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# Effects of surface charge on the anomalous light extinction from metallic nanoparticles

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ABSTRACT

The effects of extraneous surface charges on the anomalous extinction from metallic nanoparticles are studied via an application of the extended Mie theory by Bohren and Hunt. Due to the sensitivity of the higher multipolar resonance on the surface charges, it is found that quenching of the anomalous resonance can be observed with presence of only a modest amount of charges on these particles. The observed effects thus provide a rather sensitive mechanism for the monitoring of the neutrality of these nanoparticles using far field scattering approaches.



## 1. Introduction

Optical scattering from particles of sub-wavelength sizes is a well-established subject of fundamental importance in both the understanding of the propagation of light through these particulate media, and in the monitoring of these particles via optical means [1]. Within classical electromagnetic theory, such understanding has been provided by the century-old celebrated theory of Lorenz [2] and Mie [3], which is an exact solution of Maxwell's equations for spherical particles. Moreover, despite its long history of being studied as evidenced by the large amount of literature published, the Lorenz–Mie (LM) theory has kept on generating surprises and intriguing results up to the present time. Two of such examples discovered more recently are the anomalous scattering [4] and the Fano resonances [5] in the scattering/extinction cross sections of the theory [6].

In several recent studies, Tribelsky and coworkers [4,5] have discovered the possibility of an "inverted hierarchy" in the multipole contributions to the LM theory for plasmonic materials of low dissipation, leading to the invalidation of the Rayleigh approximation. In addition, Miroshnichenko has observed similar Rayleigh breakdown with particles of negative refracting medium [7]. Aside from this anomaly observed in the total cross sections, intriguing phenomenon also showed up in the angular cross sections due to interference between different scattered wave components and/or the incident wave. For example, sharp asymmetric resonance of the Fano type was obtained in the forward and backward scattering cross sections near the surface plasmon resonance frequency of a Drude sphere [5].

Moreover, most of these previous studies [4–6] were limited to a neutral sphere as within the applicability of the LM theory. On the other hand, it has been pointed out since the late 1970s that the presence of surface charge on these particles will potentially change the scattering results due to the modification of the boundary conditions in the original LM theory [8]. The motivation of such a consideration comes from the fact that many particulate systems found both in Nature and in the laboratory are not perfectly neutral. These include, for example, light scattering from intergalactic dusts, water droplets in thunderstorm clouds, …etc., as well as many colloidal systems prepared in the laboratory [9]. Thus, such "charge induced" optical effects in particle scattering has been an active research area for over three decades, including some very recent works [10–13]. Aside from the well-known small blue-shifts on the scattering/absorption resonances of these particles due to the effective increase in free charge density from the presence of the extraneous charges, some of the latest works [10–12] have focused on certain specific and intriguing aspects of the charged-particle scattering problem such as the effects due to the non-uniformity in surface charge distribution; as well as those from the interband vs intraband transitions of the surface electrons. For example, it has been found that when the surface charges are not uniformly distributed on the particle, the original extended Mie theory of Bohren and Hunt (BH, [8]) must be modified to adopt a new version of the surface current density which will lead to the incorporation of higher order modes even in the long-wavelength limit [10–11]. Furthermore, the introduction of interband transition for the surface electrons has lead to slightly

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smaller and red-shifted cross sections with additional resonance peak emerging [12]. In addition to homogeneous solid particles, charged metallic nanoshells have also been studied with intriguing effects observed on the coupled surface plasmon modes [13].

In general, it has been found that such charge-induced optical effects are rather small in most far-field scattering process except for particles of very small sizes and a large amount of surface extraneous charges (i.e. a high surface voltage). Furthermore, dielectric particles will have a better chance to reveal such effects than metallic particles can, due to their characteristic frequencies being much lower than those of metals (the plasmon frequencies of metal are often in the visible or UV range for metals). On the other hand, if one were to optically probe these charged particles via near field interactions by having a localized light source placed in the vicinity of the particle, than it is possible to observe stronger charge-optical effects since these effects are more sensitive to the higher multipole resonance of the particle which can be excited more efficiently with the near field of a localized light source [13,14]. Nevertheless, near field experiments are not as convenient as those using far field especially when one refers to remote monitoring of these charged particles.

