Theory for organic systems: the Fiesta initiative

Nowadays, the development of efficient computer codes that exploit the basic principles of quantum mechanics for the study of condensed-matter systems requires a merging of expertise between physicists, applied mathematicians and computer scientists. Collaborative work of this kind, between the Institut NÉEL and the Institute for Nanosciences and Cryogenics (INAC), has created a source code named FIESTA ("French Initiative for the Electronic Structure of Thousands of Atoms"). This code is being used to study organic systems of interest for electronics, photovoltaics, light-emission, wet chemistry and biology. The collaborating teams received the national 2014 Bull-Fourier prize for the use of computer sciences in physics.

Theoretical studies of the electronic properties of condensed matter systems rely on the basic rules of quantum mechanics. Even though these have been known since the early 20th century, the very large number of degrees of freedom (there are typically 10^{23} electrons per cm^3 of matter) precludes an exact, direct solution of the relevant equations that would yield the information needed to characterize the system of interest. It is the art of the theoretician to simplify the basic equations, and/or to reduce the number of degrees of freedom, in a way that preserves the accuracy needed for the properties or the experiment we want to describe.

A powerful approach to rationalizing how to classify the electron-electron interactions within a system by order of importance is called "many-body perturbation theory" (MBPT). This approach allows us to understand how to tune the needed accuracy by incorporating important effects before fine corrections. Such methods are built so that the first electron-electron interactions to be considered capture the most important effects while being computationally the most reasonable. This is clearly a crucial result which relies on several decades of theoretical studies.

While developed at the "pen and paper" level in the 1960s, a second step is the efficient implementation of these theories in the available computers, a crucial aspect that requires not only an expertise in physics, but also in applied mathematics, computer languages and computer architectures. Such a merging of expertise was initiated in 2011 between the Institut NÉEL and the Simulation Lab (*Laboratoire de Simulation Atomistique L_Sim*) at INAC, Grenoble. The aim was to develop a modern modelling tool, called the "Fiesta" code, devoted to studies of organic systems of interest in electronics, light-harvesting, light-emitting devices, wet chemistry and biology.

The specific many-body perturbation theory techniques implemented in the Fiesta code originate from the solid-state physics community. These methods rely on the concept of "screening" in semiconductors and metals, namely the fact that in a solid the effective interaction between two electrons is "attenuated" by the other electrons. What the Fiesta team have demonstrated is that such techniques can also be very efficient in the description of organic systems where such screening phenomena are much weaker. This leads to the description of the electronic and optical properties of a very large class of organic systems (small molecules, polymers, isolated or dense phases, etc.) to remarkable accuracy with limited computing-time cost. In particular, we have used the Fiesta code to explore the basic mechanisms behind the conversion of light energy into an electric current in organic photovoltaics (Fig. 1), and to understand how doping works in organic semiconductors. This has allowed us to discriminate between the several scenarios proposed for these phenomena.

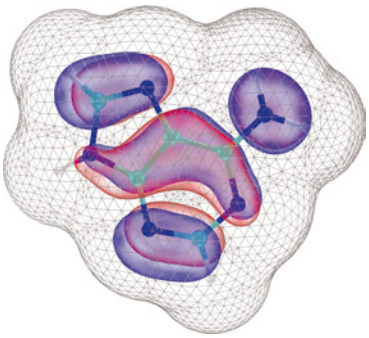

***Fig. 2**: Symbolic representation of an adenine molecule (one of the four DNA bases) placed in an effective water solvent. Here, FIESTA has described the biologically important interactions of the adenine molecule with H_2O molecules (screening, polarization, dipolar interactions, etc.) by induced effective charges on the solvation shell represented as a mesh. The colour shows the shape of the adenine's highest occupied electronic orbital (Duchemin, Jacquemin & Blase, 2016).*

Ongoing projects concern the merging of these many-body perturbation theory techniques with less-sophisticated techniques that are less accurate but more efficient in computer-time. These techniques can describe the effect of a medium (other molecules, an inorganic substrate, an electrode, etc.) that surrounds the molecule or "active subsystem" that is being described with the best MBPT methods (Fig. 2).

This is the sort of mix of quantum mechanical and semi-classical techniques that was recognized by the 2013 Nobel prize in Chemistry. Such techniques are essential steps for bridging the gap between present computer simulations and precise descriptions of a large class of systems of interest in physics, chemistry, and biology.

***Fig. 1**: Symbolic representation of the theory-to-application flow. **At left:** Many-body perturbation theory (Feynman diagrams). **Centre:** Your best computer. **At Right:** Dissociation of a photoelectron-photohole pair at a model donor-acceptor interface with proper, screened, electron-hole interactions.*

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FURTHER READING...

Review article:
"Excited states properties of organic molecules: from density functional theory to the GW and Bethe-Salpeter Green's function formalisms"

C. Faber, P. Boulanger, C. Attaccalite, I. Duchemin and X. Blase

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