Excitation and Light Emission of Localized Plasmons for Metal Nanostructures in Dielectrics by Electron Beam

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Equations on excitation and light emission of the localized bulk and surface plasmons for metal nanostructures in dielectrics by electron beam are derived using the localized plasmon theory in the random phase approximation at high frequency condition. These are applied to calculate inelastic scattering probabilities of electron beams and light emission intensities by the localized plasmon excitations for metal nanospheres and ultrathin films in dielectrics using the quasi-static and electric dipole approximations. It is also assumed that local dielectric functions for metals and dielectrics have step function shapes at the metal and dielectric interfaces. It is found that the electron beams are inelastically scattered by the localized surface and bulk plasmons with various excitation modes, but the light is emitted only from the localized surface plasmons with specific excitation modes within these approximations.

Keywords: Surface plasmon; Bulk plasmon; Light emission; Inelastic scattering; Electron beam

I. INTRODUCTION

The collective excitation of electrons in solid called plasmon has been theoretically proposed by Bohm and Pines (B. P.) [1, 2], which has been experimentally confirmed using transmission electron microscopy (TEM) [3]. Ferrell has theoretically investigated the plasmon and electron beam interaction using the B. P. theory [4]. Ritchie [5] has further shown that the collective excitation localized at thin film surfaces called surface plasmon can be excited by using the hydrodynamic method for conduction electrons. Stern and Ferrell [6] have then indicated that the surface plasmon can be also excited in the films covered with dielectrics, which has also been experimentally confirmed [7].

With the development of surface science, the interactions between low-energy electron diffraction (LEED) beam and the bulk and surface plasmons have been intensively investigated in the 1970s. Duke et al. [8–10] have investigated the interactions between the LEED beam and bulk and surface plasmons using quantum field theoretical methods. The author [11, 12] has also investigated the interactions using the distorted wave method for the LEED beam and the random phase approximation (RPA) for the plasmons in conduction electrons. These studies have indicated that the coupling between the bulk and surface plasmons plays important roles in determining the relative inelastic intensities and scattering angle dependences of the LEED beams between the bulk and surface plasmon excitations.

Moreover, with the development of the plasmonics [13, 14], the studies on the interactions between the plasmons and focused electron beams have been noticed again because they make it possible to perform microscopic studies on the plasmon excitations using TEM. García de Abajo et al. have reported detailed studies on the energy loss of focused electron beams and the light emission induced by plasmon excitations in nanostructures [15–17]. Several studies have been also performed for the quantum [18, 19] and non-local [20, 21] effects on the energy losses of focused electron beams by the
localized plasmon excitations in metal nanoparticles. Raza et al. have recently reported detailed studies on the energy losses of focused electron beams by localized plasmon excitations for metal nanoparticles in dielectrics [22].

Up to now the author has developed several theories on the localized plasmons in metal nanostructures and dielectrics, which are given respectively by

\[ \rho(r_1, \omega) = \nabla_1 \cdots \chi_0(r_1, \omega) E(r_1, \omega), \]

where \( G_0(r - r_1, \omega) \) is the retarded Green’s function of the Helmholtz equation in frequency \( \omega \) expression and \( \rho(r_1, \omega) \) is the induced charge density in metal nanostructures and dielectrics, which are given respectively by

\[ G_0(r - r_1, \omega) = \frac{\exp\left(i \frac{\omega}{c} |r - r_1| \right)}{|r - r_1|}, \]

and

\[ \rho(r_1, \omega) = \nabla_1 \cdots \chi_0(r_1, \omega) E(r_1, \omega), \]

where \( \chi_0 \) is the electric field in the Lorentz gauge where \( A_{0}(r_1, \omega) \) is the effective vector potential, \( c \) is the velocity of light, \( m_e \) and \( -e \) are the electron mass and charge, \( \nabla_1 \) represents the gradient with respect to \( r_1 \), and \( \chi_0(r_1, \omega) \) is the electric susceptibility of the dielectrics with the local position dependence and uniformity or cubic symmetry, which can be expressed by the position-dependent scalar. The Gaussian units are used in this article. \( n(r_1) \) is the local electron density in metal nanostructures, which is given by

\[ n(r_1) = 2 \sum_{n} |\Psi_n(r_1)|^2 \theta(E_F - E_n), \]

where \( \Psi_n(r_1) \) is the normalized single-electron wave function with energy \( E_n \) in metal nanostructures, \( E_F \) is the Fermi energy, and \( \theta(E_F - E_n) \) is the step function.

\( \Gamma \) in Eq. (3) is the plasmon decay frequency caused by the finite lifetime of the single electron in the metal nanostructures. To consider the plasmon decay correctly without the violation of the detailed balance condition of the electrons in the metal nanostructures, \( \omega^2 \) in the induced charge density should be replaced by \( \omega(\omega + i\Gamma) \) as indicated in the previous studies [24, 30, 31]. The plasmon decay depends on the nanostructure size and electronic state of the electrons in the nanostructures [32]. Here, the decay frequency is considered to be a phenomenological parameter to explain the experimental results, which corresponds to using the position dependent Drude dielectric function with the finite lifetime of the single electron. It is known that this method can explain experimental results in good approximation [13, 14].

