Two-dimensional nonradiative plasmon-excitons, their pulse near-field excitation and relaxation

© *V.A. Kosobukin*

Ioffe Institute,
194021 St. Petersburg, Russia

E-mail: Vladimir.Kosobukin@mail.ioffe.ru

Received April 30, 2024
Revised June 26, 2024
Accepted October 30, 2023

A theory is presented for nonradiative plasmon-excitons propagating in atomically thin metal and semiconductor layers placed nearby. For the waves of dielectric polarization of two-dimensional plasmon-excitons, the equations of motion are derived in the form to be characteristic of damped coupled oscillators excited by an external dipole. The obtained dispersion relations and optical spectra reveal the presence of pronounced anticrossing effect in the range of plasmon-exciton resonance. The transient regimes in exciting 2D plasmon-excitons by a pulse of near field and in their relaxation are discussed in terms of forced and concomitant damped oscillations with the beats.

Keywords: plasmon-excitons, polarization waves, near-field optics, pulse excitation, relaxation.

DOI: 10.61011/SC.2024.10.59944.6474A

1. Introduction

Nanostructures with plasmon-exciton interactions possess a distinctive spectrum due to easy tuning the resonant states. Many papers were devoted to optical spectroscopy of radiative plasmon-excitons (PE) and the related polaritons [1]. However, the properties of nonradiative PE unexcitable by photons stay insufficiantly explored [2,3].

This paper develops a theory of two-dimensional (2D) coupled PE propagating in neighboring semiconductor and metal layers. Properties of 2D PE are investigated using the equations of motion derived for coupled harmonic oscillators from the material relatiopnships for the polarization fields of 2D plasmons and excitons with taking account of their Coulomb interaction. The 2D PE of our interest can not be excited by light waves, but those are excited by the near field of a subwavelength probe. In conformity with the near-field optics, this work investigates the processes of pulse excitation of 2D PE and their relaxation.

2. Model and statement of the problem

Consider the waves of dielectric polarization $\mathbf{P}^{(\nu)}$ for 2D plasmons ($\nu = 1$) and excitons ($\nu = 2$) coupled owing to Coulomb interaction. Dealing with the 2D Fourier transforms $\mathbf{P}^{(\nu)}(z, \boldsymbol{\kappa}, t)$ having wavevector $\boldsymbol{\kappa} = (\kappa_x, \kappa_y)$, we apply the classical equations of motion derived in [2,3] from the material relationships between 2D polarizations $\mathbf{P}^{(\nu)}(\boldsymbol{\kappa}, \omega)$ and electric field $\mathbf{E}(\boldsymbol{\kappa}, \omega)$. Given $\boldsymbol{\kappa} = \kappa \mathbf{e}_x$, the equations of motion dependent on time t are [3]

$$\left(\frac{d^2}{dt^2} + \Gamma_\nu \frac{d}{dt} + \omega_{\nu\nu}^2(\kappa)\right) P_\alpha^{(\nu)}(z, \kappa, t) = \Omega_\nu^2 l_\nu \, \delta(z - z_\nu) \sum_{\nu'(\neq\nu)} E_\alpha^{(\nu')}(z, \kappa, t), \quad (1)$$

$$E_\alpha^{(\nu')}(z, \kappa, t) = \sum_\beta \int g_{\alpha\beta}(z - z', \kappa) P_\beta^{(\nu')}(z', \kappa, t) dz'. \quad (2)$$

Here, $\omega_{\nu\nu}(\kappa)$ are the frequencies of 2D plasmons ($\nu = 1$) and excitons ($\nu = 2$), Γ_ν are the related decay rates, $\Gamma_\nu \ll \omega_{\nu\nu}$, l_ν is the effective width of polarization confinement region near the plane $z = z_\nu$, $l_\nu \ll 1/k_0 = c/\omega$, and c is the velocity of light. Electric field (2) induced by polarization $\mathbf{P}^{(\nu')}$ in an isotropic background medium is described by quasi-static ($c \to \infty$) tensorial Green's function with components $g_{\alpha\beta}(z, \kappa)$. Parameters Ω_ν define the efficiency of exciting 2D polarizations $\mathbf{P}^{(\nu)}$ by electric field.

