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MULTIPOLAR EXCITATIONS IN SMALL METALLIC SPHERES

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ABSTRACT

A dielectric function $E(\omega,\ell)$ appropriate to a small metallic sphere is obtained within the semiclassical infinite barrier model, where ℓ is the multipole order. An excitation diagram in the ℓ,ω plane based on the structure of this function is proposed. It represents the spherical analog of the excitation structure of an infinite medium in the k,ω plane.

INTRODUCTION

It was many years ago that Fröhlich predicted that a small dielectric sphere would couple resonantly to an electromagnetic field by means of the excitation of a surface mode.[1] Such mode has been observed in particles of different materials in optical as well as electron scattering experiments.[2,3] A theory that uses a local dielectric function $\varepsilon(\omega)$ predicts an electric resonance at a frequency given by the solution of $\varepsilon(\omega) = -(\ell+1)/\ell$, where ℓ is the pole order of the applied external potential. Thus, in a uniform external field the dipole moment ($\ell=1$) is excited resonantly for $\varepsilon(\omega) = -2$. The width of the resonance is in this model determined by scattering of the surface excitations that sustain it. It is known on the other hand that nonlocal theories introduce a shift in the location of the resonance and modify its wings due to additional excitations including bulk plasmons and electron-hole pairs.[4,5] In the quantum limit of very small spheres (radius $a \lesssim 10$ Å) the spectrum is quite complex and contains many resonances due to a size effect that discretizes the energy levels in the available volume.[6] For not so small spheres ($a \sim 30$ Å or bigger) weak resonances associated with the excitation of bulk plasmons have been found assuming a bulk dielectric function may be used to characterize the response of the metal.[7] In this latter case resonances associated with quantum size effects are naturally absent.

In this paper we introduce the notion of a dispersion law in the frequency ω - angular momentum ℓ, plane. This is a useful adaptation to spherical excitations of the common ω-k representation. Its motivation is that spherical variables are more natural in the description of physical effects induced by geometry in the case of spheres. As we shall see explicitly for the case of not so small spheres a conceptually simple picture in terms of multipolar excitations emerges, emphasizing the main physical effects that take place when the particle is in the presence of an external probe that induces electromagnetic interactions.

THE DIELECTRIC RESPONSE FUNCTION $E(\ell,\omega)$

We assume that the bulk dielectric response of the metal is described by the nonlocal dielectric function $\varepsilon(\vec{k},\omega)$. The solution of the electromagnetic boundary problem for the interaction of the sphere with an external field requires in this case the specification of an additional boundary condition derived from the microscopic properties of the metal at the surface. We here adopt the one appropriate to the semiclassical infinite barrier model.[5] In this model the response of the sphere may be characterized by the sequence of multipolar polarizabilities[7]

$$\alpha_\ell(\omega) = \frac{E(\ell,\omega) - \varepsilon_o}{E(\ell,\omega) + \frac{\ell+1}{\ell}\varepsilon_o} \,. \tag{1}$$

Here ε_o is the dielectric constant of the medium the particle is placed in. This formula is identical in form to the corresponding local expression only that the dielectric function of the metal appears in the modified form

$$E(\ell,\omega) = \left[\frac{2}{\pi}(2\ell+1)a\int_o^\infty \frac{j_\ell^2(ka)}{\varepsilon(k,\omega)}\,dk\right]^{-1} , \tag{2}$$

where $j_\ell(x)$ is the spherical Bessel function of order ℓ. Notice that $E(\ell,\omega)$ equals the usual dielectric function $\varepsilon(\omega)$ when the latter is k-independent (local). We shall adopt it as a characterization of the response of the sphere to an external potential of pole order ℓ and frequency ω.

EXCITATION DIAGRAM IN THE ℓ,ω PLANE

Figure 1 represents the structure in $E(\ell,\omega)$ for a tin sphere of radius 30 Å.[8] Such structure is best brought about by the maxima in the function $R = \mathrm{Im}\left(E(\ell,\omega)-1\right)^{-1}$. Three features are included in this graph. First there is the Fröhlich resonance labeled FR and extending through large values of pole order ℓ. For the case studied it represents the most prominent resonance. It is the only feature present if a local dielectric function is assumed, a case also included in the figure and labeled D since the Drude model was used to obtain it. Notice that nonlocal effects shift the resonance far into the high energy region of the graph. A second feature is the sequence of resonances above ω_p. These correspond to the weak excitation of a bulk plasmon and its harmonics in the presence of the sphere boundary. Finally, there is the region where electron-hole pairs are created, delimited in our figure by the rising dotted lines. These are the only excitations possible at low frequencies. Unlike the other cases in which lines in the figure correspond to resonances, here we encounter a broad region where multipolar coupling is possible. The edges were arbitrarily set by the condition that the quantity R reached its maximum value divided by 80 when a relaxation time appropriate for the bulk metal is used.

