Unveiling atomic-scale features in plasmonic nanoparticles using light and electron beams

M. Urbieta[1,2]
M. Barbry[2], P. Koval[2], Y. Zhang[2], A. Rivacoba[2], D. Sánchez-Portal[2], J. Aizpurua[2] and N. Zabala[1,2]

[1] UPV/EHU, FCT/ZTF, Department of Electricity and Electronics, Barrio Sarriena s/n, 48940, Leioa, Spain
[2] CFM-MPC, Centro Mixto CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, 20018, San Sebastian, Spain; Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018, San Sebastian, Spain

mattin.urbieta@ehu.eus

Plasmonic nanoparticles (NPs) are known to produce localization and enhancement of electromagnetic fields, providing nanometer- scale effective mode volumes. Atomistic quantum calculations based on Time-Dependent Density Functional Theory (TDDFT) reveal the effect of subnanometric localization of optical fields due to the presence of atomic-scale features at the surface of metallic NPs (Fig. 1) and interparticle gaps [1]. Using classical electrodynamics (Boundary Element Method, BEM), we explain this effect as a non-resonant lightning rod effect at the atomic scale that produces an extra enhancement over that of the plasmonic background [2]. We have further studied this effect for plasmons excited with fast electrons and calculated the electron energy loss spectra (EELS) of electron beams passing nearby and through the same atomistic structures [3]. The results reveal great influence of the atomic-scale features on the localized surface plasmons (LSPs, and the failure of the classical description to address the confined bulk plasmons (CBPs) observed in the TDDFT calculations (Fig. 2). The latter are similar to CBPs observed within the spherical hydrodynamic model [4]. These findings bear out the importance of a proper consideration of the atomic-scale shape of nanoparticles in EEL spectroscopy.

References

[1] M. Barbry, et al., Nano Lett., 15, 3410-3419 (2015)
[2] M. Urbieta, et al., ACS Nano, 12, 585–595 (2018).
[3] M. Urbieta, et al. (in preparation)
[4] T. Christensen, et al., ACS Nano, 8, 1745–1758 (2014).

Figures

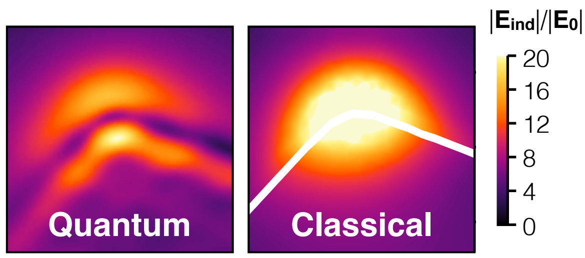

Figure 1: Zoom-in of the near-field maps around the tip of a Na icosahedral nanoparticle illuminated with linearly polarized light, at the energy of the dipolar plasmon, as calculated using TDDFT (left) and BEM (right).

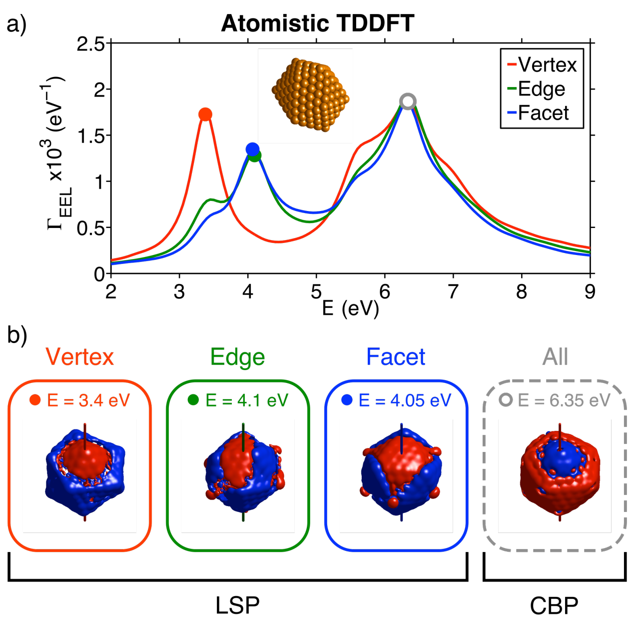

Figure 2: Electron energy loss spectra for the Na icosahedral cluster calculated using TDDFT for electron trajectories penetrating the NP through different atomic-scale features. b) Charge density isosurfaces corresponding to the main excited plasmon modes for each trajectory.