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Production of surface plasmons in electron emission from Al nanoparticles

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ABSTRACT

In this work we study the surface plasmon generation by a suddenly created electron-hole pair in nanoparticles of spherical shape. We use a previously developed model based on the Hamiltonian formulation for plasmon field.

1. Introduction

In recent years many techniques for synthesis of nanoparticles have been developed. Many of these techniques provide particles of spherical shape [1,2], the so-obtained nanospheres do have many applications, e. g. in the field of catalysis [3] or as nano-antennas [4].

In this work we use the Hamiltonian model developed in previous works [5,6] to study the plasmon production due to a suddenly created electron-hole pair. Applying the Hamiltonian formalism it is assumed that the collective electron density oscillations in the system can be described by a quantum mechanical Hamiltonian including annihilation (a) and creation (a^*) operators over the plasmon field [7–10]. In order to construct such a Hamiltonian the knowledge of the electrostatic potential as well as the boundary conditions for the particular geometry are required.

2. Theoretical model

The unperturbed Hamiltonian for a system of electronic charges under an electrostatic potential is given by Ref. [5]

$$H_0 = \frac{1}{2}\int \rho_s \phi_s d^3r + \frac{1}{2} n_0 m_e \int (\nabla\psi_s)^2 d^3r \tag{1}$$

where ρ_s is the volume charge density associated to the volume electron density at rest n_s with $\rho_s = -n_s q_e$; n_0 the volume density at rest, m_e the electron mass, q_e the electron charge, ψ_s is the field of velocities given by

$$\mathbf{v}(\mathbf{r},t) = -\nabla\psi(\mathbf{r},t)$$

where $\mathbf{v}$ is the velocity of the material electronic density, and ϕ is the electrostatic potential which for spherical bodies [11] is given by

$$\phi_s(\mathbf{r},t) = \sum_{l,m} \begin{cases} \beta_l r^l Y_{l,m}(\theta,\varphi) & r \le b \\ \alpha_l r^{-(l+1)} Y_{l,m}(\theta,\varphi) & b < r \end{cases} \tag{2}$$

where we use spherical coordinates (r,θ,φ), b is the radius of the sphere, and $Y_{l,m}$ are the spherical harmonics (See Fig. 1).

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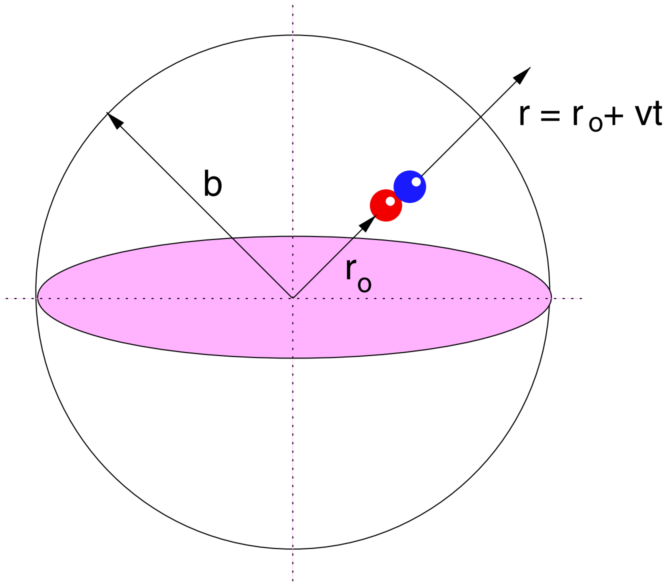

Fig. 1. Photoemission from a spherical particle. The electron-hole pair is created inside the sphere at a radial distance r_0. The hole remains stationary in that position and the electron escapes following a radial trajectory.

In the rest of this work we do use atomic units (au.), so $m_e = q_e = \hbar = 1$.

The electron density in this case is

$$n_s(r,t) = \sum_{l,m} n_l(t)\delta(r-b)Y_{l,m}(\theta,\varphi) \tag{3}$$

and the field of velocities [5] is:

$$\psi_s(\mathbf{r},t) = \sum_{l,m}\begin{cases}\psi_{l,m}(t)r^l Y_{l,m}(\theta,\varphi) & r \le b \\ 0 & b < r\end{cases} \tag{4}$$