It is hence the purpose of the present work to provide new possibilities of efficient optical monitoring of these charged metallic particles via anomalous scattering. We shall demonstrate in the following that such scattering is rather sensitive to the presence of extraneous charges on these particles, leading to realistic monitoring of these charges via far field scattering. We shall focus on the inverted hierarchy of the multipole resonances in the total extinction cross section of these particles. The physical mechanisms behind this sensitivity will be elaborated. Similar charge sensitivity on the anomalous scattering from dielectric (non-metallic) particles has been reported recently [15], based on blue-shifted magnetic scattering rather than on the inverted hierarchy as demonstrated in the present work.

## 2. Theory

Let us consider the scattering of light by a spherical particle of radius $a$ immersed in a medium with an index of refraction $n_m$. The extinction cross section is derived from the exact Mie solution [1]:

$$\sigma_{ext} = \sum_{l=1}^{\infty} \frac{2\pi}{k^2}(2l+1)\mathrm{Re}\left(a_l + b_l\right) \tag{1}$$

where summation $l$ is over all partial multipoles, $k = n_m\omega/c$ and $a_l$, $b_l$ are electric and magnetic scattering coefficients, respectively. These scattering coefficients can be written as (here we follow the notations of [4]):

$$a_l, b_l = \frac{F_l^{(a,b)}(q, \varepsilon)}{F_l^{(a,b)}(q, \varepsilon) + iG_l^{(a,b)}(q, \varepsilon)} \tag{2}$$

where $F_l^{(a,b)}$ and $G_l^{(a,b)}$ are defined in terms of the Riccati Bessel ($\psi_l$) and Neuman ($\xi_l$) functions as given in [1], $\varepsilon = \varepsilon_p(\omega)/\varepsilon_m(\omega)$ is the ratio between the dielectric function of the particle and that of the host medium, and $q$ is the dimensionless size parameter ($q = ka$). Here, $\varepsilon_m(\omega)$ is assumed to be purely real and positive, whereas $\varepsilon_p(\omega)$ is complex in general and given by $\varepsilon_p(\omega)=\varepsilon_p'(\omega)+i\varepsilon_p''(\omega)$. In order to allow for the excitation of surface plasmons, we will assume $\varepsilon_p'(\omega)$ to be negative. In addition, a necessary condition to observe anomalous scattering is with small $\varepsilon_p''(\omega)$. Thus we first consider the following idealized Drude model for the metal particle, assuming $\varepsilon_p''(\omega)=0$:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \tag{3}$$

where $\omega_p$ is the plasma frequency of the metal. As the frequency is swept, there will be a value of dielectric constant $\varepsilon$ for which $G_l^{(a)} = 0$. When this occurs, the $a_l$ coefficient in Eq. (2) will attain the maximum value of unity. For various $l$'s, this corresponds to resonant frequency of a multipole. Under the conditions of weakly absorbing metal, hierarchy in the scattering cross section of these resonances can be inverted, as referred to anomalous resonance by Tribelsky et al in [4].

In the long-wavelength or small particle size limit, we can expand the $F_l$ and $G_l$ in power series for small $q$ as follows [4]:

$$\begin{aligned}
F_l^a &\approx q^{2l+1}\frac{l+1}{[(2l+1)!!]^2}m^l(m^2-1)\\
G_l^a &\approx m^l\frac{l}{2l+1}\left\{\frac{l+1}{l} + m^2 - \frac{q^2}{2}(m^2-1)\left[\frac{m^2}{2l+3} + \frac{l+1}{l(2l-1)}\right]\right\}\\
F_l^b &\approx -\frac{mq^2}{2l+1}F_l^a\\
G_l^b &\approx -m^{l+1}\left[1 + \frac{1-m^2}{2(2l+1)}q^2\right]
\end{aligned} \tag{4}$$

where $m = \sqrt{\varepsilon_p/\varepsilon_m}$ is the relative index of refraction.