In equations (1), expression $\nu'(\neq \nu)$ in sums means the absence of contribution with number ν' coinsiding the numder ν of equation. On the other hand, the sums include field (2) of external polarization $\mathbf{P}^{(\nu')}$ with $\nu' = 0$, which generates 2D PE with wavevector $|\boldsymbol{\kappa}| \gg k_0$. The polarization $\mathbf{P}^{(0)}(\mathbf{r}, t) = \boldsymbol{\mu} f(t) \delta(z - z_0) \Phi(\boldsymbol{\rho})$ is assumed to be related with the dipole moment $\boldsymbol{\mu} f(t)$, having distribution $\Phi(\boldsymbol{\rho})$ in a nanoarea of the plane $z = z_0$. Its Fourier transform

$$\mathbf{P}^{(0)}(z, \kappa, t) = \boldsymbol{\mu} f(t) \, \delta(z - z_0) \tilde{\Phi}(\kappa). \quad (3)$$

enter Eqs. (1) and (2). In them, $\tilde{\Phi} = 1$, if $\Phi = \delta(\boldsymbol{\rho})$ or $\tilde{\Phi} = 2J_1(\kappa R)/(\kappa R) \approx 1$, if $\Phi = 1/(\pi R^2)$ within a circle of radius $R \lesssim 1/\kappa$.

In the above model with background dielectric constant ε_b, Eqs. (1)−(3) consider further the longitudinal waves of polarization $\mathbf{P}^{(\nu)} \parallel \boldsymbol{\kappa}$ with $P_\alpha^{(\nu)} = \delta_{\alpha x} P^{(\nu)}(z, \kappa, t)$. The related induced field (2) is polarized in the xz-plane, and its components $E_x^{(\nu)}$, $E_z^{(\nu)}$ just as

$$g_{x\beta}(z, \kappa) = -(2\pi\kappa/\varepsilon_b) \exp(-\kappa|z|)[\delta_{\beta x} + i\delta_{\beta z} \, \mathrm{sgn}(z)],$$

are of the zeroth order of magnitude in $k_0/\kappa \ll 1$.

Substituting Eq. (2) into (1), we guess the solutions of integro-differential equations to have the form

$$P^{(\nu)}(z,\kappa,t) = w_\nu(\kappa,t) l_\nu\, \delta(z - z_\nu). \tag{4}$$

Here, $w_\nu(\kappa,t)$ is the required time-dependent polarization of plasmons ($\nu = 1$) or excitons ($\nu = 2$) making up 2D EP with wavenumber κ, being a parameter of the problem. After integration in Eq. (1) with taking into account Eq. (4) and the conditions $z_1 = 0$, $z_2 = h$, $|z_1 - z_2| = h \ll 1/k_0$, one gets the system of time-dependent differential equations

$$\left(\frac{d^2}{dt^2} + \Gamma_\nu \frac{d}{dt} + \omega_{\nu\nu}^2\right) w_\nu(\kappa,t) + \omega_{\nu\nu'}^2\, w_{\nu'}(\kappa,t) = C_\nu\, f(t), \tag{5}$$

$\nu' \neq \nu$ in ν-th equation. Eqs. (5) describe the forced oscillations of coupled harmonic oscillators whose role is played by the waves of 2D polarization (4) with $\nu = 1, 2$. Entering the left-hand-side of Eqs. (5) is the frequency matrix with elements

$$\left.\begin{aligned} \omega_{11}^2(\kappa) &= 2\pi e^2 n_{2D}\kappa/(m\varepsilon_b) \equiv \omega_{2D}^2(\kappa), \\ \omega_{12}^2(\kappa) &= \omega_{2D}^2 (l_2/l_1) \exp(-\kappa h), \\ \omega_{21}^2(\kappa) &= \Omega^2 (2\pi/\varepsilon_b)\kappa l_1 \exp(-\kappa h), \\ \omega_{22}^2(\kappa) &= \omega_0^2 + \Omega^2(2\pi/\varepsilon_b)\kappa l_2, \end{aligned}\right\} \tag{6}$$