The factors α, β and $\psi_{l,m}$ are obtained by using the boundary conditions:

$$\frac{\partial \phi_s}{\partial r}^{\text{ext}}\Big|_{r=a} - \frac{\partial \phi_s}{\partial r}^{\text{int}}\Big|_{r=a} = -4\pi\sigma \tag{5}$$

$$\varepsilon(\omega)\frac{\partial \phi_s}{\partial r}^{\text{int}}\Big|_{r=a} - \frac{\partial \phi_s}{\partial r}^{\text{ext}}\Big|_{r=a} = 0 \tag{6}$$

where $\varepsilon(\omega)$ is the dielectric function, σ is the surface charge density, which is related to the density n_s by

$$\sigma = \sum_{l,m} n_l(t)Y_{l,m}(\theta,\varphi) \tag{7}$$

Then, from the boundary conditions Eqs. (5) and (6), and Eq. (7) we obtain

$$\alpha_l = n_l(t)\frac{4\pi\varepsilon b^{l+2}}{(l+1)(\varepsilon-1)}$$

$$\beta_l = -n_l(t)\frac{4\pi}{lb^{l-1}(\varepsilon-1)}$$

$$\psi_{l,m}(t) = \frac{\dot{n}_l(t)}{n_o}\frac{1}{lb^{l-1}}$$

and finally

$$H_0 = \frac{4\pi b^3}{2\omega_P^2}\sum_{l,m}(-1)^m\frac{1}{l}\left[\omega^2 n_{l,-m}n_{l,m} + \dot{n}_{l,-m}\dot{n}_{l,m}\right]$$

where ω_P is the frequency of the bulk plasmon.

In the frame of second quantization we should write n_l as a combination of plasmon creation and annihilation operators, a_l^* and a_l respectively. These operators act over the plasmon field absorbing and creating a plasmon of the mode l:

$$n_l = \sqrt{\frac{l\omega_P}{8\omega}}\left(a_l + a_l^*\right)$$

where l is an integer number. With this, the potential can be expressed as

$$\phi_s(\mathbf{r},t) = \sum_l F_l(t)\left(a_l + a_l^*\right) \tag{8}$$

where F_l is a real function ($F_l = F_l^*$) defined by:

$$F_l(t) = \begin{cases} P_l[\cos(\theta(t))]\xi_l(r(t)) & r \le b \\ P_l[\cos(\theta(t))]\chi_l(r(t)) & b < r\end{cases} \tag{9}$$

where the P_l are the Legendre polynomials of order l, and the functions ξ_l and χ_l are given by

$$\xi_l = \sqrt{\frac{2\pi^2 l\omega_P^2}{\omega b^3}}\frac{r(t)^l}{b^{l-1}(2l+1)}$$

$$\chi_l = \sqrt{\frac{2\pi^2 l\omega_P^2}{\omega b^3}}\frac{b^{l+2}}{r(t)^{l+1}(2l+1)}$$

In this way we get the unperturbed Hamiltonian Eq. (1) in the harmonic oscillator form:

$$H_0 = \sum_l \omega_l a_l^* a_l \tag{10}$$

For spheres [12], the dispersion ratio gives us the allowed values for the wave vector $\mathbf{k}$, so in effect, we do not have really a dispersion ratio; we have instead a relation between ω and the mode l, giving us the permitted values for ω:

$$\omega_l^2 = \omega_P^2 l/(2l+1)$$

In addition, we note that $l=0$ is not an available mode because it gives $\omega_0 = 0$. Fig. 2 shows the dispersion ratio. As we see the dispersion ratio has the form of horizontal lines which get closer and closer to $\omega/\omega_P = 1/2$ as $l \to \infty$.

In Fig. 3 we see the behavior of ω_l for many values of l; as $l \to \infty$, $\omega_l/\omega_p \to 1/\sqrt{2}$, which means that the Drude Law's relation between volume and surface plasmon frequencies is reached.

Let us suppose now that there is a charged particle traveling inside the sphere as shown in Fig. 1, with a trajectory $\mathbf{R}(t)$, then the total Hamiltonian should include an interaction term in addition to the unperturbed one (Eq. (10)). Due its electrostatic nature [5], this interaction term can be written in the form $H_I = Z\phi(\mathbf{R}(r))$.

