Unveiling the quantum nature of plasmons in metallic nanoparticles with electron beams

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Advances in electron microscopy have enabled the study of metal nanoparticles with subnanometer spatial resolution, providing a powerful tool for characterizing plasmonic excitations [1]. Most theoretical works describe the nanoparticles as spherical objects, although electron energy loss spectroscopy (EELS) which is sensitive to the shape of the target, reveals the influence of atomic scale features and faceted boundaries in the loss spectra.
We performed calculations of the EEL probability in isolated icosahedral clusters composed of 380 Na atoms using both and an efficient atomistic ab-initio TDDFT code [2], and a continuous classical BEM [3] method within a local dielectric framework. Three different shapes were considered for the latter (radius~2 nm),): a sphere, a regular icosahedron, and a smoothed irregular icosahedron resembling the electron density landscape obtained within atomistic TDDFT.
The results prove a high dependence of localized surface plasmons (LSPs) on the shape of the particles and the particular trajectory of the electrons and the failure of the classical description to address the spectral structure of confined bulk plasmons (CBPs). We use an additional spherical hydrodynamic model [4] to analyze the CBP excitations obtained in the TDDFT calculations. These findings bear out the importance of a proper consideration of the atomic-scale shape of nanoparticles in EEL spectroscopy, while highlighting the strengths and limitations of classical approximations to nanophotonics.

References

[1] A. L. Koh, K. Bao, I. Khan, W. E. Smith, G. Kothleitner, P. Nordlander, S. A. Maier, D. W. McComb, ACS Nano, 3, 3015-3022 (2009); S. Kadkhodazadeh, J. Rosenkrantz de Lasson, M. Beleggia, H. Kneipp, J. Birkedal Wagner, K. Kneipp, J. Phys. Chem. C, 118, 5478– 5485 (2014).
[2] M. Barbry, P. Koval, F. Marchesin, R. Esteban, A. G. Borisov, J. Aizpurua, D. Sánchez-Portal, Nano Lett., 15, 3410-3419 (2015); M. Urbieta, M. Barbry, Y. Zhang, P. Koval, D. Sánchez-Portal, N. Zabala, and J. Aizpurua, ACS Nano, 12, 585–595 (2018).
[3] F. J. García de Abajo, A. Howie, Phys. Rev. B, 65, 115418 (2002); U. Hohenester, Comput. Phys. Commun, 185, 1177-1187 (2014).
[4] T. Christensen, W. Yan, S. Raza, A. P. Jauho, N. A. Mortensen, and M. Wubs. ACS Nano, 8, 1745–1758 (2014).

Figures

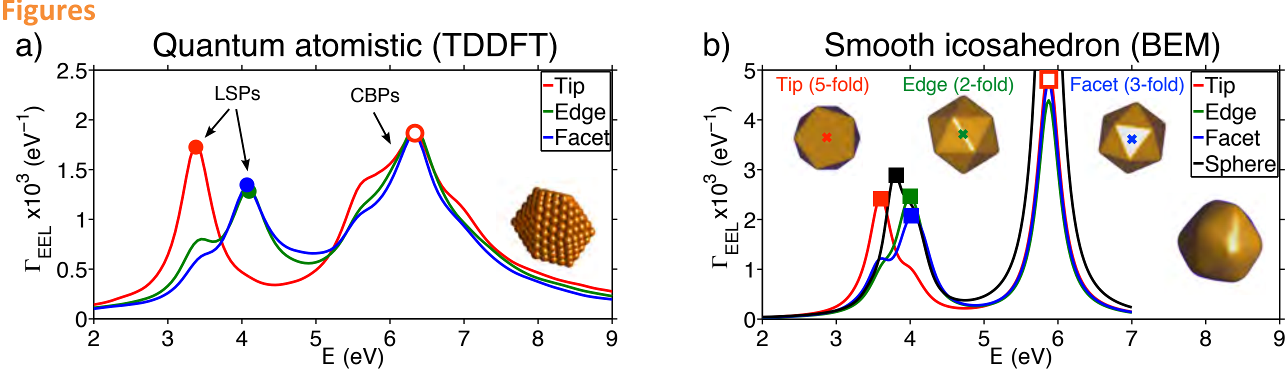

Figure 1. EEL spectra calculated for a) a Na380 cluster with TDDFT and b) an smoothed irregular icosahedron with BEM.