Tobias Benedikt Koch

Multiscale modelling of charge transport in organic materials

2021

Theoretische Physik

Multiscale modelling of charge transport in organic materials

Multiskalen-Modellierung des Ladungstransportes in organischen Materialien

Inaugural-Dissertation
zur Erlangung des Doktorgrades
der Naturwissenschaften im Fachbereich Physik
der Mathematisch-Naturwissenschaftlichen Fakultät
der Westfälischen Wilhelms-Universität Münster

vorgelegt von

Tobias Benedikt Koch

aus Lingen (Ems)

– 2021 –

Dekan:	Prof. Dr. Michael Rohlfing
Erster Gutachter:	Prof. Dr. Nikos L. Doltsinis
Zweiter Gutachter:	Prof. Dr. Andreas Heuer
Dritte Gutachterin:	Prof. Dr. Cornelia Denz
Mündliche Prüfung:	01.07.2021
Promotion:	23.07.2021

Kurzfassung

Die theoretische Untersuchung des Ladungstransports in organischen Materialien ist eine herausfordernde Aufgabe, da sie mehrere Zeit- und Längenskalen umfasst - von quantenmechanischen Ladungstransferprozessen auf molekularer Ebene bis hin zu mesoskopischen, strukturellen und dynamischen Kenngrößen, welche die Morphologie von amorphen Donor-Akzeptormaterialien bestimmen. Unser Ziel ist es hier, die Mobilität von Elektronen und Löchern in einer Multiskalen-Modellierung mittels kinetischer Monte-Carlo-Simulationen unter Verwendung bimolekularer Ladungstransferraten auf der Grundlage der Marcus-Theorie zu berechnen. Dafür sind genaue Sprungraten zwischen benachbarten Molekülen erforderlich, die abhängig sind von der inneren und äußeren Reorganisationsenergie, der Site-Energie-Differenz, den Ladungstransferintegralen und den externen Antriebskräften. Wir vergleichen verschiedene Berechnungsansätze für diese Größen und untersuchen ihre Anwendbarkeit zur Modellierung des inter- und intramolekularen Ladungstransfers in amorphen Materialien. Die Sprungraten werden daraufhin in die kinetischen Monte-Carlo-Simulationen eingespeist, die es uns ermöglichen, die Ladungsträgerdynamik im System zu überwachen und Ensemblemittelwerte der Besetzungswahrscheinlichkeit, der Ladungsträgermobilität sowie der elektronischen Ströme zu bestimmen und Pfade mit minimalem lokalem Widerstand zu ermitteln. Daher verbindet die Multiskalen-Modellierung die mikroskopische Struktur mit makroskopischen Observablen. Diese Arbeit umfasst die Entwicklung, Implementierung und Validierung von Algorithmen zur Simulation und Analyse des Ladungstransports. Hier wenden wir diesen Ansatz sowohl auf amorphes P3HT und PPDI als auch auf Mischungen von Donor : Akzeptor-Materialien in organischen Solarzellen mit Bulk-Hetero-Junction an, z.B. P3HT : DIPBI und PBDT-TS1 : PPDI.

Insbesondere in den beiden letztgenannten Materialien finden wir aufgrund abweichender morphologischer Merkmale unterschiedliche Elektronentransportmechanismen. Wir präsentieren ein Screening von Perylendiimid-Akzeptoren hinsichtlich der strukturellen und optischen Eigenschaften, des Aggregationsverhaltens und der resultierenden Ladungstransfereigenschaften für die Anwendung in organischen Solarzellen. Analog untersuchen wir organische Verbindungen und metall-organische Komplexe für die Elektrolumineszenz in organischen Leuchtdioden sowie ihr Aggregationsverhalten. Detaillierte Kenntnisse über diese Größen können dazu beitragen die Effizienz von organischer Photovoltaik und optoelektronischen Bauelementen zu verbessern.

Abstract

The theoretical study of charge transport in organic materials is challenging since it involves multiple time and length scales – from quantum-mechanical charge transfer processes at the molecular level to mesoscopic structural and dynamical parameters governing the morphology of amorphous donor-acceptor materials. Our goal here is to compute the mobility of electrons and holes in a multiscale model via kinetic Monte Carlo simulations using bimolecular charge transfer rates based on the Marcus theory. Therefore, accurate hopping rates between neighbouring molecules are mandatory, depending on the internal and outer-sphere reorganization energies, site-energy differences, charge transfer integrals, and external driving forces. We compare different computational approaches for these quantities and probe their applicability to model intermolecular and intramolecular charge transfer in amorphous materials. The hopping rates are then fed into the kinetic Monte Carlo simulations, which allow us to monitor the charge dynamics in the system as well as to get ensemble averages of the occupation probability, charge carrier mobility, electronic fluxes and pathways of minimal local resistance. Hence, the multiscale model links the microscopic structure to macroscopic observables. This thesis comprises the development, implementation, parametrisation and validation of algorithms for the simulation and analysis of charge transport. Here we apply this approach to amorphous P3HT and PPDI as well as to mixtures of donor:acceptor materials in organic bulk heterojunction solar cells, e.g. P3HT:DIPBI and PBDT-TS1:PPDI. In particular, we find distinct electron transport mechanisms in the latter two materials due to characteristic morphological differences. We present a screening of perylene diimide acceptors regarding structural and optical properties, aggregation behaviour and the resulting charge transfer properties for the application in organic solar cells. Similarly, we investigate organic compounds and metal-organic complexes for electroluminescence in organic light-emitting diodes and their aggregation behaviour. Detailed knowledge about these quantities may help to enhance the performance of future organic photovoltaics and optoelectronic devices.

