amplification and lasing 4,5 to fluorescence tagging. 6 While some applications require high QD emission efficiencies, there is a number of applications, such as ultrafast optical switching and dynamic holography, 7 that can benefit from fast nonradiative deactivation of electronic excitations in QD’s. Intrinsic relaxation in QD’s is due to radiative decay which occurs on time scales from subnanosecond to submicrosecond depending on composition, size, shape, temperature, etc. One approach to enhancing the decay rates entails the use of interactions of QD excitations with metals. As demonstrated recently, the nanoscale proximity to a metal surface can strongly affect the rates of both radiative and nonradiative relaxation of emitting species. 3,8–10 The metal nanoparticles can also serve as nanoantennas spatially concentrating electromagnetic energy on the nanoscale and transferring it to QD’s with the possibility to coherently control the excitation. 11

In the recently proposed effect of surface plasmon amplification by stimulated emission of radiation (SPASER), 12 QD’s constitute active medium, and a metal nanoparticle plays the role of laser resonant cavity. The radiationless transfer of energy from QD’s to metal is the fundamental process causing the stimulated emission of SPs that play the role of cavity photon modes for a conventional laser. The present Rapid communication will have direct application to the theory of SPASER.

Below we build theory for QD’s, though it is applicable to any dipolar emitter. The enhancement of the radiationless energy transfer from a QD to the metal in its nanometer-scale proximity occurs due to strong interaction of QD’s field with unscreened electrons in a layer of depth $r_D$ at the metal surface. For nanosystems, characteristic sizes (distances $a$ from QD’s to metal surfaces or radii of nanoparticles) are much smaller than $l_{\text{ff}}$. In this case, description of metal in DMA is not applicable. At the same time, we will not use an atomistic, ab initio theory since $a$ is much greater than the atomic scale. We will employ LRPA, a microscopic approach based on random-phase approximation (RPA), 13 where the dielectric function $\varepsilon(\omega,\mathbf{k})$ possesses both the temporal and spatial dispersion, and dissipation is due to the Landau damping 14 Earlier, approaches based on RPA (Ref. 15) and on dynamic density-functional theory 16 were developed for extremely small distances, $a \approx r_D$. In contrast, our theory is valid for the intermediate scale, $l_{\text{ff}} \approx a \approx r_D$, which is of high importance for nanooptics.

To reveal the physical meaning of LRPA vs DMA, we begin with estimates of the relaxation rate $\gamma$ (or lifetime $\tau = 1/\gamma$) of a QD in the proximity of the metal surface. The general expression for $\gamma$ for a dipolar system is

$$\gamma = \frac{1}{\hbar} \langle \hat{\mathbf{E}} \cdot \hat{\mathbf{d}} \rangle,$$  

where $\hat{\mathbf{d}}$ and $\hat{\mathbf{E}}$ are the dipole moment and electric field operators. From this expression, an estimate follows:

$$\gamma \sim \hbar^{-1} |\mathbf{E}|^2 \text{ V Im} \varepsilon(\omega,\mathbf{k}),$$

where $V$ is the metal volume occupied by field $\mathbf{E}$. 

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In DMA, the electric field created by a QD is estimated as $E \sim d/d[|e(\omega)|a^2]$, where dielectric function $e(\omega)$ possesses only the temporal dispersion, $a$ is the distance from the QD to the surface, and $V \sim a^{-1}$. Note that in the density-functional theory (DFT) there is a nanometric shift of the electron density distribution with respect to the lattice. Therefore $a$ should be treated as the distance to the electron surface. Assuming the transition frequency $\omega$ to be small compared to electron plasma frequency $\Omega_e$, we obtain from the Drude formula: $|e|^2 \sim \Omega_e^2/\omega^2$ and $\Im e \sim \gamma_m/\omega^3$, where $\gamma_m$ is the relaxation rate for electrons in the metal; $\gamma_m = v_F/l_{tr}$, and $v_F$ is the velocity at the Fermi surface. Substituting these estimates into Eq. (2), we obtain

$$\gamma = \frac{1}{2\hbar} \frac{d^2 \Im e}{a^3 |e|^2} - \frac{1}{2\hbar} \frac{d^2 v_F \omega}{a^3 \Omega_e^2}.$$  

(3)

Considering LRPA, an external field penetrates a metal mainly to a depth on order of $r_D = v_F l_{tr}/\Omega_e$. In a real metal $r_D$ is very small ($r_D \ll 1$ nm), therefore the contributing wave vectors $k \sim k_D$ are large. For such $k$, RPA yields: 

$$\Im e(\omega,k) = (3/2) \pi \Omega_e^2 \omega/(k v_F) \sim \Omega_e^2 \omega r_D^2/v_F^2.$$  

Substituting this into Eq. (1) and taking into account that $V \sim r_D a^2$, we obtain

$$\gamma = \frac{1}{2\hbar} \frac{d^2 v_F \omega}{a^3 \Omega_e^2}.$$  

(4)

The ratio of the relaxation rates in these two approximations [Eqs. (3) and (4)] is $\gamma_{LRPA}/\gamma_{DMA} \sim l_{tr}/a \sim 10^2$. The numerical estimate is obtained for silver for visible light frequencies where $l_{tr} \approx 40$ nm and distances $a \approx 1$ nm relevant for nanoscience. This estimate implies that the LRPA mechanism is dominant, and the conventional DMA is not valid even by order of magnitude.

