Nanoplasmonics by a Mixed Atomistic-Continuum Classical Approach

Pablo Grobas Illobre
Luca Bonatti, Tommaso Giovannini, Chiara Cappelli
Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy.
pablo.grobasillobre@sns.it

Most properties of plasmonic nanostructures follow from the tunability of their optical response as a function of their shape and dimensions [1-3]. The accurate description of the optical properties of the nanoparticles is crucial for a theoretical understanding of the physical phenomena occurring at the plasmon resonance frequency [4]. In this context, we have recently presented an atomistic, yet classical, approach to predict the optical properties of nanostructures of complex shapes. The approach, which is called ωFluctuating Charges Fluctuating Dipole(ωFQFμ), is based on the Drude model for conduction in metals, classical electrostatics, quantum tunneling [5] and introduce an atomic polarizability to model interband effects [6]. The model is able to reproduce all typical "quantum" size effects arising in noble metal nanoparticles, such as the sign and the magnitude of the plasmon shift, the progressive loss of the plasmon resonance for gold, the atomistically detailed features in the induced electron density, and the non-local effects in the nanoparticle response. Moreover, the approach has shown a qualitative and quantitative agreement with full *ab initio* calculations [5]. The classical nature of ωFQFμ allows for the treatment of systems composed by thousands of atoms [6-7]. However, in order to be applied to even more realistic cases (with size of tens/hundreds nm), its computational cost needs to be further decreased. In this contribution, we present a step forward in this direction by coupling ωFQFμ with the well-known Boundary Element Method (BEM) [8-10], which models the nanostructure as a homogenous continuum through its dielectric function. In the resulting ωFQFμ/BEM approach [11], the core of the nanoparticle is described at the BEM level, whereas the surface retains its atomistic nature. In this way, finite size and edge effects are preserved in a simple and affordable computational way. Here, the theoretical method is presented and applied to selected test cases, demonstrating the reliability of the approach.

This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 818064).

References

[1] V. Giannini, A.I. Fernández-Domínguez, S.C. Heck, S. A. Maier, Chem. Rev., 111 (2011) 3888
[2] K. Lee, M. A. L-Sayed, J. Phys. Chem. B, 110 (2006) 19220.
[3] L. J. Sherry, S. H. Chang, G.C. Schatz, R.P. Van Duyne, B.J. Wiley, Y. Xia, Nano lett., 5 (2005) 2034
[4] J.L. Payton, S.M. Morton, J. E. Moore and L. Jensen, Acc. Chem. Res., 47 (2013) 88-99
[5] T. Giovannini, M. Rosa, S. Corni, C. Cappelli, Nanoscale, 11 (2019) 6004
[6] T. Giovannini, L. Bonatti, P. Lafiosca, L. Nicoli, P. Grobas Illobre, S. Corni, C. Cappelli, submitted
[7] P. Lafiosca, T. Giovannini, M. Benzi, C. Cappelli, J. Phys. Chem. C., 125 (2021) 23848
[8] F. Garcia de Abajo, A. Howie, Phys. Rev. B, 65 (2002) 115418
[9] S. Corni, J. Tomasi, J. Chem. Phys., 116 (2002) 1156
[10] U. Hohenester, A. Trügler, Comput. Phys. Commun., 183 (2012) 370-381.
[11] P. Grobas Illobre, L. Bonatti, T. Giovannini, S. Corni, C. Cappelli, in preparation