Energy transfer in hybrid systems quantum dot – plasmonic nanostructures

A. V. Chaplik[1)]

Rzhanov Institute of Semiconductor Physics SB of the RAS, 630090 Novosibirsk, Russia

Novosibirsk State University, 630090 Novosibirsk, Russia

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Radiationless relaxation in hybrid systems quantum dot (QD) – plasmonic nanostructure is considered. For the system QD – 2D plasma the relaxation rate extremely steeply depends on the radius of quantum dot while in the pair QD – cylindrical wire contacting each other this dependence is logarithmic weak.

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Various forms of interaction between quantum dots (QD) and other nanostructures of different dimensions are widely discussed in the current literature. Hybrid quantum well-dots nanostructures have been considered in [1] as possible candidates for light-emitting and photo-voltaic applications. A combination of inorganic InP/ZnS core-shell quantum dots and wide bandgap ZnO nanowires which can potentially enable optoelectronic devices novel functionalities was the subject of the paper [2]. Interaction of a semiconductor (QD) with localized surface plasmons in metallic nanoparticles contains rich and interesting physics and promises numerous applications, e.g., as an all-optical ultrafast switching device [3, 4].

A very important characteristics of any hybrid system QD – plasmonic nanostructure is the rate of energy transfer between the components of the hybrid. In other words, this is the rate of radiationless relaxation of the QD electronic excitation via generation of plasmons in the neighboring nanostructure. This is the subject of the present letter. Two hybrid systems are considered: QD – 2D electron gas (quantum well) and QD – nanowire (quasi 1D electron gas). The main result is quite different (in these two cases) and surprisingly nontrivial dependence of the relaxation rate on the QD radius.

2D electron gas. First of all one has to determine the typical order of magnitude of the QD excitation energy that is converted into plasma excitation. Suppose we have a QD with the radius $a \sim 10\,\mathrm{nm}$ and the electron effective mass m_D of the order of $0.1\,m_0$ (m_0 – the bare electron mass). For the simplest model of QD – spherical potential well with hard walls – the resonant transition (i.e., allowed in the dipole approximation optical transition) connects the levels $1s$ and $1p$. The frequency of this transition Ω scales as $\hbar/m_D a^2$ and for above given values it is about $10^{13}\,\mathrm{s}^{-1}$. For the 2D electron gas we take same order of magnitude of the effective mass and typical areal density of electrons $\sim 10^{11} - 10^{12}\,\mathrm{cm}^{-2}$. Then the plasmon with the frequency $\omega(k) \sim 10^{13}\,\mathrm{s}^{-1}$ belongs to that part of the dispersion curve of the 2D plasma waves where retardation effects become already negligible (plasmon wave number k is too large) but effects of the spatial dispersion are not yet essential (k is still too small) and $\omega(k)$ can be taken in the form $\omega(k) = \sqrt{k}v_{\mathrm{F}}/\sqrt{a^*}$, where v_{F} is the Fermi velocity of the 2D electron gas, a^* is effective Bohr radius. To describe the interaction of the electron in QD with the plasmons in 2D gas one has to find the electric field created by 2D plasmon inside the QD. This can be done from the Poisson equation (not Maxwell ones because the retardation is neglected!) for the electrostatic potential φ of the 2D plasma wave:

$$\Delta\varphi = -4\pi e\widetilde{N}_s(\boldsymbol{\rho})\delta(z); \quad \widetilde{N}_s = -N_s \mathrm{div}\mathbf{u}(\boldsymbol{\rho}). \qquad (1)$$

Here $\mathbf{u}(\boldsymbol{\rho})$ is the displacement vector of the particles, $\boldsymbol{\rho}$ is the 2D vector in the plane $z = 0$ where plasma is located. We expand all quantities in Fourier series and introduce in standard fashion the normal coordinates: $\mathbf{u}(\boldsymbol{\rho}) = \sum_{\mathbf{k}} \mathbf{Q}_{\mathbf{k}} e^{i\mathbf{k}\boldsymbol{\rho}} + \mathrm{c.c.}$ Then the Fourier component of the potential is

$$\varphi_{\mathbf{k}} = -2\pi i e N_s \exp(-k|z|)(\mathbf{k}\mathbf{Q}_{\mathbf{k}})/k. \qquad (2)$$

The Hamiltonian of the free 2D plasmon field is (see [5] where this is given for 3D plasmons):

$$\hat{H} = \frac{1}{2}\sum_{\mathbf{k}} \left[\frac{P_{\mathbf{k}}P_{-\mathbf{k}}}{mN_s} + mN_s\omega^2(k)Q_{\mathbf{k}}Q_{-\mathbf{k}}\right], \qquad (3)$$

1)e-mail: chaplik@isp.nsc.ru

where $\omega^2 = 2\pi e^2 N_s k/m$, m is the electron mass of 2D gas, and P is the momentum operator. The interaction of the electrons with the plasmons is described by the operator

$$\hat{V}_{\rm int} = -2\pi i e^2 N_s \sum_{\mathbf{k}} \hat{Q}_{\mathbf{k}} e^{i\mathbf{k}\boldsymbol{\rho} - k|z|} + \text{c.c.} \quad (4)$$