A known approach to optical properties of nanoparticles is to renormalize the relaxation constant of electrons in a metal $\gamma_m \rightarrow \gamma_m + v_F/R$, where $R$ is the radius of a nanoparticle. This procedure emulates collisions of electrons with the surfaces. However, such an approach is not completely consistent since it only modifies the temporal dispersion and neglects the spatial dispersion that is of principal importance for nanoscopic optical phenomena, as demonstrated by the above estimates.

Quantitatively, we consider all sizes and distances to be much less than light wavelength $\lambda$. Then quasielectrostatic approximation is valid. For DMA, solving macroscopic quasielectrostatic equations, from Eq. (1), we get well-known result: 

$$\gamma = \gamma_r + \frac{1}{3\hbar} \frac{\Im e(\omega)}{|e(\omega)| + 1} \frac{|\mathbf{d}|^2}{a^3},$$  

(5)

where $|\mathbf{d}|^2$ is the transition dipole element for the QD and $\gamma_r$ is the rate of radiative relaxation in the presence of the metal half space. We assume an isotropic QD and average over the directions of $\mathbf{d}$.

In LRPA, we consider electrons of the metal as a degenerate electron plasma that possesses dissipation due to Landau damping and whose dielectric function depends on both $\omega$ and $k$ (temporal and spatial dispersion): 

$$e(\omega,k) - 1 = \frac{3 \Omega_e^2}{k^2 v_F^2} \bigg[ 1 - \frac{\omega}{2 k v_F} \ln \frac{\omega + k v_F}{\omega - k v_F} \bigg],$$  

(6)

where $\Omega_e = \sqrt{4 \pi N_e e^2/m}$ and complex function $\Im e(\omega,k)$ is defined as $\Im e(\omega) = \ln(\omega) - \pi i$ for $\omega < 0$. This expression is identical to the corresponding result of RPA. For $k > |\omega|/v_F$, the imaginary part of $e(\omega,k)$ is nonzero. For a spatially dispersive dielectric function, we should carefully reformulate the boundary conditions for ballistic electrons at the surface of the metal. First, even at jellium model electron density close to the surface varies smoothly with relaxation length $r_D$; second effect is that reflection of ballistic electrons from the surface modifies its interaction with electric field. In our calculations we ignore narrow region near the surface and suppose that locally the electron Fermi liquid everywhere has the same properties as in the bulk metal (the LRPA term originates from the latter assumption). We will show that variation of electron’s density close to the surface brings only small correction to our results. To take into account second effect we assume specular reflection of electron from the surface. As was shown in Ref. 21 ideal specular reflection implies that electrostatic problem with dielectric function (6) and given normal electric field $E_{int}(x,y,0)$ at this surface is equivalent to the problem in infinite space

$$\nabla \cdot (\hat{\mathbf{e}} \nabla \varphi_{int}) = 2 E_{int}(x,y,0) \delta(z),$$  

(7)

where $\varphi_{int}$ is the field potential in the metal, and $\hat{\mathbf{e}}$ is the nonlocal dielectric function whose Fourier image is $e(\omega,k)$. Note, that Dirac delta in Eq. (7) emulates boundary condition at the metal surface. Solution of Eq. (7) yields the potential distribution symmetric about the surface ($z = 0$) with a discontinuity of normal electric field $2E_{int}(x,y,0)$. Next, this electric field should be found consistently with potential distribution outside of the metal, where it obeys the Laplace equation with a dipolar singularity at point $(0,0,a)$. In Fourier space, the solution in metal is

$$\tilde{\varphi}_{int}(k_x,k_y) = 2 \tilde{E}(k_x,k_y) k^{-2} e(\omega,k)^{-1},$$  

where $\tilde{E}(k_x,k_y)$ is two-dimensional (2D) Fourier transform of $E_{int}(x,y,0)$ and $k = [k_x^2 + k_y^2 + k_z^2]^{1/2}$. As result, the 2D Fourier transform of the potential at the surface is

$$\tilde{\varphi}_{int}(k_x,k_y)_{z=0} = \frac{1}{\pi} \tilde{E}(k_x,k_y) \int_{-\infty}^{\infty} \frac{dk_z}{k_z^2 e(\omega,k)}.$$  

(8)

To find the solution in the region outside of the metal, we first find it for a unit charge at point $(0,0,a)$. Then by variation over coordinates, we find the required dipolar field. This solution for a charge is

$$\tilde{\varphi}_{exd}(k_x,k_y) = \{ -2 \tilde{E}(k_x,k_y) + 4 \pi [e^{ik_x a} + e^{-ik_x a}] \} k^{-2},$$  

(9)

and the 2D Fourier transform of the external potential at the surface has the form
where constant $C \approx 0.8$. For $\omega \ll \Omega_e$, the integral of Eq. (12) rapidly converges at the upper limit. Therefore, the result is not significantly sensitive to large $k_z$ or small distances $z \sim r_D$. 

