PHYSICAL REVIEW B **69**, 121403(R) (2004)

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

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(Received 24 October 2003; published 9 March 2004)

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.

DOI: 10.1103/PhysRevB.69.121403 PACS number(s): 78.67.−n, 68.37.Uv, 71.45.Gm

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_{tr}, 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 effect 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_{tr}. 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, $a \lesssim r_D$. In contrast, our theory is valid for the intermediate scale, $l_{tr} \gtrsim a \gtrsim r_D$, which is of high importance for nanooptics.

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

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

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

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

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

0163-1829/2004/69(12)/121403(4)/$22.50

In DMA, the electric field created by a QD is estimated as $E\sim d/[|\varepsilon(\omega)|a^3]$, where dielectric function $\varepsilon(\omega)$ possesses only the temporal dispersion, a is the distance from the QD to the surface, and $V\sim a^3$. Note that in the density-functional theory (DFT) there is a nanometric shift of the electron density distribution with respect to the lattice.[17] Therefore a should be treated as the distance to the *electron* surface. Assuming the transition frequency ω to be small compared to electron plasma frequency Ω_e, we obtain from the Drude formula: $|\varepsilon|^2\sim\Omega_e^4/\omega^4$ and $\mathrm{Im}\varepsilon\sim\Omega_e^2\gamma_m/\omega^3$, where γ_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

$$\gamma\sim\frac{1}{\hbar}\frac{d^2\mathrm{Im}\varepsilon}{a^3|\varepsilon|^2}\sim\frac{1}{\hbar}\frac{d^2v_F\omega}{a^3l_{tr}\Omega_e^2}. \tag{3}$$

Considering LRPA, an external field penetrates a metal mainly to a depth on order of $r_D\sim v_F/\Omega_e$. In a real metal r_D is very small ($r_D\lesssim1$ nm), therefore the contributing wave vectors $k\sim1/r_D$ are large. For such k, RPA yields:[14,13] $\mathrm{Im}\varepsilon(\omega,k)=(3/2)\pi\Omega_e^2\omega/(k\,v_F)^3\sim\Omega_e^2\omega\,r_D^3/v_F^3$. Substituting this into Eq. (1) and taking into account that $V\sim r_Da^2$, we obtain

$$\gamma\sim\frac{1}{\hbar}\frac{d^2v_F\omega}{a^4\Omega_e^2}. \tag{4}$$

The ratio of the relaxation rates in these two approximations [Eqs. (3) and (4)] is $\gamma_{LRPA}/\gamma_{DMA}\sim l_{tr}/a\sim10^2$. The numerical estimate is obtained for silver for visible light frequencies where $l_{tr}\approx40$ nm[18] and distances $a\sim1$ 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.[19] 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 nanoscale optical phenomena, as demonstrated by the above estimates.

Quantitatively, we consider all sizes and distances to be much less than light wavelength λ. Then quasielectrostatic approximation is valid. For DMA, solving macroscopic quasielectrostatic equations, from Eq. (1), we get well-known result:[20]

$$\gamma=\gamma_r+\frac{1}{3\hbar}\frac{\mathrm{Im}\varepsilon(\omega)}{|\varepsilon(\omega)+1|^2}\frac{|\mathbf{d}_{12}|^2}{a^3}, \tag{5}$$

where $\mathbf{d}_{12}$ is the transition dipole element for the QD and γ_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 $\mathbf{d}_{12}$.

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 ω and $\mathbf{k}$ (temporal and spatial dispersion)[14]

$$\varepsilon(\omega,k)-1=\frac{3\Omega_e^2}{k^2v_F^2}\left[1-\frac{\omega}{2kv_F}\ln\frac{\omega+kv_F}{\omega-kv_F}\right], \tag{6}$$

where $\Omega_e=\sqrt{4\pi N_ee^2/m}$ and complex function ln(u) is defined as $\ln(u)=\ln|u|-i\pi$ for $u<0$. This expression is identical to the corresponding result of RPA.[13] For $k>|\omega|/v_F$, the imaginary part of $\varepsilon(\omega,k)$ 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 jeleum 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 $E_\perp(x,y,0)$ at this surface is equivalent to the problem in infinite space