where $\Omega = \Omega_2$. In the right-hand-side of Eqs. (5), function $f(t)$ from (3) stands with coefficients

$$\left.\begin{aligned} C_1(\kappa) &= -\omega_{2D}^2 l_1^{-1} \exp(-\kappa|z_0|)[\mu_x - i\mu_z\,\mathrm{sgn}(z_0)]\tilde{\Phi}, \\ C_2(\kappa) &= -\Omega^2(2\pi\kappa/\varepsilon_b)\exp(-\kappa|z_0 - h|) \\ &\quad \times [\mu_x - i\mu_z\,\mathrm{sgn}(z_0 - h)]\tilde{\Phi}. \end{aligned}\right\} \tag{7}$$

These coefficients define the efficiencies of near-field excitation of 2D plasmons and excitons by the dipole $\boldsymbol{\mu}$ from Eq. (3) whose components lye in the xz-plane.

In Eqs. (1) and (5), the diagonal matrix elements $\omega_{11}(\kappa)$ and $\omega_{22}(\kappa)$ given by (6) express the dispersion relations of 2D plasmons and excitons, respectively. The κ-dependent contribution to $\omega_{\nu\nu}$ is due to proper electric field (2) induced by polarization $P^{(\nu)}$. Thus, the dispersion relation $\omega_{11}(\kappa) = \omega_{2D}(\kappa)$ of 2D plasmons is conditioned by the collective field of electrons having 2D density n_{2D}, effective mass m and charge e. Another term ω_{22} contains a small κ-dependent Coulomb correction $\sim (\Omega/\omega_0)^2 \ll 1$ in addition to frequency ω_0 of exciton (bound electron-hole pair). Parameter Ω is expressed through the interband dipole matrix element for the Wannier excitons [3], and through the oscillator strength of molecular transition for the Frenkel excitons.

The non-diagonal elements ω_{12} and ω_{21} from (6) express, respectively, the efficiency of plasmonic polarization excitation by the electric field of exciton and vice versa. The asymmetry $\omega_{12} \neq \omega_{21}$ reveals the difference between the two mutual effects. To add, in the region of κ near PE resonance the elements $\omega_{\nu\nu'}$ slightly depend on κ [3].

3. Solution of the problem and discussion

The problem of excitation and relaxation of 2D PE is solved using the Laplace transform [4]

$$W_\nu(p) = \int_0^\infty w_\nu(t) e^{-pt} dt, \tag{8}$$

which gives the image function $W_\nu(p)$ of complex variable p for a function $w_\nu(t)$ given for $t > 0$. Transform (8) of Eqs. (5) with initial conditions $w_\nu(0) = w'_\nu(0) = 0$ results in the system of algebraic equations for $W_\nu(p)$ of form (5) with the formal replacements $d/dt \to p$, $w_\nu(t) \to W_\nu(p)$ and $f(t) \to F(p)$.

Suppose that 2D PE are excited by the rectangular pulse

$$f(t) = \sin(\omega t)\{\vartheta(t) - \vartheta(t - \tau)\} \tag{9}$$

of duration $\tau = \pi m/\omega$ (m is an integer); the unit function equals $\vartheta(t) = 0$ for $t < 0$ and $\vartheta(t) = 1$ for $t > 0$. Then, the system of equations obtained from Eq. (5) using transform (8) has the solution

$$\begin{pmatrix} W_1(p) \\ W_2(p) \end{pmatrix} = \frac{\omega[1 - (-1)^m \exp(-p\tau)]}{(p^2 + \omega^2)D(p)} \times \begin{pmatrix} p^2 + p\Gamma_2 + \omega_{22}^2 & -\omega_{12}^2 \\ -\omega_{21}^2 & p^2 + p\Gamma_1 + \omega_{11}^2 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}, \tag{10}$$

$$D(p) = (p^2 + p\Gamma_1 + \omega_{11}^2)(p^2 + p\Gamma_2 + \omega_{22}^2) - \omega_{12}^2\omega_{21}^2. \tag{11}$$

