UNIVERSITÀ DEGLI STUDI DI SALERNO

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Ph.D. in Chemistry
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Abstract of the Thesis

Charge transfer in organic materials with potential applications in electronics

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Abstract

Search for low cost electronic materials has led towards the synthesis and the employment of organic semiconductors (OSCs), a class of materials that combine the electronic advantages of semiconducting materials with the chemical and mechanical benefits of organic compounds. Despite the intense research effort, new OSCs have usually been discovered by trial and error and, even retrospectively, it was not always possible to explain why some materials exhibit better performances than others. A more efficient approach is now required and, in this respect, the use of computer-aided materials discovery can be highly beneficial. Increasing numbers of new OSCs have already been designed and improved through computational modeling, which requires the efficient simulation of charge transport (CT) processes taking place in OSC-based devices.

In this thesis we study and compare the relative performances of different models in the simulations of charge transport in OSCs.

In the first part we focus on the different properties of organic semiconductors with respect to their inorganic counterpart, their benefits and their drawbacks, restricting our analysis to organic crystalline semiconductors, which show the highest mobilities among all OSCs. Then we describe some of the most widely studied classes of OSC materials, showing some cases in which theory-guided material design has already been applied leading towards new materials with improved electronic performances.

In the second part of this thesis we dwell on the unique physical properties of organic semiconductors and on the reasons that animates the still topical debate about the most appropriate theoretical model for the CT description in these materials. Then, we briefly analyze strengths and drawbacks of five theoretical models: the Marcus theory, the Fermi Golden Rule (FGR), the Second Order Cumulant expansion of the density matrix (SOC), the quantum dynamics, and a recently developed approach, the Transient Localization Theory (TLT). In particular we describe some approximated strategies that significantly speed up the computations still ensuring accurate results.

In the third part we apply the abovementioned models to the description of charge transport in some of the most studied OSCs, comparing their predictions with experimental data and discussing the relative performances of each method. Our results show that SOC and TLT predictions are in good agreement with experimental data, the latter being the method of choice because of its low computational cost and physically well-sound assumptions.

In the last part of this thesis we focus on the simulation of CT in DNA oligomers, a topical issue since long range charge migration makes DNA a potentially well-suited material for nanoelectronics. Our analysis reproduces in a quantitative way published experimental data and allows us to reconcile experimental results disagreeing about the role of thymine bridges in CT across DNA oligomers.