By the charge conservation law \( i\omega \rho(r_1, \omega) = \nabla_1 \cdot j(r_1, \omega) \), the induced current density is given using Eq. (3) by

\[ j(r_1, \omega) = i\omega \left[ \frac{e^2 n(r_1)}{m_e \omega (\omega + i\Gamma)} - \chi_0(r_1, \omega) \right] E(r_1, \omega). \]

Then, the following integral equation for the effective vector potential is derived:

\[ A_{0}(r, \omega) = A_{ext}(r, \omega) + \frac{1}{c} \int dr_1 G_0(r - r_1, \omega) j(r_1, \omega). \]

II. LIGHT EMISSION AND INELASTIC SCATTERING BY LOCALIZED PLASMONS
A. Equations for scalar and vector potentials

Our previous studies [28, 29] have shown that the following integral equation for the effective scalar potential \( \varphi_{ext}(r, \omega) \) and the external scalar potential \( \varphi_{ext}(r, \omega) \) for the metal nanostructures in dielectrics is derived in the RPA at the high frequency condition, i.e., the plasmon excitation condition:

\[ \varphi_{eff}(r, \omega) = \varphi_{ext}(r, \omega) + \int dr_1 G_0(r - r_1, \omega) \rho(r_1, \omega), \]

where \( G_0(r - r_1, \omega) \) is the retarded Green’s function of the Helmholtz equation in frequency \( \omega \) expression and \( \rho(r_1, \omega) \) is the induced charge density in metal nanostructures and dielectrics, which are given respectively by

\[ G_0(r - r_1, \omega) = \frac{\exp\left(i \frac{\omega}{c} |r - r_1| \right)}{|r - r_1|}, \]

and

\[ \rho(r_1, \omega) = \nabla_1 \cdots \chi_0(r_1, \omega) E(r_1, \omega), \]

\( E(r_1, \omega) \) is the electric field in the Lorentz gauge where \( A_{0}(r_1, \omega) \) is the effective vector potential, \( c \) is the velocity of light, \( m_e \) and \( -e \) are the electron mass and charge, \( \nabla_1 \) represents the gradient with respect to \( r_1 \), and \( \chi_0(r_1, \omega) \) is the electric susceptibility of the dielectrics with the local position dependence and uniformity or cubic symmetry, which can be expressed by the position-dependent scalar. The Gaussian units are used in this article. \( n(r_1) \) is the local electron density in metal nanostructures, which is given by

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\[ j(r_1, \omega) = i\omega \left[ \frac{e^2 n(r_1)}{m_e \omega (\omega + i\Gamma)} - \chi_0(r_1, \omega) \right] E(r_1, \omega). \]

Then, the following integral equation for the effective vector potential is derived:

\[ A_{0}(r, \omega) = A_{ext}(r, \omega) + \frac{1}{c} \int dr_1 G_0(r - r_1, \omega) j(r_1, \omega). \]
The effective scalar potential in Eq. (1) and the effective vector potential in Eq. (6) satisfy the Lorentz condition \( \nabla \cdot \mathbf{A}_{\text{eff}}(\mathbf{r}, \omega) = \frac{i \omega}{c} \varphi_{\text{eff}}(\mathbf{r}, \omega) \) when the external scalar potential \( \varphi_{\text{ext}}(\mathbf{r}, \omega) \) and the external vector potential \( \mathbf{A}_{\text{ext}}(\mathbf{r}, \omega) \) satisfy the Lorentz condition. The effective magnetic flux density \( \mathbf{B}_{\text{eff}}(\mathbf{r}, \omega) \) is given by \( \text{rot} \mathbf{A}_{\text{eff}}(\mathbf{r}, \omega) \). Equations (1) and (6) can be used to study the localized plasmons for any metal nanostructures in dielectrics when the retardation effect for the localized plasmons cannot be ignored.

Using the quasi-static approximation \( \omega/c \to 0 \) indicating that the retardation effect is ignored, i.e., in the case \( ka \ll 1 \) where \( k \) is the wave number of light and \( a \) is the typical size of metal nanostructures, which is considered valid for metal nanostructures [27]. Eq. (1) is transformed using \( \mathbf{E}(\mathbf{r}_1, \omega) = -\nabla \varphi_{\text{eff}}(\mathbf{r}_1, \omega) \), integration by parts and the relation \( \nabla_1^2 |\mathbf{r} - \mathbf{r}_1|^{-1} = -4\pi \delta(\mathbf{r} - \mathbf{r}_1) \) into

\[
[\varepsilon_m(\mathbf{r}, \omega) + \varepsilon_d(\mathbf{r}, \omega) - 1] \varphi_{\text{eff}}(\mathbf{r}, \omega) - \frac{1}{4\pi c} \int \text{d} \mathbf{r}' \varphi_{\text{eff}}(\mathbf{r}', \omega) \nabla_1 \frac{1}{|\mathbf{r} - \mathbf{r}'|} \nabla_1 [\varepsilon_m(\mathbf{r}', \omega) + \varepsilon_d(\mathbf{r}', \omega) - 2] = \varphi_{\text{ext}}(\mathbf{r}, \omega),
\]

where \( \varepsilon_m(\mathbf{r}, \omega) \) and \( \varepsilon_d(\mathbf{r}, \omega) \) are local dielectric functions of metals and dielectrics, respectively, which are given by

\[
\varepsilon_m(\mathbf{r}, \omega) = 1 - \frac{\omega_p^2(\mathbf{r})}{\omega(\omega + i\Gamma)},
\]

\[
\varepsilon_d(\mathbf{r}, \omega) = 1 + 4\pi \chi_d(\mathbf{r}, \omega),
\]

where \( \omega_p(\mathbf{r}) = \sqrt{4\pi e^2 n(\mathbf{r})/m_e} \) is the position dependent bulk plasmon frequency.

