

Optical spectroscopy of metallic icosahedral nanoparticles: classical versus atomistic description

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Abstract

Progress in nanotechnology has allowed control of metallic nanoparticles at the nanometer and even subnanometer scale. Some of the most fascinating properties and applications of plasmonic nanoparticles are based on the tunability of their optical response and their ability to localize the electromagnetic fields around tips or at inter particle gaps. The near-fields are commonly addressed theoretically within classical frameworks. However, in some situations the atomic structure needs to be considered to correctly determine the response of the nanosystem [1].

In this work we study the far- and near-field response of metallic nanoparticles and compare three different models. i) First, we use a classical modeling within a boundary element method (MNPBEM) [2-3], which considers abrupt boundaries between media with homogeneous and isotropic dielectric functions to solve Maxwell's equations. Because the mean free path of the electrons is comparable to the size of the particles considered, the billiard model is used to approach surface scattering effects [4-5], with the resulting increase of damping in the dielectric function. ii) Secondly, we consider a discrete dipole approximation (DDA), in which each atom of the nanoparticle is described as a dipole [6] and the atomistic structure is preserved. iii) Finally, our results are compared with atomistic ab-initio time-dependent density functional theory (TDDFT) calculations [1].

We show that the general patterns of subnanometric localization and enhancement of fields can effectively be approached by classical means. The presence of tips and sharp endings in the geometry of the particle introduces a major enhancement and localization of the near-fields. Nevertheless, for the case of close particle dimers, differences arise due to the lack of quantum tunneling effects in the classical descriptions. In Figure 1) we show the near-field enhancement and the absorption cross section for a dimer of sodium icosahedral particles of radius 1.6 nm, as calculated in the classical BEM model.

References

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Figures

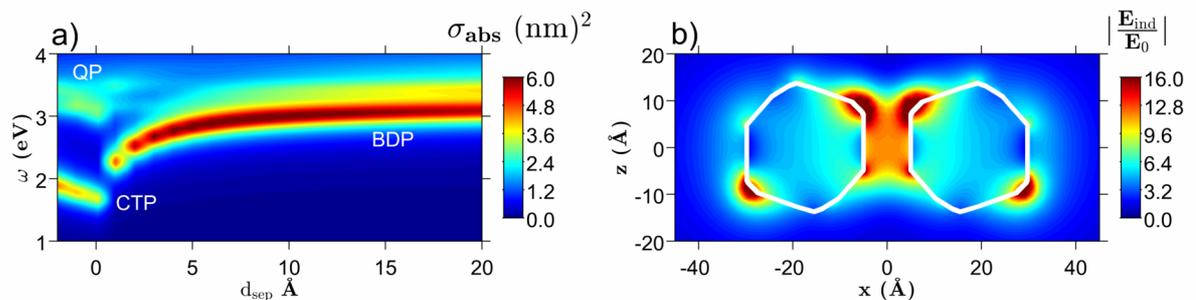


Figure 1: a) Absorption cross section of a facet-to-facet configuration of a Na icosahedral dimer for varying separation distances. The circumscribed radius of the icosahedral particles is $r = 1.6$ nm and the polarization of the external field parallel to the dimer axis. b) Field enhancement for a separation distance of $d_{\text{sep}} = 1$ nm at energy corresponding to the bonding dimer plasmon (BDP) shown in plane a).