Charge and Energy Transport in Disordered $\pi$-conjugated Systems

PROEFSCHRIFT

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Chapter 1

Introduction

ABSTRACT

In this Chapter a brief overview is given of the field of conjugated polymers, with or without dye molecules blended in. We start with a historical overview and review some basic properties regarding the conjugated character, and subsequently we discuss some important commercial applications of these materials. We continue with a more fundamental discussion about different techniques to calculate the electronic and optical properties of conjugated polymers and dye molecules. Finally, we will introduce some modelling approaches that have been applied in order to describe several characteristic features of charge and/or energy transport as found in experiments. We close this Chapter by giving an outline of the thesis.
1.1 Conjugated polymers

1.1.1 History

In the 1950s the first studies of semiconducting organic materials focussed on small organic molecules in the crystalline state. The experiments involved were photoconductivity measurements, determining the drift mobilities of electrons and holes in anthracene crystals [1, 2, 3, 4, 5]. Although the materials displayed the semiconducting properties of their inorganic counterparts, the performance was poor and the materials were considered as exotic materials with little potential for applications. In the mid-1960s [6] molecularly doped polymers with improved organic semiconducting properties appeared and they were intensively studied thereafter [7, 8]. Molecularly doped polymers are formed by including small organic pigments into an insulating polymer matrix. In this way the photoconductive properties of the pigments are combined with the mechanical properties of the polymer. Because of the ease of processing, flexibility, material variety, and environmental safety this class of materials was expected to be well-suited for xerographic applications. Indeed, since the 1970s multilayers of these organic photoconductors have replaced the amorphous-selenium and amorphous-silicon photoreceptors in electrophotographic devices like photocopiers and printers [9].

A very important step forward in the field of conducting polymers was made by accident. In the early 1970s Hideki Shirakawa of the Tokyo Institute of Technology was aiming to make the organic polymer polyacetylene. However, a visiting scientist added 1,000 times more catalyst than the recipe of Shirakawa called for. As a result he produced a peculiar film that resembled aluminum foil, but it was very stretchable. After some time the glittering silvery film arose the interest of Alan G. MacDiarmid, who visited the Tokyo Institute to give lectures and he wondered whether it could be used as a possible candidate for his goal to make a nonmetallic electrical conducting substance, a "synthetic metal". He invited Shirakawa to work at the University of Pennsylvania, and so Shirakawa joined the group of Alan G. MacDiarmid and Alan J. Heeger in 1976 [10]. Together they continued working on the substance and after doping with iodine or arsenic pentafluoride they reported an increase of the conductivity over ten orders of magnitude [11, 12]. This discovery induced a lot of research and especially the interest revived at the end of the 1980s as a result of the demonstration of high-performance electroluminescent organic multi-layer structures of vacuum-sublimed dye films at Eastman Kodak [13, 14]. Moreover, the report of field-effect transistors made from polythiophene [15, 16] and from small conjugated oligomers [17, 18] offered new perspectives. Subsequently, the discovery of electroluminescence (EL) from diodes based on the conjugated polymer poly(para-phenylene vinylene) at Cambridge University [19] initiated a lot of activity in the field of conjugated polymers, certainly because of the possible commercial applications. Below, we will first discuss some basic properties of conjugated polymers and then, in the next section, show some important commercial applications.
FIGURE 1.1: Chemical structure of the most common conjugated polymers. Hydrogen atoms are not shown and can be replaced by different sidegroups.

Fig. 1.1 shows the chemical structures of commonly used conjugated polymers. In conventional polymers (e.g. plastic bags of polyethylene (CH$_2$)$_x$) every carbon atom in the backbone is $\sigma$-bonded to four atoms in the $sp^3$ hybridized configuration. The difference with a conjugated polymer is that three of the four electrons in the outer shell of carbon occupy $sp^2$ hybridized states, creating the $\sigma$ bonds that form the strong structural backbone of the polymer. The remaining free electron occupies a $p_z$ orbital. The equivalent $p_z$ orbitals from neighboring carbon atoms overlap and form the so-called $\pi$-electron system, which in principle (ideally) extends over the full length of the polymer backbone. To lower the total energy, the polymer forms an alternating structure of single and double bonds of $\pi$ orbitals, as drawn in Fig. 1.1. Although this process costs lattice energy, because the double bonds are shorter than the single bonds, the gain in electronic energy, due to an opening of an energy gap of about 1.5 to 3.5 eV between filled bonding states (the Highest Occupied Molecular Orbital (HOMO) states or valence band) and the empty antibonding states (the Lowest Unoccupied Molecular Orbital (LUMO) states or conduction band) is larger [20]. It is this opening of an energy gap that makes the polymer a semiconducting material.

In reality a picture on a microscopic scale of a sample consisting of a conjugated polymer would look like spaghetti. Electronically, each polymer chain may be considered to consist of a number of separated conjugated segments because of the presence of twists, kinks, or impurities that disrupt the $\pi$-conjugation of the same physical chain. The term "conjugation length" is used to describe the mean length of these conjugated segments. As a result of these twists and kinks the chains cannot be aligned over their whole length and thus the polymers (can) show only a partial crystallinity. The typical size of these crystalline regions is 10-50 nm and these regions are always interconnected by amorphous regions [21]. The energies of the conjugated segments are modified by their different local arrangement, which gives rise to locally varying polarizabilities and dipole interactions between neighbor-
All these effects together will cause the charge carriers to be localized. In order to have transport of these localized charge carriers, their motion will be “hopping-like” [23]; they will “hop” from one chain to another chain in order to move through the system. This transport mechanism is different from the “band-like” transport, present in inorganic semiconductor crystals like silicon or germanium. We will come back to hopping transport in section 1.4.

1.1.2 Applications

In this section, we will briefly discuss some applications of conjugated polymers that might be most relevant from a commercial point of view: the polymer light-emitting diode (pLED), the organic field-effect transistor (FET), and the organic photovoltaic cell.

Light emitting diodes

The simplest conjugated polymer-based LED consists of a single layer of a fluorescent polymer, often a derivative of poly(p-phenylene vinylene) (PPV), sandwiched between two electrodes, one of which has to be transparent. For the single-layer device to operate, the conjugated polymer must perform three functions: hole transport, electron transport, and emission. In Fig. 1.2 we schematically illustrate the energy-level structure and the basic steps for the device to operate. Holes are injected from the anode made of the transparent

---

**FIGURE 1.2:** Basic steps of electroluminescence: (1) charge carrier injection, (2) charge carrier transport, (3) exciton formation, (4) radiative exciton decay. $\Phi_A$: anode work function, $\Phi_C$: cathode work function, $\Phi_h$: hole injection barrier, $\Phi_e$: electron injection barrier, $\Phi_{bi}$: built-in potential, $V$: applied voltage, $V_e$: effective voltage across the organic layer, $q$: elementary charge. Picture taken from Brütting *et al.* [24].
metal Indium-Tin Oxide (ITO), into the HOMO, and electrons from the cathode, e.g. a calcium electrode, into the LUMO of the polymer. The injected charges migrate through the organic layer by hopping from polymer chain to polymer chain and under the influence of the applied electric field they obtain a drift velocity. When charges of opposite sign combine on a conjugated segment they form singlet and triplet excitons. An exciton is a bound electron-hole pair of which only the singlet states decay under the emission of a photon. To have an efficient device the holes and electrons should have roughly the same mobility and injection rate. Otherwise, the charges will just pass through the polymer without recombination. It is clear that finding a single polymer that fulfils all the requirements for optimal performance is a difficult task. This immediately brings us to the existence of multi-layer structures [25, 26]. People have tried to overcome restrictions inherent to the use of specific polymers by using various polymers for different purposes. This was first accomplished by the Kodak group in the 1980s [13]. For example, in the case of a trilayer device [26], the material adjacent to the anode can be selected for good hole injection and transport, while the material adjacent to the cathode permits good injection and transport of electrons. Moreover, a third layer in between offers the possibility of selecting the emissive material independent of its transport properties.

Fourteen years after the first discovery of electroluminescence in a conjugated polymer, the first commercial applications based on these electroluminescent conjugated polymers have become available, e.g. the display on a recent shaver of Philips.

**FIGURE 1.3:** The left hand side shows a men’s shaver by Philips. Its new feature is a polymer light-emitting diode display showing information including shaving time remaining before recharge. On the right: Philips will apply PolyLED - its application of an Organic Light-Emitting Diode (OLED) display - in the new Philips 639 mobile phone. It has been introduced in the course of the second quarter of this year in selected countries. Actually, the display is at the cover. Photos: Philips.
Field-effect transistors

Nowadays logical circuits and microprocessors use field-effect transistors (FETs) instead of bipolar transistors. The bipolar transistor, invented in 1947 [27, 28], marked the birth of modern microelectronics. The concept of a FET was proposed by Lilienfield in 1930 [29] and realized in 1960 in a first practical application [30]. In a FET, the current is flowing between two electrodes, the source and the drain, and is controlled by applying a voltage to the third electrode, the gate. Single-crystalline silicon is the most widely used material in microelectronics, but the wafers are fragile, expensive and not suitable in large-area applications. For these latter applications there are three possible candidates, namely hydrogenated amorphous silicon (a-Si:H), polycrystalline Si, and organic semiconductors. In 1970 the first field effect has been observed in an organic semiconductor [31]. After the discovery of Shirakawa, MacDiarmid, and Heeger [11, 12], research in the field of organic FETs (OFETS) received more interest. The first polyacetylene OFET was reported in 1983 [32]. By that time the FET consisted of an organic material on a silicon wafer, so the big challenge was of course to build an OFET on plastic substrates.

The first ”nearly-all” organic transistor [18] was reported in 1990, the only inorganic materials being the electrodes. Finally, in 1998, the group of de Leeuw at Philips succeeded in producing an ”all-organic wafer” [33]. The device was all spincoated and built on a flexible polyimide substrate, with a poly(thiénylenevinylene) (PTV) semiconductor, a poly(vinylphenol) (PV) insulator and doped polyaniline (PANI) source and drain electrodes. The area of this large integrated circuit was 27 mm$^2$, and comprised 50 transistors on a single wafer. One of the most important parameters for the performance is the charge-carrier mobility, because this determines the clock frequency of the device. This brings us automatically to the awareness that it is unlikely that conjugated polymers will replace single-crystalline silicon in central processing units of our computers. But with a clock frequency of $10^3$ Hz they are good candidates for low-end, high-volume applications like disposable electronics, e.g. for product tagging or identification, because of their possible fabrication by low-cost technologies such as spin-coating and printing techniques.

Solar cells

During the late 1970s and early 1980s a lot of attention was paid to the research and development of photovoltaic cells. During this time the interest was also devoted to the development of organic materials for the use in photovoltaic cells. The first studied compounds were merocyanines [34] and phthalocyanines [35], which could readily be deposited as a thin film on different flexible substrates. In the previous section we discussed the physical mechanism for the pLED, and the mechanism for the photovoltaic cell is precisely the other way around. A large optical absorption in the visible spectrum generates holes and electrons, which are collected at the electrodes to produce a current. It is important to distinguish the two tasks the materials have to carry out: photoinduced charge generation and transport of created charges to the electrodes. Efficiencies of the first polymeric solar cells based on polyacetylene were very low [36]. Higher efficiencies were achieved by
using the same class of materials as in pLEDs and mixing them with electron acceptors [37]. These donor/acceptor mixtures showed solar-energy conversion efficiencies of around 1% [38]. Particularly the polymer/fullerene solid composites have been well investigated over the last few years [39]. The first truly promising results for bulk-heterojunction solar cells formed between conjugated polymers and fullerenes were obtained in 2001 by Shaheen et al. [40], and recently power conversion efficiencies >3% have been reached for polymer:fullerene bulk-heterojunction solar cells [41, 42, 43].

The reason for the interest in polymeric solar cells is the same as for the pLEDs. It is economically advantageous to make large-area photovoltaic elements on flexible substrates. This mechanical flexibility is very convenient for photovoltaic applications on curved surfaces. The low-cost technologies already developed for plastic thin-film applications can thus be used for large-scale coating of photovoltaic elements as well.

To end this section about the applications we quote a statement of Alan Heeger: As a result of the remarkable progress in the chemistry, physics and engineering (device physics) of semiconducting and metallic polymers, we are now witnessing the beginning of a revolution in ”Plastic Electronics” [44].

1.2 Polymer-dye blends

As discussed in section 1.1.2, the first commercial realizations of pLEDs are a fact. However, these are still monochrome polymer displays and nowadays we are not satisfied but with full-color displays. Production of full-color polymer displays would involve the processing of three different polymers for the three principal colors. However, due to the wide distribution of HOMO and LUMO levels in conjugated polymer systems, their emission bands are rather broad, giving rise to mixed-color light emission. This is of course highly undesirable: due to the variable color sensitivity of the human eye, e.g. any small amount of green emission in a primarily red emitting light source will lead to the perception of an orange color. Furthermore, the processing of three rheologically different polymers for the three principal colors is rather costly. To circumvent these problems a substantial research effort is put into the incorporation of dye molecules in the polymer layer [45, 46, 47, 48, 49, 50, 51, 52], exploiting the mechanism of energy transfer from polymer to dye. The functioning of such dye-doped polymers is based on the transfer of electronic excitations from the polymer to the dye. This mechanism of energy transfer will be discussed in section 1.5. By changing the dye rather than the polymer it should be possible to cover the whole visible-light spectrum. Other benefits of using dye molecules as emission centers are their narrow emission bandwidths, leading to a high color purity. An extensive (chemically oriented) review about the incorporation of various classes of dyes has been given by [53]. Moreover, recent electroluminescence experiments [54] have shown the possibility of fine-tuning the emission spectrum of e.g. dipyrrolomethene dyes,
commercially known as BODIPY dyes [55], by chemical modification of specific sidegroups [54]. The idea behind the use of these sidegroups is to manipulate the HOMO and LUMO energies by extending the $\pi$-conjugation and adding an electron-donating methoxy group. Put together, all these properties make these blends excellent candidates for further development of full-color pLEDs.

The following part of this chapter is more theoretically oriented. The presented introduction will serve as background information for the rest of this thesis, and it will enable us to more precisely formulate the goal of the study in section 1.6.

### 1.3 Electronic structure calculations

Knowledge about the electronic and optical properties of conjugated polymers is crucial in understanding and optimizing the functioning of the devices, as can be concluded from the previous sections. It would, e.g., be very useful to be able to predict (based on calculations of the electronic structure) in advance how certain conjugated systems would perform. In this section we will briefly address the issue of modelling the electronic and optical properties of conjugated polymers. It all starts with the Hamiltonian for a many (say $N$)-electron system given by (in atomic units; $\hbar = e^2/(4\pi\varepsilon_0) = m_e = 1$):

\[
\hat{H} = \sum_i \left[ -\frac{1}{2} \nabla_i^2 + v(r_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \quad (1.1)
\]

\[
= \hat{T} + \hat{V} + \hat{U}. \quad (1.2)
\]

Here $\hat{T}$ is the kinetic energy operator, $v(r)$ the external potential due to the positive nuclei, and $\hat{U}$ represents the mutual Coulomb repulsion. The corresponding Schrödinger equation is:

\[
\hat{H} \Phi = E \Phi, \quad (1.3)
\]

where $\Phi = \Phi(r_1, r_2, ..., r_N)$ with $r_i$ labeling both position and spin. A first attempt to really solve Eq. (1.3) was made by Hartree, who proposed to write $\Phi$ as:

\[
\Phi(r_1, r_2, ..., r_N) = \phi_1(r_1)\phi_2(r_2)...\phi_N(r_N), \quad (1.4)
\]

where $\phi_i$ satisfies a one-electron Schrödinger equation:

\[
\left[ -\frac{1}{2} \nabla_i^2 + v(r_i) + V_H(r_i) \right] \phi_i(r_i) = \epsilon_i \phi(r_i), \quad (1.5)
\]

with $V_H$ the Hartree potential, given by:

\[
V_H(r_i) = \sum_j \int \! dr_j \left| \frac{\phi_j(r_j)}{|r_i - r_j|} \right|^2. \quad (1.6)
\]
By writing the wave functions as in equation (1.4) the many-electron problem formulated in Equation (1.1) and (1.3) has become an effective one-particle problem. An obvious deficiency of the approximation (1.4) is that it does not take the fermionic nature of the electrons into account, i.e. the fact that their wave function should be anti-symmetric with respect to exchanging two electrons. This can be achieved by replacing the single wave function in (1.4) by a Slater-determinant:

\[
\Phi(r_1, r_2, \ldots, r_N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{c}
\phi_1(r_1) \\
\phi_2(r_1) \\
\vdots \\
\phi_N(r_1)
\end{array} \begin{array}{c}
\phi_1(r_2) \\
\phi_2(r_2) \\
\vdots \\
\phi_N(r_2)
\end{array} \begin{array}{c}
\vdots \\
\vdots \\
\vdots \\
\vdots \\
\phi_1(r_N) \phi_2(r_N) \ldots \phi_N(r_N)
\end{array} \right|.
\] (1.7)

By the use of this Ansatz for the many-body wavefunction and requiring the orbitals to be optimized, such that the Hartree-Fock (HF) energy - the energy obtained by disregarding the effect of electron correlation - is minimal under the constraint that the orbitals remain orthonormal, we end up with the so-called Hartree-Fock equations. This set of equations has to be solved self-consistently because the wave functions depend on the potential, and the potential itself depends on the wave functions. This is the reason why the Hartree-Fock approach is often called a self-consistent-field (SCF) approach. As pointed out, a fundamental shortcoming of HF theory is that electron-correlation effects are neglected. There are two major ways to cope with this shortcoming. The first is by Möller-Plesset perturbation theory [56] (often abbreviated as MP\(n\), with \(n\) the order of the perturbation theory), the second by taking into account more than one Slater determinant, called 'configuration', as is done in a multiconfiguration SCF method [57]. This latter method, Configuration Interaction (CI), where instead of just the simple HF Slater determinant also many excited configurations are taken into account, is able to give (in principle) exact results for all system properties. However, when e.g. applied to conjugated-polymer systems this is only possible for a system size of a few monomers. The major problem of the afore-mentioned methods is that they are very time-consuming, which explains why the interest in density-functional theory (DFT) grew so rapidly in the last few decades.

DFT provides a first-principles approach with very good computational efficiency. The central quantity of interest in DFT is the electron density \(n(r)\). Instead of calculating the complete wave function \(\Phi(r_1, r_2, \ldots, r_N)\), which depends upon the coordinates of all electrons, knowledge of the electron density is sufficient to obtain the ground-state energy, which was first proven by Hohenberg and Kohn [60]. The essentials of the theory are contained in the two so-called Hohenberg-Kohn theorems [60]. The first theorem states that there exists a one-to-one mapping between the external potential and the ground-state density, implying that the ground-state wave function is also uniquely defined by the ground-state density, and hence the ground-state properties. The second HK theorem states that there exists a non-universal energy functional of the electron density that is minimal for the ground-state density. Although the HK theory is exact, practically it is not very useful. The practical scheme to perform calculations was developed one year later by Kohn and Sham [61]. They derived the well-known Kohn-Sham equations, describing
a fictitious system of non-interacting electrons in an effective potential, such that the corresponding density is the same as that of the system of interacting electrons.

In our group DFT has been successfully applied to conjugated polymers [58, 59]. In order to perform the DFT calculations we make use of the computer program VASP [65, 66] (Vienna ab-initio Simulation Package). This program is especially suitable to deal with extended systems, like polymers, because it makes use of periodic boundary conditions. If we put one monomer in a unit cell and employ periodic boundary conditions we have created an extended (π-conjugated) system. VASP is currently the fastest and most accurate program to perform DFT calculations for periodic systems.

It is known that DFT can reproduce the ground-state properties correctly, but in order to obtain information about the excited-state properties one has to go beyond DFT. To perform calculations for the excited state properties we use the program EQP (Eindhoven Quasi-particle Program), developed in our group. The one-particle energies, i.e. the energies required to add or remove an electron (the latter being equivalent to adding a hole to the system), are calculated by solving the quasi-particle equation within the \( GW \) approximation [62]. From these calculations one would be able to obtain the energy to put an electron in the LUMO or take an electron from the HOMO. Of course in a real system, e.g. a pLED, the electrons and the holes are present simultaneously and interact with each other. To include this interaction between an electron and a hole one has to solve the Bethe-Salpeter equation (BSE) [63, 64] for the two-particle spectrum (electron and hole). An extensive review of how the \( GW \) and BSE methods have been implemented can be found in [67]. The \( GW \) and BSE methods have been applied in our group to conjugated polymers with great success.

However, as usual, every method has its drawbacks. In case of the polymer-dye systems, discussed in section 1.2, the dye molecules are only "small" finite objects (with respect to the polymer). If one wants to calculate the intrinsic properties of one dye molecule with the solid-state methods mentioned before, the unit cells become very big. This is because we should have enough free space around the dye molecule to be sure that there are no interactions with the periodic images. Big unit cells require a lot of memory and a lot of computational time, to (mostly) calculate irrelevant properties of free space. It turned out that the DFT calculations for our systems were tractable with VASP, but that the \( GW \) and BSE calculations became impossible. The solution was to resort to quantum-chemical methods that are especially developed to study finite systems, like atoms and molecules. For this purpose we used ADF (Amsterdam Density Functional program) [68]. With ADF ground-state calculations are possible, but the most important reason to use the ADF code is that one can perform calculations of excited-state properties as well. The method involved is the so-called time-dependent density-functional theory (TDDFT), first derived by Runge and Gross[69]. The TDDFT method is in principle an exact method to obtain the excited-state energies. The idea behind this theory is basically the same as for DFT, except that the density is now taken to be a time-dependent property. Another new method included in the ADF code to calculate the excited state properties is based on
time-dependent current-density-functional theory (TDCDFT). This new method has the potential to be better applicable in case of conjugated systems. TDCDFT is an extension of TDDFT, based on the current density instead of the electron density. In Chapter 2 we will briefly discuss some theory behind these methods. Summarized, the scheme for the calculations using the different methods looks as follows. Ground-state properties ($N$ electron system) are calculated by DFT, and then excited-state properties are calculated either via TD(C)DFT or GW/BSE, see Fig. 1.4. In table 1.1 we have shown how the different methods compare to each other with respect to computational resources, taking into account typical order of the parameters as used in the calculations. One has to realize that the structures taken for the DFT and TD(C)DFT calculations involve systems where no specific symmetries could be applied.

<table>
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</tbody>
</table>

Table 1.1: Comparison of the performance of the different methods. Note that for TDCDFT it is not exactly clear whether the given accuracy is correct. Really large systems have not yet been investigated by this method. A recent review about the performance of TDCDFT for small molecules has been given in [70].
As argued in section 1.1.1 conjugated polymers have their π-conjugated system extended along the polymer chain. As a result of this, the delocalized states extend in one direction. This is precisely the reason why conjugated polymers were initially regarded as idealized one-dimensional semiconductors. Su, Schrieffer, and Heeger (SSH) were the first who studied the dynamics of the π-electrons along the one-dimensional chain [71]. The SSH model is a simple tight-binding model for polyacetylene, neglecting Coulomb interactions and disorder effects. The coordinates and motion of the atomic nuclei are treated classically, but the π-electron dynamics is treated quantummechanically in a tight-binding approximation. The essential point of view in this model is that the coupling between neighboring nuclei is incorporated via a distance-dependent hopping term, which increases when the distance between the two nuclei decreases. It is well known that this model produces a whole zoo of exotic phenomena, like solitons, polarons, soliton-polarons, bipolarons, etc. For a detailed overview we refer to a review of Heeger et al. [71]. Although there are several outcomes of this theory that are supported by experiments [72], one of the most important drawbacks of this theory is the lack of taking into account disorder. The SSH picture might be applicable in experiments on isolated single chains, or highly ordered and stretch-oriented polymer systems, but it is well known that common conjugated polymer systems have a disordered nature (as discussed in section 1.1.1) and that the disorder plays a very important role in the charge transport. In these systems it is not possible to come up with a picture of the polymer system as a one-dimensional semiconductor. Because of the disorder, the system has no translation symmetry and this causes the formation of localized states in the energy gap between the valence band (HOMO) and conduction band (LUMO). In order to have a current through the device, charge carriers trapped at the localized states need to escape from these sites. Therefore, the conduction process involving localized states is entirely determined by the tunneling transitions of the charge carriers between the localized states, which is possible if there is sufficient overlap of the electronic wave functions. The carriers may overcome the energy differences between the sites by absorbing or emitting a phonon (or multiple phonons). Hence, the name given to this mechanism of phonon-assisted tunneling is ”hopping conduction”. It was originally proposed by Mott [73] and Conwell [74] to explain the temperature dependence of the DC conductivity as observed in compensated crystalline semiconductors. Later, the formalism was applied to the case of amorphous semiconductors [75], and nowadays the concept seems very well applicable to study the conductivity of a wide range of different materials, e.g. conjugated polymers, DNA, and high \( T_c \)-cuprate oxides [76, 77, 78, 79].

The (asymmetric) transition rate \( W_{ij} \) for hopping from a localized state \( i \) to a state \( j \) has first been calculated by Miller and Abrahams [80] and is given by:

\[
W_{ij} = \begin{cases} 
\nu_{ph} \exp\left[-\alpha |R_{ij}| - \beta (\varepsilon_j - \varepsilon_i)\right], & \varepsilon_j > \varepsilon_i \\
\nu_{ph} \exp\left[-\alpha |R_{ij}|\right], & \varepsilon_j < \varepsilon_i.
\end{cases}
\] (1.8)

Here \( \nu_{ph} \) is an intrinsic rate, \( \alpha \) is the inverse localization length, \( |R_{ij}| \) the distance between
the localized states, $\beta = 1/kT$, and $\varepsilon_i$ the energy at state $i$. In Fig. 1.5 we have tried to visualize the physics behind the wave function overlap as taken in the above-given transition rate. The tails of the wave function are the important part determining the overlap, the inner structure of the wave function does not play a crucial role in the hopping process. The tails are in a fairly good approximation described by an exponential. From the functional form of the transition rate it is clear that the conductivity will strongly depend on the energetic and structural disorder, and thus on the temperature. Moreover, the assumption behind this transition rate is that for hops downward in energy there are always phonons available to absorb the specific energy. More refined transition rates have been supposed by Emin and Marcus [81, 82], but they all lead to more difficult expressions for which it is less transparent when exactly they should be taken into account, we will elaborate more about this in chapter 5. To study theoretically the hopping transfer mechanism of positive and negative charges in disordered systems, the incoherent motion of the charge carriers for which doubly occupied electronic states are not allowed can be described by a kinetic equation known as the Pauli Master-equation:

$$\frac{\partial n_i}{\partial t} = -\sum_{j \neq i}[W_{ij}n_i(1 - n_j) - W_{ji}n_j(1 - n_i)], \quad (1.9)$$

where $n_i$ is the occupational density of site $i$, and $W_{ij}$ the transition rate given by Eq. (1.8). In this general form the master equation is nonlinear and is very difficult to handle. A natural way to overcome the problem of non-linearity is to linearize the equation in the presence of a small external electric field resulting in small deviations from equilibrium. In literature a lot of effort has been put in order to solve the linearized version of the Master-equation analytically. For completeness we will mention the standard works in which many more references can be found. These standard works can be roughly divided as based on three different methods to solve the equation: (1) by means of a mapping of the disordered system to a random resistor network [80], combined with effective medium techniques [83], or percolation techniques [84, 85, 86], (2) by use of continuous-time random walk methods [87], and (3) through Green's function methods [88, 89, 90]. The latter
method will be briefly described in Chapter 5, where we will also discuss a derivation of the Pauli Master-equation. Our solution for tackling the problem has been by solving the Pauli Master-equation in a numerically exact way, which will be discussed in Chapter 5 as well. This offers also the possibility to compare to the earlier developed methods existing in literature.