Contents

Introduction **XI**

1 Theoretical Background **1**

1.1 Born-Oppenheimer Approximation . . . 1
1.2 Electronic Structure Calculations . . . 4
  1.2.1 Hartree-Fock Theory . . . 4
  1.2.2 Density Functional Theory . . . 5
    1.2.2.1 Time-independent Density Functional Theory (DFT) . . . 5
    1.2.2.2 Kohn-Sham Theory . . . 6
    1.2.2.3 Exchange-Correlation Functional . . . 7
    1.2.2.4 Long-range Corrections in Density Functional Theory . . . 9
    1.2.2.5 Constrained Density Functional Theory (CDFT) . . . 9
    1.2.2.6 Empirical Dispersion Corrections in DFT . . . 13
    1.2.2.7 Time-Dependent Density Functional Theory (TDDFT) . . 14
    1.2.2.8 Vibronic Absorption and Emission Spectra . . . 20
  1.2.3 Density-Functional Tight-Binding (DFTB) . . . 21
  1.2.4 Semi-empirical Methods . . . 23
  1.2.5 Basis Sets . . . 25
1.3 Molecular Dynamics . . . 28
  1.3.1 Ab Initio Molecular Dynamics . . . 28
    1.3.1.1 Born-Oppenheimer Molecular Dynamics . . . 28
    1.3.1.2 Car-Parrinello Molecular Dynamics . . . 28
  1.3.2 Classical Molecular Dynamics . . . 30
  1.3.3 Verlet Algorithm . . . 32
  1.3.4 Temperature and Pressure Control . . . 33
1.4 Charge Transfer in Molecular Systems . . . 35
  1.4.1 Marcus Theory . . . 35
  1.4.2 Alternative Rate Expressions . . . 39
  1.4.3 Charge Transfer Integral . . . 40
    1.4.3.1 DIPRO Method . . . 41
    1.4.3.2 ZINDO-based Molecular Orbital Overlap Method . . . 43
    1.4.3.3 Fragment Orbital DFT . . . 44
  1.4.4 Outer-sphere Contributions in Charge Transfer Reactions . . . 46
    1.4.4.1 Reorganization Energy from Partial Charges . . . 46

1.4.4.2 Electrostatic Energy from Partial Charges 47
1.4.4.3 Electrostatic Interaction Energy from Distributed Multipoles 48
1.4.4.4 Evaluating the Induction Energy within the Thole Model . 49
1.5 Kinetic Monte Carlo Simulations for Charge Transport 50
1.5.1 Master equation 50
1.5.2 Kinetic Monte Carlo Algorithm 51
1.5.3 Macroscopic Observables 52

2 Computational Details 55
2.1 Charge Transfer Rates 55
2.2 Charge Transport in Organic Solar Cells 57
2.2.1 Workflow of the Multiscale Model 57
2.2.2 P3HT and P3HT:DIPBI 58
2.2.3 PPDI 60
2.2.4 PBDT-TS1:PPDI 61
2.3 Screening for Polyene Diimide Acceptors 62
2.4 Charge Transfer in OLED Materials 64

3 Charge Transfer Rates 67
3.1 Charge Transfer Integral 67
3.1.1 Evaluation for DIPBI Dimers within CDFT and DIPRO 67
3.1.2 P3MT Polymer Chain Partitioning in the Amorphous Phase 70
3.1.3 Comparing Different Evaluation Methods 74
3.1.4 Scaling the Charge Transfer Integral 76
3.1.5 Geometric Parametrisation 81
3.1.6 Parametrisation as a Function of the Overlap Integral 87
3.1.7 Intramolecular Charge Transfer in P3HT Polymer Chains 93
3.1.8 Conclusion: Charge Transfer Integral 96
3.2 Internal Reorganization and Site-energy Difference 97
3.2.1 Evaluation for P3HT:DIPBI within DFT 97
3.2.2 Evaluation for P3HT:DIPBI within DFTB 99
3.2.3 Evaluation for P3HT with Constraints 100
3.2.4 Evaluation in a Molecular Environment within ONIOM 102
3.2.5 Conclusion: Internal Reorganization Energy and Internal Site-energy Difference 104
3.3 Hopping Site Distance 104
3.4 Comparison of Charge Transfer Rate Expressions 107