### B. Light emission intensity

Using the induced charge density in Eq. (3), the electric dipole moment is given by [24]

\[
p(\omega) = \int \text{d} \mathbf{r} p(\mathbf{r}, \omega) d\mathbf{r} = -\int \text{d} \mathbf{r} \left[ \frac{e^2 n(\mathbf{r})}{m_e \omega(\omega + i\Gamma)} - \chi_d(\mathbf{r}, \omega) \right] \mathbf{E}(\mathbf{r}, \omega).
\]

As the vector potential term \( i\omega \mathbf{A}_{\text{eff}}(\mathbf{r}, \omega)/c \) in the electric field \( \mathbf{E}(\mathbf{r}, \omega) \) in Eq. (3) can be ignored for metal nanostructures as reported previously [27], the dipole moment is approximately given by

\[
p(\omega) \approx \int \text{d} \mathbf{r} \left[ \frac{\omega_p^2(\mathbf{r})}{4\pi \omega(\omega + i\Gamma)} - \chi_d(\mathbf{r}, \omega) \right] \nabla \varphi_{\text{eff}}(\mathbf{r}, \omega) = -\int \text{d} \mathbf{r} \varphi_{\text{eff}}(\mathbf{r}, \omega) \nabla \left[ \frac{\omega_p^2(\mathbf{r})}{4\pi \omega(\omega + i\Gamma)} - \chi_d(\mathbf{r}, \omega) \right],
\]

\[
\vec{\mathbf{p}}(\omega) = -\omega^2 \mathbf{p}(\omega),
\]

where \( \vec{\mathbf{p}}(\omega) \) is the second order derivative with respect to time of the dipole moment.

Considering the case where metal nanostructures exist in dielectrics without optical absorption, which means that the light emission frequency is far from the optical absorption one in the dielectrics and the electric susceptibility has only real part, the emitted photon number or light emission intensity with energy \( h\omega \) per unit solid angle \( \Omega \) in the \( \mathbf{r} \) direction from nanostructures is given in the electric dipole approximation by [24, 28]

\[
l_{\text{ph}}(\Omega, \omega) = \frac{1}{4\pi^2 c^3 \hbar \omega} |\mathbf{e}_r \times \vec{\mathbf{p}}(\omega)|^2
\]

\[
= \frac{1}{4\pi^2 c^3 \hbar \omega} |\mathbf{e}_r \times \int \text{d} \mathbf{r} \varphi_{\text{eff}}(\mathbf{r}, \omega) \nabla \left[ \frac{\omega_p^2(\mathbf{r})}{4\pi \omega(\omega + i\Gamma)} - \omega^2 \chi_d(\mathbf{r}, \omega) \right]|^2,
\]

where \( c_d \) is the light velocity in the dielectrics and \( \mathbf{e}_r = \mathbf{r}/r \) is the unit vector in the \( \mathbf{r} \) direction.

The previous study [24] has shown that the light emissions from the electric multipole moments \( l \geq 2 \) can be ignored in comparison with that from the dipole moment \( l = 1 \) in the case \( ka \ll 1 \), where \( l \) is the index of the moments, \( k \) is the wave number of light, and \( a \) is the typical size of metal nanostructures, because the contribution of the multipole moments to the light emission intensity is proportional to \( (ka)^{2l-1} \). For example, \( ka \) becomes about 0.06 when the wavelength of light and the nanostructure size are assumed to be 500 and 5 nm, respectively. This indicates that the contribution of the multipole moments can be ignored and Eq. (11) is a useful formula to calculate the total light emission intensity from the metal nanostructures with several nanometer sizes in good approximation.
C. Inelastic scattering probability and cross section

Following the approach of the previous study [5], the total energy loss $W$ of an electron beam with velocity $v$ in the $z$-direction, which passes at position $X_0$ in Figure 1 is given by

$$ W = e \int_{-\infty}^{\infty} dz E_z^{\text{ind}}(X_0, z, t), \tag{12} $$

where $t = z/v$ and

$$ E_z^{\text{ind}}(X_0, z, t) = - \frac{\partial}{\partial z} [\varphi_{\text{ind}}(X_0, z, t)] - \frac{v}{c_0 \partial z} [A_z(X_0, z, t)]. \tag{13} $$

