

Organic photovoltaic devices, based on small molecules or polymers as the active building blocks for capturing sun energy and generating an electrical current, represent an important paradigm for energy generation devices. The mechanisms at the heart of such systems, namely exciton generation, transport and dissociation at donor-acceptor interfaces, stand as significant conceptual and methodological challenges for theory and modeling. We have developed an efficient many-body perturbation theory *ab initio* computational tool, combining techniques developed in the solid-state physics community with specific implementations originating from quantum chemistry, allowing to study with much accuracy the electronic and optical properties of organic complexes comprising several hundred atoms. The "Fiesta project" opens further much perspectives in the study of molecular electronics and spintronics devices in hybrid systems such as functionalized nanotubes, graphene, or molecular transistors of the kind studied by several experimental groups at Institut Néel and worldwide.

From molecular electronics and spintronics to organic light-emitting or photovoltaic devices, molecular systems, either in the isolated molecule limit or in the bulk phase, offers a unique playground for exploring quantum physics at the nanoscale and provide novel paradigms for a large variety of applications. For such systems, informations at the nanoscale are still difficult to acquire experimentally and the insight from theory and modeling techniques has proven extremely useful. However, while the most successful technique for the *ab initio* modeling of condensed-matter systems, the density functional theory (DFT), has proven extremely valuable in reproducing the ground-state structural, vibrational, etc. properties of a large variety of systems, its ability to provide accurate electronic and optical properties is plagued by severe limitations. For illustration, the gap of organic molecules [1] or the energy of charge-transfer excitations, at the heart of organic photovoltaic or photosynthetic systems, [2] are wrong by up to several electronvolts within the standard implementations of DFT.

Developed in the late 80s at the *ab initio* level for inorganic semiconductors, alternative approaches based on a family of techniques labeled "many-body perturbation theory (MBPT)" such as the GW and Bethe-salpeter formalisms, have proven much more accurate in the prediction of the excited state properties of condensed matter systems, and successful applications to bulk, surfaces, or nanotubes have been demonstrated. The standard implementations of such techniques represents however a significant computational burden, in particular for open systems comprising several dozen of atoms. Benefiting from techniques developed by the quantum chemistry community – namely the use of Gaussian "auxiliary" basis and specific density or Coulomb fitting techniques to represent the quasiparticle, excitonic and various two-body operators such as the one-body Green's function and the dynamically screened Coulomb potential – we have developed in collaboration with the *L_sim* group at CEA/INAC a massively parallelized GW and Bethe-Salpeter code, the *Fiesta* package. Such developments allow the study of standard molecules such as C60, porphyrins or phthalocyanins, within one day on a very standard PC. From a "computational challenge" point of

view, and thanks to a European "supercomputing" (PRACE) grant, we could further demonstrate nearly perfect speed-up for up to 60 000 cores, allowing to treat several-hundred atoms systems within "lunch time".

Beyond computational aspects, such developments allow to tackle systems and problematics that could hardly be addressed by this family of state-of-the-art techniques a few years ago. As such, the electronic properties (frontier orbitals energy, gap, etc.) of a large variety of organic molecules of interest for photovoltaic (fullerenes, porphyrins, phthalocyanins, etc.) [1] or biological (nucleobasis) applications could be "screened out" at the GW level, showing excellent accuracy (a very few tenths of an eV error) as compared to experimental data. An important pioneering application was further to demonstrate that electron-phonon coupling matrix elements, of seminal importance in various fields such as superconductivity, hot electron lifetime, and polaron-limited mobility of carriers in organic semiconductors, was dramatically better described within the GW formalism as compared to the very widely used DFT values, as demonstrated in the well-known case of electron-doped fullerenes [2]. Finally, as another family of applications, the evolution of charge-transfer excitations in prototypical donor-acceptor organic complexes of interest for photovoltaic or photosynthetic applications, was shown to be very accurately described, curing one of the most well-known deficiency of the time-dependent extension to density functional theory (TDDFT) in the study of the optical properties of complex systems, opening the way to a better understanding of the photo-induced charge and energy transfer mechanisms in photovoltaic, photosynthetic, or photocatalytic systems.

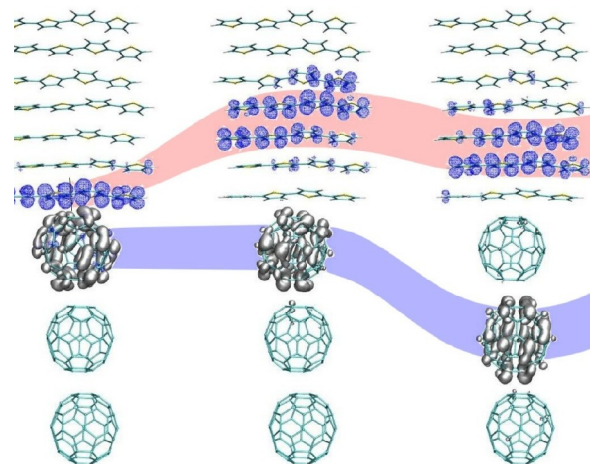


Fig. 1 : The 3 first lowest lying "Bethe-Salpeter" charge transfer excitations in a model C60/polythiophene interface showing the path for exciton dissociation (Blase, Duchemin, 2014).

- [1] Blase, Attaccalite, Olevano, PRB **83** 115103 (2011).
- [2] Faber, Jenissen, Côté, Runge, Blase, PRB **84**, 115104 (2011).
- [3] Duchemin, Deutsch, Blase, PRL **109**, 167801 (2012).
- [4] Boulanger, Jacquemin, Blase, JCTC **10**, 1212 (2014).