4 Charge Transport in Organic Solar Cells 113
4.1 Multiscale Model for Charge Transport in P3HT and P3HT:DIPBI 113
4.1.1 Introduction 113
4.1.2 kMC Simulations of Pure P3HT 115
4.1.2.1 Hole Mobility 115
4.1.2.2 Site Occupation and Current 119
4.1.3 kMC Simulations in P3HT:DIPBI 120

4.1.3.1 Morphologies . . . 120
4.1.3.2 Converging the Hole Mobility . . . 123
4.1.3.3 Sampling the Hole Mobility in Multiple Morphologies . . . 126
4.1.3.4 Comparing Simulation Approaches for Hole Mobilities . . . 129
4.1.3.5 Site Occupation . . . 131
4.1.3.6 Current and Low Resistance Pathways . . . 133
4.1.3.7 Rate Distributions in the Blend Morphology . . . 137
4.1.3.8 Electron Transport . . . 141
4.1.3.9 Conclusion P3HT:DIPBI . . . 143
4.2 Multiscale Model for Charge Transport in PPDI and PBDT-TS1:PPDI . . . 144
4.2.1 Acceptor Molecule PPDI . . . 144
4.2.2 kMC Simulations in Amorphous PPDI . . . 146
4.2.3 Electronic Structure of PBDT-TS1 . . . 150
4.2.4 Intramolecular Charge Transfer in PBDT-TS1 Polymer Chains . . . 151
4.2.5 Internal Reorganization Energy and Site-energy Difference . . . 155
4.2.6 kMC Simulations in PBDT-TS1:PPDI . . . 156

5 Screening for Perylene Diimide Acceptors 161
5.1 Introduction . . . 161
5.2 Triperilene Hexaimides (TPH / TPH-Se) . . . 164
5.3 Pentaperylene Decaimides (PPD / PPD-Se) . . . 167
5.4 Hexacene Diimides (HDI) . . . 174
5.5 PDTTI . . . 179
5.6 PHHP-AS . . . 185
5.7 Laddered Graphene Nanoribbons (PDI-Pyr) . . . 190
5.8 Comparisons of Acceptor Molecules . . . 194

6 Charge Transfer in OLED Materials 199
6.1 Introduction . . . 199
6.2 Photophysics and Aggregation of Pt Complexes . . . 201
6.3 Modelling Charge Transfer in OLED Devices with Pt Emitters . . . 209
6.4 Conclusion . . . 223

7 Conclusion and Outlook 225

A Charge Transfer Rates and Charge Transport 229

Publications:

Parts of this thesis have been submitted or are already published in the following references:

1. G. Liu, T. Koch, Y. Li, N. L. Doltsinis, and Z. Wang, "Nanographene Imides Featuring Dual-Core Sixfold [5]Helicenes", *Angew. Chem. Int. Ed.* **58**, 178–183 (2019).

2. S. Wilde, L. Stegemann, C. G. Daniliuc, T. Koch, N. L. Doltsinis, and C. A. Strassert, "Studie über den Einfluss des Fluorierungsgrades an einem tetradentaten C^N*N^C-Luminophor auf die photophysikalischen Eigenschaften seiner Platin(II)-Komplexe und deren Aggregation", *Z. Naturforsch. B* **73**, 849–863 (2018).

3. X. Cui, C. Xiao, T. Winands, T. Koch, Y. Li, L. Zhang, N. L. Doltsinis, and Z. Wang, "Hexacene Diimides", *J. Am. Chem. Soc.* **140**, 12175–12180 (2018).

4. S. Wilde, D. Ma, T. Koch, A. Bakker, D. Gonzalez-Abradelo, L. Stegemann, C. G. Daniliuc, H. Fuchs, H. Gao, N. L. Doltsinis, L. Duan, and C. A. Strassert, "Toward Tunable Electroluminescent Devices by Correlating Function and Submolecular Structure in 3D Crystals, 2D-Confined Monolayers, and Dimers", *ACS Appl. Mater. Interfaces* **10**, 22460–22473 (2018).

5. N. L. Doltsinis, J. Bachmann, T. Koch, C. Schwermann, and T. Winands, "Trendbericht Theoretische Chemie 2017: Optimierung organischer Solarzellen mit Multiskalensimulationen", *Nachr. Chem.* **66**, 320–324 (2018).

6. T. Koch, J. Bachmann, T. Lettmann, and N. L. Doltsinis, *submitted for publication*, "Multiscale modelling of charge transport in P3HT:DIPBI bulk heterojunction organic solar cells", *Phys. Chem. Chem. Phys.* (2021).

Publications that are not related to this thesis but were completed at the Institute for Solid State Theory and the Centre for Multiscale Theory and Computation at the University of Münster.

1. T. Koch, C. Höppener, and N. L. Doltsinis, "Conformation-dependent phosphorescence emission of individual mononuclear ruthenium-(ii)-bis-terpyridine complexes", *Phys. Chem. Chem. Phys.* **20**, 24921–24926 (2018).