In the following we will present a very simple but brilliant argument by Sir Nevill Mott, which circumvents the use of all kinds of advanced techniques to calculate the conductivity in a disordered system. The model is called ”Mott’s Variable Range Hopping” (VRH) model and is to be applied in the low-temperature regime. The basic assumption is that hopping transport takes place from localized states with energies $\varepsilon_i$ distributed around the Fermi level $E_F$, with $N(\varepsilon)$ the density of states (DOS) around this energy level. We can consider two limiting cases:

1. If $\beta |\varepsilon_j - \varepsilon_i| \ll 1$ for all pairs of energies, the hopping rate (1.8) is limited by $\exp(-\alpha |R_{ij}|)$ and transitions occur only between nearest neighbors, resulting in thermally activated transport.

2. If $\beta |\varepsilon_j - \varepsilon_i| \gg 1$ for all pairs of energies, in the hopping rate (1.8) the spread in energies becomes important and transitions will occur between sites with an optimal combination of $(|R_{ij}|, |\varepsilon_j - \varepsilon_i|)$. This is the situation that is called VRH.

Mott was the first who realized that at low temperatures the (as he expresses) ‘most frequent’ or ‘typical’ hopping process would not be to a nearest neighbor [73], and he formally expressed this as follows:

$$\int_0^R \int_{E_F}^{E_F+E'} dR' \int_{E_F}^{E_F+N} d\varepsilon' N(\varepsilon') \approx 1.$$ \hfill (1.10)

Thus for the typical hopping process, within a distance $R$, on average one pair of sites with absolute energy difference $E$ is present. If this is not the case, the hopping process will die, and as a result no net DC current will flow. The above stated Mott condition yields an expression for the energy $E$ in terms of $R$ and $N(\varepsilon)$, for which a constant density of states around the Fermi level $N(E_F)$ will be assumed:

$$E = \frac{R^d}{V_d N(E_F)}.$$ \hfill (1.11)

$V_d$ is the volume proportionality factor of a sphere with radius $R$ in the $d$-dimensional Euclidean space\(^1\). Using the expression for $E$ to minimize the hopping rate $\nu_{ph} \exp[-\alpha R - \beta E]$ with respect to $R$, we find for the typical hopping distance

$$R = \left( \frac{\beta d}{\alpha V_d N(E_F)} \right)^{1/(d+1)}.$$ \hfill (1.12)

The result for $R$ together with equation (1.11) gives an estimate of the typical hopping rate. This is used to identify the famous Mott law for the conductivity via the assumption

---

\(^1V_d = \frac{\pi^{d/2}}{\Gamma((d+1)/2)}\), with $\Gamma(z)$ the gamma-function
that the conductivity is determined by the single-hop rate for this optimal combination of \( R \) and \( E \):

\[
\sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/(d+1)} \right], \quad \text{with} \quad T_0 = \frac{\alpha^d [d^{1/(d+1)} + d^{-d/(d+1)}]^{d+1}}{V_d N(E_F) k}.
\]

The pre-exponential factor \( \sigma_0 \) cannot be obtained by the considered procedure, but the temperature dependence of the conductivity is obviously dominated by the exponent. This specific temperature dependence of the conductivity has been observed in many experiments and is usually referred to as "Mott" behavior.

One may criticize the above given derivation, e.g. by asking the question why only the optimal single-hops characterize the DC conductivity. In literature this led to a more systematic derivation of the temperature dependence based on percolation arguments \([84, 85, 86]\). In that work the problem of calculating the conductivity in a disordered system is mapped to that of a random resistor network. In this case the conductance between two sites \( i \) and \( j \) is given by

\[
G_{ij} = G_0 \exp[-s_{ij}],
\]

provided there is only a low bias, and the thermal energy is small compared to energy variations. Now, the argument is that the conductivity is determined by the critical percolation conductance \( G_c = G_0 \exp[-s_c] \), and as such \( \sigma = \sigma_0 \exp[-s_c] \), with \( \sigma_0 \) an (unknown) prefactor. \( G_c \) is defined as the largest conductance for which the network, after removal of all \( G_{ij} < G_c \), still contains a percolating path through the entire system. Conductances \( G_{ij} \gg G_c \) act as short circuit, while \( G_{ij} \ll G_c \) are bypassed by the current. The problem is thus reduced to determining the bond-percolation threshold \( s_c \). At the onset of percolation a critical number of bonds per sites \( B_c \) is reached. This number has been calculated, and for a three-dimensional amorphous system \( B_c \simeq 2.8 \) \([91, 182]\). This percolation criterion \( B(G = G_c = B_c) \) can be written as

\[
B_c = \frac{N_b}{N_s},
\]

where \( N_b \) is the density of bonds and \( N_s \) is the density of sites in the percolating system. The density of bonds is given by

\[
N_b = \int dR_{ij} \int d\epsilon_i \int d\epsilon_j g(\epsilon_i) g(\epsilon_j) \theta(s_c - s_{ij}),
\]

and the density of sites \( N_s \) can be estimated by excluding all sites that cannot possibly belong to an infinite cluster \([182]\):

\[
N_s = \int d\epsilon g(\epsilon) \theta(s_c kT - |\epsilon - \epsilon_F|).
\]

By solving the above-given equations one obtains a value for \( s_c \) and from that the conductivity. Applying this machinery of percolation theory in the case of a constant DOS, one
arrives at an expression for the temperature dependence of the exponent determining the conductivity, analogous to Eq. (1.13). The percolation theory presented above is in essence not an improvement of the original Mott theory, it only translates the problem to a more realistic situation of a percolating resistance network. Actually, the percolation criterion given by $B_c$ is equivalent to that of the Mott condition Eq. (1.12). Another problem is that, like in the previously discussed Mott procedure, the pre-exponential factor $\sigma_0$ cannot be obtained. In fact, in case of the percolation treatment, the prefactor of the exponent is zero exactly at the percolation threshold.

Although the VRH model has been applied successfully to describe the temperature dependence of the conductivity in conjugated polymers, it is not capable of accounting for the very often found functional form of the electric field ($E$) dependence of the carrier mobility $\mu$:

$$
\mu(E) = \mu_{E=0} \exp \left[ -\frac{\Delta}{kT} + B \gamma \sqrt{E} \right], \quad \gamma = \frac{1}{kT} - \frac{1}{kT_0},
$$

(1.18)

which is an intriguing common feature of disordered organic semiconductors. Here, $\Delta$ is the zero-field activation energy, $\mu_{E=0}$ the mobility in absence of an electric field, and $B$ and $T_0$ are parameters of the system. This empirical form of the mobility was first observed by Gill in 1972 for poly(N-vinyl carbazole) [8]. The $\sqrt{E}$ dependence of the mobility is nowadays often referred to as Poole-Frenkel behavior. Later on numerous experimental studies on different disordered organic materials have revealed similar behavior [92, 93, 94, 95, 96, 97]. The first attempt to explain this ubiquitous behavior was made by Bässler and coworkers [92, 98]. They made the assumption of a Gaussian DOS with a width $\sigma$, describing the energy disorder in conjugated polymers due to structural disorder - either static or dynamic - and local interactions. They performed Monte-Carlo simulations to test the assumption of this so-called Gaussian Disorder Model (GDM). The idea behind the use of a Gaussian DOS is the following. The polymer is a disordered system and so the energies of the localized states are randomly distributed (according to an arbitrary distribution with zero average and finite variance). Then, according to the Central Limit Theorem, the resulting distribution is a Gaussian [99]. With this assumption Bässler and coworkers were able to reproduce Eq. (1.18) for temperatures around room temperature, but only for a very narrow field range and at relatively high electric fields as compared to the experimental regime. The functional dependence of $\mu$ on temperature and electric field they found from a fit to their numerical results reads:

$$
\mu_{GDM} = \mu_{\infty} \exp \left[ - \left( \frac{2\sigma}{3kT} \right)^2 + C \left( \frac{\sigma}{kT} \right)^2 - 2.25 \right] \sqrt{E}.
$$

(1.19)

Comparison with (1.18) shows that the phenomenological parameters $\Delta$ and $\gamma$ may be related to the microscopic parameter $\sigma$. Nonetheless, a very important difference with Eq. (1.18) is the temperature-dependence of the zero-field mobility. In order to improve the regime of validity for the $\sqrt{E}$ dependence, Gartstein and Conwell [100] took into account spatial correlations between the energies of neighboring sites, which turned out
to successfully extend the Poole-Frenkel regime to lower electric fields as experimentally observed. Moreover, Dunlap et al. developed an analytical one-dimensional treatment based on long-range energy correlations due to charge-dipole interactions in the material [101], originating from the dipolar glass model [102], which improved the agreement with experiments, whereas other types of interactions give a different form. Later on, simulations have been performed for the three-dimensional case of this Correlated Gaussian Disorder Model (GDM) based on the charge-dipole interactions, resulting in the following empirical relationship [103]:

$$\mu_{CDM} = \mu_\infty \exp \left[ - \left( \frac{3\sigma}{5kT} \right)^2 + 0.78 \left( \frac{\sigma}{kT} \right)^{3/2} - 2 \right] \sqrt{e a E} \right].$$  \tag{1.20}

with $a$ the intersite spacing of the cubic lattice on which the simulations were performed. The main difference between the CDM and GDM is the predicted temperature dependence of $\gamma$. From comparison with experiments it can be concluded that the temperature dependence follows the CDM prediction, rather than the GDM. The temperature dependence of the zero-field mobility is the same and different from the activated nature as described by (1.18), but within the experimentally studied temperature range it is often not possible to distinguish between $\mu \propto \exp[-\text{const.}(\sigma/kT)^2]$ or the Arrhenius dependence $\mu \propto \exp[-(\Delta/kT)]$ [97, 104]. It is even quite often the case that $\mu \propto \exp[-(\Delta/kT)]$ seems more appropriate to describe the data in various systems, see e.g. [105, 106].

A major problem of the previously discussed theory, based on charge-dipole interactions, is that it is only applicable to systems with permanent dipole moments. Nevertheless, the $\sqrt{E}$ dependence has been observed in many conjugated polymers as well, while most of them do not have permanent dipole moments [96, 94]. This indicates that a theory based on charge-dipole interactions is ruled out as a universal explanation. An alternative mechanism based on intramolecular fluctuations of the torsion angle of e.g. benzene rings in PPV has been suggested. The resulting charge-carrier energy fluctuations with a certain spatial correlation function, containing both inter- and intramolecular restoring force constants, are shown to be responsible for a $\sqrt{E}$ dependence and a different temperature dependence, namely $\mu \propto \exp[-\text{const.}(1/kT)]$ [180, 181].

To end this section about charge transport, we show two experimental results obtained for $\pi$-conjugated systems that up to now could not be accounted for within one universal description. To come up with a unified description is exactly one of the goals of this thesis. The left panel of Fig. 1.6 shows a typical experimental result for the mobility as a function of charge-carrier density, going from the LED regime, with typical values for the density $p = 10^{15} - 10^{16}$ cm$^{-3}$, to the FET regime, where typically $p = 10^{18} - 10^{19}$ cm$^{-3}$. We have to realize that in order to inject the charges an electric field has to be applied. So in fact in this figure a dependence on electric field is present as well. The right panel shows a typical result for the conductivity as a function of temperature for different doping levels for the polymer polythiophene (PTH). We clearly see a temperature dependence that is non-Arrhenius, but $T^{-\gamma}$, where $\gamma$ changes with doping level.
1.5 Energy transfer

Important for the understanding of the functioning of polymer-dye blends are the positions of the HOMO and LUMO energy levels of the dye with respect to the polymer. If both the HOMO and LUMO energies of the dye are between those of the polymer, both electrons and holes can be trapped on the dye molecules, leading to exciton formation on the dye. If both LUMO and HOMO energies of the dye are lower than the corresponding energies of the polymer trapping may happen successively: first, electrons are trapped by the dye molecules and next the holes by their Coulomb interaction with the electrons. In the reverse situation, the roles of electrons and holes would be interchanged. In all situations these trapping processes compete with direct formation of the exciton in the polymer and subsequent Förster/Dexter transfer of the exciton to the dye. In case of Förster-type energy transfer, a dipole-dipole coupling between a donor and an acceptor [108] is assumed to be responsible for the transport of the excitation. The transfer rate $W_{ij}$ for hopping from a site $i$ to $j$ is then supposed to be given by [112, 113, 114]

$$W_{ij} = \begin{cases} k_0 \left( \frac{R_0}{R} \right)^6 \exp \left[ -\frac{\varepsilon_j - \varepsilon_i}{kT} \right], & \varepsilon_j > \varepsilon_i, \\ k_0 \left( \frac{R_0}{R} \right)^6, & \varepsilon_i > \varepsilon_j, \end{cases}$$

(1.21)

where $k_0$ is the inverse lifetime of the excitons and $R_0$ is the so-called Förster radius. The latter is a characteristic property of a donor-acceptor system, which depends on the refractive index of the medium $n$, the relative orientation of the donor and acceptor dipoles $\kappa$, the fluorescence quantum yield in the absence of an acceptor $\phi_D$, the spectral overlap integral $I$ (degree of spectral overlap between the molar absorption spectrum of acceptor
and emission spectrum of donor), and Avogadro’s constant $N_A$:

$$R_0^6 = \frac{9000(ln10)\kappa^2\phi_D I}{128\pi^5 N_A n^4}.$$  \hspace{1cm} (1.22)

It should be noted that Förster transfer can also be described by quantization of the electromagnetic field via the decay of an excitation on a site, under the emission of a virtual photon, and subsequent creation of an excitation on another site, under the absorption of the virtual photon. The Förster process can only happen if the optical gap of the dye is smaller than that of the polymer. Realization of an optimal performance for a polymer-only LED and a LED based on polymer-dye blends is reached by opposite requirements. For the polymer-only LED we want the exciton to stay on the polymer, i.e. it should have a very low mobility. However, for the polymer-dye blend the exciton should leave the polymer and reach the dye before it decays, i.e. the exciton should have a high mobility. In the latter case one should realize that the simple solution of just putting in a large amount of dyes is in fact no solution. From experiments it follows that there is a clear optimum in efficiency as a function of dye concentration.

As said before, polymers are highly disordered molecular solids and due to the more or less random positions of the chemical and conformational defects there is a broad distribution of effective conjugation lengths of the chain segments. This distribution of conjugation lengths translates into an inhomogeneously broadened density of states (DOS) for the holes and electrons, but also for the excitons. This is believed to be the case in polymers [109, 111, 50], but also in semiconductor heterostructures like GaAs [110]. This density of localized states is generally assumed to be a Gaussian for the same reasons as discussed before for the charge-carrier DOS. Once an exciton is formed within this DOS, it will relax either by tunnelling of excitons between localized states (Dexter transfer, similar to the tunnelling of holes and electrons), or by Förster transfer. The relaxation of the excitons will be towards states with lower energies [115, 111]. As a result, after each relaxation step the energy of the exciton is on average lower and hence the probability to again find a state with a lower energy decreases, because of the lower density of these states. Accordingly, the diffusion constant of the excitons is time-dependent, leading to what is called ”dispersive transport” [116, 117, 113, 114].

### 1.6 This thesis

The goal of this thesis is to get insight in the influence of experimentally controllable parameters like the charge-carrier density, the temperature, and the strength and frequency of an applied electric field on charge and energy transport in disordered $\pi$-conjugated systems. In literature a lot of effort has been put into modelling (both analytically and via simulations) the role of the above-mentioned parameters on the charge transport, but
the models often only work in limited parameter regimes. The change of the charge-carrier density by doping was what caused the birth of the field of plastic electronics. However, the nonlinear effect of doping on the mobility of the charge carriers is still not fully understood. The temperature dependence of the mobility has been investigated with Monte-Carlo simulations by Bässler and coworkers [92, 98], who found $\mu \propto \exp[-(\Delta/kT)]$. In literature this result is routinely used for fitting the experimental data, whereas it is known that deviations are observed. Bässler and coworkers were also the first to reproduce the so-called Poole-Frenkel behavior, i.e. $\mu \propto \exp[\gamma \sqrt{E}]$, which is very often claimed to be observed in $\pi$-conjugated systems. However, it is very difficult to determine whether this behavior is actually obeyed. Concerning the frequency dependence of the applied electric field, extensive simulations have been performed by Dyre and Schröder [206] for a random energy barrier model, which is the simplest possible model that reproduces many of the experimental findings, but it is not known how the results change for more realistic models. In this thesis we will try to deliver a unified description.

The contents of the thesis can roughly be divided into two parts. In the Chapters 2 through 4 we deal with ab-initio calculations. In the Chapters 5 through 10 we discuss charge or energy transport properties.

In Chapter 2 we give an overview of the quantum-mechanical formalism employed to describe the electronic and optical properties of the conjugated materials. We will briefly discuss ground-state density-functional theory (DFT), time-dependent density-functional theory (TDDFT), and time-dependent current density-functional theory (TDCDFT). The results of the ground-state density-functional theory calculations for polymer-dye blends are discussed in Chapter 3. We study the effect on the HOMO and LUMO energies of different sidegroups of the dye molecules we study (the so-called BODIPYs) and compare the results with the outcomes of cyclic-voltammetry measurements. We obtain a very satisfactory agreement between the calculations and the experiments. Moreover, we show that by calculating the HOMO and LUMO energies for the polymers poly($p$-phenylene vinylene) (PPV) and polyfluorene (PF) we can make predictions about the occurrence of charge and/or energy transport between the two polymers and dye molecules by comparing the HOMO/LUMO energies of the polymers with those obtained for the different dye molecules.

In Chapter 4 we analyze the optical gap - an excited-state property - of the same BODIPY dyes and also of an other class of molecules: TRIarylamines. The latter are used to shift the color emission from UV/blue to blue when incorporated in fluorene polymers. We examine the optical gap for these two classes of molecules within the framework of TDDFT and TDCDFT. The comparison between the results of the two different theories and the experimental data obtained from photoluminescence experiments provides a clue about how the theories compare. It is exactly this issue that has not been investigated a lot in literature because of the fact that TDCDFT is a rather new technique.

With Chapter 5 we enter the second part of the thesis dealing with charge and energy transport. Chapter 5 starts with a brief microscopic derivation of the Pauli Master-equation, which forms the basis for the following Chapters about the calculation of the charge trans-
port properties. After the introduction to this equation, the method we employed to solve it numerically exactly will be analyzed. We end this Chapter with a brief exploration about how this equation has been tackled analytically in literature.

Chapter 6 deals with an analytical theory for the doping dependence of the conductivity. This theory is a generalization of the standard Mott variable-range hopping theory in the sense that it is applicable to an arbitrary shape of the density of states. Moreover, the spatial extent of the localized states at which the charge carriers reside is taken into account (the standard Mott theory is only applicable to the case of a constant density of states and point-like sites). The predicted dependence for the conductivity is compared with experimental results and agrees very well. Additionally, from the comparison with experiments we can now understand the strong increase of the conductivity with doping by relating it to the influence of the newly incorporated parameters: the spatial extent of the localized states and the energy-dependent density of states.

Based on the results from the numerically exact solution of the Pauli Master-equation, we offer in Chapter 7 a detailed analysis of the microscopic origin behind variable-range hopping. The most important aspect is that the data reveal a hitherto never reported scaling of the temperature-dependent mobility in \((R, \varepsilon)\) space, where \(R\) is the hopping distance and \(\varepsilon\) the hop energy. The numerical findings are rationalized and we postulate a new analytical scaling theory of variable-range hopping. Finally, we will numerically validate the assumptions made in our scaling theory and compare our results with existing theories like effective-medium theory, and percolation theory. An important outcome of the comparison with percolation theory based on the random-resistor network approach, which is regarded to be the formal foundation of variable-range hopping theory, is that we find that the identification of the exponent determining the temperature dependence of the mobility with the exponent at the percolation threshold is not correct.

In Chapter 8 we study the charge-carrier mobility as a function of charge-carrier density, temperature and electric field in the case of a Gaussian density of states. The dependence of the mobility on these parameters is calculated via the Pauli Master-equation. As input for the calculations we use the experimentally determined parameters and from our results it follows that we can fully reproduce the experimentally obtained charge-carrier density dependence. Our results will be compared with newly developed semi-analytical theories that incorporate the charge-carrier density dependence. We calculate \(J-V\) characteristics for real devices via the solution of a space-charge limited current model, by using the numerically exact mobility dependence on the various parameters as input. These characteristics turn out to be in striking agreement with experiments.

Whereas the previous chapters dealt with DC transport, in Chapter 9 we will examine the AC transport properties. The nature of this chapter is more theoretical in the sense that we will not explicitly compare with experiments. Only recently the possibilities to apply our program to realistic systems have been analyzed. The reason why we started the research of AC transport is that only minor changes to the computer program developed for DC transport were needed to include the frequency dependence. Hence, this research area was entered rather accidentally. In our model we include variable-range hopping, asymmetric transition rates and the fermionic character of the charge carriers. We show a
scaling behavior for the AC conductivity in the extreme-disorder limit. The obtained master curve for the AC conductivity is compared to the one obtained by Dyre and Schrøder with a random-barrier model (only symmetric transition rates and nearest-neighbor hopping taken into account), and we conclude that the two curves seem to be the same. By a master curve we mean one single curve that is constructed by rescaling the mobility vs. frequency curves for different temperatures such that they all show the same AC response. The issue about the existence of a master curve for our model and (if it exists) how it compares to that of the random-barrier model has been an open question in literature. At the end of Chapter 9 we discuss coarse-grained analytical argument, developed to account for the temperature dependence of the slope of the frequency-dependent conductivity.

The last chapter, Chapter 10, deals with the transport of excitons in dye-doped polymers. The influence on the exciton dynamics due to the presence of dye molecules in a polymer matrix is studied by Monte-Carlo simulations. The excitation-energy transfer is assumed to be Förster-type. We find that upon increasing dye concentration a red shift is observed in the time-dependent rest-emission spectrum of the polymer, which has been confirmed by time-resolved photoluminescence experiments. Furthermore, we discuss the trends in the efficiency of electro- and photo-luminescence as a function of temperature and dye concentration. The results are found to be in qualitative agreement with experiment.
Chapter 2

Theoretical methods for electronic structure calculations

ABSTRACT

The theory behind the first-principles quantum-mechanical methods used in this work will be discussed. These are ground-state density-functional theory to calculate the ground-state geometry of the system, and time-dependent density-functional theory and time-dependent current density-functional theory to calculate the excited-state properties, like excitation energies and polarizabilities.
2.1 Ground-state density-functional theory

2.1.1 Hohenberg-Kohn theorems

The problem as formulated in section 1.3 of the introduction, is to solve the Schrödinger Equation (1.3) for the ground-state, which for simplicity will be taken to be non-degenerate. It can be shown that the formalism can be generalized for the case of a degenerate ground-state. The density in the ground-state $\Phi$ is denoted by

$$n(r) = \langle \Phi | \hat{n}(r) | \Phi \rangle,$$

and is a functional of the potential $v(r)$. The proof of this is simple and straightforward. Once the potential $v(r)$ is given, the ground-state wave function $\Phi(r_1, r_2, \ldots, r_N)$ is uniquely determined by the Schrödinger Equation (1.3) and hence also the ground-state density $n(r)$. Now the first theorem of Hohenberg and Kohn [60] states that the inverse is true as well. In order to show that $n(r)$ determines $v(r)$ they prove that $\Phi(r_1, r_2, \ldots, r_N)$ and $\Phi'(r_1, r_2, \ldots, r_N)$ are different if $v(r)$ and $v'(r)$ are different (by more than a constant) since they will not lead to the same wave function. In other words, they proved that the maps between $v(r)$, $\Phi$ and $n(r)$, are bijective. As a consequence of this bijective map every observable $O$ of the system is a unique functional of the density:

$$\langle \Phi[n] | \hat{O} | \Phi[n] \rangle = O[n],$$

where the square brackets have been used to indicate a functional dependence. We recapitulate Hohenberg and Kohn’s first theorem:

*The external potential is a unique functional of the ground-state density if the ground state is non-degenerate.*

A direct consequence of the first Hohenberg-Kohn theorem is that the external potential is a unique functional of the density and thus fixes the entire Hamiltonian. Therefore we can define the energy functional of a system, given a particular external potential $v$, as follows:

$$E[n(r)] = F[n(r)] + \int dr \ v(r)n(r), \text{ with } F[n(r)] = \langle \Phi | \hat{T} + \hat{U} | \Phi \rangle.$$  

(2.3)

$F[n(r)]$ is a universal functional, valid for any external potential and any number of particles, since the number of particles itself is a functional of $n(r)$. For a system of $N$ particles we can introduce an energy functional of the wave function $\Phi'$:

$$\tilde{E}[\Phi'] = \langle \Phi'| \hat{H} | \Phi' \rangle = \langle \Phi'| \hat{V} | \Phi' \rangle + \langle \Phi'| \hat{T} + \hat{U} | \Phi' \rangle.$$  

(2.4)
According to the variational principle, \( \tilde{E}[\Phi'] \) is minimized for the correct ground-state wave function \( \Phi \) with the restricting condition \( N[n] \equiv \int n(r) \, dr = N \). Now let \( \Phi' \) be the ground-state wave function corresponding to some external potential \( v'(r) \). Then with Equation (2.3), we get

\[
\tilde{E}[\Phi'] = \int dr \, v(r)n'(r) + F[n'(r)] > \tilde{E}[\Phi] = \int dr \, v(r)n(r) + F[n(r)].
\]  

(2.5)

This is Hohenberg and Kohn’s second theorem [60]:

There is a non-universal energy functional of the electron density that, upon minimization, gives the ground-state density.

The considerations in the previous paragraphs are very elegant, but they do not provide a practical scheme to obtain the ground-state density or energy within a good approximation, because \( F[n(r)] \) is still unspecified. This practical scheme was given in 1965 by Kohn and Sham [61].

