Density Functional Tight Binding Method for Plasmonics

Giulia Giannone[1]
Stefania D'Agostino[2]
Rosaria Rinaldi[1]
Gianaurelio Cuniberti[3]

giulia.giannone@live.it

[1]Department of Mathematics and Physics "E. De Giorgi", University of Salento, Via Arnesano, 73100 Lecce, Italy.
[2]Center for Biomolecular Nanotechnologies @ UNILE - Istituto Italiano di Tecnologia, 73010 Arnesano, Italy.
[3]Institute for Materials Science, TU Dresden, 01062 Dresden, Germany.

Electrodynamics methods have been proved to be useful and powerful tools to theoretically study localized and delocalized surface plasmons [1]. The recent progress achieved in fabrication techniques to control subnanometer structures and features has lead to search for more rigorous approaches able to theoretically describe nonlocality or the spill-out of conduction electrons, effects well visible in very narrow junctions or subnanometers gaps [2].

Standard atomistic ab-initio *Time-Dependent Density Functional Theory* (TD-DFT) is the most suitable approach for a complete quantum mechanical treatment of plasmons [3] but it becomes computationally unaffordable for particle sizes of several hundreds of atoms.

Here we alternatively propose a *Time-Dependent Density Functional Tight-Binding Method* (TD-DFTB) study [4] on silver dimers done using an optimized Slater-Koster parametrization. More in detail, we study the plasmonic response of dimers of closed-shell Ag_n (n=10, 20, 35, 56, 84 and 120) tetrahedral clusters (tip-to-tip configuration) as well as Ag_{116} cuboctahedral clusters (face to face configuration) as a function of the nanogap size (from 2 Å to 20 Å). Atom positions are fixed to the ones obtained by relaxing the isolated clusters within standard DFT (TURBOMOLE code) and geometries are re-optimized only for the smallest gaps (2 Å and 4 Å).

A red-shift in the plasmonic peak can be clearly seen in Fig. 1 by reducing the interparticle distance until 6 Å, this being due to the clusters mutual depolarization. For smaller distances, a blue-shift effect appears for both the structures, this proving the onset of a quantum mechanical effect already evidenced in literature within other approaches [5]. Moreover, it should be noted as the coupling effects, both in the near-field and in the near-touching regimes, become stronger as the number of interacting atoms becomes larger (Fig. 1b). With a computational cost much smaller with respect to standard TD-DFT one, TD-DFTB seems thus to be a useful method to overcome the limits of classical description and thus to favor the spread of computational quantum plasmonics.

References

1. S. D'Agostino et al., ACS Nano, 9, 9691 (2015).
2. W. Zhu et al., Nature Comms., 7, 11495 (2016).
3. L. R. Madison et al., Progress in Theoretical Chemistry and Physics, 29, 37 (2015).
4. C. F. A Negre et al., J Phys. Condens. Matter, 25, 125304 (2013).
5. M. Barbry et al., Nano Lett., 15, 3410 (2015).

Figures

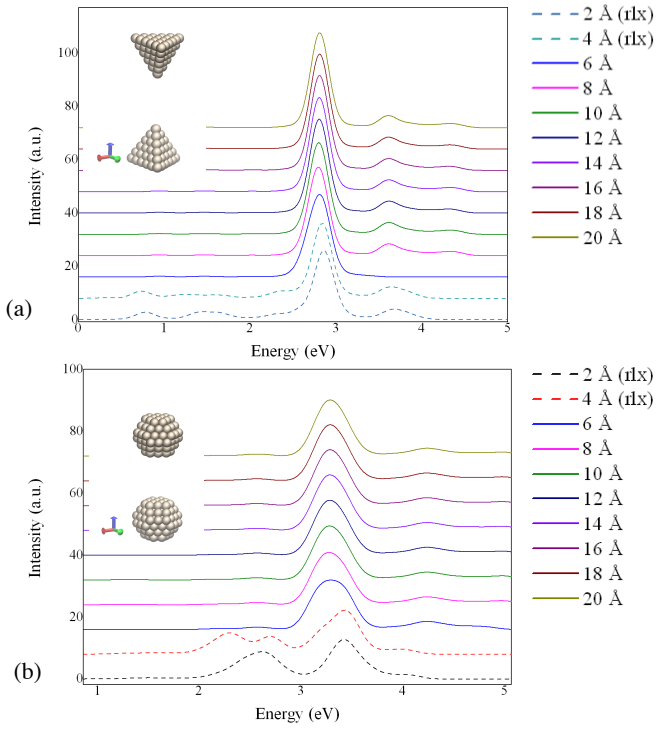

Figure 1. TD-DFTB efficiency calculated for dimers of tip-to-tip closed-shell Ag120 tetrahedrons (a) and face-to-face Ag116 cuboctahedrons (b). Separation gaps from 2 Å to 20 Å are analyzed with the spectra reported from the bottom to top side of the panels, respectively. Geometries are sketched in the insets.