2. J. Sanning, P. R. Ewen, L. Stegemann, J. Schmidt, C. G. Daniliuc, T. Koch, N. L. Doltsinis, D. Wegner, and C. A. Strassert, "Scanning-Tunneling-Spectroscopy-Directed Design of Tailored Deep-Blue Emitters", *Angew. Chem. Int. Ed.* **54**, 786–791 (2015).

   J. Sanning, P. R. Ewen, L. Stegemann, J. Schmidt, C. G. Daniliuc, T. Koch, N. L. Doltsinis, D. Wegner, and C. A. Strassert, "Rastertunnelspektroskopisch gesteuertes Design maßgeschneiderter tiefblauer Triplettemitter", *Angew. Chem.* **127**, 798–803 (2015).

3. P. R. Ewen, J. Sanning, T. Koch, N. L. Doltsinis, C. A. Strassert, and D. Wegner, "Spectroscopic mapping and selective electronic tuning of molecular orbitals in phosphorescent organometallic complexes – a new strategy for OLED materials", *Beilstein J. Nanotechnol.* **5**, 2248–2258 (2014).

Introduction

The enormous demand for energy and the fact that the supply of fossil fuels for combustion processes is limited will be one of the major challenges for our society in the following decades. As environmental awareness gets increasingly in the focus of social and political concerns, the development of alternative renewable energy sources is an essential issue [1]. The extensive use of fossil resources creates new challenges as environmental pollution and the emission of greenhouse gases trigger global climate change [2].

Nature has optimised many ways to harvest sunlight energy, e.g. by photosynthetic energy conversion [3]. Following the route of natural photosynthesis, there have been many attempts to harvest solar energy by mimicking processes as photon absorption, exciton migration [4, 5], charge separation [6] and charge transport [7, 8] in artificial devices.

Organic solar cells (OSC) [9–16] offer a desirable alternative to typical silicon-based solar cells due to their versatile properties such as their low weight, their high bendability, solution processibility and their smaller manufacturing costs [17]. The high availability of starting materials for chemical synthesis of OSC compounds and the ability to fabricate thin devices in easily scalable high-speed printing processes on flexible plastic substrates result in smaller coasts and enable shorter energy payback times compared to typical silicon-based solar cells [18]. Besides, OSCs are more environmentally friendly as they have the potential to reduce electronic waste and exhibit beneficial recyclability and biodegradability. Nevertheless, OSCs still underperform in terms of the power conversion efficiency (PCE) [19, 20]. Based on great scientific and commercial efforts in this field, the PCE of OSCs could be increased enormously to about 18% in the last decades [21–33]. OSCs have thus evolved from a promising niche existence into a genuinely competitive alternative to conventional solar cells. However, the latter are still ahead with efficiencies of more than 20% [34].

The remarkable advances in OSCs are based on the continuous development of new materials and technologies for device fabrication and the understanding of the film morphology and physical properties of the devices. In particular, conjugated polymer donors [35–46] with wide bandgaps and non-fullerene acceptors (NFAs) [26, 30, 47] have been engineered to optimise optical, electronic and crystalline properties for high-performance OSCs.

Organic materials basically consist of chemical elements such as hydrogen, carbon, nitrogen, oxygen and sometimes phosphorus, sulfur and halogens. As organic semiconductors, they form π-conjugated molecular materials, which include molecular crystals, disordered molecular materials and conjugated polymers.

Bulk heterojunction organic solar cells (BHJ-OSC) [11, 48–51] usually consist of a blend of two molecular species, the donor (D) and the acceptor molecule (A) (Fig. 1). They build an amorphous structure and form domains of different size and shape. When the sun shines on the organic solar cell, the light of an incident photon is absorbed by a molecule (1). In this process, the molecule is excited from the electronic ground state into an excited state (2). In the next step, an exciton is formed, which diffuses within the morphology until it reaches a donor-acceptor interface (3). The exciton dissociates at the interface by splitting the bound electron-hole pair into an electron at the acceptor and a hole at the donor material (4). The free hole and the electron then diffuse to the electrodes in a random walk (5). The holes are collected at the anode and the electrons at the cathode. In this manner, the excess charges are available for an external energy consumer. The introduction of electron-blocking and hole-blocking layers increases the efficiency of solar cells by preventing charge carriers generated near the electrodes from directly recombining. All these processes need to be optimised to improve the performance of the OSCs, i.e. light absorption, exciton migration, charge carrier dynamics and collection of charge carriers at the electrodes.

The main driving force for enhancing the power conversion efficiency can be attributed to chemical variation in the donor [44] and acceptor [47] species. The development was mainly guided by an empirical trial-and-error method, whereas a rational design of the components and an optimisation of the production process appears to be a desirable access pathway. Theoretical concepts and computer simulation supported research can help to gain sophisticated knowledge about the elementary photophysical processes inside OSCs. This is a major challenge due to the great variety of coupled physical processes on different time and length scales [52]. A multiscale simulation approach for charge mobilities in photovoltaic materials has been pioneered by Andrienko, Nelson and co-workers [53–58]. The fundamental concepts of our multiscale model are outlined in reference [59].