### 2.1.2 Kohn-Sham equations

Kohn and Sham considered a system of non-interacting electrons (i.e. \( U = 0 \)) moving in an external potential \( v_{s,0}(r) = 0 \). The Schrödinger Equation for such a system reads

\[
\left[ -\frac{1}{2} \nabla^2 + v_{s,0}(r) \right] \phi_i(r) = \epsilon_i \phi_i(r),
\]  

(2.6)

and the density of such a system is determined by the \( N \) lowest energy orbitals:

\[
n(r) = \sum_{i=1}^{N} \int dr \, \phi_i^*(r)\phi_i(r).
\]  

(2.7)

The central idea of Kohn and Sham is that for each interacting electron system with external potential \( v_0(r) \) an effective potential \( v_{s,0}(r) \) exists (nowadays this is called the Kohn-Sham potential) such that the density of the non-interacting system equals the density of the interacting system. In accordance with the first Hohenberg-Kohn theorem this potential must be unique. To find a useful expression for the Kohn-Sham potential \( v_{s,0}(r) \) the total energy of the interacting system is written as

\[
E[n(r)] = T_s[n(r)] + \int dr \, v_0(r)n(r) + \frac{1}{2} \int dr \, dr' \frac{1}{|r - r'|} n(r')n(r) + E_{xc}[n(r)],
\]  

(2.8)

where \( T_s[n(r)] \) is the kinetic energy of the non-interacting electron system with density \( n(r) \), and \( E_{xc}[n(r)] \) the exchange-correlation (xc) energy, which contains all unknowns. From the second Hohenberg-Kohn theorem it follows that the energy functional \( E[n(r)] \) should
not change for small deviations $\delta n(r)$ around the exact density $n_0(r)$ and thus functional minimization with respect to $n(r)$ yields (together with some algebraic manipulations) the following expression for $v_{s,0}(r)$:

$$v_{s,0}(r) = v_0(r) + \int dr' \frac{1}{|r - r'|} n(r') + \frac{\delta E_{xc}}{\delta n(r)}, \quad (2.9)$$

and hence equation (2.6) reduces to:

$$\left[ -\frac{1}{2} \nabla^2 + v_s(r) + \int dr' \frac{1}{|r - r'|} n(r') + \frac{\delta E_{xc}}{\delta n(r)} \right] \phi_i(r) = \epsilon_i \phi_i(r). \quad (2.10)$$

It is worth mentioning that

$$\frac{\delta E_{xc}}{\delta n(r)} = v_{xc}(r) \quad (2.11)$$

is called the exchange-correlation potential. Because the Kohn-Sham potential depends on the density, the equations (2.9) and (2.6) have to be solved self-consistently: One starts from an initial guess for the orbitals and then calculates the Kohn-Sham potential to get a new set of orbitals from (2.6) and a new density. This continues until a certain convergence criterion has been achieved. The ground-state energy, the Kohn-Sham energy, is given by

$$E_{KS} = \sum_i \epsilon_i - \frac{1}{2} \int d\mathbf{r} \ v_H(\mathbf{r}) n_0(\mathbf{r}) - \int d\mathbf{r} \ v_{xc}(\mathbf{r}) n_0(\mathbf{r}) + E_{xc}[n_0(\mathbf{r})]. \quad (2.12)$$

However, this scheme can only be followed once an approximation for the many-body interactions hidden in $E_{xc}$ has been made. The accuracy of DFT calculations largely depends on the approximation for the xc potential. Very often, the local density approximation (LDA) is used. The LDA is based upon the theory of a homogeneous electron gas, for which very accurate quantum Monte-Carlo simulations by Ceperley-Alder [118] are available, from which analytical parametrizations are obtained [119, 120]. The approximation is based on the assumption that the system can locally be described as a homogeneous electron gas with a density equal to the local density of the system. It is intuitively clear that this assumption is reliable for sufficiently slowly varying densities. A natural way to extend the local density approximation is to take into account gradients in the density. This is called the generalized gradient approximation (GGA) [121], which is based upon the theory of the weakly inhomogeneous electron gas. Generally, the use of GGA increases the accuracy of DFT. More detailed technical information about ground-state DFT can be found in [121]. We will apply DFT to perform structure relaxations, in order to obtain the optimized geometry. It is known that DFT performs very well for this purpose when applied to $\pi$-conjugated materials [122, 123]. From these calculation we can also get information about the position of the HOMO and LUMO energies. Although it is known that the position of the LUMO energy is underestimated, leading to a gap between the HOMO and LUMO which is typically 30 to 50 % too small, the shape of the conduction (i.e. LUMO) bands is more or less correct [140]. So the real values of the LUMO energies...
can be obtained just by a rigid shift. Summarized, the trends in the HOMO and LUMO energies are assumed to be predicted quite well within ground-state DFT [122, 123]. In order to obtain real understanding of the quantitatively correct excited-state energies one has to resort to more advanced calculations. In the next section we will discuss one of the alternatives: the time-dependent version of DFT, abbreviated with TDDFT. Next to TDDFT we have the GW and BSE methods but, as mentioned in Chapter 1, these methods turned out to be unfeasible in the application to the systems we would like to investigate: large molecules.

2.2 Time-dependent density-functional theory

2.2.1 Time-dependent Kohn-Sham equations

Now that we have derived a set of Kohn-Sham equations for the static case we will proceed by generalizing this set of equations to a time-dependent situation. The resulting so-called time-dependent density-functional theory (TDDFT) can handle excited state properties as well. The first rigorous derivation was given in 1984 by Runge and Gross [69]. They derived a density-functional formalism, comparable to ground-state DFT, for arbitrary time-dependent systems. In this section we will only give a rough outline of the derivation. Detailed proofs can be found elsewhere: e.g. in the work of Gross and coworkers [124] and in a recent review by van Leeuwen [125]. The starting point for a general time-dependent situation is logically formed by the time-dependent Schrödinger equation

\[ i \frac{\partial}{\partial t} \Phi(t) = \hat{H}(t)\Phi(t). \]  

(2.13)

The Hamiltonian \( \hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{U} \) is the same as in Eq. (1.1), apart from \( \hat{V}(t) \), which now is a time-dependent external potential.

Suppose we have solved the time-dependent Schrödinger equation (Eq. (2.13)) for a fixed initial state \( \Phi(t_0) = \Phi_0 \) and for various potentials \( v(r, t) \). We obtain a map \( F : v(r, t) \rightarrow \Phi(t) \). Next, we can calculate the densities \( n(r, t) = \langle \Phi(t) | \hat{n}(r) | \Phi(t) \rangle \) for all time-dependent wave functions resulting from \( F \). This defines another map \( G : \Phi(t) \rightarrow n(r, t) \). In order to prove that there exists a time-dependent version of the first Hohenberg-Kohn theorem, we will show that the map \( v(r, t) \rightarrow \Phi(t) \rightarrow n(r, t) \) can be inverted, up to a purely time-dependent function \( c(t) \) in the time-dependent external potential, which appears in the wave function as a phase factor, \( \Phi(t) = e^{-i\alpha(t)} \Phi[n](t) \), and under the requirement that the potential can be expanded in a Taylor series around \( t = t_0 \). So, if it is possible to establish the invertibility up to a time-dependent function, then every observable \( O(t) \) can be regarded as the expectation value of a time-dependent quantum-mechanical operator \( \hat{O}(t) \) and is a unique functional of the density (provided it does not contain derivative or
integral operators of $t$:

$$O[n(t)] = \langle \Phi[n](t)|\hat{O}(t)|\Phi[n](t) \rangle.$$  \hspace{1cm} (2.14)

This is called the Runge-Gross theorem [69], which states:

Two densities $n(r, t)$ and $n'(r, t)$ evolving from the same initial state $\Psi(t_0)$ under the influence of two (scalar) potentials $v(r, t)$ and $v'(r, t)$, both Taylor expandable around $t_0$ and differing by more than a purely time-dependent function $c(t)$ ($r$-independent), will always differ.

The proof consists of two steps. First one shows that the current densities $j(r, t)$ and $j'(r, t)$ corresponding to the potentials $v(r, t)$ and $v'(r, t)$ will differ. Then one uses the continuity equation to show that the densities $n(r, t)$ and $n'(r, t)$ must also differ. To show the first step, we use the fact that the potentials can be expanded in a Taylor series around $t_0$.

Hence, there exists a smallest nonnegative integer $k$ such that

$$\frac{\partial^k}{\partial t^k} [v(r, t) - v'(r, t)] |_{t=t_0} \neq \text{constant}.$$  \hspace{1cm} (2.15)

What has to be proven is that the current densities $j(r, t)$ and $j'(r, t)$ corresponding to $v(r, t)$ and $v'(r, t)$ are different if Eq. (2.15) is fulfilled for some $k \geq 0$. The time evolution of the current density is given by the equation of motion for a Schrödinger operator:

$$\partial_t j(r, t) = -i \langle \Phi(t)|[\hat{j}(r), \hat{H}(t)]|\Phi(t) \rangle,$$  \hspace{1cm} (2.16)

where the current operator is defined as

$$\hat{j}(r) = \frac{1}{2i} \sum_{\sigma} [\hat{\Psi}^\dagger(\sigma) \nabla \hat{\Psi}(\sigma) - (\nabla \hat{\Psi}^\dagger(\sigma)) \hat{\Psi}(\sigma)].$$  \hspace{1cm} (2.17)

Since $\Phi(t)$ and $\Phi'(t)$ evolve from the same initial state $\Phi_0$, it can be shown that Eq. (2.16) gives [69]

$$(i\partial_t)^{k+1} [j(r, t) - j'(r, t)] |_{t=t_0} = in_0(r, t_0) \nabla \left[ (i\frac{\partial}{\partial t})^k [v(r, t) - v'(r, t)] |_{t=t_0} \right] \neq 0.$$  \hspace{1cm} (2.18)

Thus, if the potentials differ at $t = t_0$ and the condition (2.15) is satisfied for a minimal integer $k \geq 0$, the currents $j(r, t)$ and $j'(r, t)$ will become different infinitesimally later than $t_0$, which completes the proof for the current densities.

The next step is to prove a similar statement for the densities by use of the continuity equation,

$$\partial_t [n(r, t) - n'(r, t)] = -\nabla \cdot [j(r, t) - j'(r, t)],$$  \hspace{1cm} (2.19)

in which the result for the current densities has to be inserted to finally show that $n(r, t)$ and $n'(r, t)$ will become different as well for times $t > t_0$. 

Now that we have shown that there exists a noninteracting system with the same density as a fully interacting system (Runge-Gross theorem), it is possible to construct the time-dependent Kohn-Sham equations for non-interacting particles:

$$i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t) = \left[ -\frac{1}{2} \nabla^2 + v_s[n](\mathbf{r}, t) \right] \phi_i(\mathbf{r}, t),$$

(2.20)

where the single-particle potential is written as

$$v_s[n](\mathbf{r}, t) = v_0(\mathbf{r}) + \int d\mathbf{r}' n(\mathbf{r}', t) |\mathbf{r} - \mathbf{r}'| + v_{xc}(\mathbf{r}, t).$$

(2.21)

Again, like in ordinary DFT, the accuracy is largely determined by the approximation of the time-dependent xc potential. In the limit that the external potential varies slowly with time, the local density approximation is used to calculate $v_{xc}$. It is approximated by the same xc potential as in ground-state DFT, but using the time-dependent density at a particular time $t$, rather than a time-independent density. This approximation is called adiabatic local density approximation (ALDA):

$$v_{xc}[n](\mathbf{r}, t) = \frac{\delta E_{xc}[\rho]}{\delta \rho}(\mathbf{r}),$$

(2.22)

with $\rho_t$ the density at time $t$. It is expected to be true for slow time-dependent processes, but practice shows that its range of applicability is quite wide [126].

### 2.2.2 Excitation energies

The TDDFT formalism from the previous section allows to set up a systematic way to calculate properties of the excited states, like excitation energies and polarizabilities. These properties cannot be accounted for by ground-state DFT. In this thesis we will especially focus on the excitation energies for various $\pi$-conjugated systems. These energies determine the emission color of the materials under consideration. Understanding how this relates to the structure may help to further improve the desired properties. It will be shown that the excitation energies can be extracted from the frequency-dependent linear response to a time-dependent external potential of a finite interacting system that has discrete poles at the excitation energies of the unperturbed system. Following Gross [127], we give a formally exact expression of the linear density response $n(\mathbf{r}, \omega)$ in terms of the Kohn-Sham response function.

We consider an external potential $v_{ext}(\mathbf{r}, t) = v_0(\mathbf{r}) + v_1(\mathbf{r}, t)$, where $v_0(\mathbf{r})$ denotes the static external potential of the unperturbed many-body state, assumed to be the ground-state corresponding to $v_0(\mathbf{r})$, and $v_1(\mathbf{r}, t)$ is a time-dependent external perturbation. The linear density response $n_1(\mathbf{r}, t)$ to the perturbation $v_1(\mathbf{r}, t)$ can be calculated from

$$\delta n_1(\mathbf{r}, t) = \int dt' \int d^3r' \chi(\mathbf{r}t, \mathbf{r}'t') v_1(\mathbf{r}'t'),$$

(2.23)
where \( \chi \) is the response function of the interacting system. Similarly, one finds that the first-order density change due to a change of the Kohn-Sham potential \( \delta v \) is, in the TDDFT case, determined by the Kohn-Sham response function \( \chi_s \):

\[
\delta n_s(r, t) = \int dt' \int d^3 r' \chi_s(rt, r't') \delta v_s(r't')
\tag{2.24}
\]

According to the Rung-Gross theorem the density changes for the interacting system and the non-interacting system are identical:

\[
\delta n_1(r, t) = \delta n_s(r, t)
\tag{2.25}
\]

Thus, the exact density change to an external time-dependent perturbation \( v_{\text{ext}}(r, t) \) can be determined either from the exact response function \( \chi \), or from the Kohn-Sham response function \( \chi_s \) and the change in the Kohn-Sham potential \( \delta v_s \). In order to determine \( \delta v_s \) we apply Eq. (2.21) to a slightly perturbed system, specified by the density \( n_0(r) + \delta n(r, t) \). As a result we find

\[
\delta v_s(rt) = v_1(rt) + \int d^3 r' \frac{\delta n(r't')}{|r - r'|} + \int d^3 r' \int dt' \int d^3 r'' \chi_s[n_0(rt, r't')] \delta n(r't').
\tag{2.26}
\]

Here, a time-dependent exchange kernel \( f_{\text{xc}} \) is defined as the functional derivative of the time-dependent exchange potential \( v_{\text{xc}}(r, t) \) with respect to the time-dependent density \( n(r, t) \):

\[
f_{\text{xc}}[n_0](rt, r't') = \frac{\delta v_{\text{xc}}[n_0](rt)}{\delta n(r't')}.
\tag{2.27}
\]

From the above-given equations we can obtain a Dyson-like response equation,\(^1\) which in the frequency domain adopts the form

\[
\chi(r, r', \omega) = \chi_s(r, r', \omega) + \int d^3 r_1 \int d^3 r_2 \chi_s(r, r_1, \omega) \left( \frac{1}{|r_1 - r_2|} + f_{\text{xc}}[n_0](r_1, r_2, \omega) \right) \chi_s(r_2, r', \omega).
\tag{2.28}
\]

The noninteracting Kohn-Sham response function \( \chi_s(r, r', \omega) \) is known in terms of the static unperturbed Kohn-Sham orbitals \( \varphi_j(r) \), including their Fermi-occupation numbers \( f_i \) (1 or zero) and their orbital energies \( \varepsilon_j \):

\[
\chi_s(r, r', \omega) = 2 \sum_{j,k} (f_k - f_j) \frac{\varphi_k^*(r) \varphi_j(r) \varphi_j^*(r') \varphi_k(r')}{\omega - (\varepsilon_j - \varepsilon_k) + i\eta},
\tag{2.29}
\]

where \( \eta \) is a positive infinitesimal, which ensures that the response function has the correct causal (retarded) structure. The noninteracting response function \( \chi_s(r, r', \omega) \) has poles at the Kohn-Sham orbital energy differences \( \varepsilon_j - \varepsilon_k \) as a function of \( \omega \). However, we

\(^1\)It has been shown that an equation with a similar structure can be derived for the BSE approach [136].
are interested in the poles of $\chi(r,r',\omega)$, given by Eq. (2.28), which determine the true excitation energies $\Omega$ of the interacting system.

Casida has shown how to recast the problem in a set of linear equations that lead to an eigenvalue equation, which determines the excitation energies and oscillator strengths of the system [128]. This is also the method as implemented in the ADF code. As a result, the whole problem of determining the excitation energies and oscillator strengths boils down to solving the following equation:

$$\mathcal{M}\mathbf{F}_k = \omega_k^2 \mathbf{F}_k. \quad (2.30)$$

The components of the matrix $\mathcal{M}$ are given by:

$$\mathcal{M}_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i)^2 + 2\sqrt{(\varepsilon_a - \varepsilon_i)K_{ia\sigma,jb\tau}}\sqrt{(\varepsilon_b - \varepsilon_j)}, \quad (2.31)$$

where $\sigma$ denotes the spin of the electrons, and the indices $i,a$ denote transitions from occupied Kohn-Sham orbitals $i$ to unoccupied Kohn-Sham orbitals $a$. $K_{ij\sigma,kl\tau}$ is defined as follows:

$$K_{ij\sigma,kl\tau} = K_{ij\sigma,kl\tau}^{\text{Coul}} + K_{ij\sigma,kl\tau}^{\text{xc}}, \quad (2.32)$$

with

$$K_{ij\sigma,kl\tau}^{\text{Coul}} = \int dr \int dr' \varphi_{i\sigma}(r)\varphi_{j\sigma}(r)\frac{1}{|r - r'|}\varphi_{k\tau}(r')\varphi_{l\tau}(r'), \quad (2.33)$$

and

$$K_{ij\sigma,kl\tau}^{\text{xc}}(\omega) = \int dr \int dr' \varphi_{i\sigma}(r)\varphi_{j\sigma}(r)f_{xc}^\sigma(r',\omega)|\varphi_{k\tau}(r')\varphi_{l\tau}(r'), \quad (2.34)$$

where a Fourier-transform of the xc kernel $f_{xc}$ is introduced. In the calculations we performed, the adiabatic local-density approximation (ALDA) to $f_{xc}$ is used, in which $f_{xc}$ reduces to a spatially local, frequency independent, real function, evaluated at the local density $n_0(r)$. Solving Eq. (2.30) yields the eigenvalues $\omega_k$, which are the excitation energies between occupied and unoccupied states, and the oscillator strengths can be obtained from the eigenvectors $F_k$ [128].

### 2.3 Time-dependent current density-functional theory

In the above-given treatment of time-dependent density-functional theory only scalar potentials were considered, thus excluding vector potentials $\mathbf{A}(r,t)$. This means that the present scheme needs to be extended in order to be able to treat electromagnetic effects. Dhara and Gosh [129, 130] developed an extension for a many-particle system subjected to an external electromagnetic field with arbitrary time-dependence. They showed that, for a given initial state, the single-particle current density $\mathbf{j}(r,t)$ uniquely determines the
external scalar potential $v(r, t)$ and vector potential $A(r, t)$. Within this extended formalism, time-dependent current-density functional theory (TDCDFT), they ended up with the time-dependent Kohn-Sham equations:

$$\left( \frac{1}{2} [-i \nabla + A_{\text{eff}}(r, t)]^2 + v_{\text{eff}}(r, t) \right) \psi_k(r, t) = i \frac{\partial}{\partial t} \psi_k(r, t),$$

(2.35)

where $v_{\text{eff}}(r, t)$ and $A_{\text{eff}}(r, t)$ are the time-dependent effective potentials. In the previous section we have shown that an exact expression for the linear charge-density response of an interacting many-electron system can be derived in terms of the corresponding non-interacting Kohn-Sham system. This derivation can be extended to the case of current-density functional theory. Since we deal with linear response theory we will work in the frequency domain. The induced charge density and current-density are then given by

$$\delta n(r, t) = \int \{ \chi_{\text{nm}}^{s}(r, r', \omega) \cdot \delta A_{\text{eff}}(r', \omega) + \chi_{\text{nn}}^{s}(r, r', \omega) \delta v_{\text{eff}}(r', \omega) \} \, dr',$$

(2.36)

$$\delta j(r, t) = \int \{ [\chi_{ji}^{s}(r, r', \omega) - \chi_{ji}^{s}(r', r, 0)] \cdot \delta A_{\text{eff}}(r', \omega) + \chi_{jj}^{s}(r, r', \omega) \delta v_{\text{eff}}(r', \omega) \} \, dr',$$

where $v_{\text{eff}}(r, t)$ and $A_{\text{eff}}(r, t)$ given by

$$\begin{align*}
\delta v_{\text{eff}} &= \delta v_H + \delta v_{\text{xc}}, \\
\delta A_{\text{eff}} &= \delta A_{\text{ext}} + \delta A_{\text{xc}}.
\end{align*}$$

(2.37)

Note that in the case of $A_{\text{xc}} = 0$ one ends up with the usual TDDFT. As in the previous section $\chi_{ab}(r, r', \omega)$ are the Kohn-Sham response functions, which can be expressed in the unperturbed Kohn-Sham orbitals $\varphi_n(r)$. They are defined as follows:

$$\chi_{ab}(r, r', \omega) = \sum_{j,k} (f_j - f_k) \frac{\varphi_k^*(r) \hat{a} \varphi_j(r) \varphi_j^*(r') \hat{b} \varphi_k(r')}{(\varepsilon_j - \varepsilon_k) + \omega + i\eta},$$

(2.38)

in which one can substitute for the operators $\hat{a}$ and $\hat{b}$ $\hat{n} = \hat{1}$, the density operator, and $\hat{j} = -\frac{i}{2}(\nabla - \nabla^\dagger)$, the paramagnetic current operator. $\varepsilon_j$ and $f_j$ are the Kohn-Sham eigenvalues, and the occupation numbers of the Kohn-Sham orbitals, respectively. We still have to specify the terms in Eq. (2.37). The first-order change in the Hartree potential, the xc potential, the xc vector potential, and the vector potential of the external electric field $E_{\text{ext}} = i\omega A_{\text{ext}}$, are represented by $\delta v_H$, $\delta v_{\text{xc}}$, and $\delta A_{\text{xc}}$ respectively. In order to perform a real TDCDFT calculation one has to solve Eq. (2.36) in a self-consistent way. It can be shown that this set of equations can be cast in an equation with a similar structure as Eq. (2.30) [70]. In this equation $v_{\text{xc}}$ and $A_{\text{xc}}$ have to be approximated. The approximation is to take for $v_{\text{xc}}$ the ALDA xc potential and for the xc vector potential we will use a particular form derived by Vignale, Ullrich, and Conti [132]. This form relates the induced xc-electric field of a weakly inhomogeneous electron gas [131] to a viscoelastic field:

$$\begin{align*}
\delta E_{\text{xc}}(r, \omega) &= \nabla \delta v_{\text{xc}}^{\text{ALDA}}(r, \omega) + i\omega \delta A_{\text{xc}}^{\text{viscoel}}(r, \omega), \\
\delta A_{\text{xc},i}^{\text{viscoel}}(r, \omega) &= \frac{i}{\omega n_{ij}(r)} \sum_j \partial_j \sigma_{\text{xc},ij}(r, \omega),
\end{align*}$$

(2.39)
where $\sigma_{xc,ij}$ has the structure of a viscoelastic stress tensor:

$$
\sigma_{xc,ij}(r, \omega) = \tilde{\eta}_{xc}(n_0(r), \omega)[\partial_j u_i + \partial_i u_j - \frac{2}{3} \delta_{ij} \nabla \cdot u] + \tilde{\zeta}(n_0(r), \omega)\delta_{ij} \nabla \cdot u.
$$

(2.40)

Here $u(r, \omega) = \delta j(r, \omega)/n_0(r)$ is the velocity field, in which $\delta j(r, \omega)$ is the induced current density, and $n_0(r)$ is the ground-state density. The coefficients $\tilde{\eta}_{xc}(n_0(r), \omega)$ and $\tilde{\zeta}(n_0(r), \omega)$ are frequency-dependent functions of the ground-state density and they represent the complex bulk and shear viscosities. Approximate expressions for these coefficients are given in [132]. Apart from the fact that we can now describe the response to an electromagnetic field, an equally important result is that with this formalism, i.e. with the current density as the basic variable, one can to treat non-local effects [151]. These are shown to be important in conjugated molecular chains [133, 134] and cannot be treated within the ALDA approximation. Non-locality in the TDCDFT formalism is realized due to the relationship between the density and the current via the continuity equation. The current density is a measure of the buildup of charges, which changes the density in the system. Thus a local functional of the current density will necessarily be a non-local functional of the density.

### 2.4 Final remarks

At the end of this chapter, concerning DFT and its extensions, we would like to mention once more that apart from the methods described in this chapter, there is an alternative to obtain the excited-state properties, namely the solution of the Bethe-Salpeter equation. This approach has been applied to $\pi$-conjugated polymers by van der Horst et al. [58, 59, 67]. This approach offers a clear physical picture and yields results that are generally in better agreement with experiments. The drawback is that it is numerically very demanding. The method as discussed in this chapter is numerically much less demanding, but the problem is to find a suitable and tractable approximation to the so-called exchange-correlation kernel $f_{xc}$, which contains all the many-body effects. Nowadays, combined studies have been performed [135, 136, 137, 138] using the BSE equation to provide a good starting point for the derivation of the exchange-correlation kernel in TDDFT calculations. It can be shown that both methods can be cast into equations with the same structure. This combined approach looks very promising in providing a computational scheme with the numerical efficiency of TDDFT and an exchange-correlation kernel $f_{xc}$ derived from the clear physical picture behind the BSE approach.
Chapter 3

*Ab-initio* study of energy-level alignments in polymer-dye blends

**ABSTRACT**

The blending of small amounts of various dyes with polymers in light-emitting devices offers an attractive possibility to tune the colors of the emitted light without varying the polymer. To understand the transport of charged or uncharged excitations from the polymer to the dye, it is important to know the alignment of HOMO and LUMO (highest occupied and lowest unoccupied molecular orbital, respectively) energy levels of polymer and dye. We present here the results of *ab-initio* calculations within density-functional theory of these energy levels for dipyrrolomethene dyes. We also calculate these energy levels for poly(phenylene vinylene) (PPV) and polyfluorene (PF), which can be used as a matrix for these dyes. Special attention is paid to the trends of the HOMO and LUMO energies of the dyes with variation of the sidegroups. The calculated values are compared to those obtained from cyclic-voltammetry experiments and a very satisfactory agreement is obtained. With the knowledge about these energies of the dyes relative to the polymer matrix we can predict the possible trapping of electrons and holes by the dye. We find, in agreement with experiment, that for the considered dyes in a PPV matrix it is favorable for holes to stay on the polymer and electrons to be trapped on the dye, although the energy gain is small. In the case of a PF matrix, we predict electron trapping for all considered dyes and hole trapping depending on the specific sidegroups of the dye.
3.1 Introduction and outline

The discovery in 1977 that polymers can be made electrically conductive [11, 12] created the new field of plastic electronics. In 1990 electroluminescence was demonstrated for the first time in a conjugated-polymer system [19], shifting the emphasis to optoelectronic properties. The first commercial applications of monochrome polymer light-emitting displays (pLEDs) are now a fact. Of course the final aim is a full-color polymer display. However, due to a wide distribution of HOMO and LUMO levels of polymers, their emission bands are rather broad, giving rise to mixed-color light emission. Furthermore, the processing of three different polymers for the three principal colors is rather costly. One of the recent ideas [50, 48, 49, 47] to circumvent these problems is to use a small fraction (∼1%) of dye molecules in a polymer matrix and to exploit the mechanism of energy transfer from polymer to dye. By changing the dye rather than the polymer it should be possible to cover the whole visible-light spectrum. Recent electroluminescence experiments [54] have shown the possibility of fine-tuning the emission spectrum of dipyrrrolomethene dyes, commercially known as BODIPY dyes [55], by chemical modification of specific sidegroups [54], see Fig. 3.1. The idea behind the use of these sidegroups is to manipulate the HOMO and LUMO energies by extending the π-conjugation by adding phenyl groups or e.g. via the addition of a methoxy group. The fact that they have relatively small bandwidths makes these dyes good candidates for the further development of full-color displays. Very important for the understanding of the functioning of such polymer-dye blends are the positions of the HOMO and LUMO energy levels of the dye with respect to the polymer. If both the HOMO and LUMO energies of the dye are between those of the polymer, both electrons and holes can be trapped on the dye molecules. If both LUMO and HOMO energies of the dye are lower than the corresponding energies of the polymer, trapping may happen successively: first electrons are trapped by the dye molecules and next the holes by their Coulomb interaction with the electrons. In the reverse situation, the roles of electrons and holes would be interchanged. In all situations these trapping processes compete with formation of the exciton in the polymer and subsequent Förster/Dexter transfer of the exciton to the dye. This latter process can of course only happen if the optical gap of the dye is smaller than that of the polymer.

