Modeling Plasmonics and Molecular Plasmonics from an Atomistic Perspective

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Abstract: This study presents an atomistic yet classical approach coupled to a QM Hamiltonian, to predict plasmonic properties of nanostructured materials. The method enables large-scale simulations, also capturing quantum effects. Remarkably, it accurately reproduces computed reference data and experiments.

The optical response of plasmonic nanostructures can be tuned by varying their shape, size, and chemical composition [1]. Peculiar phenomena arise when a molecular system is adsorbed on the surface of plasmonic materials, ranging from surface-enhanced spectroscopies to photocatalysis [2]. The accurate description of the optical properties of the plasmonic substrates is thus crucial for an understanding of the physical phenomena occurring at the plasmon resonance frequency.

We present an atomistic, yet classical, approach to predict the plasmonic properties of nanostructures of complex shapes. The method is general enough to describe any plasmonic material, including noble metal nanoparticles (Ag and Au) [3] and metal alloys [4]. The approach is also coupled to a quantum mechanical (QM) description of the molecular system adsorbed on the nanostructure surface [5]. The resulting mixed QM/classical method is then extended to various spectral signals, e.g. surface-enhanced Raman scattering.

We show that our classical approach for plasmonics can correctly reproduce reference ab initio data [3], and experimental trends [3-4], and can be applied to large-scale nanoplasmonic simulations (more than 1 million atoms). By properly accounting for the atomistic discretization of matter, we can accurately describe the nanoplasmonics of systems dominated by quantum effects, such as subnanometer junctions [3,6], geometrical defects [8], and Gold picocavities [8]. Finally, we discuss the current challenges in the prediction of surface-enhanced spectroscopies, analyzing the performance of our methods, also by comparison with experiments [5].

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).

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