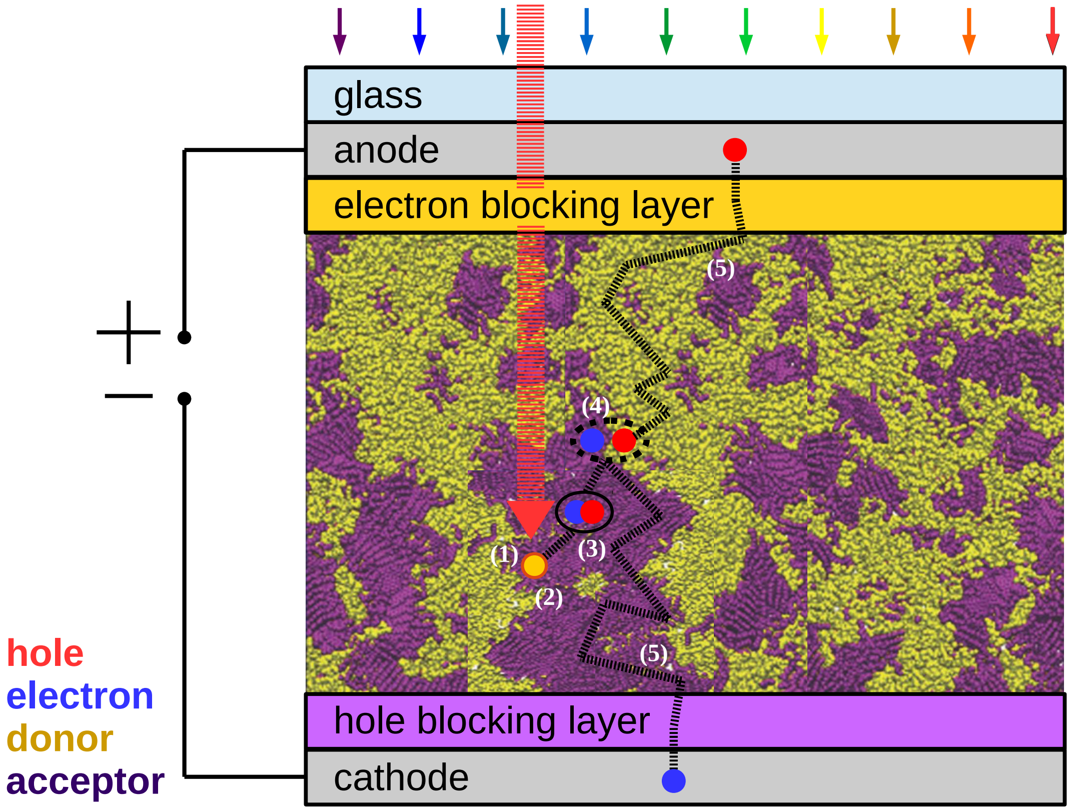

Figure 1: Fundamental physical processes inside a bulk heterojunction organic solar cell. 1) Absorption of a photon 2) formation of a charge-transfer state 3) formation and migration of an exciton to the donor-acceptor interface 4) separation of the exciton into free charge carriers 5) hole and electron transport to the electrodes.

Multiscale model The present work applies a similar multiscale model approach combining quantum mechanical (QM) methods, classical molecular mechanics (MM) on atomistic and coarse-grained (CG) level and kinetic Monte Carlo (kMC) simulations [60, 61] to gain access to macroscopic observables such as charge carrier mobilities μ and electronic current I based on molecular properties (Fig. 2). In a bottom-up approach, a classical model is parametrised on the basis of high-level quantum mechanical calculations to obtain an atomistic force field (FF) for each molecular specimen. Atomistic molecular dynamics simulations are applied to generate an amorphous donor-acceptor blend morphology. We can obtain a more realistic picture of the device morphology in a consecutive step if we reduce the number of degrees of freedom in the atomistic representation and parametrise a classical, coarse-grained model, which gives access to longer simulation times and increased length scale. A top-down approach is applied, if we make a transition from the CG back to a MM representation, and select single molecules or pairs from the morphology and perform quantum mechanical calculations. This strategy is particularly successful in the modelling of spectroscopic properties in amorphous bulk materials. The kMC simulations incorporate quantum mechanical results and the morphology to determine charge carrier mobilities μ and electronic current $\mathbf{I}$.

