Extensions to the ab-initio TDDFT code MBPT-LCAO

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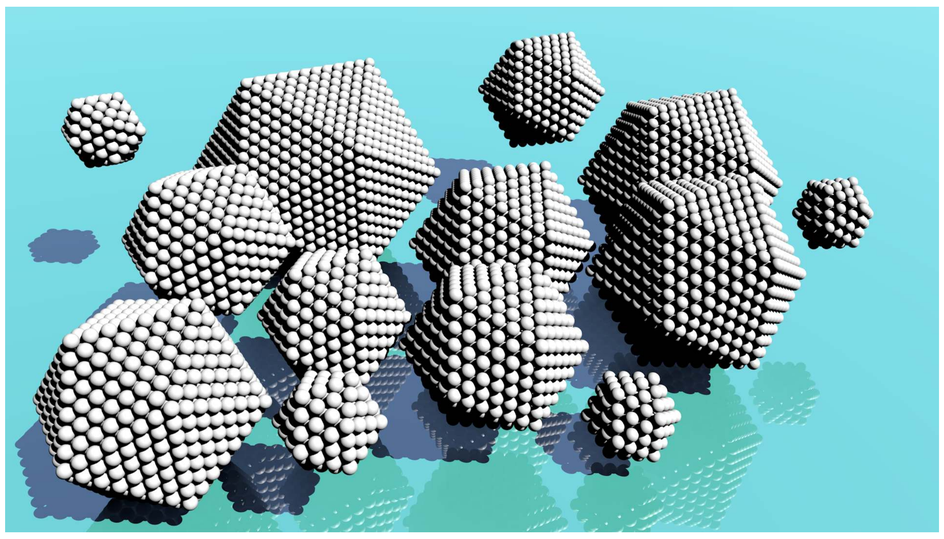
MBPT-LCAO: an efficient ab-initio program



We are currently developing an efficient ab-initio program called "mbpt-lcao" (many body perturbation theory with localized basis) that implements TDDFT, GW and BSE calculations for finite systems and is now extended to periodic systems [1, 2]. The implementation of TDDFT in the linear response regime uses the locality of atomic orbitals to expand the wave functions and employs the results of the DFT code Siesta [3], allowing the study of the optical response of systems up to thousands of atoms [4, 5].
The iterative algorithm implemented into this method has an $O(N^3)$ computational complexity [1], where N is the number of electrons in the system, and requires an $O(N^2)$ memory usage, enabling a relatively fast calculation of the interacting polarizability in plasmonic systems. Although our algorithm possesses a reasonably high asymptotic computational complexity, the method is relatively inexpensive in terms of computational resources. We successfully managed to run some tests with silver clusters of increasing sizes (from 147 to 2057 atoms) using only a few processors.

Our Goal

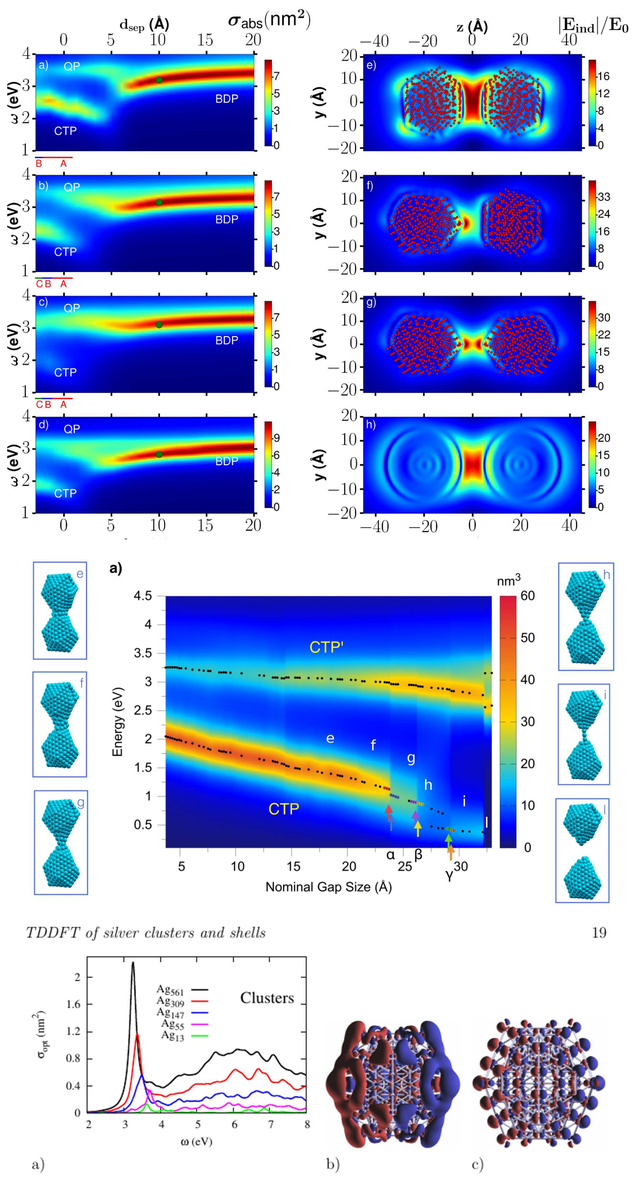
The aim of the code is to calculate the density change δn induced by an external perturbation $V_{\text{ext}}(r)$:

$$\delta n(r,\omega) = -\int \chi(r,r',\omega) V_{\text{ext}}(r') dr', \qquad (1)$$

where χ is the interacting response function.