The interaction Hamiltonian has the form:

$$H_I = -Z\phi^{(e)}\Theta(t-t_0) + Z\phi^{(h)}\Theta(t-t_0)$$

where Z is the electric charge of the particle in units of electron charge and Θ is the Heaviside step function. As we see, we have two

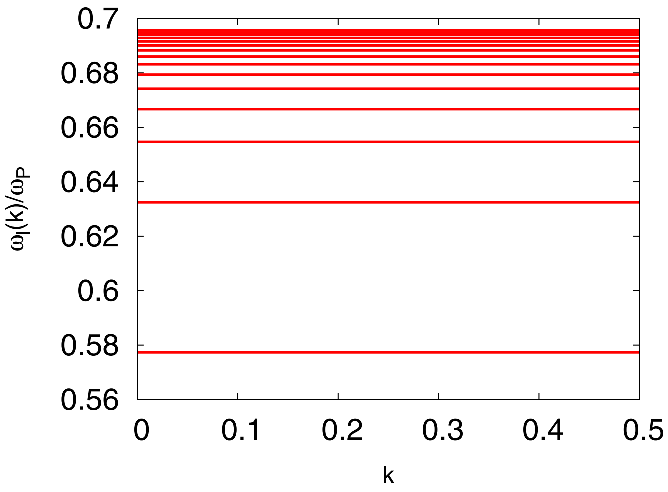

Fig. 2. Dispersion ratio for a sphere of radius $b = 20$ au. For a given value of l, ω_l does not depend on the wavenumber k. As a result, the horizontal lines in the Figure get closer to the limit value $1/\sqrt{2}$, which is the corresponding ratio ω_s/ω_P for a macroscopic body [5].

terms in the potential: one from the electron and another from the hole and according to Eq. (8) we write:

$$H_l = -\sum_l \left(f_l^{(e)} + f_l^{(h)}\right)\left(a_l + a_l^*\right)$$

with

$$f_l^{(e)}(t) = Z\Theta(t - t_0)F_l\left(\mathbf{R}^{(e)}(t)\right) \tag{11}$$

$$f_l^{(h)}(t) = Z\Theta(t - t_0)F_l\left(\mathbf{R}^{(h)}(t)\right) \tag{12}$$

where the superscripts (e) and (h) indicate electron and hole, respectively.

3. Results and discussion

We are interested now in finding the number Q of the plasmons produced, which can be obtained by Ref. [5]

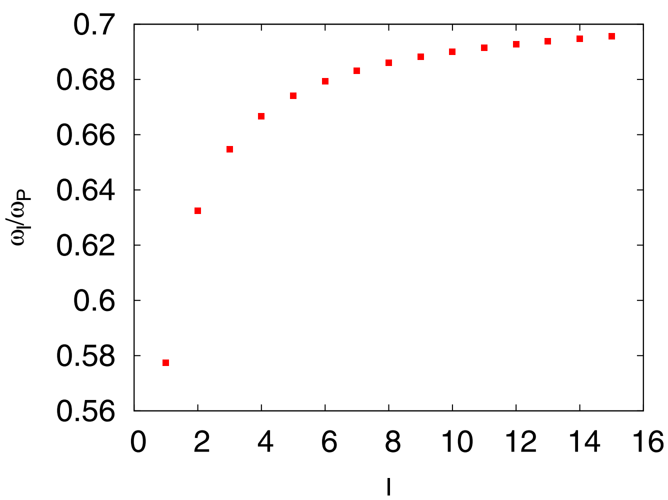

Fig. 3. Discrete set of points representing the oscillation modes of the electron gas in a sphere for l from 1 to 15. As seen in this figure, as $l \to \infty$, ω tends to $1/\sqrt{2}$, which is the value for the ratio ω_s/ω_P for macroscopic bodies.

$$Q = \frac{A}{(2\pi)^2}\int\left|X_l(\infty)\right|^2 d^2k \tag{13}$$

where $X_l(t)$ is given by Ref. [5]:

$$X_l(t) = \int_{-\infty}^{t} f_l(t')e^{-i\omega t'}dt' \tag{14}$$

Then using the Eqs. (9), (11), (12) and (14), with $t_0 = 0$:

$$X_l = \xi_l\int_0^T\left[-r^l P_l(\cos\theta) + r_h^l P_l(\cos\theta_h)\right]dt$$

in our case $r = r_0 + vt$, $\theta = \theta_0 = \theta_h = 0$ and $r_h = r_0$; then integrating:

$$X_l = -\xi_l\frac{(r_0 + vT)^{l+1}}{l+1} + \xi_l r_0^l T$$

If the time necessary for electrons to leave the sphere is $T = (b - r_0)/v$, we obtain from Eq. (13) a sum of three terms:

$$Q_l = Q_l^{(e)} + Q_l^{(h)} + Q_l^{(eh)}$$

where

$$Q_l^{(e)} = (\xi_l)^2\left(\frac{r_0 + vt}{l+1}\right)^{2(l+1)}$$

$$Q_l^{(h)} = (\xi_l)^2\left(r_0^l T\right)^2$$

$$Q_l^{(eh)} = -(\xi_l)^2\left(\frac{r_0 + vt}{l+1}\right)^{l+1}\left(r_0^l T\right)$$

Fig. 4 shows the results for an Al sphere of radius 20 au. ($\sim$1 nm) and an electron escaping with $v = 4$ au. ($\sim$108 eV), for the modes $l = 1,2,3, \ldots$; as we see, all contributions increase as the distance of the electron-hole pair creation from the surface approaches zero. Also, we note that the contributions to Q_l decrease strongly as l increases, this tendency is stronger for the electron contribution $Q_l^{(e)}$.