To study the effects of surface charge on the anomalous scattering of plasmonic particles, we apply the following modified Mie coefficients as first obtained by Bohren and Hunt [8] (in the notations of [16]):

$$\begin{aligned}
a_l &= \frac{\psi_l'(mq)\cdot\psi_l(q) - m\psi_l'(q)\cdot\psi_l(mq) - i\tau\psi_l'(mq)\cdot\psi_l'(q)}{\psi_l'(mq)\cdot\xi_l(q) - m\xi_l'(q)\cdot\psi_l(mq) - i\tau\psi_l'(mq)\cdot\xi_l'(q)}\\
b_l &= \frac{\psi_l'(q)\cdot\psi_l(mq) - m\psi_l'(mq)\cdot\psi_l(q) + i\tau\psi_l(mq)\cdot\psi_l(q)}{\xi_l'(q)\cdot\psi_l(mq) - m\psi_l'(mq)\cdot\xi_l(q) + i\tau\psi_l(mq)\cdot\xi_l(q)}\\
\tau &= iq\frac{\omega_s^2}{\omega\left(\omega + i\gamma_s\right)}
\end{aligned} \tag{5}$$

where $\gamma_s = k_B T/\hbar$ is the damping constant, and $\tau$ the charge parameter expressed in terms of the surface plasmon frequency of the extraneous charge given by $\omega_s^2 = Ne^2/m_e a^3$, with $N$, $e$, $m_e$ the total number, the charge, and the mass of the excess charge, respectively. Thus a surface potential can be defined as $V = Ne/4\pi\varepsilon_0 a$. The temperature $T$ is set to 300 K.

In the form of Eq. (2), the results in (5) can be put in the following form:

$$\begin{aligned}
a_l &= \frac{F_l^{(a)}(q,\varepsilon) + i\alpha_l^{(a)}(q,\varepsilon,\tau)}{\left[F_l^{(a)}(q,\varepsilon) - \beta_l^{(a)}(q,\varepsilon,\tau)\right] + i\cdot\left[G_l^{(a)}(q,\varepsilon) + \alpha_l^{(a)}(q,\varepsilon,\tau)\right]}\\
b_l &= \frac{F_l^{(b)}(q,\varepsilon) + i\alpha_l^{(b)}(q,\varepsilon,\tau)}{\left[F_l^{(b)}(q,\varepsilon) + \beta_l^{(b)}(q,\varepsilon,\tau)\right] + i\cdot\left[G_l^{(b)}(q,\varepsilon) - \alpha_l^{(b)}(q,\varepsilon,\tau)\right]}
\end{aligned} \tag{6}$$

where $\alpha$ and $\beta$ are correction terms to account for the surface charge and expansion to the lowest order of $q$ yields:

$$\begin{aligned}
\alpha_l^{(a)}(q,\varepsilon,\tau) &\approx \tau\cdot q^{2l}\frac{(l+1)^2}{[(2l+1)!!]^2}m^l(m^2-1)\\
\beta_l^{(a)}(q,\varepsilon,\tau) &\approx \tau\frac{l\cdot(l+1)}{2l+1}\frac{m^l}{q}\\
\beta_l^{(b)}(q,\varepsilon,\tau) &\approx -\tau\frac{m^{l+1}}{2l+1}q\\
\alpha_l^{(b)}(q,\varepsilon,\tau) &\approx \tau\frac{q^{2l+2}m^{l+1}}{[(2l+1)!!]^2}
\end{aligned} \tag{7}$$

From Eqs. (4) and (7) we observe that