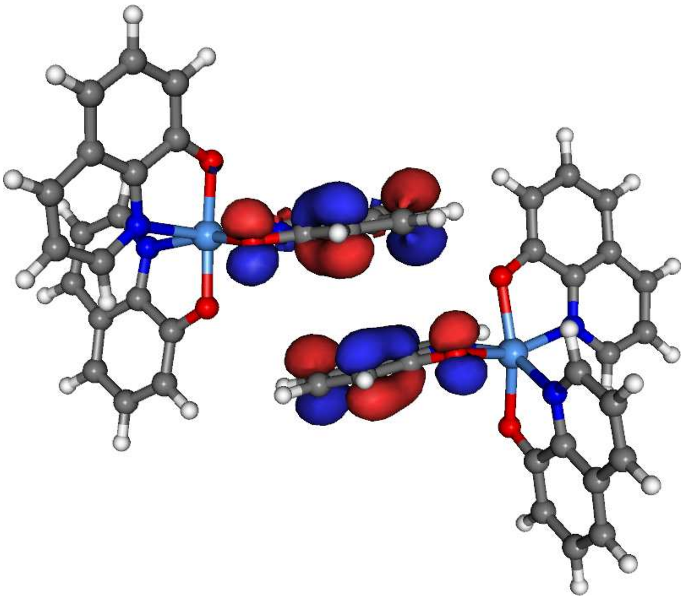
VOTCA-XTP

EXCITON TRANSPORT SIMULATIONS

USER MANUAL



compiled from: 1.3-dev (a1f39fc)

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www.votca.org

Disclamer

This manual is not complete. The best way to start using the software is to look at provided tutorials. The reference section is generated automatically from the source code, so please make sure that your software and manual versions match.

Citations

Development of this software depends on academic research grants. If you are using the package, please cite the following papers

[?] Microscopic simulations of charge transport in disordered organic semiconductors,
Victor Rühle, Alexander Lukyanov, Falk May, Manuel Schrader, Thorsten Vehoff, James Kirkpatrick, Björn Baumeier and Denis Andrienko
J. Chem. Theor. Comp. 7, 3335, 2011

[?] Versatile Object-oriented Toolkit for Coarse-graining Applications
Victor Rühle, Christoph Junghans, Alexander Lukyanov, Kurt Kremer and Denis Andrienko
J. Chem. Theor. Comp. 5, 3211, 2009

Development

The core development is currently taking place at the Max Planck Institute for Polymer Research, Mainz, Germany and TU/e Eindhoven.

Copyright

VOTCA-XTP is free software. The entire package is available under the Apache License. For details, check the LICENSE file in the source code. The VOTCA-XTP source code is available on our homepage, www.votca.org.

Contents

Chapter 1

Introduction

sec:introduction

Charge carrier dynamics in an organic semiconductor can often be described in terms of charge hopping between localized states. The hopping rates depend on electronic coupling elements, reorganization energies, and site energies, which vary as a function of position and orientation of the molecules. The purpose of the VOTCA-XTP package [?] is to simplify the workflow for charge transport simulations, provide a uniform error-control for the methods, flexible platform for their development, and eventually allow *in silico* prescreening of organic semiconductors for specific applications.

The toolkit is implemented using modular concepts introduced earlier in the Versatile Object-oriented Toolkit for Coarse-graining Applications (VOTCA) [?]. It contains different programs, which execute specific tasks implemented in calculators representing an individual step in the workflow. Figure **??** summarizes a typical chain of commands to perform a charge transport simulation: First, the VOTCA code structures are adapted to reading atomistic trajectories, mapping them onto conjugated segments and rigid fragments, and substituting (if needed) rigid fragments with the optimized copies (`xtp_map`). The programs `xtp_run` and `xtp_parallel` (for heavy-duty tasks) are then used to calculate all bimolecular charge hopping rates (via precalculation of all required ingredients). Site energies (or energetic disorder) can be determined as a combination of internal (ionization potentials/electron affinities of single molecules) as well as electrostatic and polarization contributions within the molecular environment. The calculation of electronic coupling elements between conjugated segments from the corresponding molecular orbitals can be performed using a dimer-projection technique based on density-functional theory (DFT). This requires explicit calculations using quantum-chemistry software for which we provide interfaces to `Gaussian`, `Turbomole`, and `NWChem`. Alternatively, the molecular orbital overlap module calculates electronic coupling elements relying on the semi-empirical INDO Hamiltonian and molecular orbitals in the format provided by the `Gaussian` package.

