Excited states properties for SIESTA calculations: time-dependent density functional theory and beyond.

Peter Koval
Federico Marchesin, Marc Barbry and Daniel Sánchez-Portal
Donostia International Physics Center, P° Manuel de Lardizabal 4, 20018 Donostia, Spain and Centro de Física de Materiales CSIC-UPV/EHU, P° Manuel de Lardizabal 5, 20018 Donostia, Spain

koval.peter@gmail.com

Electronic excited states in condensed matter govern many physical phenomena important for industrial applications. Such phenomena as light-matter interaction and particle-matter interaction are cricial for the operation of light-emitting diodes and photo-voltaic cells as well as for undestanding the outcomes of many spectroscopical techniques existing today. In this talk, we present the algorithms and programing solutions for SIESTA users allowing to estimate the light-absorption spectra and electron energy loss spectra within time-dependent density functional theory (TDDFT). TDDFT is a rigorous extension of density-functional theory (DFT) which is implemented in SIESTA using the parsimonious basis of numerical atomic orbitals (NAO). The algorithm relies on an iterative computation of the electron density induced by an external perturbation [1]. We use the formalism of linear response functions which is more computationally efficient than the propagation of wave-packets – the alternative method to realize TDDFT calculations developed in SIESTA. The efficiency of the linear response TDDFT allows to estimate the light absorption and electron energy loss spectra [2] of large molecules, quantum dots and metallic clusters [3,4,5] containing thousands of atoms. SIESTA is a DFT package with built-in molecular dynamics (MD) capabilities. Coupling the ab-initio MD with TDDFT allows to estimate the effects of thermal motion on the electronic spectra. The speed of our TDDFT implementation makes feasible to perform a configuration average of the optical absorption spectra [1].

Our code is written mostly in Python language allowing for a quick and compact implementation of most numerical methods and data-managing tasks with the help of Numpy/Scipy libraries and Python intrinsics. Part of the code is written in C and Fortran to achieve a competitive speed in particular sections of the algorithm. Many parts of the current algorithm and implementation are useful in other ab-initio methods for electronic excited state properties, such as Hedin's *GW*, Bethe-Salpeter equation and DFT with hybrid functionals. Corresponding proof-of-principles implementations are already part of the code and will be shortly covered in the presentaion.

References

[1] P. Koval, M. Barbry, D. Sánchez-Portal, submitted (2018).
[2] M. Barbry, P. Koval and D. Sánchez-Portal, in preparation (2018)
[3] P. Koval, et al., J. Phys.: Cond. Matter 28, (2016) 214001
[4] M. Barbry, et al., Nano Letters 354, (2015) 216
[5] F. Marchesin, et al., ACS Photonics 3, (2016)