If $\omega_{12}\omega_{21} = 0$, 2D plasmons and excitons are uncoupled; their dispersion relations $\omega_{\nu\nu}(\kappa)$ at $\Gamma_\nu = 0$ are shown by curves I and II in Figure 1,*a*. If $\omega_{12}\omega_{21} \neq 0$, appearance of mixed 2D PE becomes possible under condition $\omega_{11}(\kappa) = \omega_{22}(\kappa)$, which is satisfied at the intersection point of curves I and II. Also, presented in Figures 1,*a* and *b* are the dispersion relations $u_j(\kappa)$ and decay rates $g_j(\kappa)$ of 2D plasmon-excitons with numbers $j = 1, 2$. Figure 1,*a* demonstrates the effect of anticrossing („repulsion" of frequencies), so that $u_1 < \omega_{11}$, $\omega_{22} < u_2$.

Hereafter, used are the numerical parameters estimated for pair Ag/CdTe [3]. For 2D plasmons $n_{2D} = 15\,\mathrm{nm}^{-2}$, $\hbar\Gamma_1 = 20\,\mathrm{meV}$, $l_1 = 0.7\,\mathrm{nm}$, $\hbar\Omega_1 = 2.7\,\mathrm{eV}$ are taken, and for 2D excitons — $\hbar\omega_0 = 1.6\,\mathrm{eV}$, $\hbar\Gamma_2 = 0.3\,\mathrm{meV}$, $l_2 = 2\,\mathrm{nm} = h$, $\hbar\Omega_2 = 200\,\mathrm{meV}$, $\varepsilon_b = 10$.

Inverse Laplace transform of functions $W_\nu(p)$ from Eq. (10) using the residue method [4] gives for solutions of Eqs. (5) the following formula ($t > 0$):

$$w_\nu(t) = 2\,\mathrm{Re}\sum_{p_j} \exp(p_j t)\big[(p - p_j)W_\nu(p)\big]_{p=p_j} = \sum_{j=0,1,2} w_\nu^{(j)}(t). \tag{12}$$

Here, summation is performed over $p_j = -iu_j - g_j$ with $j = 0, 1, 2$ for three pairs (p_j, p_j^*) of complex conjugated poles of functions (10). In case of pulse (9), it follows from (10)–(12) that

$$w_\nu(t) = \vartheta(t) \sum_{j=0,1,2} w_\nu^{(j)}(t) - (-1)^m \vartheta(t-\tau) \times \sum_{j=0,1,2} w_\nu^{(j)}(t-\tau), \quad (13)$$

where $w_\nu^{(j)}(t)$ denote the functions with $j = 0, 1, 2$ calculated from (12) at $\tau \to \infty$.

For $p_{j=0} = -i\omega - 0$ and $\tau \to \infty$, Eq. (12) gives ν-contributions into (13) of the form

$$w_\nu^{(0)}(t) = |Q_\nu(-i\omega)| \sin\{\omega t - \arg Q_\nu(-i\omega)\}. \quad (14)$$

Here, $Q_\nu(-i\omega) = S_0(\omega) \sum_{\nu'} M_{\nu\nu'}(-i\omega) C_{\nu'}$, $S_0(\omega) = 1/(\Delta_1\Delta_2)$, $\Delta_j(\omega) = u_j^2 - \omega^2 - 2i\omega g_j$ $(j = 1, 2)$ with $u_j(\kappa)$ and $g_j(\kappa)$ presented in Figures 1, *a* and *b*, and $M_{\nu\nu'}(p)$ are the elements of 2×2 matrix from Eq. (10). Formula (14) describes the contribution of ν-type polarization to the forced oscillation of 2D PE with the exciting frequency ω. Depending on ω, these oscillations are resonantly enhanced near the frequencies $u_j(\kappa)$ of both 2D PE, as is shown in Figures 2, *a* and *b* by curves *1* for spectral function $S_0(\omega)$ entering $Q_\nu(-i\omega)$.