The kinetic Monte Carlo module reads in the neighbor list, site coordinates, and hopping rates and performs charge dynamics simulations using either periodic boundary conditions or charge sources and sinks.

The toolkit is written as a combination of modular C++ code and scripts. The data transfer between programs is implemented via a state file (sql database), which is also used to restart simulations. Analysis functions and most of the calculation routines are encapsulated by using the observer pattern [?] which allows the implementation of new functions as individual modules.

In the following chapter **??**, we summarize the theoretical background of the workflow of charge transport simulations and in particular its individual steps. Chapter **??** describes the structure and content of input and output files, while a full reference of programs and calculators is available in chapter **??**. For a hands-on tutorial, the reader is referred to the VOTCA-XTP project page at http://code.google.com/p/votca-xtp/.

Figure 1.1: A practical workflow of charge transport simulations using VOTCA-XTP. The theoretical background of the individual steps is given in chapter **??**. Chapter **??** describes the content of input and output files, while a full reference of programs and calculators is available in chapter **??**. fig:summary

Chapter 2

Theoretical background

sec:theory

2.1 Workflow

sec:wokflow

A typical workflow of charge transport simulations is depicted in figure **??**. The first step is the simulation of an atomistic morphology, which is then partitioned on hopping sites. The coordinates of the hopping sites are used to construct a list of pairs of molecules, or neighbor list.

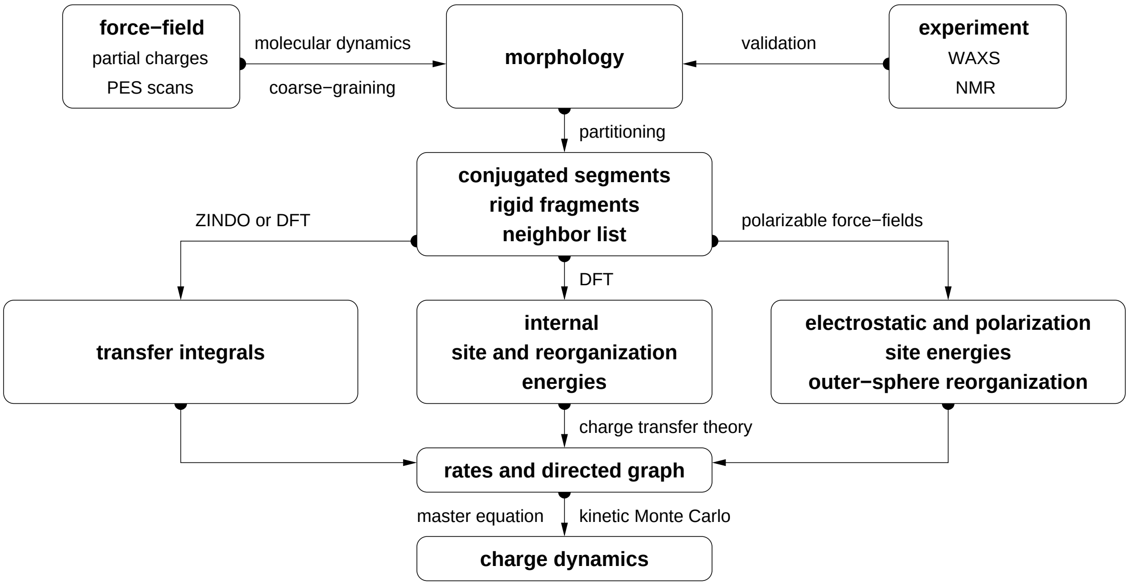
force−field
partial charges
PES scans
molecular dynamics
coarse−graining
morphology
validation
experiment
WAXS
NMR
partitioning
conjugated segments
rigid fragments
neighbor list
ZINDO or DFT
polarizable force−fields
DFT
transfer integrals
internal
site and reorganization
energies
electrostatic and polarization
site energies
outer−sphere reorganization
charge transfer theory
rates and directed graph
master equation
kinetic Monte Carlo
charge dynamics

fig:workflow

Figure 2.1: Workflow for microscopic simulations of charge transport.