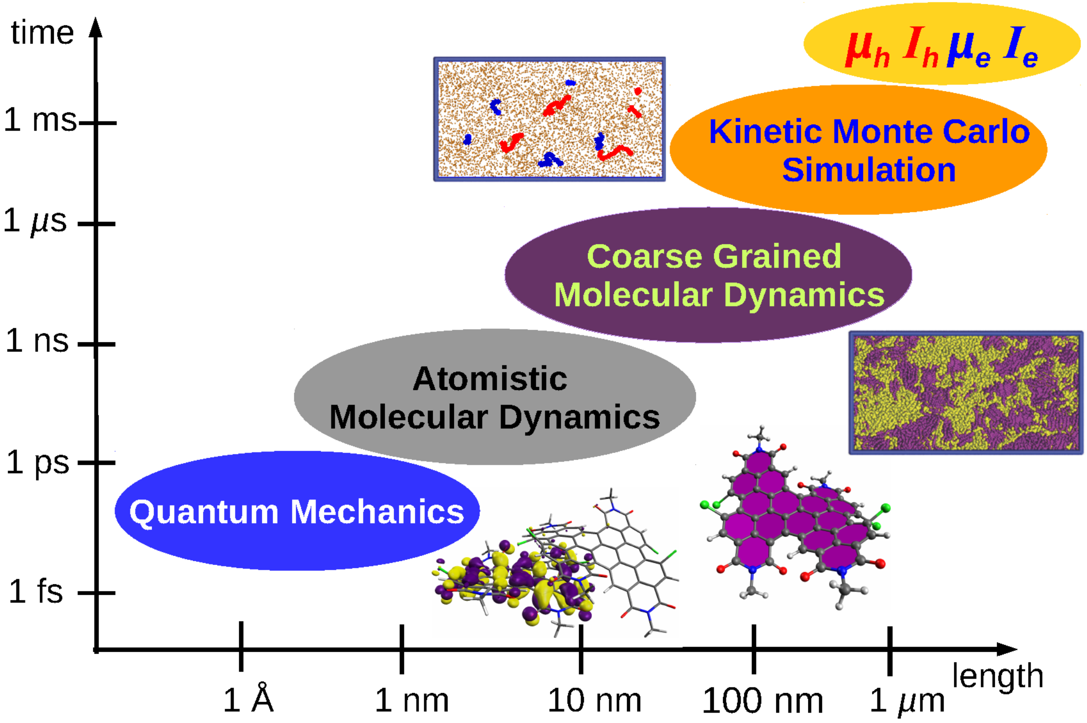
time
1 ms
1 μs
1 ns
1 ps
1 fs
μ_h I_h μ_e I_e
Kinetic Monte Carlo Simulation
Coarse Grained Molecular Dynamics
Atomistic Molecular Dynamics
Quantum Mechanics
1 Å
1 nm
10 nm
100 nm
1 μm
length

Figure 2: The multiscale model combines calculations at different time and length scales like quantum mechanical methods, classical methods on an atomistic and coarse-grained level and kinetic Monte Carlo simulations to get access to macroscopic properties like the charge carrier mobility μ and the electronic current $\mathbf{I}$.

The workflow for the multiscale model is depicted in Figure 3. The goal of our multiscale model is to compute the mobility of holes and electrons in a blend of the acceptor molecule diperylene bismide (DIPBI) [62, 63] and the donor polymer poly(3-hexylthiophene) (P3HT) [64]. Therefore a realistic description of the overall donor:acceptor blend morphology of P3HT:DIPBI is required.

