Large Scale Modelling of Photo-Excitation Processes in Materials with Application in Organic Photovoltaics

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CHAPTER 2

Objectives

2.1. General Objective

This project aims to design theoretically new optoelectronic materials with applications to organic photovoltaics (OPVs). However, as the local and charge transfer exciton dissociation in OPVs are not easy nor well understood, such a design is not straightforward. It demands a deep understanding of the microscopic processes that underly the photovoltaic operation at large scale, for which hybrid quantum mechanical/molecular mechanics (QM/MM) computational approaches are suitable.

In this thesis, the optoelectronic processes that take place in OPVs are studied theoretically and computationally, in attempts to derive materials with good charge transport properties. Following the introduction in Chapter 1, the specific research objectives are described here, ranging from the technical implementations to the applications.

2.2. Specific Objectives

In the framework of large scale modelling of the photo-excitation processes in OPVs, the excited state properties of donor:acceptor bulk heterojunctions (D:A BHJs) are studied by using a multilevel QM/MM scheme. Within this scheme, a given D:A BHJ is divided into QM and MM regions. The QM region, which comprises a D/A pair, is treated at the DFT or TD-DFT level. The MM region, which accounts for the QM surroundings, is described by the polarizable discrete reaction field (DRF) method. QM/MM calculations were performed with the Amsterdam Density Functional (ADF) modelling suite.

Further improvements on the implementation of DRF in ADF, motivated the following specific objectives:

- Implement, as an extension, new functionalities of DRF into ADF (work in collaboration with Software for Chemistry & Materials (SCM) company, Amsterdam, The Netherlands):
  - Automate DRF inputs via the graphical user interface (GUI): Set and integrate default DRF parameters (atomic charges and atomic polarizabilities)
  - Create a python script for user-flexible DRF inputs: Link the python library for automating molecular simulation (PLAMS) to ADF.

- Study charge transfer and charge separation processes in large systems, for which DFT and TD-DFT in combination with DRF are used (work in collaboration with the Theoretical Chemistry group of the University of Groningen in association with the FOM Focus Group Groningen Next Generation Organic Photovoltaics, Groningen, The Netherlands):
  - Estimate relevant photovoltaic properties like the charge transfer exciton binding energy for interesting systems consisting of polymer:fullerene derivative BHJs
  - Predict how the electron transfer processes of polymer:fullerene derivative BHJs are limited by the device morphology
  - Determine the influence of the environment in the charge generation process for polymer:fullerene derivative BHJs.

The photophysical properties of optoelectronic materials are also a subject of this thesis. TD-DFT mostly fails in the exploration of excited state potential energy surfaces (PESs) for which highly accurate electronic structure methods, such as multiconfigurational approaches, are required. As a result of the unfavorable scaling of these methods, the routine study of conventional photovoltaic materials is impractical. Instead, the luminescence properties of relatively small optoelectronic materials are studied. Specifically, the cyano-substituted distyrylbenzene (DCS) family, which comprises 33 compounds, is studied. This motivated the following specific objectives:

- Explore the PES of representative DCS molecules by using both TD-DFT and CASPT2/CASSCF approaches (work in collaboration with the quantum chemistry excited state group of the University of Valencia in association with the Madrid Institute for Advanced Studies (IMDEA), Madrid, Spain):
  - Determine the molecular basis for non-radiative mechanisms of optoelectronic materials
  - Correlate predicted non-radiative mechanisms to experimental observables, fluorescence quantum yields and decay rates, in order to find rules for emissive/non-emissive behavior
  - Define simplified computational strategies to explore PES in highly conjugated systems.

This thesis uses research methodologies that can be broadly applied to systems where excited states are of interest. Beyond the scope of this thesis, there is room for improvement concerning code and method developments. For instance, calculations derived from a potential implementation of ground state and excited DRF/QM energy gradients into ADF would complement the analysis presented here. The use of the non-orthogonal configuration interaction method (NOCI) for large systems may give further insights into the electron transfer processes. These two issues are covered as outlook for future theoretical studies.