For each pair an electronic coupling element, a reorganization energy, a driving force, and eventually the hopping rate are evaluated. The neighbor list and hopping rates define a directed graph. The corresponding master equation is solved using the kinetic Monte Carlo method, which allows to explicitly monitor the charge dynamics in the system as well as to calculate time or ensemble averages of occupation probabilities, charge fluxes, correlation functions, and field-dependent mobilities.

2.2 Material morphology

sec:morphology

There is no generic recipe on how to predict a large-scale atomistically-resolved morphology of an organic semiconductor. The required methods are system-specific: for ultra-pure crystals, for

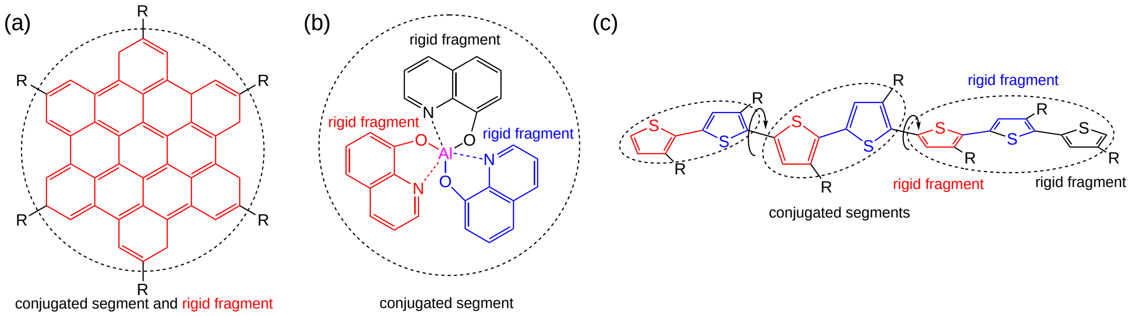

Figure 2.2: The concept of conjugated segments and rigid fragments. Dashed lines indicate conjugated segments while colors denote rigid fragments. (a) Hexabenzocoronene: the π-conjugated system is both a rigid fragment and a conjugated segment. (b) Alq_3: the Al atom and each ligand are rigid fragments while the whole molecule is a conjugated segment. (c) Polythiophene: each repeat unit is a rigid fragment. A conjugated segment consists of one or more rigid fragments. One molecule can have several conjugated segments.

fig:segment

example, density-functional methods can be used provided the crystal structure is known from experiment. For partially disordered organic semiconductors, however, system sizes much larger than a unit cell are required. Classical molecular dynamics or Monte Carlo techniques are then the methods of choice.

In molecular dynamics, atoms are represented by point masses which interact via empirical potentials prescribed by a force-field. Force-fields are parametrized for a limited set of compounds and their refinement is often required for new molecules. In particular, special attention shall be paid to torsion potentials between successive repeat units of conjugated polymers or between functional groups and the π-conjugated system. First-principles methods can be used to characterize the missing terms of the potential energy function.

Self-assembling materials, such as soluble oligomers, discotic liquid crystals, block copolymers, partially crystalline polymers, etc., are the most complicated to study. The morphology of such systems often has several characteristic length scales and can be kinetically arrested in a thermodynamically non-equilibrium state. For such systems, the time- and length-scales of atomistic simulations might be insufficient to equilibrate or sample desired morphologies. In this case, systematic coarse-graining can be used to enhance sampling [**?**]. Note that the coarse-grained representation must reflect the structure of the atomistic system and allow for back-mapping to the atomistic resolution.

Here we assume that the morphology is already known, that is we know how the topology and the coordinates of all atoms in the systems at a given time. VOTCA-XTP can read standard `GROMACS` topology files. Custom definitions of atomistic topology via XML files are also possible. Since the description of the atomistic topology is the first step in the charge transport simulations, it is important to follow simple conventions on how the system is partitioned on molecules, residues, and how atoms are named in the topology. Required input files are described in section atomistic topology.

2.3 Conjugated segments and rigid fragments

sec:segments

With the morphology at hand, the next step is partitioning the system on hopping sites, or conjugated segments, and calculating charge transfer rates between them. Physically intuitive arguments can be used for the partitioning, which reflects the localization of the wave function of a charge. For most organic semiconductors, the molecular architecture includes relatively rigid, planar π-conjugated systems, which we will refer to as rigid fragments. A conjugated segment can contain one or more of such rigid fragments, which are linked by bonded degrees of freedom.