After this the probability per unit time of the conversion of electron excitation in QD into a plasmon is given by the Fermi golden rule:

$$W = \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}} \left| \left\langle 1|\hat{V}_{\rm int}|0 \right\rangle \right|^2 \delta(\omega(k) - \Omega). \quad (5)$$

Elementary calculation results in the following relaxation rate:

$$\frac{1}{\tau} = M \frac{m\Omega^2}{\hbar N_s} \exp\left(-\frac{a^* H \Omega^2}{v_F^2}\right). \quad (6)$$

Here H is the distance between 2D gas and the center of QD, $\hbar\Omega$ is the energy separation between the levels $1p$ and $1s$ in QD, $M = |\langle 1p|e^{i\mathbf{k}\boldsymbol{\rho} - k|z|}|1s\rangle|^2$ – matrix element squared of the transition $1p - 1s$.

Though this result formally is obtained in the frame of perturbation theory (weak interaction $\hat{V}_{\rm int}$) it coincides, as it is well known (see, e.g., [6]) with the result of the Weisskopf–Wigner theory of spontaneous emission. The latter is based on a different approximation, the so-called rotating wave approach, that does not demand the weakness of interaction but exploits the resonance approximation: one neglects fast oscillating terms in the amplitude of states and keeps only slowly varying ones that actually corresponds to the energy conservation law. In the Weisskopf–Wigner theory the probability to find the QD in the initial (excited) state at the moment t equals $\exp(-t/\tau)$ with τ defined by the Eq. (6).

As Ω is proportional to $1/a^2$ the dependence of the relaxation rate on QD radius is given by the relation

$$\frac{1}{\tau} \sim \frac{1}{N_s a^4} \exp\left(-\frac{HL^3}{a^4}\right), \quad (7)$$

where $L^3 = \gamma/2\pi(m/m_D)^2 a^*/N_s$, γ is determined from the formula $\Omega = \gamma\hbar/m_D a^2$ (for $1s-1p$ transition $\gamma \approx 5$). The quantity M also depends on a while it is function of the parameter $k_0 a$ with $k_0 = a^*\Omega^2/v_F^2$ (the root of the equation $\omega(k_0) = \Omega$). For the above mentioned values of $N_s \sim 10^{11} - 10^{12}\,\text{cm}^{-2}$ we have $k_0 a \sim 1$ and, correspondingly $M \sim 1$. Then for $N_s = 10^{12}\,\text{cm}^{-2}$, $H = 20\,\text{nm}$ the Eq. (6) gives $1/\tau \sim 10^{11} s^{-1}$. However, for a very high density of 2D electrons ($N_s > 10^{13}\,\text{cm}^{-2}$) the parameter $k_0 a$ becomes small and this gives estimate $M \sim (k_0 a)^2$. Then $1/\tau$ extremely steeply depends on a: $1/\tau \sim a^{-10}\exp(-HL^3/a^4)$. Anyway, it is interesting that relaxation rate always has maximum as a function of QD radius at $a_{\max} \sim (HL^3)^{1/4}$.

Quantum wire (plasma cylinder). The subject of consideration is now mobile electrons in a cylinder of the radius R stretched along z-axis and QD (radius a) contacting with the cylinder at the point $x = R$, $y = z = 0$. Such a geometry – contact of a spherical QD and a cylindrical wire – is the most typical for experiments though, in principle, an arbitrary spatial separation between the two objects is possible. Then one more free parameter (similar to the value H of the previous paragraph) would appear in the problem. The eigenmodes of the plasma cylinder in the quasistatic approximation (infinitely large speed of light) are given by

$$\omega_n^2(k) = \omega_p^2 \frac{I_n'(kR)K_n(kR)}{\varepsilon_1 I_n'(kR)K_n(kR) - \varepsilon_2 K_n'(kR)I_n(kR)}, \quad (8)$$

where ω_p is the bulk plasma frequency of the material which the cylinder is made of, ε_1 is the background dielectric constant of the cylinder, ε_2 is the same for the outer space, k is the longitudinal (along the z-direction) plasmon momentum, n is the plasmon azimuth quantum number $n = 0, \pm1, \pm2, ...$, I and K are the modified Bessel functions of the third type and prime means derivative.