$$\nabla(\hat{\varepsilon}\nabla\varphi_{int})=2E_\perp(x,y,0)\;\delta(z), \tag{7}$$

where φ_{int} is the field potential in the metal, and $\hat{\varepsilon}$ is the nonlocal dielectric function whose Fourier image is $\varepsilon(\omega,\mathbf{k})$. 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 $2E_\perp(x,y,0)$. 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 $\tilde{\varphi}_{int}(\mathbf{k})=2\tilde{E}(k_x,k_y)k^{-2}\varepsilon(\omega,k)^{-1}$, where $\tilde{E}(k_x,k_y)$ is two-dimensional (2D) Fourier transform of $E_\perp(x,y,0)$ 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

$$\tilde{\varphi}_{sur}(k_x,k_y)|_{z=0}=\frac{1}{\pi}\tilde{E}(k_x,k_y)\int_{-\infty}^{\infty}\frac{dk_z}{k^2\varepsilon(\omega,k)}. \tag{8}$$

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

$$\tilde{\varphi}_{ext}(\mathbf{k})=\{-2\tilde{E}(k_x,k_y)+4\pi[e^{ik_za}+e^{-ik_za}]\}k^{-2}, \tag{9}$$

and the 2D Fourier transform of the external potential at the surface has the form

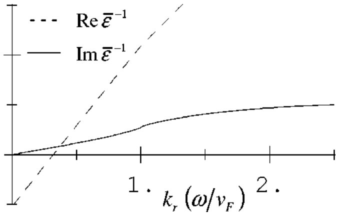

FIG. 1. Inverse surface dielectric function $\overline{\varepsilon}(\omega,k_r)^{-1}$ (the real and imaginary parts) plotted against parallel wave vector k_r for $\hbar\omega=2$ eV.

$$\tilde{\varphi}_{sur}(k_x,k_y)|_{z=0}=\frac{-\tilde{E}(k_x,k_y)+4\pi e^{-(k_x^2+k_y^2)^{1/2}a}}{(k_x^2+k_y^2)^{1/2}}. \tag{10}$$

Equating Eqs. (8) and (10), we find

$$\tilde{E}(k_r)=4\pi e^{-k_r a}[1+\overline{\varepsilon}(\omega,k_r)^{-1}]^{-1}, \tag{11}$$

$$\overline{\varepsilon}(\omega,k_r)\equiv\frac{\pi}{k_r}\left[\int_{-\infty}^{\infty}\frac{dk_z}{k^2\varepsilon(\omega,k)}\right]^{-1}, \tag{12}$$

where $k_r=(k_x^2+k_y^2)^{1/2}$.

The inverse surface dielectric function, $\overline{\varepsilon}(\omega,k_r)^{-1}$, is shown in Fig. 1 for $\hbar\omega=2$ eV. In the long wavelength limit, $k_r\ll\omega/v_F$, from Eq. (12) with logarithmic accuracy, we get

$$\frac{1}{\overline{\varepsilon}(\omega,k_r)}=\frac{1}{1-(\Omega_e/\omega)^2}-\frac{ik_r v_F\omega}{3\Omega_e^2}\ln\left(C\frac{\Omega_e}{\omega}\right), \tag{13}$$

where constant $C\approx0.8$. 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

$$\varphi_{ext}(0,0,a)=\frac{-1}{2\pi}\int_0^{\infty}[\tilde{E}(k_r)-2\pi e^{-k_r a}]e^{-k_r a}dk_r. \tag{14}$$

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

$$\gamma=\gamma_r+\frac{1}{\hbar}\frac{4}{3}|\mathbf{d}_{12}|^2\mathrm{Im}\int_0^{\infty}k_r^2e^{-2k_r a}\overline{\varepsilon}(\omega,k_r)^{-1}dk_r. \tag{15}$$

Obtaining Eq. (15), we consider visible and infrared frequencies where $|\overline{\varepsilon}(\omega,k_r)|\gg1$. For the case $a\gtrsim v_F/\omega\sim1$ nm (the numerical estimate is for silver and $\hbar\omega=1$ eV), we evaluate Eq. (15) using expansion (13)

$$\gamma=\gamma_r+\frac{1}{\hbar}|\mathbf{d}_{12}|^2\left[\frac{1}{3}\frac{\mathrm{Im}\varepsilon(\omega)}{a^3|\varepsilon(\omega)|^2}+\frac{1}{6}\frac{\omega v_F}{a^4\Omega_e^2}\ln\left(C\frac{\Omega_e}{\omega}\right)\right], \tag{16}$$

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 $a\ll l_{tr}$; 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 $\omega v_F\Omega_e^{-2}$. 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.