Here, the induced scalar potential is used by subtracting the external scalar potential from the effective scalar potential because the external scalar potential by the electron beam does not contribute to the energy loss. For the non-relativistic condition; $v/c_0 \ll 1$, the second term of Eq. (13) can be ignored. After Fourier transforms for the time $t$ and position $r$, the total energy loss $W$ of the electron beam is given by

$$ W = \frac{e}{4\pi^2 v} \int_0^\infty d\omega \left\{ \int d\mathbf{k}_\perp \text{Im} \left[ \varphi_{\text{ind}}(\mathbf{k}_\perp, \omega) \right] \exp(i\mathbf{k}_\perp \cdot \mathbf{X}_0) \right\} = \int_0^\infty \hbar \omega P(X_0, \omega) d\omega, $$

$$ P(X_0, \omega) = \frac{e}{4\pi^2 \hbar v} \int d\mathbf{k}_\perp \text{Im} \left[ \varphi_{\text{ind}}(\mathbf{k}_\perp, \omega) \right] \exp(i\mathbf{k}_\perp \cdot \mathbf{X}_0) = \frac{e}{\pi \hbar v} \int_{-\infty}^{\infty} dz \text{Im} \left[ \varphi_{\text{ind}}(X_0, z, \omega) \right] \exp \left(-i\frac{\omega z}{v} \right), \tag{14} $$

where $\mathbf{k}_\perp$ is the wave vector on the $x$-$y$ plane and $\text{Im}$ represents the imaginary part of the potential. $P(X_0, \omega)$ is the inelastic scattering probability per unit frequency for the electron beam that passes through position $X_0$. Then, after integration over $X_0$, the inelastic cross section $\sigma$ per unit frequency of the plane wave electron beam is given by:

$$ \frac{d\sigma}{d\omega} = \int dX_0 P(X_0, \omega). \tag{15} $$

III. APPLICATIONS TO METAL NANOSTRUCTURES

A. Metal nanosphere

1. Effective scalar potential

In the quasi-static approximation, the localized plasmons are studied for a metal nanosphere with the radius $a$ in a dielectric as shown Figure 1. The local dielectric function of the nanosphere and that of the dielectric are assumed to have the following step function shapes:

![Figure 1: Geometrical arrangement of the metal nanosphere and electron beam in the dielectric.](image)

**Figure 1**: Geometrical arrangement of the metal nanosphere and electron beam in the dielectric.
\[ \epsilon_m(r, \omega) = 1 - \frac{\omega_p^2}{\omega(\omega + il')} \theta(a - r), \]
\[ \epsilon_d(r, \omega) = 1 + 4\pi \chi_d^0(\omega) \theta(r_1 - a), \] (16)

where \( n_0, \chi_d^0(\omega), \theta(z_1), \) and \( \omega_p \) are the constant electron density, the homogeneous electric susceptibility, the step function, and the constant bulk plasmon frequency. The scalar potential and the Coulomb potential in Eq. (7) are expanded using polar coordinates as

\[ \varphi_{\text{ext}}(r, \omega) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \varphi_{\text{eff}}^{lm}(r, \omega) Y_{lm}(\theta, \phi), \]

\[ \frac{1}{|r - r_1|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l + 1} Y_{lm}(\theta, \phi) Y_{lm}^*(\theta_1, \phi_1) \frac{r_{\text{c}}^{l}}{r_{\text{c}}^{l+1}}, \] (17)

where \( Y_{lm}(\theta, \phi) \) is the normalized spherical harmonics, \( r_{\text{c}} = \min(r, r_1) \), and \( r_{\text{c}} = \max(r, r_1) \).

Substituting Eqs. (16) and (17) into Eq. (7), the following equations are derived using the relation \( \frac{d\theta(a - r)}{dr_1} = -\delta(r_1 - a) \) and the uniform dielectric function \( \epsilon_d^0(\omega) = 1 + 4\pi \chi_d^0(\omega) \):

1. Outside the nanosphere: \( r > a \)
   \[ \varphi_{\text{eff}}^{lm}(r, \omega) = \left( \frac{a}{r} \right)^{l+1} \frac{(2l + 1) \varphi_{\text{ext}}^{lm}(a, \omega)}{l + (l + 1) \epsilon_d^0(\omega)} - \frac{\omega_p^2 l}{\omega(\omega + il')} \varphi_{\text{ext}}^{lm}(r, \omega) - \left( \frac{a}{r} \right)^{l+1} \varphi_{\text{ext}}^{lm}(a, \omega), \] (18)

2. Inside the nanosphere: \( 0 \leq r \leq a \)
   \[ \varphi_{\text{eff}}^{lm}(r, \omega) = \left( \frac{r}{a} \right)^l \frac{(2l + 1) \varphi_{\text{ext}}^{lm}(a, \omega)}{l + (l + 1) \epsilon_d^0(\omega)} - \frac{\omega_p^2 l}{\omega(\omega + il')} \varphi_{\text{ext}}^{lm}(r, \omega) - \left( \frac{r}{a} \right)^l \varphi_{\text{ext}}^{lm}(a, \omega). \] (19)

Equation (18) coincides with Eq. (19) at \( r = a \), which is given by

\[ \varphi_{\text{eff}}^{lm}(a, \omega) = \frac{(2l + 1) \varphi_{\text{ext}}^{lm}(a, \omega)}{l + (l + 1) \epsilon_d^0(\omega)} - \frac{\omega_p^2 l}{\omega(\omega + il')}. \] (20)