In the ω vs k representation one gets an approximate expression for the electron-hole edges by requiring that energy and momentum be conserved when the incoming photon takes an electron above the Fermi surface and a hole is left behind. We can here use this same condition to sketch our edges if we keep in mind that the wavelength of an excitation at the surface is approximately the sphere perimeter over ℓ, or $ka = \ell$. Using these relations we get

$$\omega_{\pm} = \frac{\hbar}{ma^2} (\ell \pm 2ak_F)\ell \tag{3}$$

where k_F is the Fermi wave vector, m the electron mass and ± refers to the left (right) edge. We remark that, as Eqs. (2) and (3) show explicitly the details of the ω vs ℓ graph depend on the radius of the sphere as well as the metal the particle is made of. The curves given by (3) are the rising dashed lines in the figure. The small discrepancy at the right edge is a manifestation of the arbitrariness of the criterion used in drawing the dotted lines, as explained above. The slope of these lines is correctly given by (3), however, providing evidence that the physical picture conveyed by our diagram is essentially correct.

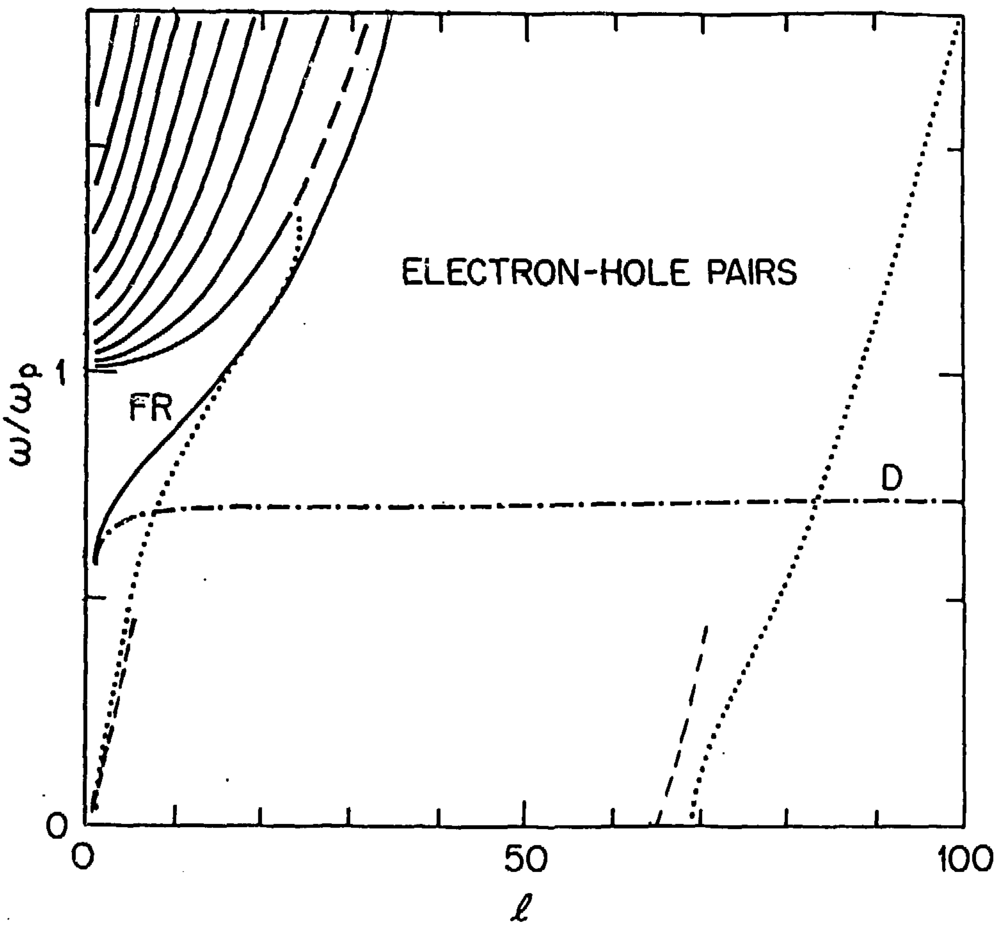

Fig. 1. Dispersion curves of the multipolar resonances for a 30 Å radius tin sphere in the multipole order ℓ - frequency ω, plane. Full lines follow resonances for the Lindhard-Mermin model while the dash-dotted line is the Fröhlich resonance (FR) in the Drude (D) model. The dashed lines rising from the bottom follow Eq. (3).

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