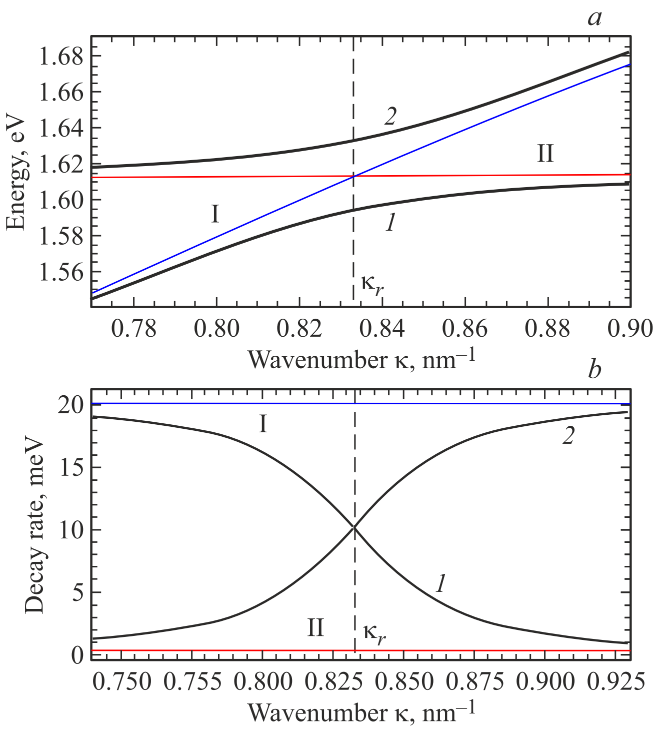

Figure 1. (*a*) Dispersion relations $\hbar\omega_{11}$ of 2D plasmons (I), $\hbar\omega_{22}$ of 2D excitons (II) and $\hbar u_1$ (*1*), $\hbar u_2$ (*2*) of 2D plasmon-excitons at $\Gamma_1 = \Gamma_2 = 0$. (*b*) Decay rates $2\hbar g_1$ (*1*) and $2\hbar g_2$ (*2*) of 2D PE at $\hbar\Gamma_1 = 20$ meV (I) and $\hbar\Gamma_2 = 0.3$ meV (II). Parameters of calculation are given in the text.

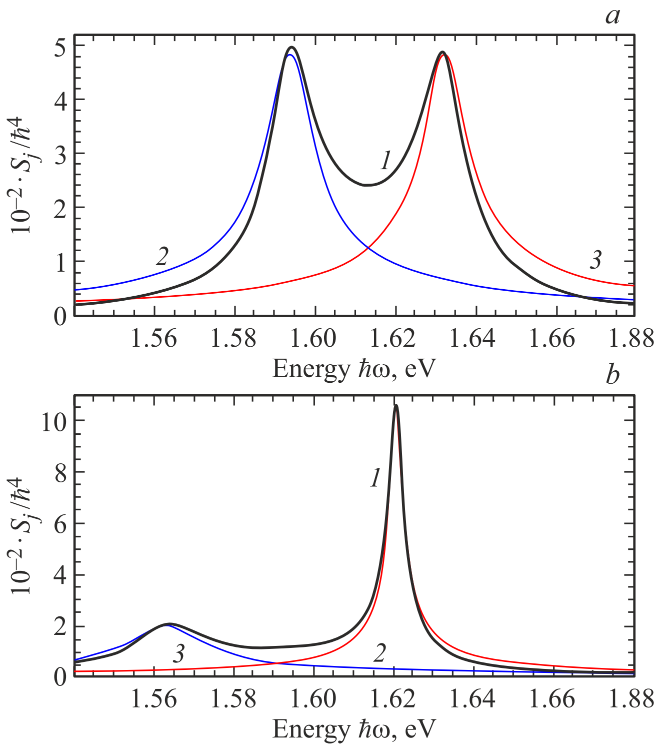

Figure 2. Spectral functions $10^{-2} \cdot S_j/\hbar^4$ with $j = 0$ (*1*) from (14), with $j = 1$ (*2*) and $j = 2$ (*3*) from (15) for 2D PE with wavenumbers (*a*) $\kappa_r = 0.832\,\text{nm}^{-1}$ (at $\omega_{11} = \omega_{22}$) and (*b*) $\kappa = 0.79\,\text{nm}^{-1}$. Calculated with the same parameters as in Figure 1.