We note also that the interference term $Q_l^{(eh)}$ is negative and larger than the hole term, $Q_l^{(h)}$ which is smaller for the mode $l = 0$, than $Q_l^{(e)}$; in such a way we cannot separate the intrinsic (hole) and extrinsic (electron) terms. We note that as l increases, the electron contribution decreases strongly being even smaller than the hole contribution, at the same time the interference (electron-hole) term becomes very important in production of surface plasmons.

4. Concluding remarks

In this work we used the Hamiltonian formalism for studying the plasmon production in a spherical nanoparticle of aluminum. Such a model is a very suitable way for the study of plasmon generation and decay due to a suddenly created electron-hole pair in nanoscaled bodies [5,13], and it has the advantage of giving a more complete view of the system from the point of view of quantum mechanics. The advantage of the Hamiltonian formalism consists in describing the production and decay of plasmons in terms of operators creation a^*, and absorption a of plasmon, respectively, over the plasmon field. However this method requires more complex mathematics, which is not always easy to apply.

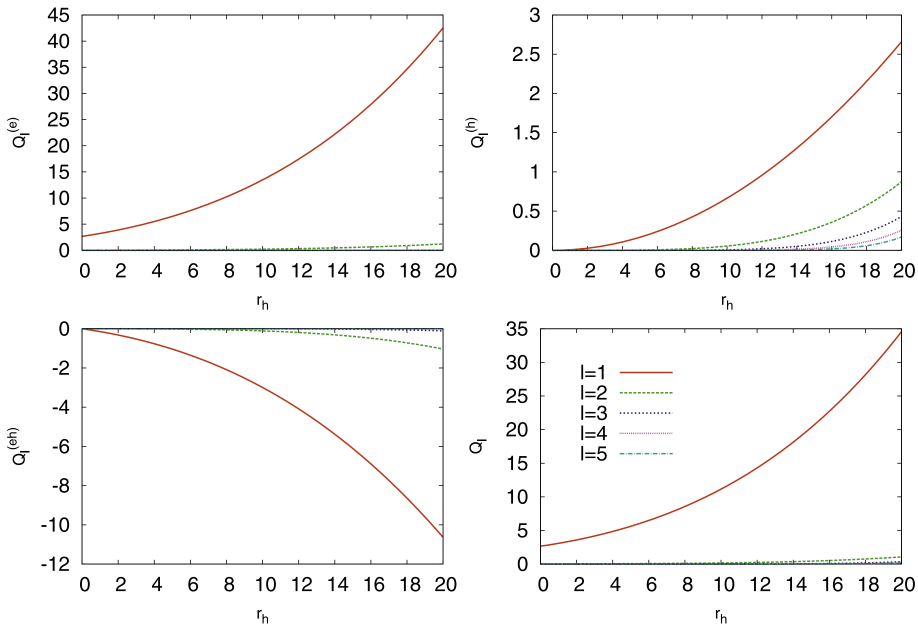

Fig. 4. Contributions to the average number of plasmons produced $Q_l^{(e)}$, $Q_l^{(h)}$, $Q_l^{(eh)}$ and Q_l respectively, from the electron, the hole, the interference (electron-hole) and total, for the values $l = 1, 2, 3, 4$ and 5; as a function of r_h, the radial distance at which the electron-hole pair is created; for an Al sphere of radius 20 au. (~1 nm) and an electron escaping with $v = 4$ au. (~108 eV).

As expected for spherical particles, the plasmon production increases as the site of the electron-hole pair generation approaches the surface.

We see that the hole term in the expression describing the average number of plasmons produced is very small compared with the electron one and due to the interference term, the obtained average number of the surface plasmons produced shows us that for nanospheres it is not possible to distinguish between the plasmon generation processes of intrinsic (hole) and extrinsic (electron) type, which was previously indicated in the case of nanocylinders, so one should be very careful when trying to interpret the respective plasmon spectra in terms of intrinsic and extrinsic excitations [14,13].

In addition, it is very important to note that these values do not depend on the size of the sphere, which is a very different behaviour from other geometrical shapes i. e. cylindrical [13].

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