Unveiling atomic-scale features in plasmonic nanoparticles using electron beams

M. Urbieta[1,2]
M. Barbry[2], E. Ogando[3], P. Koval[2], A. Rivacoba[2], D. Sánchez-Portal[2], J. Aizpurua[2] and N. Zabala[2,4]

[1] *UPV/EHU, Faculty of Engineering Gipuzkoa, Department of Applied Physics I, Otaola Etorbidea 29, 20600, Eibar, 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*
[3] *UPV/EHU, FCT/ZTF, Department of Physics, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain*
[4] *UPV/EHU, FCT/ZTF, Department of Electricity and Electronics, Barrio Sarriena s/n, 48940, Leioa, Spain*

mattin.urbieta@ehu.eus

Electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM), together with optical spectroscopies, has played a crucial role in understanding the properties and dynamics of plasmons in nanoparticles (NPs). In particular, technical progress in the performance of STEM-EELS microscopy in the last two decades has enabled sub-nanometer resolution and sub-eV energy sensitivity in EELS, opening new opportunities for characterization of novel materials and nanostructures. In this sense, *ab initio* atomistic methods such as Time-Dependent Density Functional Theory (TDDFT) provide an appropriate quantum framework to consider sub-nanometric atomistic features in plasmonic NPs [1,2]. Indeed, most of the classical and semiclassical theories rely on spherical descriptions of the NP's geometry, disregarding any dependence of the NP's shape and orientation on the electron energy loss (EEL) spectra. We have studied within atomistic TDDFT the influence of atomic-scale features in small plasmonic NPs on the EEL spectra of electron beams passing nearby and through atomistic NPs, revealing that EEL spectra strongly depend on the orientation of the atomistic clusters (Fig 1). Moreover, we show that classical electrodynamics (Boundary Element Method, BEM) models are able to reproduce the EEL spectra corresponding to localized surface plasmons (LSPs), if the shape of the NP is properly described, but fail to address the confined bulk plasmons (CBPs) observed in the TDDFT calculations [3]. The CBPs show correspondence with those observed within hydrodynamical models for spherical NPs [4]. These findings bear out the importance of a proper consideration of the atomic-scale shape of nanoparticles in EEL spectroscopy.

References

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Figures

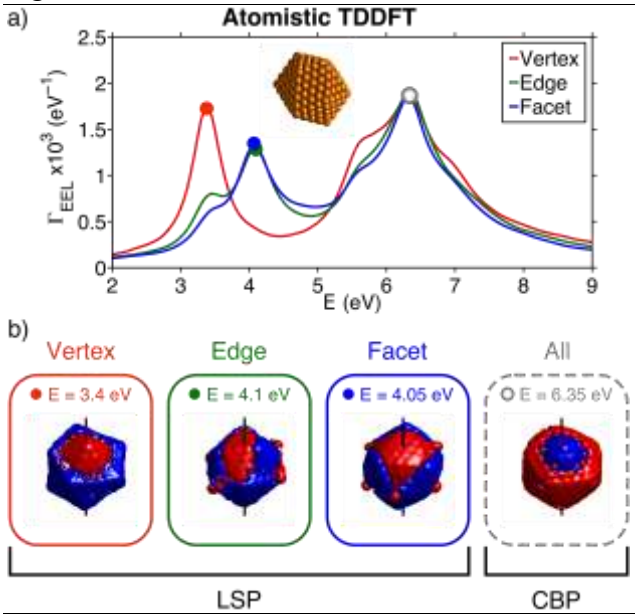

Figure 2: Electron energy loss spectra for the Na icosahedral cluster calculated using TDDFT for electron trajectories penetrating the NP through different atomic-scale features. b) Charge density isosurfaces corresponding to the main excited plasmon modes for each trajectory.