Metallic nanofilms optical response description based on self-consistent theory

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Abstract. In this paper an interaction of ultrathin (~1 nm) metal film (called metal nanofilm) with external optical radiation theoretically considered. It’s shown that metal nanofilms have a substantially nonlocal optical properties. A frequency, angular and polarization dependencies of optical response considered.

1. Introduction

Recently a self-consistent microscopic theory of metal nanofilms optical response have been developed [1-2] in case of unbacked ultrathin (~1 nm) metal film interacting with external plane 2D electromagnetic wave. Consideration was carried out in formalism of density functional theory in time-dependent local density approximation. A jellium model for ions was used. Both of longitudinal and transverse electromagnetic field components have been taken into account in calculations. It was shown that optical response of metal nanofilms have substantially nonlocal character.

But constructed theory doesn’t allow to obtain an explicit expressions coupling an optical response (field distribution and angular and frequency dependence of absorption coefficient) with both of non-excited potential parameters (quantum well characteristics) and external field parameters (frequency and incidence angle) because there are no analytical expressions for non-excited wave functions in this theory. So, in this theory a basic formulas and equations can be analytically obtained but matrix elements contained in these expressions can be calculated only numerically.

In this paper a non-excited wave functions calculated analytically in case of rectangle quantum well: it’s assumed that full potential (including exchange-correlation part) can be approximated by such form. It allows to calculate an explicit expressions for field spatial distribution and absorption, transmission and reflection coefficients. Also a generalization of self-consistent theory on case of 3D incident wave and some of its consequencies considered.

2. Self-consistent microscopic theory for optical response

The electron motion in ultrathin metal film can be described by the following Schrödinger-type equation (called as basic equation below):

\[ i\hbar \frac{\partial \Psi_n}{\partial t} = \frac{-\hbar^2}{2m} \Delta \Psi_n + e\phi \Psi_n + \nabla \Psi_n + \frac{i\hbar e}{2mc} (\nabla \tilde{A} + \tilde{A} \nabla) \Psi_n + \frac{e^2}{2mc^2} \tilde{A}^2 \Psi_n, \]

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where $\phi$ and $\tilde{A}$ are the field potentials, $V$ is the exchange-correlation potential, $\Psi_n$ is the $n$-th electron wave function. In the steady-state case this equation transforms to Kohn-Sham equation [3]. For solution of this equation a perturbation theory used (in assumption that external field much smaller than internal film field). Wave function written as

$$\Psi_n = \Psi_{0n} + \Psi_{1n} + \Psi_{2n} + ..., \quad \text{where } \Psi_{0n} \text{ is the wave function without external field, and } \Psi_{1n} \text{ and } \Psi_{2n} \text{ is the excited wave functions.}$$

The coefficients at field harmonics can be expressed in terms of Kohn-Sham eigenfunctions $\Phi_k$ ($c^\pm_{mn} = \sum_{m} c^\pm_{p,nm} \Phi_m$) with the help of the recurrence procedure applied to basic equation.

The field potentials and exchange-correlation potential were represented analogously. It’s assumed that the electron is initially in the ground state. The discrete-discrete transitions are only taken into account. The probability of electron transitions from discrete to continuous spectrum assumed to be negligible. For induced exchange-correlation potentials time-dependent (adiabatic) local density approximation used.

Obtained from basic equation wave functions allow to calculate current and charge densities:

$$\rho = e \sum_n |\Psi_n|^2,$$

$$\bar{J} = -\frac{e}{mc} \tilde{A} \rho + \frac{ihe}{2m} \sum_n (\Psi_n \nabla \Psi_n^* - \Psi_n^* \nabla \Psi_n),$$

which also expands into perturbation series similarly to expansion of potentials. In these formulas summation is implied over all of quantum well states and $\tilde{k}_i$. A degenerate electron gas approximation is used in zero-temperature limit. Charge and current density distributions include local and nonlocal electron subsystem response. Local part is defined by first item and depends on field at the same point. Nonlocal part is caused by quantum well transitions and depends on field distribution inside the film.

Obtained expressions for current and charge densities used then in wave equations:

$$\frac{d^2 A_{ki}}{dz^2} + 2^{(k-1)} \left( \frac{\omega^2}{c^2} - \tilde{q}_i^2 \right) A_{ki} = -\frac{4\pi}{c} J_{ki} + \frac{2^{k-1} \pi}{\omega^2} (k\omega + i\gamma) \tilde{q}_i \rho_k,$$

$$\frac{d^2 A_{kc}}{dz^2} + 2^{(k-1)} \left( \frac{\omega^2}{c^2} - \tilde{q}_c^2 \right) A_{kc} = -\frac{4\pi}{c} J_{kc} + \frac{4\pi}{\omega^2} (\gamma - k\omega) \frac{d\rho_k}{dz}, \quad k = 1, 2.$$

Here $\omega$ is an incident wave frequency and $\tilde{q}_i$ is a tangential component of wave vector; $\gamma \equiv \gamma_{nm}$ is a transverse relaxation rate, which doesn’t depend on initial and final eigenstates; $z$ is the normal coordinate. For scalar potential the following gauge condition is used:

$$\phi - \phi_0 = 0.$$

Wave equations solution can be obtained through Green’s functions method using [1-2].

