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# ON THE MECHANISM OF DEPHASING OF ELECTRON COLLECTIVE OSCILLATIONS IN METALLIC NANOPARTICLES

**A.H. Melikyan[1], H.R. Minassian[2], V.A. Paployan[1*]**

[1]*Russian-Armenian (Slavonic) University, Yerevan, Armenia*
[2]*A.Alikhanian National Laboratory, Yerevan, Armenia*
**e-mail: vahagn.paployan@gmail.com*

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**Abstract** - A mechanism of dephasing of collective oscillations of electrons in metallic nanoparticles, leading to the absorption line width proportional to the ratio of the Fermi velocity to the radius of the particle is proposed. The mechanism is associated only with elastic collisions of electrons with the surface of the particle, which leads to an uncontrolled jump in the oscillation phase. The mean period of time during which the free oscillations take place determines the width of the spectrum. Thus the proposed mechanism initiates dephasing of the oscillations without energy dissipation.

Keywords: metallic nanoparticles, electron collective oscillations, dephasing

## 1. Introduction

Collective oscillations of electrons in metallic nanoparticles (MNP) are of great interest due to the so-called plasmon resonance. It turns that the optical properties of the particles are determined by two factors. The first is the interband transitions, and the second - plasmon resonance. The position of the plasmon peak is determined by many factors. The same is true for the second important parameter of resonance - the spectral width of the peak. There are surprisingly large number of effects which lead to 1/R dependence of the spectral width on the particle radius [1,2]. In particular this includes scattering of electrons by the surface of the particle, which may be diffuse, purely elastic or inelastic. It should be emphasized that the 1/R–law is experimentally confirmed in most cases (e.g. see [3]).

In this communication we discuss a mechanism of broadening of the plasmon resonance, similar to collisional broadening of atomic spectra in gases.

**2. Theory**

Consider a metallic nanosphere of radius R, in which the conduction electrons make coherent collective oscillations. Motion of each electron is a superposition of the chaotic and ordered oscillatory motions. The amplitude of the latter is typically a few tenths of an angstrom, and speed - much less than the Fermi velocity. Suppose that the oscillating electron approaches the boundary of the sphere and undergoes an elastic collision with the surface. As a result of the collision phase of the oscillation changes, and after the collision the electron will oscillate with a phase different from the phase of collective oscillations. This dephasing leads to the breakdown of collective motion, however, the total energy of the oscillations of all the electrons remains unchanged. In addition, the emission spectrum of oscillating electrons is broadened, since the coherence time of the oscillation becomes finite. To determine the width of the oscillation spectrum we proceed in the same way as is done in atomic spectroscopy. Let us calculate the Fourier component of the oscillating part of the electron coordinate between two collisions with the surface of the sphere which gives

$$x_\omega \sim \frac{\sin\left[\left(\omega_0 - \omega\right)\tau\right]}{\omega_0 - \omega}, \tag{1}$$

where $\omega_0$ is the oscillation frequency, $\omega$ is the current frequency, $\tau$ is the time interval between two successive collisions. The latter can be presented as follows - $\tau = 2\sin\left(\alpha/2\right)\cdot R/v$, where - $\alpha$ is the angle between the radii connecting the center of the sphere with the points on the surface where the collision took place, and $v$ is the electron speed. Now the expression (1) must be averaged over the angle $\alpha$ between zero and $\pi$ and over the velocity with the Fermi partition function which leads to the following expression:

$$\left\langle x_\omega \right\rangle \sim \frac{1}{2\Delta}\int_0^a\int_0^\pi \sin\left(2\frac{\Delta}{u}\sin\frac{\alpha}{2}\right)u^2 du\, d\alpha \equiv f\left(\Delta\right), \tag{2}$$

where $a$, $\Delta$, and $u$ are dimensionless ratio of Fermi velocity and the sphere radius, detuning from the resonance frequency, and the ratio of the electron velocity and the sphere radius correspondingly. At first glance, it seems unlikely that this formula gives a linear dependence of the spectral width on $v_F/R$ with factor of 0.95, but this is indeed the case. Below we show the plots for $\langle x_\omega \rangle^2$ vs detuning Δ for the three values of the radius - 20 nm (Fig. 1a), 10 nm (Fig. 1b) and 5 nm (Fig. 1c) at the same Fermi velocity -$10^8$ m/ s.

