

Optical Properties of Noble Metal Clusters: Comparing Non-local Classical and TDDFT Calculations

Rajarshi Sinha Roy^{1,2,3}, H.-Ch. Weissker^{1,2}, P. García González^{2,3}, A.I. Fernández-Domínguez³

¹CINaM & Aix-Marseille Université, 13288 Marseille, France.

²European Theoretical Spectroscopy Facility (ETSF)

³Departamento de Física Teórica de la Materia Condensada and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid (UAM), E-28049 Madrid, Spain.

sinharoy@cinam.univ-mrs.fr

The Localized Surface-Plasmon Resonance (LSPR) in quantum-sized noble metal clusters (~1-3nm) is being widely used in numerous applications in biological sensing/detecting technology. The LSPR depends on size, composition and geometry of the clusters. It is well known that the resonance energy of the LSPR is strongly red-shifted with increasing aspect ratio of the clusters as is well described by classical local theory [1-3]. In model clusters of Au and Ag, full quantum calculations using time-dependent density-functional theory (TDDFT) have shown deviations from this classical behavior [4]. The different contributions to the spectra have also been analyzed [5,6]. To study the deviations in the behavior of the LSPR in particles having very small sizes (~1nm), the non-local nature of the bulk dielectric response has been incorporated into classical electrodynamics through a density-dependent hydrodynamic model [7]. Moreover, good agreement with experiments is found by using these non-local effects described in the local analogue model (LAM) [8].

In this work we present a comparative study of the full quantum analysis of model noble-metal nanorods of different sizes and aspect ratios with classical local and non-local calculations. For the non-local classical calculations, where the non-locality is described by the LAM, complex Lorentz-Drude fitted dielectric functions [9] are used. On the other hand, the TDDFT calculations are carried out using the time evolution method by means of the octopus code.

References:

- [1] J. Alan Creighton and Desmond G. Eadont, *J. CHEM. SOC. FARADAY TRANS.*, 1991, 87(24), 3881-3891
- [2] M. A. El-Sayed, *Acc. Chem. Res.*, 2001,34, 257
- [3] T. Jun, L. Yong-Hua, Z. Rong-Sheng, L. Kai-Qun, X. Zhi-Guo, L. Zhao-Feng, L. Sheng-Li, W. Pei, M. Hai, *Chin. Phys. Lett.* 2008, Vol. 25 Issue (12): 4459-4462
- [4] X. López Lozano, H. Barron, C. Mottet and H.-Ch. Weissker, *Phys. Chem. Chem. Phys.*, 2014, 16, 1820–1823
- [5] Emilie B. Guidez and Christine M. Aikens, *J. Phys. Chem. C*, 2013, 117, 12325–12336
- [6] G. M. Piccini, R. W. A. Havenith, R. Broer, M. Stener, *J. Phys. Chem.C*, 2013, 117, 17196–17204
- [7] S. Raza, G. Toscano, A.-Pe. Jauho, M. Wubs, N. A. Mortensen, *PRB* 84, 121412(R) (2011)
- [8] Y. Luo, A. I. Fernandez-Dominguez, A. Wiener, S. A. Maier, J. B. Pendry, *PRL* 111, 093901 (2013)
- [9] A. D. Rakic, A. B. Djurišić, J. M. Elazar, M. L. Majewski, *APPLIED OPTICS / Vol. 37, No. 22 / 1 August 1998*. doi: 10.1364/AO.37.005271