From Eqs. (9) and (11), the induced potential at point $(0,0,a)$ is

$$\varphi_{\text{ind}}(0,0,a) = -\frac{1}{2\pi} \int_0^\infty \left[ \tilde{E}(k_r) - 2\pi e^{-k_r a} e^{-k_r a} dk_r \right].$$

From this, we find the induced field at the QD. Averaging over the dipole orientation, from Eq. (1), we obtain the relaxation rate

$$\gamma = \gamma_r + \frac{4}{3} \frac{1}{d_{12}^2} \Im \tilde{\varepsilon}(\omega, k_r) \int_0^\infty k_r^2 e^{-k_r a} e^{-k_r a} dk_r.$$  \hfill (15)

Obtaining Eq. (15), we consider visible and infrared frequencies where $|\tilde{\varepsilon}(\omega, k_r)| \approx 1$. For the case $a \approx v_F / \omega - 1$ nm (the numerical estimate is for silver and $h \omega = 1$ eV), we evaluate Eq. (15) using expansion (13)

$$\gamma = \gamma_r + \frac{1}{h} |d_{12}^2| \left\{ \frac{1}{3} \frac{1}{a \vert \tilde{\varepsilon}(\omega, k_r) \vert^2} + \frac{1}{6} \frac{\omega v_F}{a^2 \Omega_e^2} \ln \left( \frac{\Omega_e}{\omega} \right) \right\}.$$  \hfill (16)

where $\varepsilon(\omega)$ is the macroscopic dielectric function (without the spatial dispersion). Here, the first term in the brackets describes the macroscopic contribution and is in agreement with Eqs. (3) and (5). The second term, $\propto a^4$, is the result of LRPA and originates from the Landau damping. It is dominant for $a \ll \lambda_0$; its prelogarithmic factor agrees with the estimate of Eq. (4). The same dependence on the distance ($\propto a^4$) was obtained in Ref. 22. However, the result of Ref. 22 does not contain the large logarithm and has an inaccurate prefactor, $\omega(k_F \Omega_e)^{-1}$, in contrast to ours $\omega v_F \Omega_e^{-1}$. This stems from the fact that Ref. 22 incorrectly assumes that only electrons from a surface layer of width $\sim k_F^{-1}$ interact with the external field.

The metal not only causes radiationless relaxation, but also affects (renormalizes) the radiative decay rate. From Eqs. (5.159) and (5.160) of Ref. 23, one can calculate the radiative rate for a QD in the presence of metal half space considered as an ideal mirror that reasonably emulates noble metals at not very high frequencies ($\omega \ll \Omega_e$). Fluorescence of QD will, consequently, be strongly quenched, its quantum yield $\gamma_r / \gamma \sim 10^{-1} - 10^{-3}$ for $h \omega > 0.5$ eV.
yields a very strong dependence on the emitter distance from the metal surface, $\gamma \propto a^{-4}$ for $a \ll \lambda$. This is in sharp contrast with the conventional DMA where $\gamma \propto a^{-3}$. Importantly, the present LRPA theory not only predicts a qualitatively different behavior, but also quantitatively predicts a much higher relaxation rate. Physically, this enhancement of relaxation is due to the fact that for an emitter close to the metal surface, a significant number of metal electrons are within the Debye screening length, affected by an unscreened field of the emitter. This unscreened interaction is very strong, leading to efficient coupling to surface plasmons and subsequent dissipation due to Landau damping. The relaxation in LRPA is enhanced with respect to that in DMA by a factor $l_{tr}/a$ that is very large for good metals and nanometric distances $a$.

The present theory is directly applicable also to metal nanoparticles whose curvature is large enough, $r \gg a$ and $r \gg r_D$, as for some cases in the experiment of Ref. 9. For SPASER,\textsuperscript{12} the enhanced coupling of QD’s with metal that follows from the present theory implies lower threshold and shorter pulse time, which we will consider elsewhere. Our theory can be further developed to take into account the modification of the metal electron liquid properties close to the surface. The DFT yields also the Friedel oscillations of electron density.\textsuperscript{17} Such oscillations are found to be important for optical responses of metallic nanoshells described by time-dependent local density approximation of DFT.\textsuperscript{24} These effects may be important for theory of QD’s close to a metal surface; we intend to consider them elsewhere.

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\textsuperscript{11}Electronic address: klimov@lanl.gov
\textsuperscript{14}V.V. Klimov, M. Ducloy, and V.S. Letokhov, Eur. Phys. J. D 20, 133 (2002).
\textsuperscript{24}G. D. Mahan, \textit{Many-Particle Physics} (Plenum, New York, 1990).
\textsuperscript{35}E. Prodan and P. Nordlander, Chem. Phys. Lett. 352, 140 (2002).}