Ignoring the plasmon decay frequency \( \Gamma \), the pole of Eq. (20) gives the surface plasmon frequency as shown previously [28]:

\[ \omega_1 = \omega_p \sqrt{\frac{l}{l + (l + 1) \epsilon_d^0(\omega)}}, \] (21)

The first and second terms in the right side of Eq. (19) correspond to the surface and bulk plasmon excitations, respectively. The bulk plasmon term disappears at the outside of the nanosphere; \( r > a \), which indicates that the bulk plasmon contribution vanishes by the surface plasmon screening effect. The induced scalar potentials are given by subtracting \( \varphi_{\text{eff}}^{lm}(r, \omega)/\epsilon_d^0(\omega) \) from \( \varphi_{\text{ext}}^{lm}(r, \omega) \) in Eq. (18) at \( r > a \) and by subtracting \( \varphi_{\text{ext}}^{lm}(r, \omega) \) from \( \varphi_{\text{eff}}^{lm}(r, \omega) \) in Eq. (19) at \( 0 \leq r \leq a \).

2. External scalar potential

Considering the case where an electron beam with velocity \( v \) passes through position \( X_0 \) on the \( x-y \) plane, as shown in Figure 1, the external scalar potential from the electron beam is given using the light velocity in dielectrics \( c_d \) by
\[
\varphi_{ext}(r,t)x_0 = \frac{-e}{\sqrt{(z-\nu t)^2 + \left[1 - \left(\frac{\nu}{c_d}\right)^2\right](X-X_0)^2}},
\]
\[r = (X,z),\]

where the external charge density of \(\rho_{ext}(r,t) = -e\delta(r - r'(t))\); here, \(r'(t)\) is the trajectory of the electron beam, and the retarded Green’s function of Eq. (2) in the time \(t\) expression was used to derive the above result [24]. By expanding the external scalar potential using the normalized spherical harmonics, \(\varphi_{ext}(r,\omega)x_0\) is given by

\[
\varphi_{ext}^{lm}(r,\omega)x_0 = \int_{-\infty}^{\infty} dt \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \frac{-eY_{lm}^*(\theta,\phi) \exp(i\omega t)}{\sqrt{(z-\nu t)^2 + \left[1 - \left(\frac{\nu}{c_d}\right)^2\right](X-X_0)^2}}.
\]

After the calculation shown in the previous study [24], the following result is obtained:

\[
\varphi_{ext}^{l0}(r,\omega)x_0 = -\frac{e}{\pi \nu} \int d\mathbf{k}_\perp \sum_{l=0}^{\infty} \frac{[4\pi (2l+1)]^{1/2} i^l j_l}{k^2 + \left[1 - \left(\frac{\nu}{c_d}\right)^2\right] \left(\frac{\omega}{\nu}\right)^2} \exp(-i \mathbf{k}_\perp \cdot \mathbf{X}_0).
\]

where \(j_l(x)\) is the spherical Bessel function and only the \(m = 0\) term contributes to the external scalar potential.

3. Light emission intensity

Using Eqs. (10) and (20), the electric dipole moment is given by

\[
\mathbf{p}(\omega) = -e\mathbf{e}_x 2\pi a^2 \left[\frac{\omega^2 - \omega_d^2}{4\pi \omega (\omega + i\Gamma)} + \omega^2 \chi_d^0(\omega)\right] \sum_{l=0}^{\infty} \frac{(2l+1)}{4\pi} ^{1/2} \phi_{ext}(a,\omega) \int d(\cos \theta) P_{l0}^0(\cos \theta) \cos \theta
\]

\[
= -e\mathbf{e}_x \left[\frac{\omega^2 - \omega_d^2}{4\pi \omega (\omega + i\Gamma)} + \omega^2 \chi_d^0(\omega)\right] \phi_{ext}(a,\omega),
\]

where \(\mathbf{e}_x\) is the unit vector in the \(x\) direction, and the orthogonal property of the associated Legendre function \(P_{l0}^0(\cos \theta) = \cos \theta\), indicating that only the term of \(l = 1\) (electric dipole) at \(r = a\) contributes the dipole moment. However, when the local electron density depends on \(\theta\), i.e., the spherical symmetry of the electron density is broken, the orthogonal property in Eq. (25) cannot be applied and the multipole moments \(l \geq 2\) also contribute to the light emission. Using Eqs. (11), (20), and (24), the emitted photon number when an electron beam with velocity \(\nu\) passes in the \(z\)-direction through position \(X_0\) is given by

\[
I_{ph}(\Omega,\omega)x_0 = \frac{36a^4 e^2 \sin^2 \theta}{\pi^2 c_d^3 h \nu^2} \left[\frac{\omega^2}{4\pi} + \omega^2 \chi_d^0(\omega)\right] \int d\mathbf{k}_\perp \left\{\frac{j_l a}{\sqrt{k^2 + \left[1 - \left(\frac{\nu}{c_d}\right)^2\right] \left(\frac{\omega}{\nu}\right)^2}} e^{-i \mathbf{k}_\perp \cdot \mathbf{X}_0} \right\}^2 \frac{\omega^3 + \omega \Gamma^2}{\omega^2 - \frac{\omega_d^2}{1 + 2e_d^b(\omega)}},
\]

where \(\theta\) is the angle between \(\mathbf{e}_x\) and \(\mathbf{e}_y\), and \(i\Gamma\) shown in Eq. (25) is neglected because this is negligibly small.