To be precise I consider a metallic wire with ω_p about 3 orders of magnitude larger than Ω. Then the ratio $\omega_p R/c$ (c is the speed of light) becomes equal to or larger than unit for $R \geq 30\,\text{nm}$. Hence, for such wire radii the quasistatic approach becomes inapplicable and retardation effects have to be accounted for. Formally this can be done by substitution $k \to \sqrt{k^2 - \omega^2/c^2}$ in the Eq. (8). As $\omega_p \gg \Omega$ only the long wavelength plasmons with $n = 0$ and $kR \ll 1$ can be excited by QD. Their dispersion relation with logarithmic accuracy has the form

$$\omega_0^2(k) = \frac{\omega_p^2 (kR)^2 \Lambda}{1 + \omega_p^2 R^2 \Lambda/c^2}, \quad (9)$$

where $\Lambda = \ln 2/kR$ (for the sake of simplicity I put $\varepsilon_1 = \varepsilon_2$, after that the denominator in the Eq. (8) gives the Wronskian of I and K equaled to $1/kR$). All the rest plasmon branches with $n \neq 0$ look like optical phonons – they have $\omega \sim \omega_p \gg \Omega$ for all values of k and cannot be in resonance with the electron transition in QD.

Our next step is quantization of the plasma waves in the cylinder. One has to consider longitudinal vibrations with the displacement vector $u_\varphi = u_\rho = 0$, $u_z \neq 0$ which effectively interact with electrons. Expansion

$$u_z(\rho, \varphi, z) = \sum_{n,k} Q_{k,n} I_n(k\rho) e^{in\varphi + ikz} \quad (10)$$

is to be put in the Maxwell equation for the electric potential φ^{in} inside the cylinder

$$\frac{d^2\varphi_{nk}^{in}}{d\rho^2}+\frac{1}{\rho}\frac{d\varphi_{nk}^{in}}{d\rho}-\left(\kappa^2+\frac{n^2}{\rho^2}\right)\varphi_{nk}^{in}= = Q_{kn}(4\pi iekN_v)I_n(\kappa\rho), \quad (11)$$

where $\kappa^2=k^2-\omega^2/c^2>0$, φ_{nk}^{in} is the Fourier component of the potential, N_v is the bulk density of electrons. The solution of the inhomogeneous equation (11) is looked for in the form $\varphi_{nk}^{in}=c(\rho)I_n(\kappa\rho)$ by the method of variation of constants. The result reads

$$\varphi_{nk}^{in}(\rho)=4\pi iekN_vI_n(\kappa\rho)\int_0^{\rho}\frac{d\rho'}{\rho' I_n^2(\kappa\rho')}\times \times\int_0^{\rho'}I_n^2(\kappa\rho'')\rho''d\rho''Q_{kn}. \quad (12)$$

For $n=0$, $\kappa\varrho\ll1$ this gives $\varphi_{0k}^{in}=i\pi ekN_v\rho^2Q_{k0}$. This solution for φ^{in} has to be matched with the solution in outer space $\varphi^{\rm ext}=BK_0(\kappa\rho)$ at $\rho=R$. The operator of the electron-plasmon interaction $\hat V_{\rm int}$ is $e\varphi^{\rm ext}(\rho)e^{ikz}$ where $\rho=\sqrt{(R+a+x)^2+y^2}$. Here x and y are the coordinates in the equatorial plane of QD $z=0$ counted from the QD center. Usually one can suppose $a\ll R$, then $x,y,z\sim a$ and the leading term in the matrix element of $\hat V_{\rm int}$ takes the form (one can put $e^{ikz}=1$):

$$\langle\hat V_{\rm int}\rangle=i\pi ekN_v\langle\hat Q_{k0}\rangle\langle x\rangle_{1s,1p}\frac{K_0'(kR)}{K_0(kR)}. \quad (13)$$

Moreover, for the cylinder radius much larger than 30 nm, $\omega_pR\gg c$ and the plasmon dispersion relation becomes linear: $\omega=ck$. After integration over k, remembering that $kR\ll1$ one obtains:

$$\tau\sim\ln^2(\hbar/ma^2\omega_p). \quad (14)$$

We see now a much slower dependence of the relaxation rate $1/\tau$ on the QD radius compared with the system QD – 2D plasma. It is worth to stress that exponential dependence in the Eq. (6) is not an asymptotical behavior for large distance H but it is the exact result and the exponent $a^*H\Omega^2/v_F^2$ can be of any magnitude. In the case of plasma cylinder the similar exponential behavior appears in the limiting case $kR\gg1$ (see Eq. (13)) while here the opposite limit is considered when McDonald function K_o has the logarithmic asymptotics. With the logarithmic accuracy the dependence (14) holds also for a wire of essentially smaller radius when the quasistatic limit $\omega_pR\ll c$ is achieved. Indeed, the dispersion law of the quasistatic 1D plasmon very weakly differs from the linear one: $\omega\sim k\sqrt{\ln2/kR}$ while in the opposite limit $\omega=ck$. But just linear law $\omega(k)$ leads to the relation (14). Such a drastic difference between the cases of 2D gas (quantum well) and 1D electron system (quantum wire) stems from the different dispersion laws of plasmons in these structures and different dimension of the phase space of the excited plasmons (2D and 1D).

In conclusion, the rate of radiationless relaxation of QD excitation in hybrid structures QD – quantum well and QD – quantum wire is found as a function of the QD radius.

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