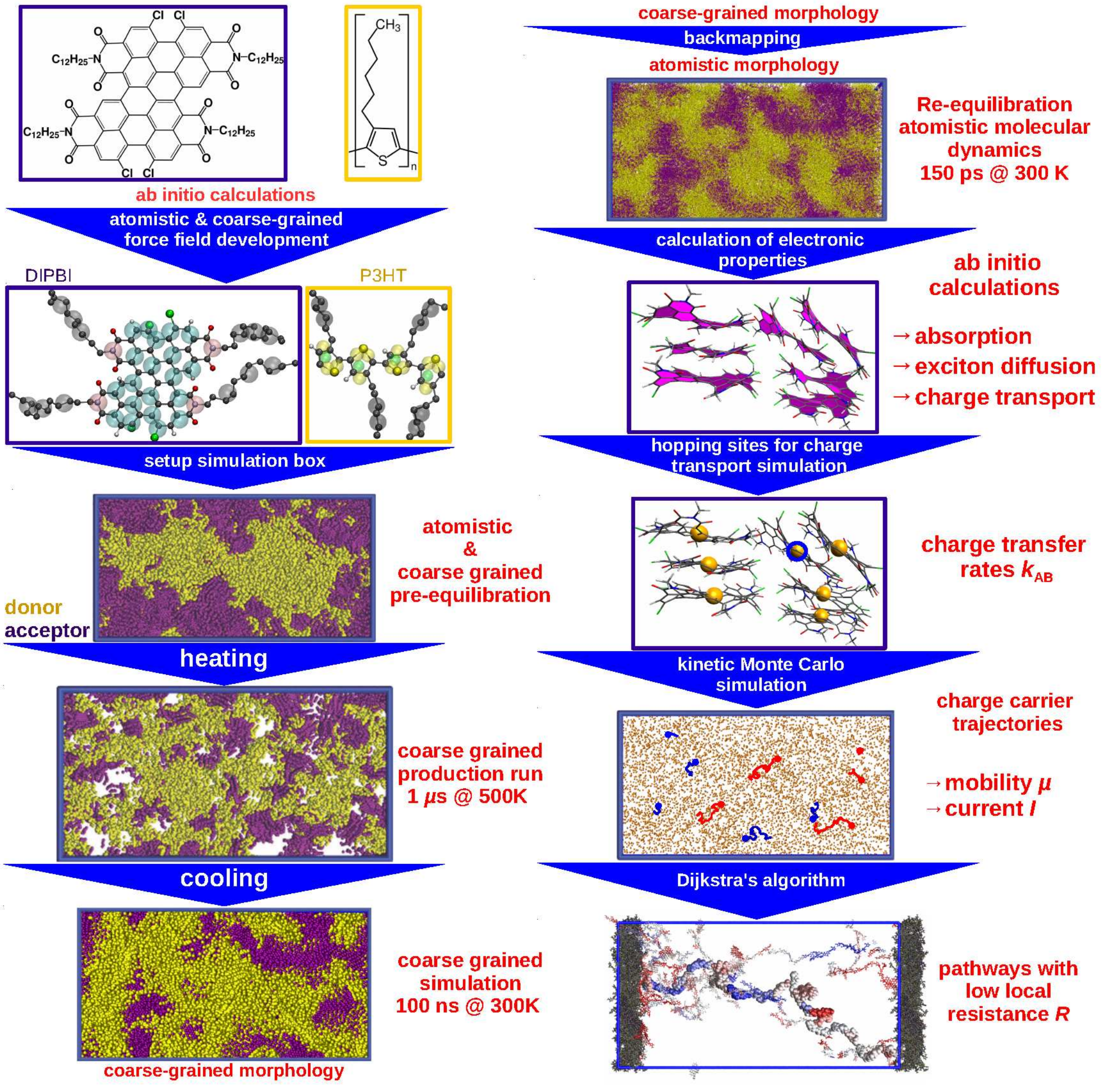
ab initio calculations
atomistic & coarse-grained force field development
DIPBI
P3HT
setup simulation box
atomistic & coarse grained pre-equilibration
donor
acceptor
heating
coarse grained production run 1 µs @ 500K
cooling
coarse grained simulation 100 ns @ 300K
coarse-grained morphology
coarse-grained morphology
backmapping
atomistic morphology
Re-equilibration atomistic molecular dynamics 150 ps @ 300 K
calculation of electronic properties
ab initio calculations
→absorption
→exciton diffusion
→charge transport
hopping sites for charge transport simulation
charge transfer rates k_{AB}
kinetic Monte Carlo simulation
charge carrier trajectories
→mobility µ
→current I
Dijkstra's algorithm
pathways with low local resistance R

Figure 3: Workflow of the multiscale model for a P3HT:DIPBI bulk-heterojunction OSC.

We start with the chemical structure of individual DIPBI molecules and the polymer P3HT. With the help of *ab inito* calculations, one can generate atomistic force fields. A force field is a parametrisation of the potential energy and interactions of a chemical system as a function of the nuclear configuration. It provides analytical expressions for intermolecular and intramolecular interactions, which are parameterised depending on, e.g. bond length, bond angles and dihedral angles.

In principle, the morphology is generatable by atomistic molecular dynamics simulations, but to adequately address the mixing of components and the process of domain formation, it is necessary to proceed to a coarse-grained level. In coarse-grained force fields, several atoms or functional groups of atoms are replaced by effective particles called beads [65, 66]. The interaction potentials between the beads are adjusted so that the atomistically generated trajectories are reproduced in a coarsened representation by a corresponding coarse-grained molecular dynamics (CG-MD) simulation. Only considering Lennard-Jones and electrostatic interactions, these beats are designed to reproduce the physical properties of molecules in an averaged manner using a reduced number of degrees of freedom.

For instance, we set up a three-dimensional orthorhombic simulation box containing e.g. 1248 DIPBI molecules and 416 P3HT chains with a length of 32 thiophene rings each. We start the creation of the morphology with a pre-equilibration scheme using atomistic and coarse-grained molecular dynamics [64]. The simulation box is then expanded in combination with the heating of the system to 500 K in CG-MD simulations to obtain a mixture of the components. Depending on the simulation protocol, one can size control of the domain formation in the CG production run and in the subsequent cooling of the system back to 300 K, which is accompanied by a shrinking of the simulation box. The CG simulations can achieve a simulation time of over one microsecond, which is required to obtain a suitable morphology. In the next step, the respective CG structure is backmapped onto an atomistic representation and re-equilibrated in an atomistic MD run to obtain the positions of individual atoms inside the simulation box [67]. On closer examination of the equilibrated morphology, we can identify the formation of ordered DIPBI π-stacks and large interconnected, disordered domains of P3HT polymers.

We extract individual molecules (and pairs) from the final morphological structure to perform electronic structure calculations using density functional theory (DFT). In particular, we use linear-response time-dependent density functional theory (TDDFT) [68] to calculate ultraviolet-visible (UV-Vis) absorption spectra of the materials [69, 70]. One aim is to find a relationship between the absorption spectra and the underlying morphology. Furthermore, the structure can be used to study exciton diffusion [71] and charge transport [72]. This enables the extraction of experimental observables from the simulation.