When the two-dimensional density of the electron beams on the \(x\)-\(y\) plane is expressed as \(N_e\), the emitted photon number with the energy \(\hbar \omega\) per unit solid angle of \(\Omega\) is given by

\[
I_{ph}(\Omega,\omega) = N_e \int d\mathbf{X}_0 I_{ph}(\Omega,\omega)x_0
\]

\[
= \left[\frac{12}{a^4 e^2 N_e \sin^2 \theta}{\pi^2 c_d^3 h \nu^2} \left[\frac{\omega^2}{4\pi} + \omega^2 \chi_d^0(\omega)\right] \int d\mathbf{k}_\perp \left\{\frac{j_l a}{\sqrt{k^2 + \left[1 - \left(\frac{\nu}{c_d}\right)^2\right] \left(\frac{\omega}{\nu}\right)^2}} \right\}^2 \frac{\omega^3 + \omega \Gamma^2}{\omega^2 - \frac{\omega_d^2}{1 + 2e_d^b(\omega)}},
\]

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The emitted photon number corresponds to the case when a plane wave electron beam passes through the nanosphere. The term of \(1 - (v/c_d)^2\) is caused by the relativistic effect on the electron beam.

4. Inelastic cross section

The inelastic scattering probability per unit frequency \(P(X_0, \omega)\) of the electron beam that passes in the z-direction through position \(X_0\) is given by the Fourier transform of the induced scalar potential with respect to \(z\) as shown in Eq. (14). The induced scalar potential is expanded by the normalized spherical harmonics \(Y_{lm}(\theta, \phi)\) and the inelastic scattering probability is given by

\[
P(X_0, \omega) = e \frac{\omega}{\pi \hbar v} \sum_{l=0}^{\infty} \int_{-\infty}^{\infty} dz \, \text{Im} [\phi_{\text{ind}}^{l,0}(r, \omega) Y_{l0}(\theta, \phi)] \exp \left(-\frac{i \omega z}{v}\right),
\]

where only the terms \(m = 0\) contribute to the inelastic scattering probability because the probability does not depend on the rotational angle \(\phi\) around the \(z\)-axis.

Equations (18), (19), and (28) reveal that the electron beam is inelastically scattered only by the surface plasmon at \(X_0 \geq a\) but by both of the surface and bulk plasmons at \(X_0 < a\). This has been observed by the previous experimental studies [18, 22]. The \(l\) dependence of \(r\) in Eqs. (18) and (19) indicates that the multipole surface plasmons \((l \geq 2)\) are more localized than the dipole surface plasmon \((l = 1)\) at the interface, which has also been observed in the experiment study [22].

The studies [18, 22] have also reported that the surface plasmon excitation energies increase with the decrease of the metal nanoparticle size. It has been reported that the local electron density increases near the metal nanoparticle surface with the decrease of the nanoparticle size by the quantum interference effect [33]. When the increase of the local electron density near the metal surface is expressed by the step function-like shape, the surface plasmon frequencies are given by using the increased local electron density (not shown). This may explain the blue-shift of the surface plasmon frequency with the decrease of the nanoparticle size.

Substituting Eqs. (18), (19), and (24) into Eq. (15), the inelastic scattering cross section per unit frequency is given by

\[
\frac{d\sigma}{d\omega} = \frac{4e^2 \omega^2 a^2}{\pi \hbar v^2} \sum_{l=0}^{\infty} \frac{(2l + 1)^3 \, l}{[l + (l + 1) \epsilon_d(\omega)]^2} \int dk_z \left[ \frac{\omega}{\omega^2 - \omega_i^2} \right] \exp \left(-\frac{\omega^2}{\omega_i^2}\right) \frac{\omega_i^2}{\omega^2} \sum_{l=0}^{\infty} (2l + 1) \int dr \frac{r^2}{k_z^2 + (\omega_i^2/\gamma) r} \left[ j_l \left( \frac{k_z^2 + (\omega_i^2/\gamma) a}{\epsilon_d(\omega)^2} \right) \right]^2 \times \frac{\omega_i^2}{(\omega^2 - \omega_i^2)^2 + \omega^2 \Gamma^2},
\]

where the decay of the localized plasmons is considered. The first and second terms correspond to the surface and bulk plasmon excitations, respectively. The bulk plasmon cross section has a negative term indicating that the bulk plasmon excitation is reduced by the surface plasmon excitation near the metal surface. It is noted that the result of Eq. (29) coincides with that calculated by the quantum mechanical method when \(\epsilon_d(\omega) \approx 1\) and \(\Gamma \to 0\) [23].