### 3. Optical properties of metal nanofilms

An obvious analytic expressions for field vector potential, exchange-correlation potential and for electron and current densities shown that optical response of ultrathin metal film have substantially nonlocal character and defines not only by quantum well interlevel transitions but also by collective electron excitations.

Obtained formulas demonstrate a polarizaion dependence for optical response. One of interesting effect in this case is a second harmonic generation. It can be shown that in case of s-polarized 2D (i.e. $q_x = 0$) incident laser beam an s-polarized response at second harmonic of incident frequency absent [2]. It caused by electron density and exchange-correlation potential excitations absence at this frequency. So, an optical response in this case can be selected by polarization: s-polarized response contains only fundamental frequency and p-polarized response contains only doubled one. Another
situation take place in case of 3D laser beam. It can be shown that in this case a second harmonic response include both of s- and p-polarized components. And in this case both of electron density and exchange-correlation potential excitations at fundamental frequency present in system. Analogously, it can be shown by direct analytical calculation that in case of p-polarized 2D incident laser beam only p-polarized response obtained at both of fundamental and doubled frequencies [2]. In case of 3D incident laser beam an s-polarized component at doubled frequency appeared in optical response.

4. Matrix elements calculation
All of expressions obtained in this work contain a matrix elements of any variables by Kohn-Sham eigenfunctions $\Phi_n$. These functions cannot be calculated analytically. So, an obvious dependencies for vector potential, electron density etc. which couple these values with quantum well parameters and incident wave parameters (frequency and incidence angle) cannot be obtained. But these matrix elements can be calculated analytically in case of eigenfunctions approximation by any analytical expression caused by potential approximation by corresponding formula. Below a results shown obtained in case of potential approximation by rectangle quantum well.

The wave function of n-th level for rectangle potential can be expressed by follow formula:

$$\Phi_n(z) = \begin{cases} A_n^- \exp(\kappa_n (L/2 + z)), & z < -L/2, \\ A_n^0 \cos\left(\frac{\pi}{2} \delta_{(n (mod 2))} - k_n z\right), & -L/2 \leq z \leq L/2, \\ A_n^+ \exp(\kappa_n (L/2 - z)), & z > L/2, \end{cases}$$

where $A_n^- = A_n^+ = A_n^0 \cos\left(\frac{\pi}{2} \delta_{(n (mod 2))} - \frac{k_n L}{2}\right)$ (levels numbered from 0). So, a Green’s functions and it’s matrix elements can be calculated using this formula.

Obtained in considered calculations expressions are very intricate and become complicated by number of quantum well levels increasing. So, only two-level quantum well with one (ground, even) level under and one (excited, odd) level upper Fermi level considered below. (Although all of formulas can be obtained for case of any number of levels.) Analogously, only s-polarization incident field considered.

For Green’s function a follow expression [1-2] using:

$$G_{nm}(z) = \frac{1}{w} \left( e^{i\theta_0} \int_{-\infty}^{\infty} dz' e^{-i\theta_0 z'} + e^{-i\theta_0} \int_{-\infty}^{\infty} dz' e^{i\theta_0 z'} \right) \Phi_n(z') \Phi_m^*(z'),$$

where $w = 2iq_{z0}$, $q_{z0} = \frac{\hbar}{\epsilon} \cos \theta$, $\theta$ - incidence angle (between wave vector and z-axis which normal to film plane).

Green’s function matrix elements can be written as:

$$[G_{nm}]_{kl} = \frac{P_{1,\text{nmkl}}(q_{z0}) - ie^{i\theta_0 L/2} \left( P_{1,\text{nmkl}}^2(q_{z0}) \cos q_{z0}L + P_{1,\text{nmkl}}^3(q_{z0}) \sin q_{z0}L \right)}{q_{z0}(\kappa_k + i\kappa_l - iq_{z0}) \left( (\kappa_k + \kappa_l)^2 + q_{z0}^2 \right)(k_k + k_l)^2 - q_{z0}^2(k_k^2 - k_l^2)^2 - q_{z0}^2 \left( (k_k + k_l)^2-q_{z0}^2 \right) \left( (k_k - k_l)^2-q_{z0}^2 \right)}$$