In this work, we will calculate the single particle HOMO and LUMO energies of the dyes shown in Fig. 3.1 and the polymers poly(p-phenylene vinylene) (PPV) and polyfluorene (PF), by Density-Functional Theory in the Local Density Approximation (DFT-LDA). The HOMO energy is given by the highest Kohn-Sham energy of the occupied states in a DFT calculation. In principle, DFT cannot be used to calculate LUMO energies, due to the well-known band-gap problem. In particular, energies of unoccupied states are generally underestimated in DFT [139, 140]. However, we will concentrate here not on absolute values but on trends in HOMO and LUMO energies and assume that these are well described in DFT [122, 123]. We will especially pay attention to the trends in the calculated values for the HOMO and LUMO energies of the dyes with variation of the sidegroups and compare with measured values from cyclic-voltammetry experiments. We
will finally discuss the relative positions of the HOMO and LUMO levels of the dyes and those of the polymers and the consequences for charge and energy transport.

### 3.2 Computational details

The DFT-LDA calculations were performed with the program VASP [65, 66]. A full relaxation of the geometric structure was performed and after that a determination of the HOMO and LUMO energies. In the appendix we will give structure information of the simplest dye molecule, dye I. Our calculations were performed with a supercell geometry, using an orthorhombic lattice with such lattice parameters that in the direction of the $\pi$-lobes perpendicular to the molecules (polymers) the distance between two molecules (polymers)
is at least 15 Å, and in the other directions at least 10 Å. This guarantees that our results reflect those of a single molecule (polymer). For the polymers the Brillouin sampling was done with 3 \( k \)-points in the polymer-chain direction. A check with a set of 7 \( k \)-points led to a downward shift of only 6 meV and 3 meV for HOMO and LUMO energies, respectively. The cutoff energy in the plane-wave basis set used by VASP was about 500 eV for the dyes and about 300 eV in case of the polymers. We checked that for the dye molecules a 30\% increase of the cutoff energy resulted in a downward shift of about 8 meV and 7 meV for the HOMO and LUMO energies, respectively. Concerning the polymers, the same increase in cutoff energy led to a downward shift of the HOMO of 2 meV and an upward shift of the LUMO of 3 meV.

The convergence of the HOMO and LUMO energies as a function of the size of the supercell is very slow. A way to overcome this problem is to calculate the Hartree potential in the middle between the molecules or polymers, which should be zero in vacuum, but is still not negligible for our supercells (about 0.14 eV or less). This value for the potential is subtracted from the calculated energies [141] and the resulting final value converges much faster. In this way, we obtain reliable results without needing excessively large supercells.

### 3.3 Results and discussion

The calculated values for the HOMO and LUMO energies of all the dyes shown in Fig. 3.1 are given in Table 3.1. From this table we can already make some qualitative conclusions when only looking at the trend in the band gap. The addition of a phenyl group has only a small effect, and the addition of larger sidegroups (including the addition of a methoxy group) shows up in a red-shift. We will proceed with a more detailed analysis of the energies presented in Table 3.1. In Table 3.2 we present a comparison between the

<table>
<thead>
<tr>
<th>Structure</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>band gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-5.99</td>
<td>-3.95</td>
<td>2.04</td>
</tr>
<tr>
<td>II</td>
<td>-5.89</td>
<td>-3.84</td>
<td>2.05</td>
</tr>
<tr>
<td>III</td>
<td>-5.57</td>
<td>-3.82</td>
<td>1.75</td>
</tr>
<tr>
<td>IV</td>
<td>-5.34</td>
<td>-3.79</td>
<td>1.45</td>
</tr>
<tr>
<td>V</td>
<td>-5.31</td>
<td>-3.75</td>
<td>1.46</td>
</tr>
<tr>
<td>VI</td>
<td>-5.24</td>
<td>-3.79</td>
<td>1.45</td>
</tr>
<tr>
<td>VII</td>
<td>-5.14</td>
<td>-3.78</td>
<td>1.36</td>
</tr>
<tr>
<td>VIII</td>
<td>-5.11</td>
<td>-3.82</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Table 3.1: Calculated values of the HOMO and LUMO energies for the dyes shown in Fig. 3.1.
calculated HOMO and LUMO energies of the dyes and the (available) experimental values. The experimental values have been obtained from cyclic-voltammetry measurements in a dichloromethane solution. Because of the different environment of the dyes in the calculated and in the experimental situation it is not possible to compare the results on an absolute scale. The fact that DFT underestimates the magnitude of band gaps also prohibits a direct comparison of the differences between HOMO and LUMO energies. Therefore, it is best to make a separate comparison of the HOMO and LUMO energies with respect to those of the reference dye IV. From the tables 3.1 and 3.2 the following observations can be made: (1) excluding the first two structures, addition of the phenyl group at the head of the dipyrromethene group does not significantly affect the HOMO and LUMO energies, (2) addition of phenyl and naphtyl groups to the sides of the dipyrrolomethene group leads to a decrease of the HOMO energy, (3) addition of a methoxy group leads to a further decrease of the HOMO energy. The first observation is explained from the fact that in the optimized geometries the phenyl group always makes an angle of about 70 degrees with the plane of the dipyrrrolylomethene group. Consequently, just a small interaction will occur between the π-orbitals of those groups. Relatively, this small interaction has the largest effect for the smallest dyes (I, II in Table 3.1). In principle, the second observation could be explained from the fact that the attachment of larger side groups provides an opportunity for the π-system to extend its conjugation length. Consequently, an increase of the HOMO energy [142, 143] will be the result. However, the same argument apparently does not apply to the LUMO. In good agreement with the experiments, the LUMO energies are rather unaffected by all the changes. To check whether this is a result of the fact that the LUMO wavefunction on the side groups has a small contribution in comparison to the dipyrrolomethene group, we calculated $|\psi_{\text{lumo}}(\vec{r})|^2$ on both the side group and the dipyrrolomethene group. After comparing the two values for the contributions with $|\psi_{\text{lumo}}(\vec{r})|^2$ of the total molecule, no significant difference could be found. The addition of a methoxy group at the naphthyl side group, going from dye VI to VIII, leads to a further lowering of the HOMO energy due to the electron-donating character of this group. One clearly observes these trends both in the calculations and the experiments.
As already noted, it is not possible to directly compare the values for the calculated band gaps of the dyes to the measured ones. It is, however, useful to check the possibility to obtain the experimental values for the HOMO-LUMO gap by multiplying the calculated HOMO-LUMO gap by an overall scaling factor, in order to get another justification of the consistency of the trends in the calculations. If we use a scale factor of 1.45 we find an agreement within 3% or less with the experimental values, obtained from cyclic-voltammetry. By comparing the HOMO and LUMO energies of the dyes to those of the polymers, see Fig. 3.2, we can draw some important conclusions about the charge- and energy-transport properties of the polymer-dye blends. It is clear from Fig. 3.2 that in the case of a PPV-dye blend the only energetically favorable transfer is electron transfer from PPV to the dye. Hence, one expects trapping of the electrons on the dye molecules, which has also been confirmed experimentally [54, 146]. We conclude that exciton formation on dye molecules in these blends is a result of sequential charge trapping. The presence of an electron on the dye leads to a Coulomb attraction of a hole and finally transfer of the hole from the polymer to the dye. It should be stressed that one cannot naively draw the conclusion that because the HOMO-LUMO gap of PPV is smaller than that of the dyes, it would not be favorable at all for an exciton to be on the dyes. From the experiments we know that the optical gap of the dyes is smaller than that of PPV. This brings us to the conclusion that the exciton binding energy for the dyes is significantly larger than for the polymer, which is intuitively expected because of larger delocalization on the polymer.

In the case of a PF-dye blend, electron transfer from the polymer to the dye is also energetically advantageous. But in the case of dyes IV and V it is favorable for holes as well to be transferred from the polymer to the dye. It would be very interesting to have an experimental verification of this.

<table>
<thead>
<tr>
<th></th>
<th>PPV</th>
<th>Dyes</th>
<th>PF</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO [eV]</td>
<td>-3.54</td>
<td>-3.8 all</td>
<td>-3.03</td>
</tr>
<tr>
<td>HOMO [eV]</td>
<td>-4.70</td>
<td>-5.1 VII, VIII</td>
<td>-5.21</td>
</tr>
</tbody>
</table>

**FIGURE 3.2:** Schematic drawing of HOMO and LUMO energies of the various dyes with respect to those of the polymers PPV and PF. Typical values of the HOMO for the experimentally used PPV and PF are -5.3 eV and -5.8 eV, respectively [144, 145]. The arrows denote possible transfer of either a hole or an electron from the polymer to a suitable dye.
3.4 Summary and conclusions

Using a DFT-LDA approach we have been able to calculate the HOMO and LUMO energies of a series of dipyrrolomethene dyes and of the polymers PPV and PF. The shifts of these energies for the dyes with varying sidegroups are in agreement with cyclic-voltammetry measurements. By comparison with the HOMO and LUMO energies of the polymers we are able to make predictions about the transfer of charges and energy from polymer to dye. In PPV-dye blends only electrons can be trapped on the dye. In PF-dye blends electrons can be trapped on the dye, but, for the dyes with methoxy sidegroups, also holes can be trapped. These conclusions are an important starting point for further modelling of transport of charge and energy in these systems.
3.5 Appendix

Here we show the information regarding the geometry of the simplest dye structure, dye I. In Fig. 3.3 we show the molecule with the numbered atoms.

**FIGURE 3.3:** Numbering of the atoms for the structure of dye I.

In Table 3.3 we have put the positions of the atoms in Cartesian coordinates in Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>1.44759</td>
<td>2.69276</td>
<td>0.48144</td>
<td>B(1)</td>
<td>1.07894</td>
<td>0.16531</td>
<td>0.39136</td>
</tr>
<tr>
<td>C(2)</td>
<td>2.50617</td>
<td>3.60890</td>
<td>0.51248</td>
<td>F(1)</td>
<td>0.20492</td>
<td>0.11426</td>
<td>1.45447</td>
</tr>
<tr>
<td>C(3)</td>
<td>3.67104</td>
<td>2.87202</td>
<td>0.50368</td>
<td>F(2)</td>
<td>0.40429</td>
<td>0.11245</td>
<td>0.80875</td>
</tr>
<tr>
<td>C(4)</td>
<td>3.29996</td>
<td>1.51191</td>
<td>0.47185</td>
<td>H(1)</td>
<td>2.40579</td>
<td>0.46899</td>
<td>0.54270</td>
</tr>
<tr>
<td>C(5)</td>
<td>4.04891</td>
<td>0.35191</td>
<td>0.47779</td>
<td>H(2)</td>
<td>4.69231</td>
<td>3.24782</td>
<td>0.52546</td>
</tr>
<tr>
<td>C(6)</td>
<td>3.45157</td>
<td>-0.89273</td>
<td>0.48808</td>
<td>H(3)</td>
<td>5.04716</td>
<td>-2.44301</td>
<td>0.56449</td>
</tr>
<tr>
<td>C(7)</td>
<td>3.98721</td>
<td>-2.19590</td>
<td>0.53777</td>
<td>H(4)</td>
<td>2.95385</td>
<td>-4.15478</td>
<td>0.60085</td>
</tr>
<tr>
<td>C(8)</td>
<td>2.92152</td>
<td>-3.07041</td>
<td>0.55624</td>
<td>H(5)</td>
<td>5.14019</td>
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<tr>
<td>C(9)</td>
<td>1.75855</td>
<td>-2.29151</td>
<td>0.51377</td>
<td>H(6)</td>
<td>0.71266</td>
<td>-2.59126</td>
<td>0.50726</td>
</tr>
<tr>
<td>N(1)</td>
<td>2.07810</td>
<td>-1.00088</td>
<td>0.47527</td>
<td>H(7)</td>
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<td>2.86310</td>
<td>0.47265</td>
</tr>
<tr>
<td>N(2)</td>
<td>1.92314</td>
<td>1.45038</td>
<td>0.45965</td>
<td>H(8)</td>
<td>0.71266</td>
<td>-2.59126</td>
<td>0.50726</td>
</tr>
</tbody>
</table>

**Table 3.3:** Positions of the atoms with respect to each other (in Cartesian coordinates in Å) for the relaxed structure of dye I.
Chapter 4

Calculation of excitation energies of complex dye molecules: TDDFT vs. TDCDFT

ABSTRACT

In this chapter we present the results of first-principles calculations of excitation energies of two classes of complex dye molecules. The first are the dipyrrrolomethene dyes, used for applications in full-color polymer light-emitting diodes, and the second are the so-called TRIarylamines which are used to shift the color emission from UV/blue to blue when incorporated in fluorene polymers. The methods employed to calculate the excitation energies are time-dependent density-functional theory (TDDFT) and time-dependent current density-functional theory (TDCDFT). Because up to now little is known about how these methods compare, the focus will be especially on the trends produced by the two methods. We compare the outcomes of both methods with results obtained from photoluminescence experiments. We find that for the dipyrrrolomethene dyes both methods give good results as compared to experiment, apart from one specific molecule in the case of TDCDFT. For the TRIarylamines we don’t find consistent results with both methods.
Chapter 4

4.1 Introduction

Nowadays, calculations of ground-state properties of many-electron systems are well-established. Most often, techniques based on density-functional theory (DFT) in the local density approximation (LDA) [60, 61] are employed. Although DFT has been successfully applied to a wide variety of systems, it has some drawbacks. It is limited to the calculation of ground-state properties, and is not able to produce correct excitation energies. The efficient calculation of excited state properties is still a challenge for computational methods. Accurate calculations involve sophisticated techniques such as the configuration-interaction (CI) method [57], or Green’s function methods based on the GW approximation [62, 63, 64]. In spite of the fact that these methods provide very good agreement with experiments [58, 59, 147, 148], they suffer from the computational demands and it is very hard or impossible to apply them to large systems, especially large molecules, see Table 1.1 in Chapter 1. A promising candidate to handle large systems is the, in principle exact, method of Time-Dependent Density-Functional Theory (TDDFT) [69, 125]. With this method good accuracy may be obtained of various dynamic response properties for different materials [149, 150]. Until now, mainly the adiabatic local density approximation (ALDA) is used, in which the exchange-correlation (xc) potential $v_{xc}$ is a local functional in space and time of the electron density. However, it has been shown that this approximation leads to large overestimations of the polarizabilities in case of long molecular chains [151, 152]. The reason is already to be expected from its name: it is the locality in space of the approximation that gives rise to problems (there is not much information available about the influence of the assumption of locality in time). For long molecular chains, the potential at the center of the chain is insensitive to changes in the charge at the endpoints of the chain, while these changes turn out to have important global effects for the exact exchange-correlation potential [152, 151, 133]. A way to overcome the problem is to include nonlocality by the use of current functionals. Vignale and Kohn (VK) [131] and Vignale, Ullrich, and Conti [132] were the first to show that the nonlocality problem could be circumvented by working with the current density rather than the density as a basic variable. Basically, their arguments boil down to the fact that the relationship between the longitudinal current and the density is nonlocal, as follows from the continuity equation, and thus a local functional of the current is necessarily a nonlocal functional of the density [153]. By describing ordinary TDDFT in terms of a vector potential $A_{xc}$ and the current density $j$ these authors end up with a formulation in which ordinary TDDFT is a special case of the Time-Dependent Current-Density-Functional Theory (TDCDFT).

In the present chapter we would like to focus on a comparison between results from photoluminescence experiments [157] and results obtained either by making use of the ALDA or the VK approximation in TDDFT calculations of the optical gap of various complex molecules. By VK we mean the xc-current functional as first derived by Vignale and Kohn for a weakly inhomogeneous electron gas [131]. Since TDCDFT is a rather new method it is important to examine its applicability. Despite some successful applications to e.g. optical spectra of solids and small ($\pi$-conjugated) organic molecules [133, 134, 153, 154],...
there is very few practical or quantitative information regarding the applicability of TD-
CDFT. The purpose of the present work is to investigate for the first time the applicability
of TD(C)DFT on very large molecules, with no symmetries involved. The molecules we
investigate are built up from conjugated units. The first class of molecules consists of
dipyrrolomethene dyes, commercially known as BODIPY dyes [55]. They have possible
technological relevance for applications as dyes in full-color polymer light-emitting diodes.
The other class are the so-called TRIarylamines, which can be used to shift the color emis-
sion from UV/blue to blue when incorporated in fluorene polymers. From a theoretical
point of view it is important that the properties of interest for the molecules under con-
sideration (and for which we have experimental data) cover a large enough regime, so that
we are able to distinguish a clear trend. In fact it will turn out that, e.g. for the BODIPY
dyes, it would have been desirable to study structures with even larger sidegroups than the
ones studied here. The structures of the molecules are shown in Fig. 4.1. Technical details
about implementation of the TDCDFT method can be found in [134], where the TDCDFT
formalism has been applied successfully for the first time to conjugated oligomers.

4.2 Computational details

All calculations were performed with a modified version of the Amsterdam Density Func-
tional (ADF) program [68]. In these calculations we made use of the standard ADF basis
set collection. The ground-state geometries have all been calculated with the Generalized
Gradient-Approximated (GGA) functional by Becke [155] for exchange and Perdew [156]
for correlation, and with basis set V, which is a triple zeta Slater-type orbital basis set aug-
mented with two polarization functions [68]. Concerning the ALDA calculations for the
excitation energies we used basis set V as well, but in case of the VK calculations we used
a smaller basis set, namely IV, which is a triple zeta Slater basis set augmented with one
polarization function. The use of the smaller basis set was inevitable because of restricted
computational resources. The influence of the smaller basis set was checked in the ALDA
case and turned out to be of minor importance; it introduced errors of about 10 meV. For
all the calculations cores were kept frozen up to 1s, and for Sulfur (S) and Bromine (Br) up
to 2p and 3p respectively. In the case of the TRIarylamines we have tried to improve the
ALDA results by making use of a different approximation for the xc functional, namely the
one obtained with the statistical averaging of (model) orbitals potentials (SAOP) [158]. All
integrals (e.g. for obtaining the density and the Coulomb potential) have been evaluated
with at least four significant figures, which should be enough [134].
4.3 Results and discussion

We will first show and discuss the results obtained for the BODIPY dyes and then treat the results for the TRIarylamines.

BODIPY dyes

Fig. 4.2 presents a comparison between the calculated values for the optical gap, either from the ALDA or VK calculations, and the experimental values obtained from the photoluminescence spectra [157]. Along the vertical axis we plot the values for the optical gap obtained by both calculations and experiments and along the horizontal axis we plot the experimental values. In this way it is possible to compare the trend in the calculated results with the trend as found in experiment. In the experiments, we identify the peak
Calculation of excitation energies of complex dye molecules

FIGURE 4.2: Comparison between the calculated and experimental values for the optical gap. The results for the calculations have been obtained by employing TDDFT, within the ALDA approximation and by application of TDCDFT, with the VK functional.

position in the photoluminescence spectrum as the magnitude of the optical gap. For our calculations, we identify the excitation energy of the transition with the largest oscillator strength as the value for the optical gap, in order to compare with the experimental values. The transitions turned out to always have a strong HOMO→LUMO character both for the ALDA and VK calculations, except for dye III, which has HOMO-1→LUMO as strongest contribution in the case of the VK calculation. Another important remark is that the calculated oscillator strengths for this molecule are all of the same order, and for none of the calculated excitations a dominating HOMO→LUMO character could be found. We would like to stress that the focus is on the observed trends. One should not try to make claims about the absolute magnitude of the results, because we performed our calculations for isolated molecules in vacuum, while the experiments are performed in a dichloromethane solution. The trend in the ALDA calculations is not in good agreement with the experiments. The ordering for the decreasing excitation energies as predicted by the ALDA calculations is: I, IV, II, III, whereas the experiment tells us: I, II, III, IV. Moreover, the scatter present in the data is as large as the total decrease in the values for the optical gap as obtained from experiments. In the case of the VK results the energies are much higher. However, the trend in the changes of the energies relative to each other, as compared to experiment, is captured reasonably well. We use the word ‘reasonably’ because of the surprising outcome for dye III. For this molecule a sudden drop in the value for the optical gap with respect to the others is observed. It is not clear to what effect this drop should be attributed. The only difference with the other species is the character of the transition involved, as just remarked. But there is no explanation yet for the fact that this results in a huge drop of the energy. Summarized, it appears that the trend in
the optical gap is better described by the VK than the ALDA calculations. A similar conclusion was reached in [70]. However, it would have been desirable to conclude this on the basis of more data, e.g. data for molecules with more benzene rings, in order to see whether indeed a strong HOMO→LUMO character of the transition correlates with a good description by VK.

TRIarylamines

A comparison of the experimental values for the optical gap of these materials with the calculated results is presented in Fig. 4.3, where we have chosen to plot the same quantities along the axes as in Fig. 4.2. The experiments [157] have, just as for the BODIPY dyes, been performed in a dichloromethane solution, while the calculations are again performed for isolated molecules in vacuum. Therefore, straightforward comparison of the experimental results and the calculations is again difficult. Dye I can be viewed as different from the other structures, simply because of its smaller size, leading to a larger optical gap. For this dye the excitation energies are much larger than those of the other structures, which is in contrast to the trend as observed in the experiments. For the dyes II to V the ALDA results do not predict the trend as seen in experiment, either. The ALDA calculations predict a
small scatter around a constant value for the optical gap. The calculated dispersion of the value for the optical gap is 0.11 eV, no matter what happens with the side groups, while from the experiments a monotonous decrease of 0.42 eV is obtained when going from dye I to V. We have indicated the dispersion for the ALDA calculations with the hatched region. The results of the VK calculations for the dyes II to IV show the same dependence as is found for ALDA, albeit that the energies are all shifted upwards. The reason why we give two values for the optical gap of dye III is that both transitions have comparable oscillator strengths. We have indicated the dispersion for the VK results with the cross-hatched region. Because of the fact that both ALDA and VK did not give results that compare well with experiment, we have tried to improve upon the ALDA-TDDFT results. To improve upon the results of the ALDA approximation, we use the SAOP approximation for the xc functional [158]. This functional is currently one of the best available functionals for ground-state DFT calculations and because of the improvement on the ground-state calculation it often improves the calculations for excitation energies as well. However, but it has the drawback that the calculations become more expensive. The results are given in Fig. 4.3 as well, indicated with SAOP. The outcome is clear: we do not improve the trend as compared to the experiments. The only effect of using the SAOP functional is a uniform shift of about 0.15 eV. As a final result we show the outcomes of the ground-state DFT calculations. They show a trend that is somewhat similar to the trend found in the VK calculations, apart from the fact that for the latter we have two data points for dye III. So, our final conclusion is that, when compared to experiment, the trend as found for the dyes II, III, and IV is described best by ground-state DFT.

4.4 Summary and Conclusions

We applied TDDFT and TDCDFT to calculate the optical gap of two different classes of molecules: derivatives of dipyrrolomethene dyes and a family of TRIarylamines. We compared the results with photoluminescence experiments. For the TDDFT calculations we used two different approximations for the xc functional: ALDA and SAOP, while for the TDCDFT calculations we use the current functional derived by Vignale and Kohn to treat the xc-effects. In the case of the dipyrrolomethene dyes, the ALDA results give energies closer to experimentally found values, but the trend is not predicted well, while the VK results largely overestimate the energies. Although the trend as found for the VK results compares well with experiment, dye III is an exception that cannot be treated correctly. At present the behavior of dye III is not understood. The second class, the TRIarylamines, cannot be described consistently, neither by ALDA and SAOP, nor by VK. However, we have to realize that experience with TDCDFT calculations is still in its infancy, and that the molecules we considered are more complex than the systems investigated up to now. The final conclusion of this chapter it that neither TDDFT nor TDCDFT provides a good prediction for the systems we studied. Our study indicates that further development of TDCDFT and improvement of the VK functional is necessary.
Chapter 5

Computational method to calculate the hopping mobility/conductivity

ABSTRACT

This chapter is concerned with the modelling of charge transport, via the Pauli Master-equation approach, as studied in the next three chapters. We start with a short survey of how the Master-equation can be derived from the Hamiltonian describing charge transport on a microscopic scale. Then we present our methods to solve this equation numerically exactly in order to study the charge-transport properties. In the last part of this chapter we outline an important analytical approach to solve the Master-equation as developed by Movaghar and Schirmacher.
5.1 Background behind the model

In this section we will report briefly on the general theory behind the description of hopping (phonon-assisted tunnelling) conduction in disordered solids. Extensive discussions by Böttger and Bryksin can be found in [172, 173, 174, 170], so we will only present some basic results. Our focus will be especially on the origin of the Master-equation and on the actual assumptions that are made. This is important in order to see how the influence of the microscopic structure enters the equation.

Analogous to Böttger and Bryksin, we start the discussion for a coupled electron-phonon system from the following Hamiltonian:

\[
\hat{H} = \hat{H}_e + \hat{H}_{ph} + \hat{H}_{e-\text{ph}},
\]

(5.1)

where

\[
\hat{H}_e = \sum_m \varepsilon_m a_m^\dagger a_m + \sum_{m' \neq m} J_{mm'} a_{m'}^\dagger a_m,
\]

(5.2)

\[
\hat{H}_{ph} = \sum_q \hbar \omega_q (b_q^\dagger b_q + 1/2),
\]

(5.3)

\[
\hat{H}_{e-\text{ph}} = \sum_m a_m^\dagger a_m \sum_q \hbar \omega_q [u_m(q) b_q + u_m^*(q) b_q^\dagger].
\]

(5.4)

Here \(\varepsilon_m\) is the electronic energy of the localized state at position \(\mathbf{R}_m\), \(\omega_q\) is the frequency of a phonon with wave vector \(\mathbf{q}\), \(a^\dagger (a)\) and \(b^\dagger (b)\) are, respectively, the electron and phonon, creation (annihilation) operators, and \(J_{mm'}\) is the transfer integral between the sites \(m'\) and \(m\). The aim of the present thesis is to describe transport in conjugated polymers, hence by a localized state we mean a state localized on a conjugated polymer segment, from which the carrier can only escape by hopping. We will call the conjugated region where the charge carrier resides a site. The quantity \(u_m(q)\) is related to the dimensionless electron-phonon coupling constant, \(\gamma_m(q)\), by

\[
u_m(q) = \frac{1}{\sqrt{2N}} \gamma_m(q) \exp(-i \mathbf{q} \cdot \mathbf{R}_m).
\]

(5.5)

Note that we have neglected a term \(\hat{H}_{ee} = -\sum_q \sum_{m \neq m'} \hbar \omega_q u_m(q) u_{m'}^*(q) a_{m'}^\dagger a_m a_m^\dagger a_m\), describing the indirect attractive interaction between electrons located at different sites due to the virtual exchange of phonons (an analogous mechanism gives rise to Cooper pairs in superconductors). Furthermore, we assume the Hubbard repulsion to be so strong that a double occupation of sites does not occur.