Comparing the surface plasmon term in Eq. (29) with Eq. (27) at non-relativistic case \(v/c_d \ll 1\), it is found that they have the same \(k_z\) dependence at \(l = 1\). This indicates that the light emission is accompanied with the inelastic scattering of the electron beam by the surface plasmon excitation. The electron beam can excite the dipole \((l = 1)\) and multipole surface plasmons \((l \geq 2)\) and also the bulk plasmon, but the light emission takes place only from the dipole surface plasmon within the electric dipole approximation shown in Eq. (11).
B. Metal ultrathin film

1. Effective and external scalar potentials

In the quasi-static approximation, the localized plasmons are studied for a metal ultrathin film in a dielectric, which has a thickness $d$ in the $z$-direction and spreads on the $X = (x, y)$ plane as shown in Figure 2. The local electron density in the metal ultrathin film and the local electric susceptibility of the dielectric are assumed to have the following step function shapes:

$$
\varepsilon_m(r_1, \omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}[\theta(z_1) - \theta(z_1 - d)],
$$

$$
\varepsilon_d(r_1, \omega) = 1 + 4\pi\chi_d^0(\omega)[\theta(-z_1) + \theta(z_1 - d)].
$$

The scalar potential and the Coulomb potential in Eq. (7) are expanded using the Fourier transform with respect to $k_\perp$ as

$$
\varphi_{\text{eff}}^{\text{ext}}(X, z, \omega) = \frac{1}{(2\pi)^2} \int dk_\perp \varphi_{\text{eff}}^{\text{ext}}(k_\perp, z, \omega) e^{i k_\perp \cdot X},
$$

$$
\frac{1}{|r - r_1|} = \frac{1}{(2\pi)^2} \int dk_\perp \frac{2\pi}{k_\perp} e^{-k_\perp |z - z_1|} e^{i k_\perp \cdot (X - X_1)}.
$$

The effective scalar potentials $\varphi_{\text{eff}}(k_\perp, z, \omega)$ have been calculated previously [28], which are not shown here but only the potentials at the interfaces are shown. The effective scalar potential at $z = 0$ is given by

$$
\varphi_{\text{eff}}(k_\perp, 0, \omega) = \left[ 1 - \frac{\omega_p^2}{2\omega(\omega + i\Gamma)} + 2\pi\chi_d^0(\omega) \right] \varphi_{\text{ext}}(k_\perp, 0, \omega) - \left[ \frac{\omega_p^2}{2\omega(\omega + i\Gamma)} + 2\pi\chi_d^0(\omega) \right] e^{-k_\perp d} \varphi_{\text{ext}}(k_\perp, d, \omega).
$$

The effective scalar potential at $z = d$ is given by

$$
\varphi_{\text{eff}}(k_\perp, d, \omega) = \left[ 1 - \frac{\omega_p^2}{2\omega(\omega + i\Gamma)} + 2\pi\chi_d^0(\omega) \right] \varphi_{\text{ext}}(k_\perp, d, \omega) - \left[ \frac{\omega_p^2}{2\omega(\omega + i\Gamma)} + 2\pi\chi_d^0(\omega) \right] e^{-k_\perp d} \varphi_{\text{ext}}(k_\perp, 0, \omega).
$$

Figure 2: Geometrical arrangement of the metal ultrathin film and electron beam in the dielectric.
Ignoring the plasmon decay frequency \( \Gamma \), the localized surface plasmons frequencies are given by the poles of Eq. (32) or Eq. (33) [28]:

\[
\omega_{k_\perp}^{\pm} = \omega_p \sqrt{\frac{1 \pm e^{-k_\perp d}}{2 + 4\pi \chi_0^2(\omega_p) (1 \mp e^{-k_\perp d})}},
\]

where the frequencies \( \omega_{k_\perp}^{\pm} \) correspond to the antisymmetric mode \( (+) \) with antisymmetric induced charge distribution in the \( z \) direction and the symmetric mode \( (-) \) with the symmetric induced charge density, respectively. The bulk plasmon term exists only at the inside of the film; \( 0 \leq z \leq d \), which indicates that the bulk plasmon contribution vanishes by the surface plasmon screening effect at the outside of the film as shown in the previous study [28].

Considering the case where an electron beam with velocity \( v \) passes in the \( z \)-direction through position \( X_0 \) on the \( x-y \) plane as shown in Figure 2, the Fourier component of the external scalar potential of Eq. (22) with respect to \( X \) and \( t \) is given by

\[
\varphi_{\text{ext}}(k_\perp, z, \omega)_{X_0} = \int_{-\infty}^{\infty} dt \int dX \frac{-e}{\sqrt{(z - vt)^2 + \left(1 - \frac{v}{c_d} \right)^2}} \exp(-i k_\perp \cdot X + i\omega t) = -\frac{4\pi e \exp(-i k_\perp \cdot X_0 + i\omega z)}{v k_\perp^2 + \left[1 - \left(\frac{v}{c_d}\right)^2\right] \left(\frac{\omega}{v}\right)^2}.
\]

(35)

2. Light emission intensity

Our previous study [28] has given the following dipole moment when the electron beam passes through the position \( X_0 \):

\[
\mathbf{p}(\omega)_{X_0} = e_z \left\{ \frac{\varphi_{\text{ext}}(0, 0, 0, \omega)_{X_0} - \varphi_{\text{ext}}(0, d, \omega)_{X_0}}{1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}} \left[ \frac{\omega^2 \omega_p^2}{4\pi \omega(\omega + i\Gamma)} + \omega^2 \chi_0^2(\omega) \right] \right\},
\]