For $p_j = -iu_j - g_j$ with $j = 1, 2$, the contributions in (13) at $\tau \to \infty$ are expressed by formulas

$$w_\nu^{(j)}(t) = (-1)^j \exp(-g_j t) |S_j(\omega)| \times \sum_{\nu'} |M_{\nu\nu'}(p_j)|\, |C_{\nu'}| \sin(u_j t - \alpha_{\nu\nu'}^{(j)}). \quad (15)$$

Here, $S_j(\omega) = \omega/(u_j \Theta_j \tilde{\Delta}_j)$ with $\tilde{\Delta}_j(\omega) = u_j^2 - \omega^2 - 2iu_j g_j$, $\Theta_j = u_2^2 - u_1^2 - 2iu_j(g_2 - g_1)$, $M_{\nu\nu'}(p_j)$ are the elements of 2×2 matrix entering Eq. (10), and $\alpha_{\nu\nu'}^{(j)} = \arg\big(S_j(\omega) \times M_{\nu\nu'}(p_j) C_{\nu'}\big)$.

Given κ, it follows from Eqs. (14) and (15) that the polarization $w_\nu = \Sigma w_\nu^{(j)}$, induced by a dipole from Eqs. (3), (9), consists of three contributions: forced $w_\nu^{(0)}$ oscillation with exciting frequency ω and two $(j = 1, 2)$ concomitant $w_\nu^{(j)}$ oscillations with frequencies $u_j(\kappa)$ of 2D PE. The latter oscillations decay for times $\sim 1/g_j$, therefore, the transient processes under pulse excitation of 2D PE have duration $\sim \max(1/g_j)$. Substituting Eqs. (14) and (15) written as $w(t) = A \sin(\varpi t - \alpha)$ into formula $p(x, t) = \text{Re}[\exp(i\kappa x) w(t)]$, one finds two waves of polarization $p_\mp(x, t) = A \sin(\varpi t \mp \kappa x - \alpha)/2$, running in opposite directions of the x-axis.

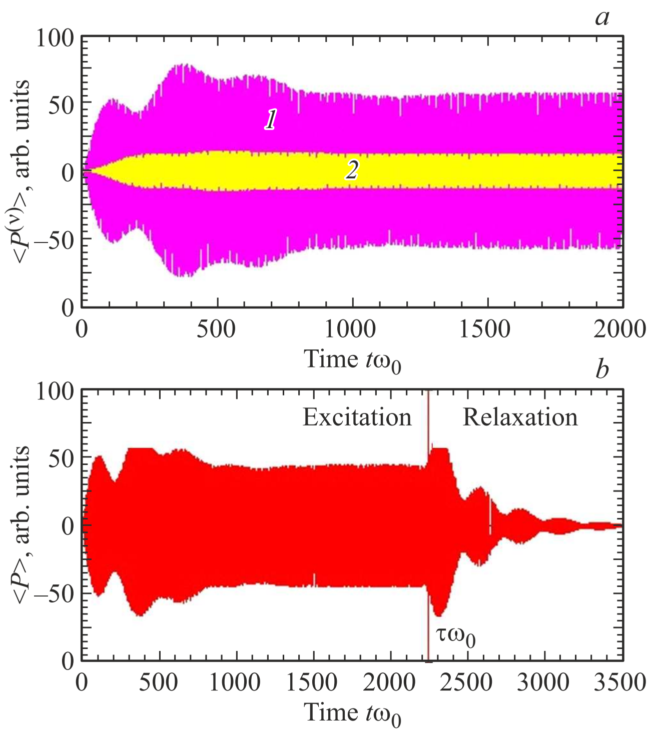

Figure 3. Dependences on time $\omega_0 t$ of 2D PE polarization: (a) $\langle P^{(\nu)}\rangle$ from (16) and (b) $\langle P\rangle$ from (17) excited at $t = 0$ by pulse (9) with duration $\tau = 700\pi/\omega$. Calculated at exciting frequency $\omega = u_{\text{II}}(\kappa_r)$, $\kappa_r = 0.832\,\text{nm}^{-1}$, and presented in arbitrary units normalized by $\mu_x\tilde{\Phi}$ at $\mu_z = 0$ in Eq. (3).