To handle the Hamiltonian \(\hat{H}\) it turns out to be very useful to apply a polaron canonical transformation (Lang and Firsov [175]), leading to a transformed Hamiltonian

\[
\hat{H}' = \sum_m \tilde{\varepsilon}_m a_m^\dagger a_m + \sum_q \hbar \omega_q (b_q^\dagger b_q + 1/2) + \sum_{m' \neq m} J_{mm'} a_{m'}^\dagger a_m \hat{\Phi}_{m'm}.
\]

(5.6)
Here $\tilde{\varepsilon}_m$ is $\varepsilon_m - E_p(m)$, and $E_p(m)$ is called the 'polaron shift', which describes the lowering of the energy when an electron is present at site $m$, caused by a 'polarization' of the surroundings:

$$E_p(m) = \frac{1}{2N} \sum_q \hbar \omega_q |\gamma_m(q)|^2.$$  

(5.7)

The quantity $\hat{\Phi}_{m'm}$ is the multiphonon operator describing the transfer of a polaron between sites $m$ and $m'$, which includes both phonon-emission and -absorption processes, and is given by

$$\hat{\Phi}_{m'm} = \exp \left( \sum_q \left[ b^\dagger_q (u^*_m(q) - u^*_{m'}(q)) - b_q (u_m(q) - u_{m'}(q)) \right] \right)$$

$$\equiv 1 + \left( \sum_q [-] \right) + \frac{1}{2!} \left( \sum_q [-] \right)^2 + \ldots.$$  

(5.8)

To calculate the conductivity for a disordered system described by Eq. (5.6) and coupled to an external electric field $E(t)$ through the Hamiltonian

$$\hat{H}_E = -e \sum_m E(t) \cdot R_m a^\dagger_m a_m,$$  

(5.9)

we need to do a configurational averaging, which can be done via the density operator, defined as

$$\hat{\rho} = \exp[-\beta(\hat{H} - \mu \hat{N})]/\text{Tr}\{\exp[-\beta(\hat{H} - \mu \hat{N})]\},$$  

(5.10)

where $\mu$ is the chemical potential, and $\hat{N} = \sum_m a^\dagger_m a_m$ is the operator for the total particle number. The configurational average of an operator $\hat{A}$ is given by $\text{Tr}[\hat{\rho} \hat{A}]$. The diagonal elements of the density matrix $\rho_{mm} = \langle U^\dagger(t) a^\dagger_m a_m U(t) \rangle$, where $U(t)$ is the time-evolution, have a clear physical meaning. The quantity $\rho_{mm}$ describes the time evolution of the thermodynamically averaged concentration of charge carriers at site $m$ after turning on the electric field. The time-dependence of the density matrix is described by the quantum Liouville equation

$$i\hbar \frac{d\rho_{mm'}}{dt} = \sum_{m''} (\langle m | \hat{H}' + \hat{H}_E | m'' \rangle \rho_{m''m'} - \langle m'' | \hat{H}' + \hat{H}_E | m' \rangle \rho_{mm''}), \quad \rho_{mm'} = \langle m | \hat{\rho} | m' \rangle.$$  

(5.11)

The current density of a system with volume $\Omega$ is given by

$$j = \frac{e}{\Omega} \sum_m R_m \frac{d\rho_{mm}}{dt},$$  

(5.12)

from which it is possible to construct an expression for the conductivity via $\sigma = j/E$. 
The off-diagonal elements of the density matrix, which are related to extended states, will be neglected henceforth. Moreover, a Hartree approximation is employed. In this approximation, the correlation between the occupational probabilities of sites between which a hopping event can occur is neglected and the prohibition of an electron transfer to an occupied neighbouring site is approximated by a finite transition probability, which decreases with increasing average occupation of that site. Hence, this approximation neglects the effect of correlated multiple hops. Furthermore, the dwell time of a carrier on a given site is assumed to be long enough for the phonon system to equilibrate, so that the so-called Markovian limit is valid. This means that the system has no memory, so that the current does not depend on the initial state at which the electric field is turned on. With these approximations one finds the following expression for the time dependence of the thermodynamically averaged concentration of the charge carriers [170]:

$$\frac{\partial \rho_m}{\partial t} = - \sum_{m' \neq m} [W_{mm'} \rho_m (1 - \rho_{m'}) - W_{m'm} \rho_{m'} (1 - \rho_m)],$$

(5.13)

This is the Pauli Master-equation as stated in Chapter 1, Eq. (1.9), now derived in a more formal way. It describes the incoherent motion of the carriers on a lattice under the influence of an external electric field. The transition rate $W_{mm'}$, following from the perturbation by $\hat{H}_E$, is calculated by Böttger and Bryksin via a diagram technique and reads

$$W_{mm'} = \frac{|J_{mm'}|^2}{\hbar^2} \exp\left[-2 S_T(mm')\right] \exp(\beta \epsilon_{mm'} / 2) \int_{-\infty}^{\infty} dt' \exp\left(\frac{i \epsilon_{mm'} t'}{\hbar}\right) \times$$

$$\left[ \exp\left(\sum_q |\gamma_m(q)|^2 [1 - \cos(q \cdot R_{mm'})] N \sinh(\hbar \omega_q \beta / 2) \cos(\omega_q t') \right) - 1 \right],$$

(5.14)

with

$$S_T(mm') = \frac{1}{2N} \sum_q |\gamma_m(q)|^2 [1 - \cos(q \cdot R_{mm'}) \coth(\hbar \omega_q \beta / 2)],$$

(5.15)

and $\epsilon_{mm'} = \epsilon_{m'} - \epsilon_m - e \mathbf{E}(t) \cdot (\mathbf{R}_{m'} - \mathbf{R}_m)$.

The important message is that the use of Eq. (5.13) provides a very powerful method to describe the hopping motion of the charge carriers in the Markovian limit. But, as mentioned before, this limit only holds when the timescale is such that the electron distribution at a site reaches equilibrium with the phonon subsystem. A typical estimate of this time is the reciprocal phonon frequency, i.e. $\approx 10^{-12}$s. Thus, Eq. (5.13) is valid for frequencies of the external electric field up to the infrared region. From the expression Eq. (5.14) for $W_{mm'}$ it is clear that, formally, the microscopic nature of the coupling of the electrons and phonons is of crucial importance to get the right dynamics of the charge carriers. It can be shown that under the conditions of weak electron-phonon coupling, low temperature
where \textit{one-phonon processes} dominate, and under the assumption that the transfer integral behaves like \( J_{mm'} = J_0 \exp[-\alpha |R_{mm'}|] \), one obtains a rather simple expression for the transition rate:

\[
W_{mm'} = \begin{cases} 
\nu_{\text{ph}} \exp[-\alpha |R_{mm'}| - \beta (\varepsilon_{m'} - \varepsilon_m)], & \varepsilon_{m'} > \varepsilon_m, \\
\nu_{\text{ph}} \exp[-\alpha |R_{mm'}|], & \varepsilon_{m'} < \varepsilon_m,
\end{cases} \quad (5.16)
\]

with \( \nu_{\text{ph}} \) given by

\[
\nu_{\text{ph}} = \frac{J_0^2 \pi}{\hbar^2 N} \sum_q |\gamma_m(q)|^2 \left[ 1 - \cos(q \cdot R_{mm'}) \right] \delta(\omega_q - |\varepsilon_m - \varepsilon_{m'}| / \hbar). \quad (5.17)
\]

This is precisely the Miller-Abrahams transition rate we have been talking about in Chapter 1, see Eq. (1.8). Now it is clear what has been neglected if we use Eq. (5.16) with \( \nu_{\text{ph}} \) independent of \( \varepsilon_m \) and \( \varepsilon_{m'} \) instead of Eq. (5.14). The dependence of \( \nu_{\text{ph}} \) on \( \varepsilon_m \) and \( \varepsilon_{m'} \) is accounted for in the more refined theory of Marcus [82]. At high temperatures the assumption that \textit{only} one-phonon processes are involved in the electronic transition breaks down. Emin showed that the highest temperature for which only one-phonon processes need to be considered decreases with increasing electron-phonon coupling strength [81]. He also showed that in many disordered systems the coupling is strong, \(|\gamma|^2 \gg 1\), and thus multi-phonon processes are important. However, he also noted that even with strong coupling there is a temperature below which no mixed absorption-emission processes occur. In the case of disordered \( \pi \)-conjugated polymer systems we typically have \(|\gamma|^2 \ll 1\) [185], which corroborates our one-phonon approximation for the transition rate. Despite the assumption of a constant rate, most of the dominant physical processes are apparently included, which follows from the favorable comparison with experiments that will be demonstrated.

As can be seen, \( \nu_{\text{ph}} \) contains information about the microscopic parameters like inter-site distance, electron-phonon coupling strength, phonon density of states, temperature, etc. To include all this microscopic information, we should have detailed knowledge about all these parameters. The study of the charge transport with input about the electronic and phononic structure from e.g. \textit{ab-initio} calculations may be the subject of future research, which is beyond the scope of the present work.

### 5.2 Numerical solution of the Pauli Master-equation

We will now discuss how we solve Eq. (5.13) numerically. In the seventies Butcher [184, 183] started the numerical work to solve the hopping problem by mapping the problem to a Miller-Abrahams random-resistor network for which he solved Kirchhoff’s equations. In this section we will discuss a method in which this mapping is circumvented. The new aspect of our approach is that we numerically solve the linearized Master-equation in an efficient way, so that we can handle much larger systems and perform averages over more
disorder configurations than could be done before. We start, following [182], by taking
the linear approximation with respect to the external electric field $E$ that is contained in $W_{mm'}$. In the case that $E$ is equal to zero we have the following (stationary) situation:

$$0 = - \sum_{j \neq i} W_{ij}^0 n_i^0 (1 - n_j^0) + \sum_{j \neq i} W_{ji}^0 n_j^0 (1 - n_i^0),$$

(5.18)

where $n_i^0$ is the occupational density of site $i$, with position vector $\mathbf{R}_i$ and energy $\varepsilon_i$, and $W_{ij}^0$ is the (asymmetric) transition rate for hops from site $i$ to $j$. The occupational density $n_i^0$ is given by the Fermi-Dirac distribution function, because of detailed balance. Using Eq. (5.16), we have for $W_{ij}^0$:

$$W_{ij}^0 = \left\{ \begin{array}{ll}
\nu_{ph} \exp[-\alpha |\mathbf{R}_{ij}| - \beta(\varepsilon_j - \varepsilon_i)], & \varepsilon_j > \varepsilon_i, \\
\nu_{ph} \exp[-\alpha |\mathbf{R}_{ij}|], & \varepsilon_j < \varepsilon_i.
\end{array} \right.$$

(5.19)

Now we apply in the $x$-direction an external time-dependent electrical field $E \exp(-i\omega t)$. $W_{ij}$ will change because now includes a contribution $-e \mathbf{E} \cdot \mathbf{R}_{ij}$ from the external time-dependent electrical field, with $e$ the particle charge. If we want to examine the DC case, we can just put $\omega = 0$. If we linearize with respect to the electric field, we arrive at the following equation for $n'_i = n_i - n_i^0$, with $n_i' \in \mathbb{C}$ ($n_i' \in \mathbb{R}$ in DC case):

$$\sum_{j \neq i} [W_{ij}^0 (1 - n_i^0) + W_{ij}^0 n_i^0] n_j' - \left[ \sum_{j \neq i} [W_{ij}^0 (1 - n_j^0) + W_{ji}^0 n_j^0] + i\omega \right] n_i' = \sum_{j \neq i} [W_{ij}' n_i^0 (1 - n_j^0) - W_{ji}' n_j^0 (1 - n_i^0)],$$

(5.20)

where $n_i^0$ is the equilibrium Fermi-Dirac distribution, $W_{ij}^0$ is the transition rate at zero electric field, and $W_{ij}' = (\partial W_{ij}/\partial E)|_{E \to 0}$. The above-stated equation can be cast in a very simple form:

$$\mathbf{M} \mathbf{n}' = \mathbf{b},$$

(5.21)

where $\mathbf{M}$ has diagonal elements $M_{ii} = - \sum_j M_{ij} + i\omega$ and off-diagonal elements $M_{ij} = M_{ji}$ for $i \neq j$. Here we have defined $M_{ij} = \Gamma_{ij}/F_i$, with $\Gamma_{ij} = W_{ij}^0 n_i^0 (1 - n_j^0)$, $F_i = n_i^0 (1 - n_i^0)$, and $b_i = \sum_{j \neq i} [W_{ij}' n_i^0 (1 - n_j^0) - W_{ji}' n_j^0 (1 - n_i^0)]$. As a result, we just have to solve a system of linear equations, with a sparse matrix $\mathbf{M}$. The sparsity of the matrix $\mathbf{M}$ is achieved by taking into account only a limited number of hopping sites $j$ around $i$. This is justified by the exponential decay of the transition rates Eq. (5.19).

In our numerical calculations, we first generate randomly distributed energies on each site of an array of lattice constant $R_0$ and size $L^d$, $d = 1, 2, 3$. In case of an energy-independent DOS $g_{D}$, we sample the energies $\varepsilon$ from an interval $|\varepsilon| \leq \varepsilon_0/2 \equiv (2R_0^d g_{D})^{-1}$, and charge is introduced into the system by setting the chemical potential in the Fermi-Dirac distribution equal to zero. In case of a Gaussian DOS we sample from a normalized Gaussian
distribution with a width $\sigma$, and again charge is introduced by setting the chemical potential to a desired value. To solve the set of linear equations we use standard routines for sparse matrices from the NAG library. Actually, we solve the problem for $n'_i/F_i$. This rescaling of $n'_i$ turned out to be computationally convenient in the low-temperature regime. The mobility $\mu$ can be calculated from the current between all sites $(i, j)$:

$$\frac{L^{d-1} < n^0_i >}{R_0} \mu = \sum_i \sum_j [R_{ij} W_{ij} n_i (1 - n_j) + (i \leftrightarrow j)]. \quad (5.22)$$

In the previous part we discussed how to solve the Pauli Master-equation in the case of a small applied external electrical field. The condition of a small electric field was needed in order to linearize the equation. When the external applied electrical field is large, our linearization procedure breaks down. In order to be able to still analyze the regime of Fermi-Dirac statistics combined with larger electric-field strengths, we use a numerical approach developed by Yu et al. [180, 181]. This approach is based on a very efficient iteration procedure to solve the nonlinear Master-equation in the steady state. In this approach, $n_i$ is expressed as

$$n_i = \frac{\sum_j W_{ij} n_j}{\sum_k W_{ki}} \left[ 1 - \frac{\sum_j (W_{ji} - W_{ij}) n_j}{\sum_k W_{ki}} \right]^{-1}. \quad (5.23)$$

Based on this equation, $n_i$ is updated using implicit iteration until a certain accuracy criterion has been satisfied. More specifically, when $n_i^{(n-1)}$ with $(1 \leq i \leq N)$ is the solution after step $n - 1$, then the next step (step $n$) $n_i$ is calculated as follows. The right hand side of Eq. (5.23) is taken to consists of $n_j^{(n)}$ for $j < i$ and $n_j^{(n-1)}$ for $j > i$. This proves to be superior to using explicit iteration, i.e. $n_j^{n-1}$ for all $j$, because then the iteration scheme does not converge [180, 181].

To conclude this section, one might ask a very relevant question: 'Why not use Monte-Carlo simulations?' The reasons why we used a Master-equation and not a Monte-Carlo approach are:

1. The Master-equation ensures a stationary solution, and since the mobility is a property of the steady state, it is very advantageous to solve the stationary Master-equation.
2. For Monte-Carlo simulations the simulation time required for convergent results increases rapidly when the temperature decreases, because of the transition rates involved ($W_{ij} \propto e^{-\beta \epsilon_{ij}}$). In other words, when the temperature of the system becomes very low, it is very difficult to obtain stationary solutions by means of Monte-Carlo simulations. And it is exactly the low-temperature or strongly-disordered regime that we want to study.
5.3 Analytical work based on the Pauli Master-equation

In this section we will summarize some important analytical results based on the Pauli Master-equation that have been derived by Movaghar and Schirmacher in 1981 [88]. They treated the situation of a symmetric as well as an asymmetric hopping model by means of effective medium theories, in terms of a perturbation expansion of the Green function $G(i\omega)$ for the linearized Master-equation. The frequency-dependent hopping conductivity $\sigma(\omega)$ following form the linearized Master-equation Eq. (5.20) is given by Butcher [182]

$$\sigma(\omega) = \frac{e^2(i\omega)^2}{6\Omega kT} \left\langle \sum_{ij} F_i R^2_{ij} G_{ij}(\omega) \right\rangle,$$

with $\Omega$ the volume of the system, $e$ the elementary charge, the angular brackets denoting a configurational average, and the rest of the notation as in the previous section. The quantity $G_{ij}(\omega)$ can be interpreted as a Green function of the operator $(i\omega I - H)^{-1}$, where $H$ is a Hamiltonian with diagonal elements, $H_i = \sum_n H_{in}$ and off-diagonal elements, $H_{ij} = \Gamma_{ij}/F_i$. In another interpretation, $G_{ij}$ is the Fourier-Laplace transform of the time-dependent Green function $G_{ij}(t)$ of the linearized Master-equation with asymmetric transition rates $H_{ij}$ and $H_{ji}$. In order to analyze the problem in a more quantitative way Movaghar and Schirmacher developed the following perturbation expansion for $G_{ij}(\omega)$:

$$G_{ij}(\omega) = G_{ii} \delta_{ij} + G_{ii} g_{ij} G_{jj}(ij) + \sum_{l \neq i \neq j} G_{ii} g_{il} G_{ll}(il) g_{lj} G_{jj}(il;lj) + \ldots,$$

where $G_{jj}(il;lj)$ refers to the exact local Green function with transitions to sites $i$ and $l$ excluded and the bonds $(i-l)$ and $(l-j)$ removed from the system. Here we have defined

$$g_{il} = \frac{H_{il}/H_{li}}{1/H_{ii} + G_{ll}(il)} \quad \text{and} \quad g_{lj}^{(i)} = \frac{H_{lj}/H_{jl}}{1/H_{jj} + G_{jj}(il;lj)}.$$

It is possible to write the quantities $G_{ii}$ and $G_{jj}(ij)$ in the following form:

$$G_{ii} = \left( i\omega + \sum_k g_{ik} - C_i \right)^{-1} \quad \text{and} \quad G_{jj}(ij) = \left( i\omega + \sum_{k \neq i} g_{jk}^{(i)} - C_j^{(i)} \right)^{-1},$$

with

$$C_i = \Delta_i - \sum_l H_{il} H_{il}^{(i)} H_{li}.$$ 

$\Delta$ represents the closed-loop self-energy contributions involving three sites or more. Up to here all equations are exact, regardless of the structure of the lattice. However, in practice it is very difficult to compute all terms exactly, and hence one has to resort to approximate schemes. This can be done either in the summation of the terms in the
perturbation expansions or by the structure of the lattice used for the computations. The latter procedure has been used by Movaghar and Schirmacher in order to provide a clue for developing an approximate scheme for the real 2D and 3D systems. By approximating the lattice topology by a Cayley tree of coordination number $Z$, for which closed loops are absent, implying that the $C$'s in the Eqs. (5.27) are identically zero, it is possible to obtain exact results. As discussed by Movaghar and Schirmacher, inspired by the exact results for the Bethe lattice, they approximate the closed loop terms (prohibiting exact results) by breaking them up into products of two-site contributions. By this procedure they take into account repeated forward and backward hopping. This approximation is called a 'two-site self-consistent approximation'. With this procedure they arrive at the same equations as (5.27) with $C = 0$, but with reduced $g_{ik}$'s. From this result it is possible to apply a 'two-site effective-medium approximation' directly to the Green function expansion with the reduced $g_{ik}$'s. We will summarize the resulting expressions for the frequency-dependent conductivity in case of the symmetric energy-dependent case ($W_{ij} = \nu_{ph} \exp[-\alpha |R_{ij}| - \beta |\varepsilon_{ij}|]$) and in the more complex case of an asymmetric transition rate (5.19). The symmetric transition rate is a generalization of the hopping rate for the random-barrier model, where only nearest neighbor hopping has been taken into account. The application of this model will be discussed in Chapter 9. In the symmetric case the frequency-dependent conductivity reads

$$\sigma(\omega) = \frac{e^2}{kT} \frac{\nu_c(1 - n_c)}{\Omega} \frac{\langle R^2(\omega) \rangle}{6a_p} \sigma_1(\omega), \quad (5.29)$$

where $\sigma_1(\omega)$ satisfies the following self-consistency equation:

$$\sigma_1(\omega) = n_c a_p \left[ \sigma_1(\omega) + i\omega \right] \int \int g(E) g_c(R_{ij}) W_{ij} \frac{dR_{ij} dE}{i\omega + \sigma_1(\omega) + W_{ij}}, \quad (5.30)$$

and $\langle R^2(\omega) \rangle$ is given by

$$\langle R^2(\omega) \rangle = \frac{W_{ij}}{i\omega + W_{ij} + \sigma_1(\omega)} \left( \frac{W_{ij}}{i\omega + W_{ij} + \sigma_1(\omega)} \right)^{-1}, \quad (5.31)$$

with $n_c = N_c/N$ the average number of hopping particles per site, $N_c$ the total number of particles, $N$ the total number of sites, $a_p = e$ with $e$ the natural logarithm base, $g(E)$ the density of states, and $g_c(R_{ij})$ the pair correlation function.

In the case of an asymmetric hopping model one arrives at the following expression for the frequency-dependent conductivity:

$$\sigma(\omega) = \frac{e^2}{kT} \frac{n_c^2}{6} \int \int \frac{g(E) g(E') g_c(R_{ij}) R_{ij}^2}{\Gamma(E, E'; R_{ij})^{-1} + [i\omega F(E') + \sigma_1(E', \omega)]^{-1}} dR_{ij} dE dE', \quad (5.32)$$

where $\sigma_1(E', \omega)$ satisfies the integral equation

$$\sigma_1(E', \omega) = n_c a_p \int \frac{g(E'') g_c(R_{ij})}{\Gamma(E', E''; R_{ij})^{-1} + [i\omega F(E'') + \sigma_1(E'', \omega)]^{-1}} dR_{ij} dE''. \quad (5.33)$$
Here $\Gamma(E)$ and $F(E)$ are defined as in the previous section. Applications and implications of these equations concerning their DC and AC results will be compared and discussed in later chapters.
Chapter 6

Generalized Mott theory - Application to the doping dependence in conjugated polymers

ABSTRACT

Standard variable-range hopping (VRH) theories for the DC conductivity neglect the spatial extension of the sites at which the charge carriers are localized and the energy dependence of the density of states (DOS). In the present work we will show how to take into account both these effects analytically in order to arrive at an exact generalized VRH relation for the conductivity. Both dependencies will be shown, by comparison with experimental data, to be of crucial importance for the understanding of the strong doping dependence of the conductivity in PPV, doped in solution with iron(III)chloride, FeCl₃.
6.1 Introduction

The discovery of a strong increase in conductivity upon doping of conjugated polymers was the first revolutionary step to the increased activity in the field of plastic electronics and this effect has been demonstrated many times since. Different ways of doping can be considered. One can think of chemical doping, ‘photo-doping’, and doping by charge injection from electrodes, which is most convenient for devices like LEDs and FETs. A nice review about doping of conjugated polymers can e.g. be found in [159]. The importance of the effect of doping in devices like LEDs and FETs has been pointed out recently by Tanase et al. [165]. They showed that the hole mobility in these devices (based on conjugated polymers) increases as a function of charge-carrier density, and that this dependence can explain the large difference in hole mobilities between the two devices, based on the same polymers. However, the nonlinear functional relation between dopant concentration and conductivity in the non-metallic state has not been fully understood [11, 12, 160, 161, 162]. In this chapter we will show how to derive an analytical expression for the doping and temperature dependence of the conductivity. It turns out that this result is mathematically applicable to any shape of the density of states (DOS). The procedure is based on Mott’s (three-dimensional) variable-range hopping theory for point-like localized states. We generalize this idea to the situation of an arbitrary energy-dependent DOS, and spatially extended localized regions, without the need of specifying the exact nature of the charge carriers involved. A strong argument (as will be shown later from the comparison with experiments) in favor of an approach beyond the point-site model is the fact that the conductivity at high temperatures $T$ and at high doping concentrations $c$ is only one order of magnitude below the value of Mott’s minimum metallic conductivity [163]. The minimum metallic conductivity is obtained from the Ioffe-Regel condition [164], stating that the mean free path of a charge carrier is equal to the distance between the atoms. The conductivity is then given by $\sigma_{\text{min}} = \text{const.} \times \frac{e^2}{h a}$, with $e$ the electron charge, $h$ Planck’s constant, and $a$ the distance between atoms. We will apply the obtained exact relation for the conductivity to discuss the outcome for experimentally relevant shapes of the DOS, e.g. a near-constant DOS, an exponential DOS, and a Gaussian DOS. We will discuss a quantitative comparison of our theory with experiments in the situation of a near-constant DOS. Before discussing the analytical work, let us first try to qualitatively understand the strong superlinear dependence of the conductivity $\sigma$ on the concentration $c$ of doped charges. As mentioned in Chapter 1, due to the disordered nature of the system, charge transport takes place via localized electronic states with randomly distributed energies. One can consider two important contributions to $\sigma(c)$: (1) an energy-dependent DOS, and (2) an increasing size of the localized region, both of which we will discuss on the basis of Figure 6.1.

(1) In the undoped situation an energy-dependent DOS has, in contrast to a constant DOS (which is indicated by the dotted line) more states available at higher energies. Within the Mott theory this results in critical hops with lower energy, and hence in an increasing conductivity. Similarly, in a doped system more states become available at the new Fermi energy $E_F(c)$, with the same effect. Moreover, this difference in Fermi energy leads to
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Figure 6.1: (a) Density of states $g(E)$ vs. $E$. After doping up to concentration $c$, states between $E_F(c)$ and $E_{\text{hop}}(c)$ are available for hopping. (b) Increase of the extent $A(c)$ of the localized states as a function of doping, here from $A_1$ in the case of no doping to $A_2$ for a doped situation, leading to an increase of the number of available states within $R_{\text{hop}}$.