In the next step, we want to calculate the time-evolution of charge carriers within the morphology. Therefore, one needs to solve the master equations, e.g. by using a kinetic Monte Carlo algorithm. For this purpose, the overall morphology is then divided into different hopping-sites, representing the centres of the probability density for the excess charges in the conjugated π-system. The excess charge can thus jump from one hopping site to another in the simulation.

The kMC algorithm requires accurate hopping rates between neighbouring molecules. Since the contributions to the hopping rates vary as a function of position and orientation of the molecules in the amorphous material, the rates have to be calculated individually for every donor-acceptor charge-transfer pair.

At the beginning of each kMC simulation, we distribute different charges in the simulation box. For each occupied hopping site, the total escape rate is determined. In the first step, a charge is selected for the jump using random numbers, and in the second step, the jump destination is determined. The selected charge is transferred, and the rates to the nearest neighbours are updated again. The kMC simulations allow monitoring the charge dynamics and obtaining ensemble averages of occupation probability, charge flows, correlation functions and pathways with low local resistance using Dijkstra's algorithm [73].

All in all, we aim to demonstrate that a multiscale model as a combination of coarse-grained molecular dynamics, atomistic molecular dynamics, electronic structure calculations based on density functional theory and kinetic Monte Carlo simulations can provide a powerful toolbox to gain insight into the physical processes within an organic solar cell. Since the description of charge transport in OSCs is a multilayered, complex problem, we are confident that the multiscale model can provide information for design strategies of novel compounds that can contribute improving the performance of bulk heterojunction solar cells and electroluminescent devices in the future.

In this thesis, we introduce theoretical methods (Ch. 1), apply and compare different approaches to determine charge transfer rates (Ch. 3) and charge transport properties (Ch. 4), we provide a screening of several acceptor molecules for OSCs (Ch. 5) and investigate properties of compounds in organic light emitting diodes (Ch. 6). This work builds on earlier research by Marcus Böckmann [69, 70] and Thorsten Winands on force field development and the equilibration of morphology [64], Frank Lengers on charge transfer [74], Tobias Lettmann on CDFT [75], Dana Brünink and Christian Schwermann on Pt complexes [76, 77] and in particular by Jim Bachmann [78] on kMC simulations, combining ideas from across the Doltsinis group [59].

Thesis outline Chapter 1 summarises the theoretical background underlying the work of the dissertation. The main focus is on electron structure calculations such as DFT. We present molecular dynamics simulations from an *ab initio* and classical perspective. Charge transfer is introduced based on the Marcus theory. The rates are compared to Jortner and Weiss-Dorsey, and calculation methods for components such as the charge transfer integral, the internal and outer-sphere contributions to the reorganization energy and site-energy difference are presented. These serve as the basis for charge transport simulations using kMC.

In chapter 2, we outline the computational details for the subsequent simulations, including the workflow of the developed charge transport package.

In chapter 3, we analyse and compare different approaches to evaluate the components of charge transfer rates. We concentrate on the charge transfer integral $|J_{\mathrm{AB}}|$ and start with DIPBI dimers, present a partitioning scheme for polymers like P3HT, compare methods, e.g. CDFT, DIPRO in conjugation with DFT, DFTB and semiempirical methods. We propose a linear scaling schema of $|J_{\mathrm{AB}}|$ as well as a geometry-dependent and an overlap-dependent parametrisation of $|J_{\mathrm{AB}}|$. CDFT is used for intramolecular charge transfer in P3HT. The reorganization energy and internal site-energy differences are evaluated using DFT, DFTB, employing additional geometric constraints or a molecular cavity of the environment. We also compare measures for the hopping-site distances. We evaluate charge transfer using different rate types and discuss limitations for transitions at the donor/acceptor interface.

In chapter 4, we simulate charge transport in organic solar cells using the multiscale model for two amorphous materials P3HT and PPDI as well as to mixtures of donor:acceptor materials in organic bulk heterojunction solar cells, e.g. P3HT:DIPBI and PBDT-TS1:PPDI. We combined intramolecular and intermolecular hole/electron transport in these materials and compare different parametrisation schemes (rate distributions, convergence of the mobility) and obtain quantities as the charge carrier mobility, site-occupation probabilities, local currents, pathways low local resistance.

In chapter 5, we present a screening of thirteen perylene diimide acceptors regarding their chemical structure (conformations, chirality, stability), spectral properties (bulk, solution, film), aggregation behaviour and the resulting charge transfer properties for the application in OSCs.

Similarly in chapter 6, we investigate six metal-organic complexes and three organic compounds concerning the impact of chemical modifications on absorption, photoluminescence, the character of the emissive state, zero-field splitting, aggregation motives associated binding energies, charge transfer properties, for electroluminescence in organic light-emitting diodes.

Finally, in chapter 7, we summarise our findings and give an outlook on possible next steps for this research.