(36)

where only the antisymmetric mode \( \omega_{k_\perp}^{+} = \omega_p \) at \( k_\perp = 0 \) contributes to the dipole moment. Then, using Eqs. (11), (32), (33), and (35), the emitted photon number with the energy \( \hbar \omega \) per unit solid angle \( \Omega \) is given by

\[
I_{\text{ph}}(\Omega, \omega) = \frac{8e^2 \sin^2\theta}{c_d \hbar v^2} \left\{ \frac{\omega_p^2}{4\pi} + \omega^2 \chi_0^2(\omega) \right\}^2 \left[ 1 - \cos\left(\frac{\omega d}{v}\right) \right]^2 \left(\frac{\omega^3 + \omega \Gamma^2}{(\omega^2 - \omega_0^2)^2 - (\omega \Gamma)^2} \right).
\]

(37)

3. Inelastic scattering probability

The inelastic scattering probability per unit frequency for the electron beam that passes in the \( z \)-direction through position \( X_0 \); \( P(X_0, \omega) \) in Eq. (14) can be calculated using the \( \varphi_{\text{ind}}(k_\perp, z, \omega)_{X_0} \) given in the previous study [28] and \( \varphi_{\text{ext}}(k_\perp, z, \omega)_{X_0} \) in Eq. (35), which is represented by

\[
P(X_0, \omega) = P_{\text{asy}}(X_0, \omega) + P_{\text{sy}}(X_0, \omega) + P_{\text{b}}(X_0, \omega),
\]

(38)

where \( P_{\text{asy}}(X_0, \omega) \), \( P_{\text{sy}}(X_0, \omega) \), and \( P_{\text{b}}(X_0, \omega) \) are the inelastic scattering probabilities for the antisymmetric and symmetric surface plasmon excitations and the bulk plasmon excitation, respectively. They are given by

\[
P_{\text{asy}}(X_0, \omega) = \frac{4e^2}{\pi \hbar v^2 \chi_0^2(\omega)} \int dk_\perp \frac{1 + e^{-k_\perp d}}{2 + (1 - e^{-k_\perp d})} \frac{\omega \Gamma}{2(1 - e^{-k_\perp d})} \left[ (1 - \cos\left(\frac{\omega d}{v}\right) \right]^2 \left\{ \frac{1 + e^{-k_\perp d}}{2 + (1 - e^{-k_\perp d})} \right\} + \omega^2 \Gamma^2.
\]

(39)
It is noted that the inelastic scattering probabilities are independent of the position \( X_0 \) because of the translational invariance of the system on the \( x-y \) plane. Comparing the surface plasmon excitation probability in Eq. (39) with the emitted photon number in Eq. (37) at the non-relativistic case \( v/c \ll 1 \), it is found that they have the same \( k_{\perp} \) and \( 1 - \cos(\omega d/v) \) dependences at \( k_{\parallel} = 0 \) when the relation \( 1 - e^{-k_{\perp}d} \approx k_{\perp}d \) is used. This indicates that the light emission is accompanied with the inelastic scattering of the electron beam by the antisymmetric surface plasmon excitation. The terms of \( 1 - \cos(\omega d/v) \) and \( 1 + \cos(\omega d/v) \) in Eqs. (39) and (40) are caused by the interaction between the localized charges at the two surfaces. The cosine terms are cancelled with each other when the thickness becomes infinite, i.e., \( k_{\perp}d \rightarrow \infty \).

The electron beam can excite the antisymmetric and symmetric surface plasmons with any \( k_{\perp} \) value and also the bulk plasmon, but the light emission takes place only at \( k_{\perp} = 0 \) for the antisymmetric surface plasmon within the electric dipole approximation shown in Eq. (11). The bulk plasmon scattering probability has a positive term that is proportional to the thickness \( d \) and also a negative term as shown in Eq. (41). This indicates that the bulk plasmon excitation is reduced by the surface plasmon excitations near the metal ultrathin film surfaces.

IV. CONCLUSIONS

Equations on excitation and light emission of the localized bulk and surface plasmons for metal nanostructures in dielectrics by electron beam were derived using our localized plasmon theory in the random phase approximation at high frequency condition. Inelastic scattering probabilities of electron beams and light emission intensities by the localized plasmons for metal nanospheres and ultrathin films in dielectrics were calculated using the quasi-static and electric dipole approximations. It was also assumed that the local dielectric functions for metals and dielectrics had step function shapes at the metal and dielectric interfaces. It was found that the electron beams were inelastically scattered by the localized surface plasmons with the modes of \( l \geq 1 \) and bulk plasmons with the modes of \( l \geq 0 \) for the metal nanosphere, and with any \( k_{\perp} \) value for the metal ultrathin film. The light emissions, however, occurred only from the dipole surface plasmon with \( l = 1 \) for the metal nanosphere, and from the antisymmetric surface plasmon with \( k_{\perp} = 0 \) for the metal ultrathin metal in these approximations. These specific properties for the light emissions, however, are not maintained when the retardation effect cannot be ignored in the metal nanostructures, i.e., failure of the quasi-static approximation or the electric dipole approximation cannot be used.

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