(2) The size of the localized regions may grow with increasing $c$ and thus with increasing $E_F$. This can be expected from the fact that states with high energy $E$ are less strongly bound by the random potential and as a matter of fact become spatially more extended. As can be seen from Fig. 6.1b, the number of states within a given hopping distance $R$ from these more extended states increases with this increase in the localization volume. The result is again a larger VRH conductivity $\sigma$. The assumption of the increasing extent of the localized states can be also be understood from the fact that by filling, higher lying energy states start to act as "virtual stepping stones", due to hybridization between the actual hopping sites, which manifests itself in an increased wave function overlap.
6.2 General theory

We will now derive an expression for the concentration-dependent VRH conductivity in a system with an arbitrary shape of the density of states \( g(E) \) and volume \( V_0 \) of the localized region. The procedure we follow is analogous to what has been discussed in Chapter 1. The charge carrier is considered to be located at the Fermi level, from where the transport takes place. The hopping probability depends exponentially both on the hopping distance \( R \) between the localized regions and on the activation energy difference \( E - E_F \) [73]. The density of final states \( \mathcal{N} \) that can be reached with activation energy less than \( E - E_F \) is given by

\[
\mathcal{N}(E, E_F) = \int_{E_F}^{E} dE' g(E').
\] (6.1)

We take into account a dependence on the doping level via the Fermi energy \( E_F(c) \)

\[
\int_{E_F(0)}^{E_F(c)} dE' g(E') = c.
\] (6.2)

In this relation we ignore Fermi-Dirac statistics and as such the model is a zeroth order approximation just in order to keep the problem analytically tractable. According to Mott, the DC conductivity \( \sigma \) is governed by those hops for which \( E \) and \( R \) are such that about one state lies within a volume \( V \):

\[
V \mathcal{N} \approx 1.
\] (6.3)

The physical interpretation behind this criterion is very intuitive: to have a nonzero conductivity the hopping process should not die out after several hops. From the Mott condition (6.3) we can define the hopping volume \( V \) as a function of \( E \) and \( E_F \), namely

\[
V = V(E, E_F) = \mathcal{N}^{-1}(E, E_F).
\] (6.4)

Now, the hopping distance \( R \) is a unique function, which will be specified later, of \( V \) and of some length \( A \), schematically indicated in Fig. 1b. For the moment we define:

\[
R = R(V, A) = R(E, E_F, A).
\] (6.5)

So we just have defined the functional forms and conditions for the variables playing a major role in the hopping process. In order to find the optimal hop energy \( \tilde{E} \), and the associated hopping distance \( \hat{R} \), we need to minimize the expression \( \alpha R + \beta E \) (as discussed in Chapter 1), resulting in

\[
\alpha \left( \frac{\partial R}{\partial E} \right)_{E_F, A} + \beta = 0 \quad \text{for} \quad E = \tilde{E}.
\] (6.6)

From differentiation of Eq. (6.3) with respect to \( E \) we have

\[
\left( \frac{\partial V}{\partial R} \right)_A \left( \frac{\partial R}{\partial E} \right)_{E_F, A} \mathcal{N} + V g = 0 \rightarrow \left( \frac{\partial R}{\partial E} \right)_{E_F, A} = -V^2 g \left( \frac{\partial R}{\partial V} \right)_A.
\] (6.7)
So together with Eq. (6.6) the condition for \( \tilde{E} \) becomes:

\[
\frac{1}{V^2} \left( \frac{\partial V}{\partial \tilde{R}} \right)_A = \frac{\alpha}{\beta} g(E) \quad \text{for } E = \tilde{E}.
\]  

(6.8)

With the solution of this equation we have established an expression for the optimal hop energy \( \tilde{E} \) and optimal hopping distance \( \tilde{R} \):

\[
\tilde{E} = E(\beta, E_F, A), \quad \tilde{R} = R[\tilde{E}(\beta, E_F, A), E_F, A],
\]

(6.9)

which yields the final form for the system’s conductivity:

\[
\sigma = \sigma_0 \exp[-\alpha \tilde{R} - \beta(\tilde{E} - E_F)],
\]

(6.10)

where the conductivity ultimately depends on \( c \) via \( \sigma_0, E_F, \) and \( A \).

In order to gain a deeper insight into the explicit dependence on \( c \) via \( E_F \) and \( A \), we can write:

\[
\left( \frac{\partial \log(\sigma/\sigma_0)}{\partial c} \right)_{\beta} = \left( \frac{\partial \log(\sigma/\sigma_0)}{\partial E_F} \right)_{\beta, A} \frac{dE_F}{dc} + \left( \frac{\partial \log(\sigma/\sigma_0)}{\partial A} \right)_{\beta, E_F} \frac{dA}{dc}.
\]

(6.11)

To proceed the analysis of this expression, let us start considering the first term:

\[
\left( \frac{\partial \log(\sigma/\sigma_0)}{\partial E_F} \right)_{\beta, A} = -\alpha \left( \frac{\partial \tilde{R}}{\partial E_F} \right)_{\beta, A} - \beta \left( \frac{\partial \tilde{E}}{\partial E_F} \right)_{\beta, A} + \beta
\]

\[
= -\alpha \left[ \left( \frac{\partial \tilde{R}}{\partial E_F} \right)_{\tilde{E}, A} + \left( \frac{\partial \tilde{R}}{\partial \tilde{E}} \right)_{E_F, A} \left( \frac{\partial \tilde{E}}{\partial E_F} \right)_{\beta, A} \right] - \beta \left[ \left( \frac{\partial \tilde{E}}{\partial E_F} \right)_{\beta, A} - 1 \right]
\]

\[
= -\alpha \left( \frac{\partial \tilde{R}}{\partial E_F} \right)_{\tilde{E}, A} + \beta.
\]

(6.12)

In the last step we have used Eq. (6.6), the condition for the optimum critical hop. In order to arrive at an expression for the explicit dependence of \( \tilde{R} \) on \( E_F \) we can make use the functional dependence of \( \tilde{R} \) on \( \tilde{V}(\tilde{E}, E_F) \):

\[
\left( \frac{\partial \tilde{R}}{\partial E_F} \right)_{\tilde{E}, A} = \left( \frac{\partial \tilde{R}}{\partial \tilde{V}} \right)_A \left( \frac{\partial \tilde{V}}{\partial E_F} \right)_{\tilde{E}}
\]

\[
\left( \frac{\partial \tilde{V}}{\partial E_F} \right)_{\tilde{E}} = \frac{d\tilde{V}}{dN} \left( \frac{\partial N}{\partial E_F} \right)_{\tilde{E}} = \tilde{V}^2 g(E_F).
\]

(6.13)

Combining the above two equations we end up with the expression for the explicit dependence of \( \tilde{R} \) on \( E_F \), i.e.

\[
\left( \frac{\partial \tilde{R}}{\partial E_F} \right)_{\tilde{E}, A} = \tilde{V}^2 g(E_F) \left( \frac{\partial \tilde{R}}{\partial \tilde{V}} \right)_A = \frac{\beta}{\alpha} \frac{g(E_F)}{g(\tilde{E})}.
\]

(6.14)
Now that we have an expression for \( \left( \frac{\partial \tilde{R}}{\partial E_F} \right)_{E_F,A} \) we are able to deliver the final outcome for the first term of Eq. (6.11) which has a very simple structure, namely
\[
\left( \frac{\partial \log(\sigma/\sigma_0)}{\partial E} \right)_{E_F,A} = \beta \left[ 1 - \frac{g(E_F)}{g(E)} \right]. \tag{6.15}
\]
To finish our exploration of Eq. (6.11) the second term has to be investigated as well. The same line of reasoning as above leads to
\[
\left( \frac{\partial \log(\sigma/\sigma_0)}{\partial A} \right)_{\beta,E,F} = -\alpha \left( \frac{\partial \tilde{R}}{\partial A} \right)_{\tilde{E},E,F} - \beta \left( \frac{\partial \tilde{E}}{\partial A} \right)_{\tilde{E},E,F} - \beta \left( \frac{\partial \tilde{E}}{\partial A} \right)_{\tilde{A},E,F}
\]
\[
= -\alpha \left( \frac{\partial \tilde{R}}{\partial A} \right)_{\tilde{E},E,F} \tag{6.16}
\]
where in the last step we again used Eq. (6.6). By use of the definition for \( \tilde{R} \) it follows from Eq. (6.5) that \( \tilde{R} \) is a function of \( A \) and \( V \) only, so
\[
\left( \frac{\partial \tilde{R}}{\partial A} \right)_{\tilde{E},E,F} = \left( \frac{\partial \tilde{R}}{\partial A} \right)_{\tilde{V}}. \tag{6.17}
\]
For the three variables \( R, V, \) and \( A \) we can make use of the well-known ’-1 rule’:
\[
\left( \frac{\partial R}{\partial A} \right)_V \left( \frac{\partial A}{\partial V} \right)_R \left( \frac{\partial V}{\partial R} \right)_A = -1 \quad \rightarrow \quad \left( \frac{\partial R}{\partial A} \right)_V = -\left( \frac{\partial V}{\partial A} \right)_R. \tag{6.18}
\]
To learn more about the \( A \)-dependence of \( \tilde{R} \) we now make a more specific assumption about the shape of the hopping volume:
\[
V = V_0(A + R) - V_0(A), \tag{6.19}
\]
where \( V_0 \) is still arbitrary. With this assumption we get
\[
\left( \frac{\partial V}{\partial A} \right)_R = V'_0(A + R) - V'_0(A), \quad \left( \frac{\partial V}{\partial R} \right)_A = V'_0(A + R), \tag{6.20}
\]
and as a result we arrive at the following equation for \( \left( \frac{\partial \tilde{R}}{\partial A} \right)_{\tilde{E},E,F} \):
\[
\left( \frac{\partial \tilde{R}}{\partial A} \right)_{\tilde{E},E,F} = - \left[ 1 - \frac{V'_0(A)}{V'_0(A + \tilde{R})} \right]. \tag{6.21}
\]
So, we can write down the final expression for the second term of Eq. (6.11):

\[
\frac{\partial \log(\sigma/\sigma_0)}{\partial A} = \alpha \left[ 1 - \frac{V'_0(A)}{V'_0(A + \tilde{R})} \right].
\] (6.22)

Having found an expression for the two terms of Eq. (6.11), we arrive at the final exact expression for the dependence of \(\sigma/\sigma_0\) on \(c\):

\[
\frac{\partial \log(\sigma/\sigma_0)}{\partial c} = \beta \left[ 1 - \frac{\tilde{E}}{g(\tilde{E})} \right] + \frac{1}{g(\tilde{E})} \left[ 1 - \frac{V'_0(A)}{V'_0(A + \tilde{R})} \right] \frac{dA}{dc},
\] (6.23)

This equation can be put in a form that is more instructive in illustrating the \(c\)-dependence, namely by replacing \(\frac{dE_F}{dc}\) by \(\frac{1}{g(E_F)}\); see Eq. (6.2), which leads to the following equation:

\[
\frac{\partial \log(\sigma/\sigma_0)}{\partial c} = \beta \left[ 1 - \frac{\tilde{E}}{g(\tilde{E})} \right] + \alpha \left[ 1 - \frac{V'_0(A)}{V'_0(A + \tilde{R})} \right] \frac{dA}{dc},
\] (6.24)

where \(\tilde{E}\) and \(\tilde{R}\) are found from Eqs. (6.6)-(6.9). The first term represents the effect on the conductivity of the energy dependence of the DOS, while the second term accounts for changes in the spatial extend of the localized states. Note (once more) that this is an exact relation, valid for arbitrary shape of the density of states. At this stage we are able to examine experimentally relevant situations.

### 6.3 Instructive limits

In order to describe \(\sigma(T, c)\) fully by integration of Eq. (6.24), we also need an expression for \(\frac{\partial \log(\sigma/\sigma_0)}{\partial \beta}\). In this section we will discuss the temperature dependence of the conductivity by straightforward application of Eq. (6.10) for two important assumptions for the shape of the density of states (omitting for the moment the \(c\) dependence): (1) a nearly constant density of states, \(g(E_F) \approx g(\tilde{E})\), and (2) a strongly energy-dependent DOS, \(g(\tilde{E}) \gg g(E_F)\).

Furthermore, we assume a \(T\)-dependent Fermi level (i.e. the initial level from where the hopping takes place), which is a good approximation if thermal equilibration is fast. The variables in Eq. (6.10) are given by

\[
\tilde{E} = E(\beta, E_F, A), \quad \tilde{R} = R[\tilde{E}(\beta, E_F, A), E_F(\beta, A)].
\] (6.25)

So, we have:

\[
\frac{\partial \log(\sigma/\sigma_0)}{\partial \beta} = -\alpha \left( \frac{\partial \tilde{R}}{\partial \tilde{E}} \right) \frac{d\tilde{E}}{d\beta} - \alpha \left( \frac{\partial \tilde{R}}{\partial E_F} \frac{dE_F}{d\beta} - \beta \frac{d\tilde{E}}{d\beta} + \beta \frac{dE_F}{d\beta} - (\tilde{E} - E_F) \right)
\]

\[= -(\tilde{E} - E_F) + \left[ -\alpha \left( \frac{\partial \tilde{R}}{\partial E_F} \right) \frac{dE_F}{d\beta} + \beta \frac{dE_F}{d\beta} \right]
\]

\[= -(\tilde{E} - E_F) + \beta \left[ 1 - \frac{g(E_F)}{g(\tilde{E})} \right] \frac{dE_F}{d\beta},
\] (6.26)
with $\tilde{E}$ defined as in Eq. (6.8). In the first step in obtaining Eq. (6.26), a cancellation occurred and in the second step we rewrote the last term, using similar arguments as in the previous section.

We observe from Eq. (6.26) that if we deal with a constant DOS, we immediately end up with Mott’s law, because the only remaining term is $\tilde{E} - E_F$, which satisfies Mott’s solution given by $\tilde{E} - E_F \sim \beta^{n-1}$, where $\gamma \equiv 1/(d+1)$, with $d$ the dimensionality of the system. If we now consider case (1) and make the assumption $g(\tilde{E}) - g(E_F) \approx (\tilde{E} - E_F)g'(E_F)$, we have from Eq. (6.26)

$$
\frac{\partial \log(\sigma/\sigma_0)}{\partial \beta} = -(\tilde{E} - E_F) \left[ 1 - \beta \frac{dE_F}{d\beta} \left( \frac{d \log g(E)}{dE} \right)_{E_F} \right].
$$

(6.27)

If, furthermore, we assume the case of low doping and a spherical localization volume, we have $A \ll R$, and hence $V_0'(A + R) \gg V_0'(A)$. Then, the last term of Eq. (6.24) reduces to $\alpha(c)$, which leads to $\sigma \propto \exp(\alpha A(c))$. Combining this with Eq. (6.27), we recover Mott’s law, however, with an important extra factor $\exp(\alpha A(c))$:

$$
\sigma = \sigma_0 \exp(\alpha A(c)) \exp \left[ - \left( \frac{T_0(c)}{T} \right)^{1/4} \right].
$$

(6.28)

This relation is what we call the generalized Mott formula, including a spatial extension of the localized states, indicating that at a given temperature the growth of the localized regime $A$ has a considerable influence on the conductivity. In fact, this expression can also easily be found from the original Mott argument by just replacing the hop distance $R$ by $R + A$, and assuming that the additional volume spanned by $A$ is negligible compared to that spanned by $A + R$.

Considering case (2), $g(\tilde{E}) \gg g(E_F)$, Eq. (6.26) reduces to

$$
\frac{\partial \log(\sigma/\sigma_0)}{\partial \beta} = -(\tilde{E} - E_F) + \beta \frac{dE_F}{d\beta}.
$$

(6.29)

If we assume a general relation for the temperature dependence of the Fermi level, $E_F \sim \beta^\zeta$, with $\zeta > 0$, we can that the temperature dependence of the conductivity will be $\sigma \propto \exp(\text{const} \beta^{\zeta+1})$ (because the first term in Eq. (6.29) has a much weaker temperature dependence than the second term). Thus if $\zeta$ is small compared to unity, we end up with an activated-like temperature dependence of the conductivity.

### 6.4 Quantitative verification of the theory for doping dependence

We will start our discussion with an application of the theory developed above in the case of a constant density of states, and compare with experiments [76], as shown in Fig. 6.2.
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Figure 6.2: Experimental results of $\sigma$ vs. $T^{-1/4}$ for doping concentrations $0.005 \leq c \leq 0.17$ in OC$_1$C$_{10}$-PPV (two samples have $c$ close to 0.6). $c$ is expressed as the number of charge carriers per monomer. At low temperatures Mott’s law for 3D VRH is clearly obeyed. The dashed lines are fits of the theory and are discussed in the main text. The inset shows a power-like dependence of $\sigma$, indicated by the dashed line $\sigma \propto c^8$, for $0.01 \leq c \leq 0.1$ at 200 K.

The experiments have been performed on the conjugated polymer OC$_1$C$_{10}$-PPV doped in solution with iron(III)chloride, FeCl$_3$. Ideally, the following redox reaction should then take place: PPV$+2$FeCl$_3$ $\rightarrow$ PPV$^+$ + FeCl$_2$ + FeCl$_7^-$. The doping level $c$ is defined as the number of added charge carriers per monomer, which makes the total amount $c_0 + c$, where $c_0$ is taken to be the amount of charge carriers already present in the undoped sample. The measured temperature dependence of $\sigma$ is presented in Fig. 6.2, where $\sigma$ is plotted vs. $T^{-1/4}$ on a log-linear scale. The straight lines at sufficiently low temperature clearly indicate that Mott’s VRH law for three dimensions holds, as frequently reported in doped conjugated polymers [162, 167, 168, 169, 77]. From the inset in Fig. 6.2, representing the conductivity as a function of doping concentration at a fixed temperature around 200 K, we see a clear and steep power-law dependence of $\sigma$ on $c$. We obtain $\sigma \propto c^p$, with $p$ around 8, from which we can draw the conclusion, by looking to the generalized Mott formula Eq. (6.28), that $A$ depends logarithmically on $c$. In the analysis that follows, we will neglect the $c$-dependence of $\sigma_0$, because it is expected to be weak [170]. It is possible to reconstruct the density of states at the Fermi level from the experiments and to use this knowledge as input in fitting the generalized Mott formula Eq. (6.28) to the data. The density of states $g$ is obtained via $kT_0 \propto \alpha^3/g$, where $T_0$ is the slope of the data as presented in Fig. 6.2. For $\alpha^{-1}$ we take 0.2 nm [97]. The dashed lines in Fig. 6.2 represent the fits according to Eq. (6.28) of the data, which are shown to be in very good quantitative agreement with the experimental
data. From the fitting procedure we obtain $A$ as a function of doping concentration. The results for the reconstructed energy-dependent density of states and the doping dependence of $A$ are shown in Fig. 6.3. As can be seen from Fig. 6.3a, the $c$ dependence of $\sigma$ clearly necessitates the assumption of a strong increase in $g(E)$. However, this is not enough to achieve the quantitative fits as given in Fig. 6.2. We have to include the dependence of $A$ on $c$ as given in Fig. 6.3b. From this figure $A$ is shown to vary between 1 and 5 nm and follows a logarithmic dependence, indicated by the dotted line, as expected from the inset of Fig. 6.2. The range of values for $A$ compares fairly well with conjugation lengths obtained for chemically undoped PPV by the use of voltage modulated millimeter-wave spectroscopy [171]. At very low doping concentrations we of course encounter the lowest length scale set by the conjugation length of the polymer itself, namely a few monomers along the chain and one monomer in the perpendicular direction. Since we did not include anisotropy, the effective size has to be larger than that of one monomer. The saturation as found for high doping concentrations can easily be explained. For very high doping concentrations the localized regions start to consume the total available volume of the polymer.

### 6.5 Application to an exponential and Gaussian DOS

Let us now discuss the applicability of Eq. (6.24) in the case of an exponential density of states. Although in general disordered polymer systems are described by a Gaussian DOS, it is always possible to locally approximate the tails of the Gaussian by an exponential DOS.
In organic FET materials the temperature and gate bias dependencies are often described by hopping in an exponential DOS [165, 166]. In this section we will apply the generalized Mott theory to the two different functional forms of the exponential and Gaussian DOS and in this way derive a relation for the conductivity. For this section it is important to note once more that we ignore Fermi-Dirac statistics and as such the model is a zeroth-order approximation, in order to keep the problem analytically tractable. To be more specific, this means that in the case of a strongly energy-dependent DOS, e.g. exponential or Gaussian, we will finally run into problems due to the neglect of Fermi-smearing. For an average polymer system with a Gaussian DOS of width $\sigma$, we will typically have at room temperature $\beta\sigma = 4$. At this temperature the effects on the relation for the doping level, Eq. (6.2), due to the Fermi-Dirac statistics, are negligible or at most $O(1)$ for $E_F < 4\sigma$. The approximation becomes better at lower temperatures. The typical lowest concentrations involved at room temperature are then 0.005. In the case of an exponential DOS the neglect of Fermi-Dirac statistics is less harmful. The typical width of an exponential DOS as follows from experiments is about 1.5 times or more the thermal energy at room temperature [165]. We then typically underestimate the concentration by an amount $O(1)$. Just like for the case of the Gaussian DOS, the approximation becomes better at lower temperatures.

We assume the exponential DOS to have the following functional form

$$g(E) = g_0 \exp \left[ \frac{E}{E_0} \right].$$ \hfill (6.30)

In the particular case of this DOS, Eq. (6.10) can be rewritten as

$$\sigma = \sigma_0 \exp(-\alpha \tilde{R}) \left[ \frac{g(E_F)}{g(E)} \right]^{\beta E_0}$$

$$= \sigma_0 \exp(-\alpha \tilde{R}) \left\{ \frac{g[E_F(0)]}{g(E)} \right\}^{\beta E_0} \left\{ \frac{g[E_F(c)]}{g[E_F(0)]} \right\}^{\beta E_0}. \hfill (6.31)$$

If we integrate the exponential DOS with the integration running from $E_F(0)$ to $E_F(c)$, we find the following useful expression:

$$\frac{g[E_F(c)]}{g[E_F(0)]} = 1 + \frac{c}{c_0}, \quad c_0 = E_0 g[E_F(0)]. \hfill (6.32)$$

This relation can be substituted in Eq. (6.31), leading to an exact result for the conductivity in an exponential DOS:

$$\sigma = \sigma_0 \exp(-\alpha \tilde{R}) \left\{ \frac{g[E_F(0)]}{g(E)} \right\}^{\beta E_0} \left( 1 + \frac{c}{c_0} \right)^{\beta E_0}. \hfill (6.33)$$

However, this formula still contains the unknown variables $\tilde{R}$ and $\tilde{E}$. To make the expression for $\sigma$ more transparent, we introduce the following approximation in the case of an
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exponential DOS: \( \mathcal{N} = E_0[g(E) - g(E_F)] \approx E_0g(E) \). As in Section 6.2, we again have to solve the Mott equations

\[
\frac{1}{V^2} \left( \frac{\partial V}{\partial R} \right)_A = \frac{\alpha}{\beta} g(E), \quad VN = p_c \quad \text{for } E = \tilde{E},
\]

(6.34)

together with \( V = v_0 R^d \), where \( d \) is the dimensionality, and with \( p_c \) the value for the Mott percolation condition. From these equations we can easily find a relation for \( R \):

\[
R = \left( \frac{p_c}{v_0 E_0} \right)^{1/d} [g(E)]^{-1/d}.
\]

(6.35)

This relation can be used in the Mott equations to find their solution, which is given by:

\[
g(\tilde{E}) = \frac{p_c}{v_0 E_0} \left( \frac{p_c \alpha}{d E_0 \beta} \right)^d, \\
\tilde{R} = \frac{d E_0 \beta}{p_c \alpha}.
\]

(6.36)

Now that we have solved the Mott equations, it is easy to write down the final expression for the conductivity, which reads

\[
\sigma = \sigma_0 \left\{ \exp \left( -\frac{d}{p_c} \right) \right\} \frac{v_0 c_0}{p_c} \left( \frac{d E_0 \beta}{p_c \alpha} \right)^d \beta E_0 \left( 1 + \frac{c}{c_0} \right)^{\beta E_0}
\]

(6.37)

This relation shows two important features. First, there is a power-law dependence on the charge carrier density, where the power \( \beta E_0 \) is an increasing function of the inverse temperature, proportional to the width \( E_0 \) of the distribution. Second, for densities of the order \( c_0 = E_0g[E_F(0)] \) the mobility tends to a constant value. Both characteristics are observed in experiments [165]. Our expression should be compared with an analytical expression derived from percolation theory by Vissenberg and Matters [166], which gives for the mobility

\[
\mu_{FE}(p, T) = \frac{\sigma_0}{e} \left( \frac{(T_0/T)^4 \sin(\pi T/T_0)}{(2\alpha)^3 B_c} \right)^{T_0/T} p^{T_0/T-1},
\]

(6.38)

where \( e \) is the elementary charge, \( \sigma_0 \) a prefactor for the conductivity, \( \alpha^{-1} \) the effective overlap parameter between localized states, \( T_0 \) a measure for the width of the exponential density of states, and \( B_c \) a critical number for the onset of percolation. The conclusion we can draw from the comparison is as follows. Apart from the power-law dependence, which is the same for both expressions, we have derived a general expression, of which the Vissenberg-Matters expression is a special case, namely for \( c \gg c_0 \). Note that the pre-factor they find is different from what we find, which has to do with the fact that we did not take into account Fermi-Dirac statistics, whereas these authors did.
We now consider the case of Gaussian DOS, for which we take the following functional form:

\[
g(E) = g_0 \exp \left[ -\frac{(E - E_m)^2}{2\sigma^2} \right],
\]

(6.39)

where \( \sigma \) and \( E_m \) are width and the mean of the distribution, respectively. In physically realistic situations the parameters are such that the transport takes place in the tail of the Gaussian distribution. So, we can substitute \( E = E_F + \Delta E \) in the expression for \( g(E) \), resulting in

\[
g(E) = g_0 \exp \left\{ \frac{[(E_F(0) - E_m) + \Delta E]^2}{\sigma^2} \right\}
\approx g(E_F(0)) \exp \left[ \frac{E_m - E_F(0)}{\sigma^2} \Delta E \right],
\]

(6.40)

provided that \( \Delta E \ll E_m - E_F(0) \). Hence, we have reduced the problem of a Gaussian DOS to that of an exponential DOS with \( E_0 \) replaced by \( E_0 = \frac{\sigma^2}{E_m - E_F} \). This situation has been discussed above. The same features for the conductivity in case of an exponential DOS, namely a power law and a tendency to saturation, are thus to be expected for the Gaussian DOS. The value for the power is again \( \beta E_0 \), but with \( E_0 = \frac{\sigma^2}{E_m - E_F} \), and the point \( c_0 \) where saturation starts is now defined in terms of this \( E_0 \) times the density at the Fermi level \( g(E_F(0)) \).

6.6 Conclusions

We have developed an analytical generalization of the Mott theory for variable-range hopping, see Eq. (6.24), which is mathematically applicable to any shape of the DOS and takes into account the spatial extent of the localized states. With the help of this theory it is possible to obtain insight into the strong doping dependence of the conductivity as observed in experiments, by relating it to two dominant effects: an increasing DOS at higher doping concentrations, and the growth of the delocalized regions as a function of doping. In the specific comparison with measurements performed on doped PPV, it has been shown that, in order to describe the \( c \) and \( T \) dependence of \( \sigma \) as found in experiment, one has to take into account the explicit \( c \) dependence of both the density of states \( g(E) \) and the size of the delocalized regions \( A(c) \).

