9th International Conference on Molecular Electronics
Paris, France
December, 17-21st 2018

Constrained density functional theory: a versatile tool for studying charge dynamics in organic materials

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Constructing a materials-specific theory of charge dynamics in organic single materials is a complex problem, where the computation of accurate structural and vibrational properties needs to be coupled to ways of determining the charge mobility characteristics. In particular one needs an accurate method for describing excitations, which is also scalable to reasonably large systems. Here I will discussed how different flavours of constrained density functional theory (CDFT) can achieve such goal.

Firstly I will consider the most conventional form of CDFT, which allows one to calculate the energy of systems with displaced electron densities (e.g. in a charge transfer process). Such scheme can be used to extract a number of quantities important for charge dynamics. Here I will make examples of the calculation of 1) the charge transfer energies of molecules on surfaces, so to derive accurate level alignments[1,2]; 2) the quasi-particle gap renormalisation in molecular crystals[3]; 3) the reorganisation energy of molecules in the gas phase and on surfaces[4].

Then I will move to show a recently implemented scheme, which uses CDFT to compute elementary excitations in molecules[5]. This method, which we have named excitonic DFT (XDFT), calculates the M-particle excited state of an N-electron system, by optimizing a constraining potential to confine $N - M$ electrons within the ground-state Kohn-Sham valence subspace. The efficacy of XDFT will be demonstrated by calculating the lowest single-particle singlet and triplet excitation energies of the well-known Thiel molecular test set, with results which are in excellent agreement with time-dependent density functional theory (TDDFT).

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