$$\equiv \frac{P_{1,\text{nmkl}}(q_{z0}) - \left( P_{1,\text{nmkl}}^2(q_{z0}) \cos q_{z0}L + P_{1,\text{nmkl}}^3(q_{z0}) \sin q_{z0}L \right)}{q_{z0}(\kappa_k + i\kappa_l - iq_{z0}) \left( (\kappa_k + \kappa_l)^2 + q_{z0}^2 \right)(k_k + k_l)^2 - q_{z0}^2(k_k^2 - k_l^2)^2 - q_{z0}^2 \left( (k_k + k_l)^2-q_{z0}^2 \right) \left( (k_k - k_l)^2-q_{z0}^2 \right)},$$

where $P_{M,\text{nmkl}}(q_{z0})$ - polynomial functions of $q_{z0}$ ($M$ - degree of polynomial) numbered by index $s$. Coefficients of these polynomials contain a quantum well parameters and can be expressed analytically. For Green’s function in case of second harmonic [2] an analogical expression can be written with replacement of $q_{z0}$ by $2q_{z0}$. 


Based on this expression a field spatial distribution can be written in the following form:

\[
A_{1x}(z) = A_0 e^{iq_{z0}z} + A_0 \frac{\left[ e^{iq_{z0}z} \right]_1 [G_{12}]_{12} - \left[ e^{iq_{z0}z} \right]_2 [G_{12}]_{11} + [G_{11}]_1 - \left[ e^{iq_{z0}z} \right]_1 [G_{11}]_{12} G_{12}(z)}{[G_{11}]_1 [G_{12}]_{12} - [G_{12}]_{11} [G_{11}]_{12}} \equiv A_0 \left( e^{iq_{z0}z} + \alpha(q_{z0}) G_{11}(z) + \beta(q_{z0}) G_{12}(z) \right),
\]

where \( A_0 \) - incident field amplitude. Coefficients \( \alpha \) and \( \beta \) can be expressed as follows:

\[
\alpha = \frac{2q_{z0}^2(2\kappa_0 - i\gamma_{q_{z0}})\left( 4\kappa_0^2 - q_{z0}^2 \right) \left( \Pi_0'(q_{z0}) \cos \frac{q_{z0}L}{2} + \Pi_1'(q_{z0}) \sin \frac{q_{z0}L}{2} - i e^{i\theta_{q_{z0}}/2} \left( \Pi_1'(q_{z0}) \cos q_{z0}L + \Pi_1'(q_{z0}) \sin q_{z0}L \right) \right)}{\Pi_0'(q_{z0}) + \Pi_1'(q_{z0}) \cos q_{z0}L + \Pi_1'(q_{z0}) \sin q_{z0}L + \Pi_1'(q_{z0}) \cos q_{z0}L + \Pi_1'(q_{z0}) \sin q_{z0}L \sin 2q_{z0}L},
\]

\[
\beta = \frac{2q_{z0}^2(4\kappa_0^2 - q_{z0}^2)\left( 4\kappa_0^2 - q_{z0}^2 \right) \left( \Pi_0'(q_{z0}) \cos \frac{q_{z0}L}{2} + \Pi_1'(q_{z0}) \sin \frac{q_{z0}L}{2} - i e^{i\theta_{q_{z0}}/2} \left( \Pi_1'(q_{z0}) \cos q_{z0}L + \Pi_1'(q_{z0}) \sin q_{z0}L \right) \right)}{2(\kappa_0 + i\gamma_{q_{z0}})\left( \Pi_0'(q_{z0}) + \Pi_1'(q_{z0}) \cos q_{z0}L + \Pi_1'(q_{z0}) \sin q_{z0}L + \Pi_1'(q_{z0}) \cos q_{z0}L + \Pi_1'(q_{z0}) \sin 2q_{z0}L \right)}.
\]

Functions \( \Pi_j'(q_{z0}) \) are polynomial functions which expressed through polynomial functions \( P_{M,\text{pol}}(q_{z0}) \). In case of \( \theta = \pi/2 \) corresponding to wave propagation parallel to film plane coefficients \( \alpha \) and \( \beta \) vanish. It’s clear from formulas obtained that field distribution can be represented as a decimal with numerator and denominator both represented as a superposition of functions \( \cos n q_{z0}L \) and \( \sin n q_{z0}L \) \( (n = 0,1,2) \). Coefficients at these functions are a polynomial of \( \gamma_{q_{z0}} \) with, in general, complex coefficients.

Based on field spatial distribution an absorption, transmission and reflection coefficients can be calculated by corresponding formulas. An obvious expressions based on these formulas for corresponding coefficients obtained but it very large and cannot be written here. These expressions show that coefficients demonstrate a significantly non-monotonic frequency and angular dependencies.

5. Conclusion

Thus, in this paper a self-consistent theory for metal nanofilms optical response considered. It’s shown that metal nanofilms optical response have a substantially nonlocal character and non-monotonic frequency and angular dependence. A two polarizations of incident wave discussed and optical response properties analyzed for them. An approach considered which allows to construct an obvious analytical expressions for field spatial distribution through quantum well and incident field parameters.

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References

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