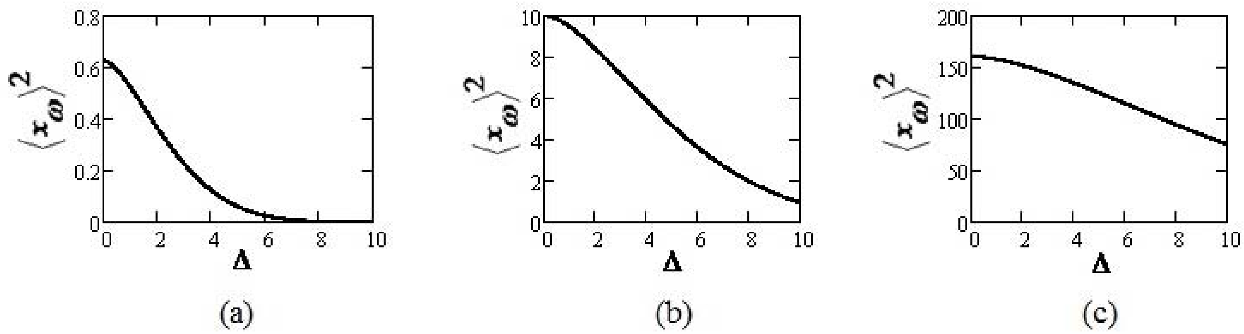


**Fig.1.** Dependences of the $\langle x_\omega \rangle^2$ on detuning Δ for the three values of the radius 20 nm (a), 10 nm (b) and 5 nm (c) at the same Fermi velocity -$10^8$ m/ s.

It is obviously clear, that the full width $\Gamma$ behaves as $\Gamma = 0.95 v_F/R$.

Now we can perform an analogous calculation for a spherical nanoshell with the internal radius $R_{in}$ and the external radius $R_{ext}$. In this case, the maximum distance that an electron can pass without collision with the boundaries of nanoshells equals to $2\sqrt{R_{ext}^2 - R_{\text{int}}^2}$. Correspondingly we will integrate over the angle $\alpha$ from zero to $\alpha_{\max} = 2\arcsin\sqrt{1-\left(R_{\text{int}}/R_{ext}\right)^2}$, i.e.

$$\langle x_\omega \rangle \sim \frac{1}{2\Delta}\int_0^a\int_0^{\alpha_0}\sin\left(2\frac{\Delta}{u}\sin\frac{\alpha}{2}\right)u^2 du\, d\alpha \equiv f_1\left(\Delta,\alpha_0\right). \tag{3}$$

We consider the following values the radii: a) $R_{in}$=3, $R_{ext}$=5; b) $R_{in}$=9, $R_{ext}$=10; c) $R_{in}$=15, $R_{ext}$=20.

The expected dependence $\Gamma = 0.95 v_F \big/ \sqrt{R_{ext}^2 - R_{\text{int}}^2}$ doesn't hold. The reason for such descripancy is that we do not take into account the processes of successive collisions of electrons with the outer and the inner edge of the shell. For this issue, we hope to return in the future.

## 3. Conclusion

It is shown that the widely discussed 1/R–law, describing the dependence of the width of the spectrum of collective oscillations of electrons in a metal nanosphere on the radius of the sphere can be derived from simple physical reasoning. Namely, it is obtained under the assumption that the electrons elastically collide with the boundary of nanospheres, and the phase of the oscillation of electron changes chaotically. However, in the case of nanoshells for the calculation of the width successive collisions of an electron with the outer and inner boundaries of the sphere must be taken into account as well.

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