New Trends in Computational Plasmonics

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Plasmonics has seen an incredible boost during the past few decades as a promising route for nanophotonic devices. Metallic elements act as optical antennas and can strongly enhance the efficiency of several photophysical phenomena.
The resonant coupling between light and metallic (or heavily doped semiconductor) nanostructures enables the possibility to squeeze the electromagnetic fields in sub-wavelength volumes, greatly enhancing optical absorption and scattering phenomena. Electrodynamics methods have been proven to be useful and powerful tools to theoretically investigate and optimize plasmonic systems with respect to their macroscopic interactions with absorbers or emitters placed in their proximities[1]. Anyway, with the help of new fabrication techniques it is nowadays possible to realize very narrow junctions or nanogap features between larger metallic elements, so that control of light-matter interactions can be achieved at the sub-nanometer scale. This requires to adopt new theoretical schemes able to overcome the limits of the classical vision and to go towards "quantum".

Recent experimental studies have demonstrated in fact, that quantum mechanical effects, such as *electron spill-out* and *tunneling* as well as *nonlocal screening*, cannot be neglected as distances between metallic elements approach the sub-nanometer length-scale[2]. Such quantum mechanical effects have thus operated a revolution in plasmonics, stimulating a number of theoretical and experimental studies aiming to describe the atomistic structure of matter. In this talk, an overview on the last developments in computational plasmonics, highlighting their limits and potentialities, is given with the idea to stress the trends and identify the challenges in the field. Several efforts have already been done to include quantum effects in the calculation of the optical properties of nanoparticles by introducing non-local corrections to the classical dielectric constant[3] or by recurring to the *Jellium-Model* based TD-DFT (*Time Dependent Density Functional Theory*) approach[4]. However, such calculations neglect the atomistic nature of matter and as a consequence they do not success in describing experimental results, highlighting the need for better models to take into account the quantum behavior of electrons. Standard TD-DFT seems to be, thus, the most suitable approach for a complete quantum mechanical treatment of nano-plasmonic systems but it becomes computationally unaffordable for particle sizes of the order of several hundreds or thousands of atoms. To this regards, *Density Functional-based Tight-Binding Approximation*, together with its Time-Dependent (DFTB) derivation, seems to be a promising frontier of computational plasmonics[5]. DFTB is based on the second order expansion of the *Kohn-Sham* energy functional around a reference density of neutral atomic species and it can be proved to be an efficient scheme for describing the optics of plasmonic systems under particular conditions. With an appropriate choice of the *Slater-Koster* parametrization, results that are in good agreement with *Ab Initio* calculations can be achieved at a much reduced computational cost. This opens the avenues towards a new era of plasmonics and, in particular, molecular plasmonics.

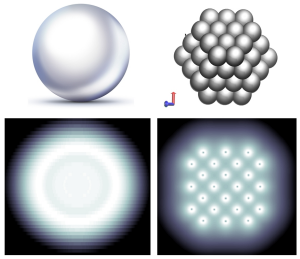

Figure 1. Jellium model (left) and fully-atomistic (right) groundstate electron density for a NP within DFT.

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[2] W. Zhu et al., Nature Comms., 7 (2016) 11495
[3] C. Ciracì et al., Phys. Rev. B 93 (2016) 205405
[4] D. C. Marinica et al., Nano Lett., 13 (2013) 5972
[5] C. F. A Negre et al., J Phys Condens Matter. 25 (2013), 125304.