Integrating expressions (4) over z, introduce the functions

$$\langle P^{(\nu)}(\kappa, t)\rangle = \sum_{j=0,1,2} \int P_j^{(\nu)}(z, \kappa, t)dz = l_\nu \sum_j w_\nu^{(j)}(\kappa, t). \tag{16}$$

At $t = 0$ one has $w_\nu^{(j)}(\kappa, 0) \neq 0$ at all j, but the necessary initial zero condition is satisfied by superposed polarization (16), i.e. $\langle P^{(\nu)}(\kappa, 0)\rangle = 0$ [2,3]. This result is clearly seen from Figure 3,a, showing the dependencies of $\langle P^{(\nu)}(\kappa, t)\rangle$ on t in exciting by dipole $\boldsymbol{\mu} = \mu\mathbf{e}_x$ from (3). For the two types of polarization with $\nu = 1, 2$ these dependencies are similar: at first $\langle P^{(\nu)}\rangle$ grows from zero, nonmonotonously because of beats, and at $t > 1/g_j$ ($j = 1, 2$) it passes to the regime of forced steady oscillations $\langle P_{j=0}^{(\nu)}\rangle = l_\nu w_\nu^{(0)}$.

Finally, let us discuss a process which includes excitation of 2D PE by pulse (9) and subsequent relaxation after $t > \tau$. Figure 3,b shows the time dependence of superposition

$$\langle P(\kappa, t)\rangle = \sum_\nu \langle P^{(\nu)}(\kappa, t)\rangle = w_1(\kappa, t)l_1 + w_2(\kappa, t)l_2 \tag{17}$$

under the same conditions as for $\langle P^{(\nu)}\rangle$ in Figure 3,a and at $\tau = 700\pi/\omega$. For $0 < t < \tau$ oscillations (17) have the same features as $\langle P^{(\nu)}\rangle$ in Figure 3,a. In relaxation process ($t > \tau$) the forced oscillations $w_\nu^{(0)}$ disappear in accordance with (13), and decay of polarization is realized by transient oscillations $w_\nu^{(j)}$ with $j = 1, 2$. As well, seen in Figures 3,a and b are the beats related to energy transfer between 2D PE components complicated by weak dissipative losses. To note, the beats in inital and final transient processes predicted in two-oscillator model do not appear in one-oscillator model [3].

4. Conclusions

This paper presents the theoretical study of two fundamental aspects for mixed-state 2D plasmons and excitons. One concerns the properties of nonradiative coupled 2D PE as such, independently of the way of their excitation. Another aspect is near-field optical excitation of 2D PE by pulses of any duration and relaxation of them. For the model of coupled harmonic oscillations, it is shown that 2D PE excited under action of external oscillating dipole include a forced and two damped oscillations. Predicted are a considerable anticrossing effect and the presence of beats in transient processes conditioned by Coulomb interactions between components of 2D PE. Appearance of the polarization beats in the two-oscillator model of plasmon-excitons proves the existence of energy transfer between the components of mixed-state 2D PE having close frequencies.

Conflict of interest

The author declares that he has no conflict of interest.

References

[1] M. Sukharev, A. Nitzan. J. Phys. Condens. Matter **29**, 443003 (2017). doi: 10.1088/1361-648X/aa85ef.
[2] V.A. Kosobukin. Solid State Communs. **342**, 114638 (2022). doi: 10.1016/j.ssc.2021.114638.
[3] V.A. Kosobukin. Physica B: Condensed Matter **674**, 415541 (2024). doi.org/10.1016/j.physb.2023.415541.
[4] M.A. Lavrent'ev, B.V. Shabat, Methods of Complex Variable Theory, Nauka, Moscow, 1987.