When the room is the elephant: chemical environment in quantum chemical calculations

MICHELE TURELLI[1], ILARIA CIOFINI[1] and CARLO ADAMO[1]

[1]Chimie ParisTech, PSL Research University, CNRS, Institute of Chemistry for Life and Health Sciences, Paris F-75005, France
michele.turelli@chimieparistech.psl.eu

ABSTRACT

Density functional theory (DFT) in its most widely employed instantiations, like B3LYP or PBE0, still represents the go-to simulation method in a large number of situations ranging from purely theoretical investigations to molecular simulations carried out to help the interpretation of experimental data. This means that DFT is put to the test in a large set of specific situations that vary across a range of conditions (i.e., pressure or temperatures) and chemical environments (i.e., aggregation phase, solvation). Attaining a more accurate molecular modelling in these cases means identifying the interactions with the chemical environment that have the largest impact on the properties of interest and include in the Hamiltonian interaction terms with simplified degrees of freedom representing the environment.

Here, we present a few examples where DFT and (LR)TD-DFT have been used in combination with a modeling of the chemical environment for the simulation of the optical response of molecules in organic crystalline solids. To build the environment representation, periodicity is exploited to perform a high-level periodic-DFT calculation from which a charge population is extracted for the unit cell. This periodic distribution is then mapped into a finite-size charge distribution reproducing the bulk electrostatic potential in a specific region of at the center of a box derived from a crystal supercell. An explicit molecular model for the optically active unit (e.g., monomer, dimer) is placed inside this region and properties are predicted with the inclusion of the crystalline electrostatic potential. Results consistently show a better agreement with the experimental data for absorption and emission spectra when the model for the environment is included for the systems investigated.