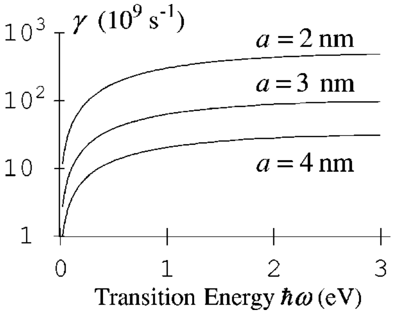

FIG. 2. Relaxation rate γ of QD at a distance a from metal surface as a function of transition energy $\hbar\omega$. The distances a to the surface are indicated at the corresponding curves. The computations are made for a constant $d_{12}=28\times10^{-18}$ esu, which corresponds $\gamma_0=10^9$ s^{-1} at $\hbar\omega=2$ eV.

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 ($\omega\ll\Omega_e$),

$$\gamma_r=\gamma_0\left[1-\frac{2\alpha\cos(2\alpha)-(1-2\alpha^2)\sin(2\alpha)}{4\alpha^3}\right], \tag{17}$$

where $\alpha=a/\bar{\lambda}$ and γ_0 is the decay rate of an isolated QD. For simplicity, here and below, we do not take into account the nonradiative decay of an isolated QD setting $\gamma_0=4|\mathbf{d}_{12}|^2/(3\hbar\bar{\lambda}^3)$, where $\bar{\lambda}\equiv c/\omega$. Note that $\gamma_r\rightarrow(2/3)\gamma_0$ for $a\ll\bar{\lambda}$.

The results of numerical computations from Eq. (15) of the metal-induced enhancement of relaxation rate γ for silver at $a=2$, 3, and 4 nm are shown in Fig. 2. The metal in such a close proximity accelerates the relaxation in QD *by orders of magnitude*. Fluorescence of QD will, consequently, be strongly quenched, its quantum yield $\gamma_r/\gamma\sim10^{-1}$–$10^{-3}$ for $\hbar\omega>0.5$ eV.

In Fig. 3, we show relative decay rate γ/γ_0 for silver as a function of the relative distance $a/\bar{\lambda}$ computed from Eqs. (15) and (17) along with the asymptotics from Eq. (16). The long-dash line is the LRPA contribution [the second term in brackets of Eq. (16)] that falls off with distance as a^{-4}; it is in a good agreement with the full computation result (bold line) for small distances ($a\lesssim0.05\bar{\lambda}$). Thus, the LRPA mechanism dominates the QD relaxation in such a close proximity to the surface. In contrast, the DMA rate (the

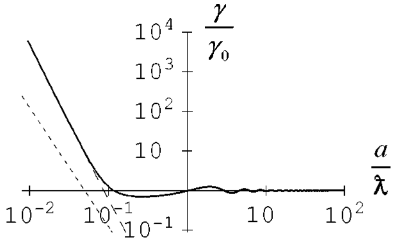

FIG. 3. Relaxation rate γ of QD at a distance a from metal surface relative to γ_0 for isolated QD computed from Eqs. (15) and (17) by numerical integration for $\hbar\omega = 2$ eV (bold line). The long-dash line is the asymptotic given by the second term and short-dash line by the first term in the brackets of Eq. (16). Note the double logarithmic scale.

short-dash line) is always negligible despite its weaker fall off as a^{-3}. Note that these two asymptotics cross at $a \sim l_{tr}$; however, at such large distances the radiative term actually dominates over both of them. The decay rate γ oscillates significantly (with the relative amplitude of $\approx 30\%$) at $a \gtrsim \bar{\lambda}$ due to destructive/constructive interference of QD radiation with that of the QD mirror image. These oscillations are in an agreement with Ref. 10.