Moreover, we have shown that based on our general analytical theory we can derive a relation for the conductivity as a function of doping concentration in case of an exponential or Gaussian DOS. This relation, in case of the exponential DOS, compares very well with the relation found by Vissenberg-Matters [166] apart from a pre-factor which originates from effects of Fermi-Dirac statistics.
Chapter 7

Scaling in DC Variable-Range Hopping

ABSTRACT

By a numerically very efficient Master-equation approach we study the low-temperature mobility of a charge carrier in a disordered energy landscape, and demonstrate Mott-type variable-range hopping (VRH) in $d=1$, 2 and 3. The $T$-dependent distribution of hops over distances and energies is shown to obey a hitherto never reported universal scaling. The data and the origin of Mott-type temperature behaviour are explained by a new scaling theory in which the typical Mott hops mark the end of the scaling regime. This interpretation sheds new light on the roles of different hops in the overall mobility, and of the percolation path.
Chapter 7

7.1 Introduction

It is by now well-established that the low-temperature charge mobility in many disordered semiconductors deviates from Arrhenius-type behaviour, and obeys a temperature dependence of the form \( \mu \propto \exp[-(T_0/T)^\gamma] \), \( \gamma < 1 \). Originally, the phenomenon has been much studied in Si- and Ge-based systems, III-V compounds, and glasses[75]. The same universal behaviour is now also recognized in completely different systems, e.g. in high-\( T_C \) cuprate oxides[79], in conjugated polymers[76, 77], and in DNA[78]. The discrete range of values \( \gamma = 0.25, 0.33, 0.50 \) observed experimentally is a striking feature. Following the first observations of the phenomenon, Mott[73] presented an explanation based on so-called Variable-Range Hopping between localized states, and in particular showed that \( kT_0 = a(d)\alpha^d/\varrho_F \), and \( \gamma = 1/(d + 1) \), with \( a(d) \) a constant of order unity, \( \alpha \) the inverse localization length, \( \varrho_F \) the (constant) density of states at the Fermi level, and \( d \) the spatial dimension. Mott thereby considers the single-hop rate of the form \( \nu_{ph} \exp(-\alpha R - \beta \varepsilon) \) (\( \beta = 1/kT \), \( R \) is the hopping distance, and \( \varepsilon \) is the hop energy) first introduced by Miller and Abrahams[80]; hence from now on we will refer to it as Miller-Abraham factor. This expression accounts both for tunneling through a region in which the tail of the wave function is well approximated by an exponential, and for jumps upward in energy via phonon-assisted thermal activation. The central but very brief argument in the Mott theory is to identify the overall mobility with that of a single hop \((R_M, \varepsilon_M)\) which on the one hand is ‘typical’ or ‘most frequent’ [73] and optimizes the exponent but at the same time is the ‘most difficult’ hop in the sense that statistically it will just percolate: \( R_M^d \varepsilon_M \approx 1/\varrho_F \). Although the essential correctness of the VRH functional form is in no way in doubt, both the theoretical basis and the interpretation of the experimentally accessible and morphology-related parameter such as \( T_0 \) have remained a much-discussed topic; this also applies to extensions of the theory, e.g. to include Coulomb effects and non-constant \( \varrho(\varepsilon) \), and new contributions to the theory continue to appear[176, 76, 177, 178, 77, 117, 179]. Very early on already[84, 85, 86] the statistical basis of the Mott argument has been criticized, in particular the focus on a single representative bond; attempts were made to base the Mott formula more rigorously on the statistics of percolation theory. In that picture bonds are artificially introduced in decreasing order of conductance; \( R_M \) and \( \varepsilon_M \) then define a maximum in \((R,\varepsilon)\) space with a critical probability for bond percolation; introducing only bonds with a higher Miller-Abrahams factor is supposed to give rise to isolated islands while introducing also bonds with a Miller-Abrahams factor less favorable than \((R_M, \varepsilon_M)\) has no further effect since they are short-circuited. However, precisely at the percolation point there will be a dramatic difference in mobility between the real network (which has a nonzero and size-independent \( \mu \)) and the fractal network with the short-circuited bonds ignored (which has \( \mu \) size-dependent and vanishing). To avoid this complication and to arrive at an estimate for the prefactor of the mobility, the percolation approach necessitates more detailed arguments considering the ‘nodes-links-blobs’ organization of bonds beyond the percolation point[86, 186, 187, 188]. In Fig. 7.1 a schematic picture of the ‘nodes-links-blobs’ model is given for an infinite cluster, i.e. a system just above the percolation threshold. The
nodes indicate a subset of sites in the system that are at a typical average distance of each other (this distance is called the correlation length), whereas the thick lines indicate the bond segments between chains of sites. The loops are called the blobs, and they should be interpreted as different ways in parallel in order to connect the bond segments. The thin lines are dead ends, which do not contribute to the percolating path through the system. So if in the 'nodes-links-blobs' model the thick lines would not contain blobs, the system would be exactly at the percolation threshold. It is known that at the percolation threshold the mobility is strongly size-dependent and different from its bulk value. The picture as given in Fig. 7.1 explains this size-dependence in terms of adding new bonds above the percolation threshold, leading to the blobs, which open reservoirs of more favorable bonds causing the mobility to increase to and saturate at its bulk value.

The original aim of the present work has been to contribute to a clarification of some of the profound open issues. We chose the approach of direct numerical evaluation on a Miller-Abrahams network; since precisely at low temperatures a Monte-Carlo simulation becomes very time-consuming we employed the linearized Master equation for the site-to-site transport, which proves numerically far superior[181]. Our numerical results indeed clearly distinguish between the roles of different hops, in particular the most frequent, dominant and critical hops. More importantly, the data reveal a hitherto never reported scaling of the $T$-dependent mobility in $(R, \varepsilon)$ space. To rationalize the numerical findings we postulate a new analytical scaling theory of VRH. Finally, we will numerically validate the assumptions made in our scaling theory, and compare our results with effective-medium theory and percolation theory.
7.2 Results

To show the numerical results for the temperature dependence of the mobility we introduce units for the particle charge $e$, the lattice constant $R_0$, the intrinsic rate $\nu_{ph}$, and the energy span $\varepsilon_0$ of the DOS: $e = R_0 = \nu_{ph} = \varepsilon_0 = 1$. In Fig. 7.2 we have plotted $\mu^*$

![Figure 7.2: Mobility as a function of temperature for three spatial dimensions. Array sizes $L^d$ used for calculations: $L = 10000$, 200 and 60 for $d = 1, 2, 3$ respectively. The number of neighbors $N$ taken into account is $N = 79$, 99, 215 for $d = 1, 2, 3$. Averaging over different disorder realizations is performed to get error bars smaller than the symbol size; for $d = 3$ the error bar is of the order of the symbol size. The inset shows the 2D high-$T$ activated behavior.](image)

(the reason to use a superscript star will be indicated below) vs $T$ for all three spatial dimensions. With the values chosen for $\alpha$ we observe that at high temperature nearest-neighbor hopping takes place and at lower temperature variable-range hopping, which is also observed in experiments. Although it is known from experiments that $\alpha$ is quite often around 10, our value for $\alpha$ of 3.6 correctly describes the physics and is numerically more convenient. Clearly in each dimension the numerical data of $\mu^*$ follow a straight line for low temperatures only if the temperature is plotted as $\beta^{1/(d+1)}$. This is a direct consequence of the VRH character of the charge transport in a constant density of states, as derived by Mott[73]. At high temperatures the mobility follows a simple activated behavior (see e.g. inset for the 2D case). The slopes of the curves give prefactors $a(d) = 2.81 \pm 0.02, 1.24 \pm 0.03, 1.20 \pm 0.1$ for the relation between $kT$ and $\alpha^d/\varrho_F$. McInnes and Butcher[184] have investigated this temperature dependence of the mobility as well.

Despite the fact that we retrieve VRH behavior it does not inform us about what actually happens in $(R, \varepsilon)$ space. However, our simulations enable us to study $\mu^*$ in the form

$$\mu^*(\beta) = \int dR \int d\varepsilon \mu(R, \varepsilon; \beta),$$  \hspace{1cm} (7.1)
with the distribution $\mu(R, \varepsilon; \beta)$ following from the summand in Eq. (5.22). So we use $\mu^*$ to indicate the total mobility and $\mu$ to denote the distribution function. Fig. 7.3 shows a typical example of the distribution in 1D ($\alpha = 1, (\beta \alpha / \varrho F)^{1/2} = 7.3$) and in 2D ($\alpha = 3.6, (\beta \alpha^2 / \varrho F)^{1/3} = 9.3$). From Fig. 7.3 the similarity between the 1D and 2D results is clear; because of computational demand, the 3D distribution is still under investigation, but first results look qualitatively the same. Fig. 7.3 clearly shows a peak at a point $(R_p, 0)$ giving the dominant contribution to the mobility; the figure has a mirror image for $\varepsilon < 0$, understandable from energy conservation. Around the peak the distribution falls off more slowly than exponentially. Only beyond $\alpha R + \beta \varepsilon \approx 20$ in the 1D situation and beyond $\alpha R + \beta \varepsilon \approx 12$ in the 2D situation, equidistant lines reflecting the Miller-Abrahams factors can be recognized. From similar plots at higher temperatures it is seen that the peak shifts to smaller distances. For the 1D system the temperature dependencies of the average hop distance $\alpha \langle R \rangle$ and of the typical energy spread $\beta \langle \varepsilon^2 \rangle^{1/2}$, each weighted with $\mu(R, \varepsilon; \beta)$, are visualized in Fig. 7.4; they show as nearly parallel straight lines vs $\beta^{1/2}$. One may be tempted to call this a verification again of the Mott VRH theory because 'typical' hops should behave in this way. However, with our detailed results we are now able to distinguish between hops that are dominant, most frequent, or critical. First we note that, if the slopes in Fig. 7.2 are to be attributed to critical hops $(R_M, \varepsilon_M)$, then for $d = 1, \alpha = 1, (\beta \alpha / \varrho F)^{1/2} = 7.3$, we have $\alpha R_M + \beta \varepsilon_M = 20.5 (= a(d) \times (\beta \alpha^d / \varrho F)^{1/(d+1)})$, far from the value $\alpha R_p + \beta \varepsilon_p = 5$ at the peak in Fig. 7.3, at the boundary zone where the logarithmic contours become equidistant. The same can be done for the 2D case where we have $\alpha R_M + \beta \varepsilon_M = 11.5$, far from the maximum at the peak $\alpha R_p + \beta \varepsilon_p = 5$. 

FIGURE 7.3: Distribution of hops $(\alpha R, \beta \varepsilon)$ and their contribution to the mobility at a fixed temperature. The left-hand picture shows the situation for $d = 1, \alpha = 1, (\beta \alpha / \varrho F)^{1/2} = 7.3$, and the right-hand side for $d = 2, \alpha = 3.6, (\beta \alpha^2 / \varrho F)^{1/3} = 9.3$. Both plots are normalized on the peak and have contour lines with decreasing values: 0.9, 0.5, 0.1, and then one per decade.
FIGURE 7.4: Temperature dependence for the average hop distance $\alpha\langle R \rangle$, together with the average energy spread $\beta\langle \varepsilon^2 \rangle^{1/2}$ ($d = 1$, $\alpha = 1$).

To study the full $(R, \varepsilon)$ picture as a function of temperature, we have scaled in Fig. 7.5 the distributions $\mu(R, \varepsilon; \beta)$ of two higher temperatures ($d = 1$, $\alpha = 1$, $(\beta\alpha/\varrho_F)^{1/2} = 5.3$ and 6.6) and $d = 2$, $\alpha = 3.6$, $(\beta\alpha^2/\varrho_F)^{1/3} = 7.2$ and 8.8) by plotting $\mu_{\text{scaled}} = \mu/\mu^*$ vs scaled variables $R_{\text{scaled}} = R\beta^{-1/(d+1)}$, $\varepsilon_{\text{scaled}} = \varepsilon\beta^{d/(d+1)}$. The result is quite striking, the contours from different temperatures coincide not only around the average hop, as should already be on the basis of Fig. 7.3, but in a much larger $(R, \varepsilon)$ domain. In fact, significant deviations from this scaling behavior only emerge when $\alpha R + \beta \varepsilon$ approaches values where the logarithmic contours become equidistant, values which in Fig. 7.3 were identified as critical. Obviously, beyond these critical values the exponential decay precludes scaling. The cross-over from the scaling regime to the exponential regime, around Miller-Abraham factors that are equal to equal to the critical Mott values, is first observed at the highest temperature. Simultaneously, for the one dimensional case we have divided out from $\mu$ a factor $R^2$, thus better visualizing the effective jump frequency of the diffusive hops, which is plotted in Fig. 7.6. Note from Fig. 7.6 that $\mu/R^2$ increases to a constant near the origin $(R_0, 0)$, showing that this is the region of the most-frequent hops.

### 7.3 Scaling Theory

The following part of this chapter is about the interpretation of the data shown in the previous section. We will start by putting forward an analytical scaling theory based on the variable $\xi = \alpha R_{ij} + \beta \varepsilon$. After that the crucial statements for the scaling theory will be verified numerically. In literature the theory by Ambegaokar et al. [84] is regarded as the formal derivation of the variable-range hopping problem. This theory is based on percolation arguments and consists of a mapping of the disordered system onto a random-resistor network. The relevant variable in this case is $\xi_{\text{rrn}} = \alpha R_{ij} + \beta(\varepsilon_i - \varepsilon_F) + |\varepsilon_j - \varepsilon_F|$.
FIGURE 7.5: Scaled hop rate $\mu_{\text{scaled}}(R_{\text{scaled}}, \varepsilon_{\text{scaled}})$ (contour lines are normalized to the peak, and from $10^{-1}$ decreasing per decade) for three different temperatures in the Mott regime. Left-handed contour plot shows ($d=1$, $\alpha=1$): $(\beta \alpha / \varrho F)^{1/2} = 5.3$ (solid), 6.6 (dashed), 7.3 (dotted) and right-handed contour plot shows ($d=2$, $\alpha=3.6$): $(\beta \alpha^2 / \varrho F)^{1/3} = 7.2$ (dotted), 8.8 (dashed), 9.3 (solid).

FIGURE 7.6: Scaled hop rate $\tilde{\mu}(\tilde{R}, \tilde{\varepsilon}) / R_{\text{scaled}}^2$ (contour lines per decreasing decade w.r.t. origin) for three different temperatures in the Mott regime ($d=1$, $\alpha=1$): $(\beta \alpha / \varrho F)^{1/2} = 5.3$ (dotted), 6.6 (dashed), 7.3 (solid).

It is important to realize that this expression is strictly speaking only exact in the limit that thermal energies $kT$ are smaller than the appearing energies [84].
This means that in the region where $\beta \varepsilon_i \leq 1$, one should be careful when analyzing the results. In our calculations we will take $\varepsilon_F = 0$ but this does not affect the results when dealing with a constant DOS. During the research period also an alternative view has developed which analyzes the same numerical data as shown in the previous section in terms of the variable $\xi_{rrn}$. It is clear that the parameter $\xi_{rrn}$ is only equal to $\xi$ if $\varepsilon_i$ and $\varepsilon_j$ are on opposite sides of the Fermi level. This is exactly the reason why people often take just $\xi$; the hard hops (determining the dc mobility) will be those between sites on either side of the Fermi level[86]. Formally, we can express this as $\xi = \xi_{rrn} - \Gamma$ with $\Gamma \equiv 0$ if $\varepsilon_i \cdot \varepsilon_j < 0$ and $\Gamma \equiv \min(|\varepsilon_i|, \varepsilon_j)$ if $\varepsilon_i \cdot \varepsilon_j > 0$. So in general we can state: $\xi \leq \xi_{rrn}$. When examining the results in terms of $\xi_{rnn}$, again a scaling behavior is found. Note that the difference between the two views is about interpretation, not about the characteristics of the ultimately experimentally measured mobility.

Let us now rationalize the findings of the previous section. A natural energy scale in the problem is $\varepsilon_0 = (R_0^d \varrho_F)^{-1}$ where $\varrho_F$ is the (constant) density of states near the Fermi level. From this expression it follows that for $\beta \varepsilon_0 \leq 1$ there is nearest-neighbor hopping, but for $\beta \varepsilon_0 \gg 1$ the charge carrier is forced to hop further away to find a percolating path. If, like Mott stated, there are maximum hops, characterized by $R_M(\beta)$ and $\varepsilon_M(\beta)$, that still contribute and should be taken into account in order to finally obtain a current on a macroscopic length-scale, we can make the following two assumptions:

(I) for $(R, \varepsilon)$ beyond this maximum we have a contribution $\mu \equiv \mu_> >$ that becomes negligible, simply because the distribution will represent single hops with an unfavorable Miller-Abrahams factor, which will effectively be short-circuited.

(II) in the remaining $(R, \varepsilon)$ space the only relevant scales in the contributions to $\mu \equiv \mu_<$ are $R_M$ and $\varepsilon_M$, the Mott scales.

With these characteristic properties of the Mott scales $(R_M, \varepsilon_M)$ we can write down the following relation for $\mu^*(\beta)$

$$
\mu^*(\beta) = \int dR \int d\varepsilon \mu(R, \varepsilon; \beta) = \int_{R_M} dR \int_{\varepsilon_M} d\varepsilon_\mu(R, \varepsilon; \beta) + \int_{R_M} dR \int_{\varepsilon_M} d\varepsilon_\mu(R, \varepsilon; \beta).
$$

Bearing in mind that the second term must be negligible if $\beta \varepsilon_0 \equiv kT R_0^d \varrho_F \ll 1$ we demand that

$$
\eta \equiv \frac{1}{\mu^*(\beta)} \int_{R_M} \int_{\varepsilon_M} dR d\varepsilon_\mu_>(R, \varepsilon; \beta) = O\left(\frac{1}{\beta \varepsilon_0}\right) \to 0 \quad \text{if} \quad T \to 0.
$$

As stated already the only characteristic scales are $(R_M, \varepsilon_M)$ themselves. Because the external scales $R_0$ and $kT$ are out of the relevant range, the $\beta$-dependence of the distribution function must be via $R_M$ and $\varepsilon_M$; the only $\beta$-dependence may be via a normalization factor $C(\beta)$ in front of the distribution. The choice of the normalization factor $C(\beta) = \mu^*(\beta)$ is postulated in order to express the self-consistent character of the theory; as a generalization of the high-temperature limit $\beta \varepsilon_0 \to 1$, where $\mu_<(R, \varepsilon; \beta)$ should become $\delta$-peaked around $R_0$ and $\varepsilon_0$. This choice can actually be justified within an effective-medium theory, see next section. The above given consideration can be summarized by the following scaling
Ansatz, supported by the results in Fig. 7.5

\[
\mu_<(R, \varepsilon; \beta) = \mu^*(\beta) \varrho_F h \left[ \frac{R}{R_M(\beta)}, \frac{\varepsilon}{\varepsilon_M(\beta)} \right], \quad \text{for } \alpha R + \beta \varepsilon < \alpha R_M + \beta \varepsilon_M
\]

\[
\mu_>(R, \varepsilon; \beta) = \mu_0 \varrho_F \exp(-\alpha R - \beta \varepsilon), \quad \text{for } \alpha R + \beta \varepsilon > \alpha R_M + \beta \varepsilon_M.
\] (7.4)

Here \( h(x, y) \) is a scaling function which is of order unity in the central part of \((R, \varepsilon)\) space. The prefactor \( \mu_0 \) in the expression for \( \mu_> \) sets the natural scale of the mobility via a factor \( \beta e R_0^2 \nu_0 / 2d \). In general this prefactor may also contain a different temperature dependence.

It may be easily verified that expressions exactly of these forms are implicit in a self-consistent effective-medium theory of VRH[88]; in that case \( h(x, y) \) is a trivial function, see next section. With this Ansatz we have to be aware that exactly at \((R_M, \varepsilon_M)\) a transition to the exponential regime of negligible contribution to the mobility \( \mu^*(\beta) \) occurs. This transition implies, as usual in scaling theories, a non-analytical connection in \((R_M, \varepsilon_M)\) of the asymptotic function \( \mu^*(\beta) \varrho_F h(x, y) \) in the inner region to the asymptotic exponential regime beyond \((R_M, \varepsilon_M)\). For finite temperatures a crossover region is observed and the width of the crossover region should shrink with decreasing temperature and vanish in the limit \( T = 0 \), leading to a singularity at \((R_M, \varepsilon_M)\).

Given the expressions for the different regimes, new information can be obtained by the requirement of continuity at the crossover which dictates

\[
\mu^*(\beta) = \frac{\mu_0}{h(1,1)} \exp(-\alpha R_M - \beta \varepsilon_M).
\] (7.5)

So the temperature dependence of the mobility \( \mu^*(\beta) \) is indeed via a single-hop of the Miller-Abrahams form with the scaling parameters \( \alpha R_M(\beta) \) and \( \beta \varepsilon_M(\beta) \), as supposed by Mott, however, with an additional factor \( 1/h(1,1) \), which numerically may be considerably larger than unity. More information can be obtained by applying the self-consistency condition

\[
\mu^*(\beta) = \frac{1}{1 - \eta} \int_{R_M}^{R} \int_{\varepsilon_M}^{\varepsilon} dR d\varepsilon \mu^*(\beta) \varrho_F h \left[ \frac{R}{R_M(\beta)}, \frac{\varepsilon}{\varepsilon_M(\beta)} \right],
\] (7.6)

where the condition for \( \eta \) as given in Eq. (7.3) can be put in a more instructive way, related to the scaling function

\[
\eta \equiv \frac{1}{\mu^*(\beta)} \int_{R_M}^{R} \int_{\varepsilon_M}^{\varepsilon} dR d\varepsilon \mu_>(R, \varepsilon; \beta) = \frac{h(1,1)}{\alpha^d \beta \varrho_F}.
\] (7.7)

So \( \eta \) is indeed small, but only vanishes in the limit \( T \to 0 \). In view of the symmetry between \( \alpha R_M(\beta) \) and \( \beta \varepsilon_M(\beta) \) in determining the upper boundary of the scaling regime we postulate that there is in fact one scaling parameter: \( \alpha R_M(\beta) = \beta \varepsilon_M(\beta) \equiv \xi_M(\beta) \). The \( \beta \)-dependence of \( \xi_M(\beta) \) then follows from the integral given in Eq. (7.6):

\[
\xi_M(\beta) \approx \left[ \frac{\alpha^d \beta}{\varrho_F} / \int_{|x|+|y|<2} dx dy h(x, y) \right]^{1/4} + O(\eta).
\] (7.8)
This replaces the Mott percolation condition, since at percolation a first new natural scale enters the problem. Of course the expressions \( \mu_\text{<} \) and \( \mu_\text{>} \) are only asymptotically equal to \( \mu(R, \varepsilon) \) sufficiently below and above \( \alpha R_M + \beta \varepsilon M \), respectively. For increasing \( T \) or \( \alpha^{-1} \) the width of the crossover region indicated by \( \eta \) increases, and hence the deviation from scaling near \((R_M, \varepsilon_M)\) will increase, as was observed in Fig. 7.5. Note that in constructing Fig. 5 the limit form of (7.8) has already been used, which introduces additional errors of \( O(\eta) \) as follows from Eq. (7.8). In order to summarize this section, the findings for the scaling theory can be put in a simple way:

\[
\begin{align*}
\mu^*(\beta) &= \frac{1}{1-\eta}\frac{\rho_0}{h(1,1)} \exp[-2\xi_M(\beta)] \\
\xi_M(\beta) &= \left[ \frac{\alpha^d \beta}{\varepsilon \rho_F} \int_{|x|+|y|<2} d\mathbf{x} dy h(x, y) \right]^{1/d+1} \rightarrow \text{Mott.} \tag{7.9}
\end{align*}
\]

### 7.4 Connection with effective-medium theory

As followed from the previous paragraph, the crux of the scaling theory is the self-organizing character of the current distribution. This self-consistent mechanism has been discussed in Chapter 5 where we summarized the findings of Movaghar and Schirmacher [88]. However, the self-consistent mean field theory of Movaghar and Schirmacher (sometimes also called effective-medium theory) leads to rather difficult equations. An instructive example to make a connection with effective-medium theory is by looking at a self-consistent relation for the effective conductivity in case of a continuous inhomogeneous medium (e.g. isolator/conductor mixture), derived first by Bruggeman in 1935 [189]. Basically the derivation is by calculating the effective response of the medium to an external field and by representing the electric field as a sum of the incident field propagating through a homogeneous medium with conductivity \( \sigma^* \) and the local fluctuations in the field due to the inhomogeneities. This can be put in the requirement that the local fluctuations in the current density, associated with the deviation of the local conductivity \( \sigma(r) \) from the effective conductivity \( \sigma^* \), vanish on average

\[
\langle (\sigma(r) - \sigma^*)E \rangle = 0, \tag{7.10}
\]

Treating the case of spherical particles and solving for the local electric field leads to the Bruggeman equation (in 3 dimensions\(^1\)):

\[
\left\langle \frac{\sigma - \sigma^*}{\sigma + 2\sigma^*} \right\rangle = 0, \tag{7.11}
\]

where the self-consistency enters by the fact that \( \sigma^* \) can be determined via the constriction that the volume average of the ”excess polarizability” equals zero. It can easily be shown that, provided we have a two component system with \( \sigma_1 = 0, \sigma_2 \neq 0 \), and with volume

\[\frac{\sigma - \sigma^*}{\sigma + (d-1)\sigma^*}, \text{ for system in } d \text{ dimensions}\]
fractions $\phi_1, \phi_2 = 1 - \phi_1$ this system will have a percolation threshold at $\phi_{2,c} = 1/3[210]$. If we apply the above given theory to a $\infty$-component system and assign to every component a Miller-Abrahams conduction $\sigma(R, \varepsilon) = \sigma_0 \exp(-\alpha R - \beta \varepsilon)$ and replace the volume average by an average over $R$ and $\varepsilon$, the self-consistent effective-medium condition on $\sigma^*$ follows from Eq. (7.11)

$$1 = \frac{1}{N \rho_F} \int_0^\infty dR \int_{-\infty}^\infty d\varepsilon \frac{1}{\frac{2\sigma^*}{\sigma(R, \varepsilon)} + 1}, \quad \text{with} \quad N = \theta_F \int_0^\infty dR \int_{-\infty}^\infty d\varepsilon. \quad (7.12)$$

In fact $N$ is normalization factor describing the total amount of states in the system, and for practical reasons the integration boundaries can be replaced with a cut-off in energy and distance. In order to treat the right-hand side of Eq. (7.12) we can handle the two cases of $\sigma \gg \sigma^*$ and $\sigma \ll \sigma^*$ separately, because of the broad distribution of $\sigma(R, \varepsilon)$. As a result the integral splits up into two pieces given by

$$\sigma^* = \frac{1}{N \rho_F} \int_0^{R_M} dR \int_{\varepsilon_M}^{\varepsilon_M} d\varepsilon \sigma^* + \frac{1}{N \rho_F} \int_{R_M}^\infty dR \int_{\varepsilon_M}^{\varepsilon_M} d\varepsilon \frac{3}{2} \sigma_0 \exp(-\alpha R - \beta \varepsilon). \quad (7.13)$$

The correspondence with Eq. (7.2), which we used as a starting point for the scaling theory, and the way $\varepsilon_M$ and $R_M$ play part in largest scales to be taken into account is evident. We obtain the same cross-over function as postulated, with $h(x, y) = \text{const}$ in this case. To determine the scales $\varepsilon_M$ and $R_M$ we only need the first term in Eq. (7.13) giving

$$\frac{1}{N \rho_F} \int_0^{R_M} dR \int_{\varepsilon_M}^{\varepsilon_M} d\varepsilon = \frac{1}{3}. \quad (7.14)$$

This means that we end up exactly with the same percolation threshold as predicted from the Bruggeman theory. Moreover, it means that we can conclude that within this mean-field theory no problem concerning a fractal structure will occur. Another important result is obtained if we recall from the previous section that $\alpha R_M(\beta) = \beta \varepsilon_M(\beta) \equiv \xi(\beta)$. We then, from Eq. (7.14), immediately arrive at $\xi(\beta)^{d+1} \sim \alpha d / \theta_F$, which gives the Mott formula, see Eq. (7.9).