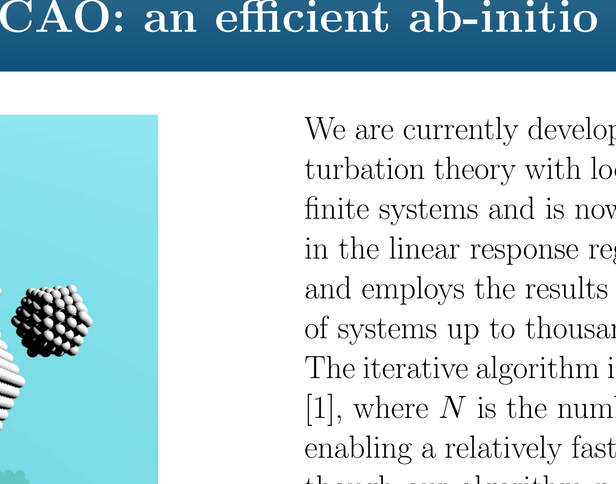
Optical response of small sodium and silver clusters

Until recently, we worked with Na dimers containing up to 760 atoms and 561 atoms for Ag clusters.



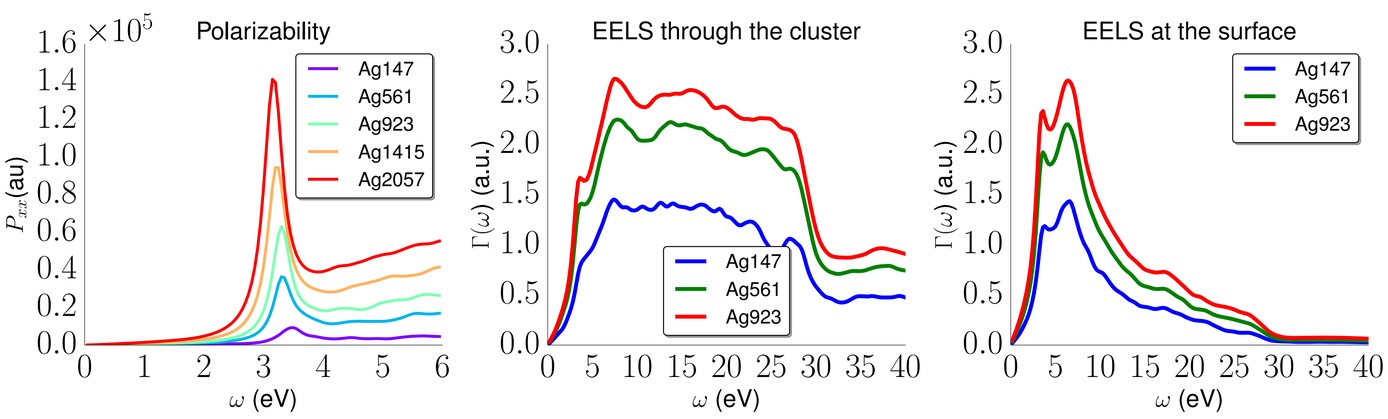
The top plot represents the polarizability of 380 Na dimers with different gap sizes between the clusters (left column) and the electric field distribution along the dimer axis at resonance (right column) from [4]. The middle plots represent the polarizability of a 380 Na dimer but with relaxed geometry while the two clusters, that have entered into contact, are retracted and a metal neck that connects both clusters has formed [5]. The last row represents the polarizability of Ag clusters (left column) and the density change distributions (right column) from [2].

Electron Energy Loss from small sodium clusters



EELS spectra for several trajectories and an electron with an energy of 100 keV. The electron trajectories are going from the center of the cluster until far away from the cluster surface (Figure e). The dashed line represents the position of the cluster surface. The Figures b, c, and d show the density change at the surface of the cluster for the energy and impact parameters represented by the dots α, β, δ on Figure a.

Optical response and EELS from large silver clusters



Conclusion

- With the MBPT-LCAO program, we managed to show the influence of the geometry on the field distribution in the neighborhood of sodium dimers [4], and how the plasmonic response of the system can be dramatically modified by structural changes involving single atom motions [5].
- A method to compute EELS was implemented, allowing us to use the external potential created by a fast moving charge. The computation of EELS spectra for sodium clusters reveals the excitation of many modes that are silent to light excitation.
- Recent improvement to the code allowed us to reach cluster sizes that could not be addressed before (more than 2000 silver atoms) and we will be soon able to get the polarizability of systems up to 5000 atoms.

References

[1] P. Koval et al., J. Chem. Theo. Comput. 6, 2010.
[2] P. Koval et al., J. Phys.: Condens. Matter 28, 2016
[3] J. M. Soler et al., J. Phys.: Condens. Matter 14, 2002
[4] M. Barbry et al., Nanolett. 15, 2015
[5] F. Marchesin et al., ACS Photonics 3, 2016

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