To briefly summarize the main results, we have developed LRPA theory to describe a nanosize dipolar emitter placed in a nanometer-scale proximity of a metal surface and calculated its relaxation rate γ [Eqs. (15) and (16)]. We predict *strong enhancement of this relaxation by up to three orders of magnitude* (in comparison with radiative transition of an isolated emitter). The dominant mechanism is radiationless transfer of energy to the metal with excitation of surface plasmons that undergo Landau damping. This mechanism yields a very strong dependence on the emitter distance from the metal surface, $\gamma \propto a^{-4}$ for $a \ll \bar{\lambda}$. 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,[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.[17] Such oscillations are found to be important for optical responses of metallic nanoshells described by time-dependent local density approximation of DFT.[24] These effects may be important for theory of QD's close to a metal surface; we intend to consider them elsewhere.

This work was supported by the Chemical Sciences, Biosciences, and Geosciences Division of the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, and Los Alamos LDRD Funds. We are grateful to W. Kohn and J. E. Sipe for useful discussions.

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[1] J.E. Sipe, Surf. Sci. **105**, 489 (1981).

[2] J. Gersten and A. Nitzan, J. Chem. Phys. **75**, 1139 (1981).

[3] V.V. Klimov, M. Ducloy, and V.S. Letokhov, Eur. Phys. J. D **20**, 133 (2002).

[4] V.I. Klimov, A.A. Mikhailovsky, S. Xu, A. Malko, J.A. Hollingworth, C.A. Leatherdale, H.-J. Eisler, and M.G. Bawendi, Science **290**, 314 (2000).

[5] S. Fafard, K. Hinzer, S. Raymond, M. Dion, J. McCaffrey, Y. Feng, and S. Charbonneau, Science **274**, 1350 (1996).

[6] M. Bruchez, Jr., M. Moronne, P. Gin, S. Weiss, and A.P. Alivisatos, Science **281**, 2013 (1998).

[7] B. Kraabel, A. Malko, J. Hollingsworth, and V.I. Klimov, Appl. Phys. Lett. **78**, 1814 (2001).

[8] K.T. Shimizu, W.K. Woo, B.R. Fisher, H.J. Eisler, and M.G. Bawendi, Phys. Rev. Lett. **89**, 117401 (2002).

[9] E. Dulkeith, A.C. Morteani, T. Niedereichholz, T.A. Klar, J. Feldmann, S.A. Levi, F.C.J.M. van Veggel, D.N. Reinhoudt, M. Möller, and D.I. Gittins, Phys. Rev. Lett. **89**, 203002 (2002).

[10] R.M. Amos and W.L. Barnes, Phys. Rev. B **55**, 7249 (1997).

[11] M.I. Stockman, S.V. Faleev, and D.J. Bergman, Phys. Rev. Lett. **88**, 067402 (2002).

[12] D.J. Bergman and M.I. Stockman, Phys. Rev. Lett. **90**, 027402 (2003).

[13] G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1990).

[14] E. M. Liftshitz and L. P. Pitaevskii, *Physical Kinetics* (Butterworth-Heinemann, Oxford, 1997).

[15] A.G. Eguiluz, Phys. Rev. Lett. **51**, 1907 (1983).

[16] P. Gies and R.R. Gerhardts, Phys. Rev. B **37**, 10 020 (1988).

[17] N.D. Lang and W. Kohn, Phys. Rev. B **7**, 3541 (1973).

[18] P.B. Johnson and R.W. Christy, Phys. Rev. B **6**, 4370 (1972).

[19] U. Kreibig and L. Genzel, Surf. Sci. **156**, 678 (1985).

[20] H. Morawitz, Phys. Rev. **187**, 1792 (1969).

[21] M. Wilkinson and B. Mehlig, J. Phys.: Condens. Matter **12**, 10 481 (2000).

[22] A. Liebsch, Phys. Rev. Lett. **54**, 67 (1985).

[23] J. R. Wait, *Introduction to Antennas and Propagation* (P. Peregrinus Ltd., London, 1986).

[24] E. Prodan and P. Nordlander, Chem. Phys. Lett. **352**, 140 (2002).