Report on the ETSF Training Project

Improvement of the theoretical background for the study of the optical properties of TiO_2 nanostructures

During my training project I calculated the optical spectrum of a TiO_2 cluster made of 29 molecular units, within the TDDFT framework, with a real time and real space approach implemented in the Octopus code[1]. I initially tested the computational demand with respect to the number of atoms in the cluster and then the dependence of the optical spectra with respect to different pseudopotentials, with and without semicore states. This test highlighted the importance of employing reliable semicore pseudopotentials in order to obtain meaningful results. Since the final goal is to study the interaction of a dye molecule with a TiO_2 nanostructure, I did recognized the systems that can be effectively calculated with respect to the computing features of the Octopus code in a multiprocessors machine.

I performed TDDFT calculations both within the time propagation and the Casida approach, to estimate both the accuracy of the optical properties calculation and the computing efforts with respect to the theoretical scheme. The Casida approach results to be faster than the time propagation, but more difficult to converge with respect to the number of unoccupied bands. In any case, it is useful to identify the onset and the low energy part of the optical spectrum. To highlight the role of a proper description of electronic corraletion on optical properties, I also planned the use of a many-body scheme based on the GW correction and the Bethe-Salpeter equations, as implemented in the Yamboo code[2]. These methods were used first to calculate the optical spectrum of the TiO_2 anatase crystal phase. Then I started to apply them to the cluster TiO_2, also to produce reference results for the calculations of the optical properties of the complex made up of a TiO_2 nanostructure with a dye molecule. The calculations of GW+BSE for this kind of nanostructure are however extremely computationally demanding, and they are still going on.

This training project allowed me to have direct clarifications on the theoretical aspects of the TDDFT applied to finite systems, to be aware of the technicality surrounding the computation of complex systems optical properties, and to be ready to perform productive calculations on systems of scientific interest.

[1] www.tddft.org.

[2] www.yambo-code.org.