It is illustrative to see how the resulting self-consistent equations derived by Movaghar and Schirmacher as discussed in Chapter 5 compare with Eq. (7.12). We treat their results in the case of a symmetric energy-dependent hopping model. Then the dc-conductivity can be calculated analytically if we assume a constant density of states of width $W_0$ and a complete randomness approximation, i.e. $g_c(R_{ij}) = 1$. In this case we obtain the following self-consistent equation for the conductivity

$$\frac{4\pi k n a_p T}{\alpha^3 W_0} \int_0^{W_0/kT} \int_0^\infty \frac{x^2}{(\sigma/\nu_0) \exp(x + y) + 1} dx dy = 1, \quad (7.15)$$

which, as can be seen, has a completely similar structure as Eq. (7.12), with $\sigma = \sigma(R, \varepsilon)$, although derived in a much more complicated way. Assuming a low-temperature limit
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$W_0/kT \to 0$, the regime where variable-range hopping is valid, it can be solved for $\sigma$ leading to

$$\sigma = \nu_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/(d+1)} \right], \quad \text{with} \quad T_0 = \frac{3\alpha^3 a_p W_0}{\pi k n}.$$  (7.16)

This expression is again in complete agreement with the Mott formula. So from this self-consistent equation we can indeed derive the Mott formula.

7.5 Validation for assumptions and interpretation of scaling theory

We will now verify the crucial statements for the scaling theory to be justified: can we visualize the existence of Miller-Abrahams single hops for hops beyond the critical "length-scale" $\alpha R_M + \beta \varepsilon_M$, which we indicate by $\xi_M$, and is $\eta$ given by Eq. (7.3) indeed small, decreasing with temperature, and finally vanishing for $T = 0$?

In Fig. 7.7 we show the results for the scaled mobility distribution (normalized to the peak) along the cross-section $\tilde{\varepsilon} = 0$ through Fig. 7.5 for different temperatures, both for a one dimensional system and a system in two dimensions; in case of the latter we will also investigate the effect of different values for $\alpha$. The clear fact is that in both one and two

![Cross-section of the scaled contour plot](image)

FIGURE 7.7: Cross-section of the scaled contour plot for $(d = 1, \alpha = 1)$: $(\beta \alpha/\varrho_F)^{1/2} = 5.3$ (squares), $6.6$ (circles), $7.3$ (triangles) and for $d = 2$: $\alpha = 2.0$: $(\beta \alpha^2/\varrho_F)^{1/3} = 5.3$ (down triangles), $6.5$ (squares), $\alpha = 3.6$: $(\beta \alpha^2/\varrho_F)^{1/3} = 7.2$ (circles), $9.3$ (diamonds), and $\alpha = 7.0$: $(\beta \alpha^2/\varrho_F)^{1/3} = 17.0$ (up triangles). The 2D graphs are constructed such that the peaks are at the same position. The inset shows the same plots but represented in a linear fashion.

dimensions the curves for different temperatures are nicely on top of each other until $\xi_M$
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(like expected from Fig. 7.5) and then start to follow a straight-line dependence for which the slope numerically agrees well with the Miller-Abrahams factor, i.e. with an exponential cut-off as given in Eq. (7.4). The slopes decrease when $\beta$ increases, indicating a possible diverging slope for $T \to 0$. Especially in the graph for the two dimensional system, where the case $\alpha = 7$ has twice a lower temperature than the lowest temperature involved for the cases of $\alpha = 2$ and $\alpha = 3.6$, supports this viewpoint. Another interesting feature is the observation of a clear point of intersection for the drawn lines. This point is identified with the scaled variable $\xi_M$, separating the regime where the scaling function $h$ defined in Eq. (7.4) is observed from the exponential regime. As such this picture backs up the scaling Ansatz (Eq. 7.4). The statement about the existence of an intersection point separating two regimes is easily verified e.g. with the help of the scaled distribution function for the one dimensional system; the contour lines practically coincide till $\alpha R_M + \beta \varepsilon_M = 2\xi_M = 20$, about the same place where the drawn lines intersect! Furthermore, in the case of two dimensions we have as well plotted results for different values of $\alpha$ in order to investigate and clarify the influence of $\alpha$ on the intersection point. The outcome is settled easily, the scaling functions for the various $\alpha$’s have the same shape and their Miller-Abrahams factors, when extrapolated above the scaled length-scale $\xi_M$, have a common crossing point. This result corroborates the view that scaling in $\alpha$ is satisfied as well, so the only relevant scaling parameter is given by

$$\xi_M = a(d) \times (\beta a^d / \varrho_F)^{1/(d+1)}.$$ 

An important issue we should mention is the observation that for all the graphs in Fig. 7.7 the transition from a scaling region to an exponential region is via a crossover region. A glance of this phenomenon can be obtained by the insets of Figure 7.7, showing the same graphs but in a linear representation. They indeed show that the exponential tails are almost vanished at the intersection point, confirming the assumption of a negligible contribution (but still finite) of $\mu >$. A better way of assessing this issue is by calculating the integral as given in Eq. (7.3) for $\eta(\beta)$. In Fig. 7.8 we have plotted the results for 1 and 2 dimensions. The trend is clear, $\eta$ is a monotonously decreasing function of $\beta$, extrapolating to 0.2% (4%) for $d = 2$ ($d = 2$) in the limit $T \to 0$. We mention that $\eta$ is evaluated by integrating from the point $\xi_M$, while we observe that a small shift of this point into the crossover region already decreases the values found for $\eta$. This crossover is of course always present at finite temperatures. The dependence of the error $\eta$ on the accuracy in $\xi_M$ can already be inferred from Eq. (7.8), where higher order effects introducing errors of $O(\eta)$ have not been taken into account. So we have to conclude that the determination of $\eta$ is rather sensitive to the error we make in identifying $\xi_M$. The effect has been visualized by the error bars plotted in Fig. 7.8, they are the result of including an error of 5 % in the value of $\xi_M$. The reason why we choose 5 % is that such an error is not visible in Fig. 7.7, while it has a huge effect on $\eta$. Moreover, a reason to have a larger $\xi_M$ is realized from the fact that when fitting the exponential region in Fig. 7.7 more weight may be attributed to points far from $\xi_M$, because these are certainly well described by the exponent. This would results in a small shift of the crossing point to the right. Another important point to make about the value of $\eta$ is that, from Eq. (7.6), it introduces only algebraic temperature corrections to the Mott behavior as normally deduced from the existence of a linear dependence of $\log \mu$ when plotted versus $T^{1/(d+1)}$. This means that it is (experimentally) possible to find an apparent Mott law, but
FIGURE 7.8: The left-hand graph shows the temperature dependence of $\eta$ for the 1D case with $\alpha = 1$, the right-hand side also shows $\eta(\beta)$, but for 2D with $\alpha = 3.6$. The error bar indicates the effect on $\eta$ when an error of 5 % enters in the determination of $\xi_M$.

In fact the mechanism is variable-range hopping within a range $\alpha^{-1} > R_0$. Besides, when the hopping distance $R$ approaches $R_0$ deviations from variable-range hopping will appear as well.

Having validated the important assumptions forming the foundations of our scaling theory, we will try to come up with a physical picture. From the analysis from Movaghar and Schirmacher which turns out to be similar to a Bruggeman type approach we can qualitatively interpret the integrand of Eq. (7.12). Let us consider a charge carrier passing by an "easy" hop (i.e. advantageous Miller-Abrahams factor); in this case the chance of returning and repeating the same hop is rather big just because of the large probability to encounter a "difficult" hop subsequently. We can look to this as if a resistance is put in series with itself several times, and the easier the hop the more often this is the case. On the other hand, once a charge carrier has passed a "difficult" hop, it has a large probability of encountering an environment with "easy" hops, and as a result it will not return. The consequences for the accompanying currents can be put in the following way:

- **easy hops**: effective current is smaller than expected from the Miller-Abrahams factor solely; as a result the effective currents between "easy" and "very easy" hops will flatten mutually.

- **difficult hops**: effective current determined by Miller-Abrahams factor.

The important thing to realize is that the border between "easy" and "difficult" hops is determined by the average environment, i.e. in a self-consistent way exactly via $\mu^* (\sigma^*)$. This statement can be clarified from Eq. (7.12). In the effective-medium approximation the
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effective conductivity is the average, i.e. the sum (integral), of effective local conductors in parallel. The local conductivity in the integrand is the result of two resistive processes in series: a direct process (whence $2/\sigma(R, \varepsilon)$), followed by a contribution from effective local conductors ($1/\sigma^*$) in parallel but excluding the initial site (see [88] Eq. (3.14)). So the effective conductivity can be viewed as the overall average over effective local conductivities, where locally two steps are considered sequentially: the direct process + all possible following processes. This latter process is self-consistently equal to the overall process.

The new point of our work is, that we have been able to show that the current distribution possesses a self-organization into a distribution only determined by scaled variables up to a boundary given by $\xi_M$. Within this scaling regime of relatively easy passages the effective hop probabilities are well below the corresponding single-hop Miller-Abrahams factors, which can be understood as being due to iterative hops before local escape. At the boundary there is a cross-over to a Miller-Abrahams-type single-bond hopping distribution, i.e. to an exponential cut-off. The scaling regime grows with lower temperature and diverges at $\beta^{-1} = 0$. Most-frequent hops occur around the origin while there is a peak of dominant contributions well inside the scaling region. The position of the boundary is determined by the Mott percolation condition, which enables global escape and which introduces a first new scale above the nearest-neighbor regime. It is this position which is temperature-sensitive; due to the self-organized scaling up till the boundary, this temperature dependence enters the total mobility. In the above sense the critical bond for percolation, with its Miller-Abrahams form, does indeed determine the total mobility. A retrospect to Fig. 7.7 now indeed substantiates our physical interpretation. Below the intersection point identified with the scaled variable $\xi_M$ we find indeed an effective mobility which is well below the value of the extrapolated Miller-Abrahams straight line; the effective mobility is flattened for the values $\xi < \xi_M$. Above the scaled variable $\xi_M$ we find precisely the individual Miller-Abrahams factors, given by the straight lines.

7.6 Relation of scaling theory with percolation theory

In this section we will make a connection with percolation theory, which has been extensively used to derive and examine properties concerning Mott variable-range hopping theory. As discussed in the previous sections, we defined the bulk mobility as $\mu^* = \int \int dR d\varepsilon \mu(R, \varepsilon)$ and for our scaling theory we made the assumption that the mobility, which we will now call $\mu_s^*$, is given by $\mu_s^* = \mu_s^*(\xi) = \mu^* + O(1/\beta \varepsilon_0)$, with $\xi_M(\beta \varepsilon_0)$ as defined previously. To calculate $\mu_s^*(\xi)$, we thus neglect the contributions in the integral of all hops $> \xi = \alpha R_{ij} + \beta |\varepsilon_i - \varepsilon_j|$ in the distribution function.

Historically, variable-range hopping has been derived on the basis of percolation arguments via a mapping of the disordered system on a random-resistor network by Ambegaokar et al.[84]. The relevant variable in this case is $\xi^{mn} = \alpha R_{ij} + \beta/2(|\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F| + |\varepsilon_i - \varepsilon_j|)$, with $\varepsilon_F$ the Fermi energy. In the work of Ambegaokar et al. it is stated that
the temperature dependence of mobility (apart from pre-factors) can be obtained via the identification $\mu^* \sim \mu_p^*(\xi_{\text{rrn}}) \sim \exp[-\xi_{\text{rrn}}]$. So, the temperature dependence of the mobility is taken to be given by the exponent of the percolation threshold $\xi_{\text{rrn}}$.

A similar method has been developed in the case of treating only nearest-neighbor hopping (NNH) in a disordered system, in which case the relevant variable is given by $\xi = \beta|\epsilon_i - \epsilon_j|$. Moreover, for the problem of nearest-neighbor hopping it has been shown by Týc and Halperin [190, 191] that the identification of the temperature dependence of the mobility to be given by the exponent of the percolation threshold is exact. The statement is that in the case of an exponential distribution of conductances, which is e.g. the case for thermal hopping over barriers, the temperature dependence of the conductivity is given by percolation conductance, $\mu_{\text{NNH}} = \mu_{\text{NNH},p}(\xi_p) \sim \exp[-\xi_p]$. Our goal is to study now the more general case of variable-range hopping. We want to check the statement as applied for the random-resistor network, and explore the possibility to extend the ideas of Týc and Halperin to the case of variable-range hopping.

In our calculations for the percolation problem, the mobility $\mu_p^*$ is determined by neglecting all hops above some $\xi$. If $\xi$ is sufficiently large, say $\xi_\infty$, the mobility has reached its plateau value. For $\xi$ is much smaller than $\xi_p$, we have $\mu_p^*(\xi) = 0$ based on percolation arguments. We define a percolation threshold $\xi_c < \xi_\infty$. The same definitions are used for the variable $\xi_{\text{rrn}}$. In Fig. 7.9 we have plotted the results for the different mobilities $\mu_s^*(\xi)$, $\mu_p^*(\xi)$, and $\mu_p^*(\xi_{\text{rrn}})$. It is very important to realize once more that the two functions $\mu_s^*(\xi)$, $\mu_p^*(\xi)$, $\mu_p^*(\xi_{\text{rrn}})$ are related to physically different systems. $\mu_s^*(\xi)$ is determined by integrating the exact solution $\mu(R, \epsilon)$ up to $\xi$, where the distribution $\mu(R, \epsilon)$ is influenced by hops

**FIGURE 7.9:** Comparison between the mobilities $\mu_s^*(\xi)$, $\mu_p^*(\xi)$ and $\mu_p^*(\xi_{\text{rrn}})$ as a function of $\xi$ ($\xi_{\text{rrn}}$), where $\mu_s^*(\xi)$ and $\mu_p^*$ are defined in the text, for a 2D system with $\alpha = 3.6$ and $(\beta \alpha^2 / g_F)^{1/3} = 9.3$. The full line indicates the position of $\xi_M$ ($\xi_c$), whereas the dotted line indicates the position of $\xi_{\text{rrn}}$. 

and $\mu_p^*(\xi_{\text{rrn}})$ are related to physically different systems. $\mu_s^*(\xi)$ is determined by integrating the exact solution $\mu(R, \epsilon)$ up to $\xi$, where the distribution $\mu(R, \epsilon)$ is influenced by hops.
larger than \( \xi \). Whereas \( \mu_p^*(\xi) \) and \( \mu_p^*(\xi^{rrn}) \) are obtained by solving the master equation for a system in which bonds beyond \( \xi \) \((\xi^{rrn})\) are disregarded.

Fig. 7.9 shows three important features. 1) There is a large difference between the values around the percolation threshold between \( \mu_p^* \) and \( \mu_p^* \), about two orders of magnitude. However, in the limit \( \xi \) \((\xi^{rrn}) \to \infty \) the mobilities all have the same value which means that the pre-factor is not correct in the percolation description. 2) It is suggested that \( \xi_M \) and \( \xi_c \) seem to be the same. 3) The value of the percolation threshold following from the mapping to a random-resistor network \( \xi^{rrn} \) is definitely different from \( \xi_M \).

Let us now look more carefully into the three observations listed above. First we note that in the following discussion we use the definition for \( \xi \) \((\xi^{rrn}) \): \( \xi = a(d) \times (\beta a^d / \varrho_F)^{1/(d+1)} \). The consequence is that we can then easily speak about a slope \( a(d) \) of the mobility when logarithmically plotted versus temperature, if the identification \( \mu^* \sim \exp[-\xi] \) is made. The first observation can be handled shortly: the approach followed by focussing on \( \mu_p^*(\xi_M) \) gives the right value for the bulk mobility (at this finite temperature already within 90 \%) and does not suffer from a pre-factor problem, which in percolation approaches is only achieved by taking into account contributions above the percolation threshold. This is a big problem for percolation theories because it is not known how to define \( \xi_{\infty} \), in order to get the plateau value. From the second observation \( \mu_p^* \sim \exp[-\xi_c] \), with \( \xi_c = \xi_M \), we may speculate that it is still possible to extend the ideas of Halperin to the case of variable-range hopping. From \( \xi_c \) we can extract a value \( a(d) = 1.20 \pm 0.07 \), more accurate calculations should be performed in order to decrease the error bar. Nevertheless, it seems that indeed the mathematical statement that the temperature dependence of conductivity can be identified with the exponent of the critical conductance is true. If indeed \( \xi_c = \xi_M \) this would mean that \( \xi_c \) is the first new relevant scale above \((R_0, kT)\) which is in fact the basic idea of Mott, as speculated in section 7.3. But, we have to be very careful with drawing these conclusions, because the problem is that it is not evident that percolation theory as applied for the nearest-neighbor problem is applicable; in case of variable-range hopping the coordination number of the lattice is not fixed (or it is \( \infty \)). Concerning the third observation, a we find from the position of \( \xi_c^{rrn} \) the value \( a(d) = 1.43 \pm 0.03 \), whereas from Fig. 7.1 we found \( a(d) = 1.24 \) meaning a different slope. The values \( a(d) = 1.43 \) and \( a(d) = 1.24 \) have been confirmed by independent calculations[192, 193]. In the case of [193] invasion percolation has been used which enables one to study very carefully the effect of adding bonds just above the percolation threshold. Our final conclusion is that at the percolation threshold \( a(d) = 1.44 \pm 0.01 \) and at the plateau value of the conductivity we find \( a(d) = 1.24 \pm 0.01 \). Thus the percolation arguments as used in the random-resistor network approach[84, 194] where \( \xi_c^{rrn} \) has to be identified with the temperature dependence of the conductivity via \( \mu_p^* \sim \exp[-\xi_c^{rrn}] \), is not valid. It simply gives the wrong slope for the temperature dependence of the conductivity. In order to be somewhat more specific, the statement used in the random-resistor network approach is that the identification of the temperature dependence of the conductivity with \( \xi_c^{rrn} \) is only exact in the limit \( T \to 0 \). For small but finite \( T \) it has been shown that bonds somewhat larger than \( \xi_c^{rrn} \) should be taken
into account[194] and that these corrections on $\xi^r_{\text{rrn}}$ decrease with lower temperatures such that for $T \to 0$ it is equal to $\xi_c$. In order to check the predictions as stated in [194, 84] we performed calculations for decreasing temperature[193]. The results are given in Fig. 7.10. Instead of the appearance of a step function as expected from [194, 84] we seem to observe

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{The conductivity $\sigma^*(\xi^r_{\text{rrn}})$ as a function of $\xi^r_{\text{rrn}}/(\beta\alpha^2/\theta_F)^{1/3}$ for decreasing temperatures, i.e. increasing $(\beta\alpha^2/\theta_F)^{1/3} = 7.19.011.3$ with $\alpha = 3$. The dashed line denotes the position of the percolation threshold at which the tendency towards a step function is expected.}
\end{figure}

the development of a scaling curve close to the threshold value towards the plateau value, although we are not fully in the scaling regime. This result indicates that even in the limit $T \to 0$ one does have to take into account bonds beyond $\xi^r_{\text{rrn}}$. The physical picture behind this phenomenon is that inclusion of these bonds opens the possibility to sample easier bonds which are not only needed for the conductivity to reach its plateau value, but they are also necessary to obtain the right slope for the temperature dependence of the conductivity, i.e. the coefficient $a(d)$.

Summarizing, from our scaling theory it follows that taking into account bonds up to $\xi_M$ when integrating the self-organized current-distribution function leads to a correct value of bulk mobility. For the temperatures we have studied this agreement is already within $90\%$, and for lower temperatures the agreement is assumed to become better and better. Whereas for the case of percolation theory it is obvious that we have to take into account bonds beyond $\xi_c$ (up to $\xi_p$) in order to have a good description of the bulk mobility. But, it is still unclear how to determine $\xi_p^r$. From the observation $\mu_p^* \sim \exp[-\xi_c]$, with $\xi_c = \xi_M$, we may speculate that it is still possible to extend the ideas of Halperin to the case of variable-range hopping. In the case of the picture of a random-resistor network it follows that the value for the slope $a(d)$ of the temperature dependence of the conductivity is not correctly accounted for when only taking bonds up to the percolation threshold $\xi^r_{\text{rrn}}$. 
7.7 Alternative view

In this section we present an alternative way of treating the results obtained in section 7.2 [195]. Disordered systems are often viewed as random-resistor networks. In the mapping onto a random-resistor network, the conductance of the bond between $i$ and $j$ was shown to become, in the limit that thermal energies $kT$ are smaller than the appearing energies [84]:

$$G_{ij} = \frac{e^2}{kT} \nu_0 \exp[\alpha R_{ij} + \beta/2(|\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F| + |\varepsilon_i - \varepsilon_j|)]. \quad (7.17)$$

This equation expresses not only the fact that, in order to have a high conductance between $i$ and $j$, the energies $\varepsilon_i$ and $\varepsilon_j$ should be close to each other, but also that $\varepsilon_i$ and $\varepsilon_j$ separately should be close to the Fermi energy $\varepsilon_F$. In order to make a better connection with this picture of a random-resistor network, the current distribution as given in Fig. 7.2, should be plotted versus the variables: $R = R_{ij}$ and $E = (|\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F| + |\varepsilon_i - \varepsilon_j|)/2$. Of course for hard hops [86] i.e. between states at either side of $\varepsilon_F (\varepsilon_i < \varepsilon_F, \varepsilon_j > \varepsilon_F)$ the only thing that matters is the energy difference between two sites, meaning that we end up with the previous way of plotting $\varepsilon = \varepsilon_i - \varepsilon_j$. The results are shown in Fig. 7.11. We again see that most of the current is not carried by the high-conductance bonds near $R = E = 0$, but by bonds near a peak $R = R_p, E = E_p$. The difference with Fig. 7.3 is clear, the peak position has shifted along the energy axis (right axis), which is just a result of using the new variable for $E$. Upon decreasing the temperature the peak moves downward along the energy axis, indicating that the important sites taking part in the hopping process are those closer to the Fermi Energy. However, in terms of the scaled variables, due to the Fermi-Dirac function, the important states are those with small occupation numbers $n_i$ with $\varepsilon_i > \varepsilon_F$ and large occupation numbers $n_j$ with $\varepsilon_j < \varepsilon_F$.

Another interesting feature can be observed if we look at the current distribution function $I$ when plotted versus the dimensionless scaling variables $\rho \equiv \alpha R/l$ and $\epsilon \equiv \beta E / l$ along the horizontal and left axis respectively, where $l = [\alpha d \beta / g_F]^{1/(d+1)}$. It is clear that although $\alpha$ and $\beta$ are varied, when plotted in this way the distribution functions appear to collapse onto a single scaling function $f(\rho, \epsilon)$ as was observed in section 7.2. The scaled distribution functions have a common scaled peak position is at $(\rho_p, \epsilon_p) = (0.69, 0.36)$, which again means that $R \sim \beta^{1/(d+1)}$, and $E \sim \beta^{-d/(d+1)}$. The difference with the scaling function as given in section 7.2 is that we now have a peak along the energy axis as well. Another import difference is the interpretation that should be given to the variable $\xi = \alpha R_{ij} + \beta|\varepsilon_i - \varepsilon_j|$ as used in sections 7.3 and 7.5, when plotting in the way we just discussed. One should realize that the parameter $\xi^{rrn} = \alpha R_{ij} + \beta E$ with $E = |\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F| + |\varepsilon_i - \varepsilon_j|)/2$ is only equal to $\xi$ if $\varepsilon_i$ and $\varepsilon_j$ are on opposite sides of the Fermi level. Formally, we can express this as $\xi = \xi^{rrn} - \Gamma$ with $\Gamma \equiv 0$ if $\varepsilon_i \cdot \varepsilon_j < 0$ and $\Gamma \equiv \min\{|\varepsilon_i|, |\varepsilon_j|\}$ if $\varepsilon_i \cdot \varepsilon_j > 0$. So in general we can state: $\xi \leq \xi^{rrn}$. As a consequence we do thus find that if a certain hop in the $(R, \varepsilon)$ representation is characterized by $(R_1, \varepsilon_1)$ then in the $(R, E)$ representation this hop is characterized by $(R_1, E_1)$. The latter point will thus be positioned on the same place if $\varepsilon_i \cdot \varepsilon_j < 0$ and will be pushed upward if $\varepsilon_i \cdot \varepsilon_j > 0$. This difference will also
FIGURE 7.11: Current distributions in $d = 2$. Bottom axis: $\rho$, left axis: $\epsilon$, top axis: $R/R_0$, and right axis: $E/E_0$, where $E_0$ is the width of the energy distribution and $R_0$ the lattice constant. Where $\rho$ and $\epsilon$ are defined as $\rho \equiv \alpha R/l$ and $\epsilon \equiv \beta E/l$ with $l = [\alpha^d \beta / \varrho F]^{1/(d+1)}$. The displayed results for different $\beta$ and $\alpha$ are averaged over 200 configurations, and are interpolations on a $R-E$ grid. The drawn lines are $R-E$ values of the critical conductance in percolation theory as found by Skal and Shklovskii [196]. The currents have been normalized by the maximum current. For all plots the values of the contour lines have decreasing values: 0.9, 0.5, 0.1, 0.01, 0.001, 0.0001.

make it difficult to check predictions about the value $\xi$ when results are presented in a $(R, E)$ representation. In fact up to know it is not really clear how to define a similar boundary analogous to $\xi$ in the $(R, E)$ representation, if possible at all. Anyway, from the fact that scaling behavior is found in both representations we may conjecture that the main contribution is due to hops between states at either side of the Fermi level, because then we have $\epsilon = E$. 
The drawn lines in Fig. 7.11 indicate the value \( \alpha R + \beta E \) for which the conductance following from Eq. (7.17) is equal to the critical conductance according to percolation theory [84, 196]. Skal and Shklovskii [196] found the values \( a(d) = 1.51, 1.28 \) \( (d = 2, 3) \) by means of Monte-Carlo simulations via which they solved the percolation problem. The slight failure of percolation theory is no surprise, since its application to variable-range hopping is not exact, because at finite temperatures one also has to take into account bonds above the percolation threshold, as shown in the previous section. Their values are larger than the values we found obtained from fitting Mott’s law directly, \( a(d) = 1.24, 1.20 \) \( (d = 2, 3) \), meaning that the lines drawn in Fig. 7.11 for our values would be even closer to the conductance at the peak position. In fact, the actual conductivity corresponds to values of \( R \) and \( E \) that are 20% below the drawn lines. This means that the actual conductivity is determined by the lines corresponding to the critical conductance which are almost on top of the peak position.

From the fact that we have a scaling function for \( \alpha R + \beta E < a(d) \) we can easily observe a peculiar counter-intuitive result. If e.g. we draw the line \( \rho + \epsilon = 1 \) which can be identified with a resistance of \( \exp(l) \) and do the same for \( \rho + \epsilon = 1/2 \), and take the ratio between the two resistances we end up with \( \exp(1/2) \). This ratio will of course increase as a function of decreasing temperature, because then \( l \) increases. How can it be that the ratio between the currents for \( \rho + \epsilon = 1 \) and \( \rho + \epsilon = 1/2 \) have the same ratio, as follows from the scaling behavior? The only answer should be that the voltage over these resistors changes accordingly, which is a manifestation of the self-organized current distribution. To assess the scaling behavior we will use a scaling argument to demonstrate universality of the current distributions as a function of \( \alpha R \) and \( \beta E \) with the same \( l \). To prove this we have to show that \( l \) is the only relevant variable. Universality in transformations where \( \beta \) and \( \rho F \) are varied such that \( \beta/\rho F \) remains constant, \( \beta \rightarrow \beta' = s\beta \) and \( \rho F \rightarrow \rho' F = s\rho F \), is trivial in view of the fact that the relevant parameter in the hopping process is \( \beta E_i \). The universality when \( \alpha^d \) and \( \rho F \) are varied such that \( \alpha^d/\rho F \) remains constant can be rationalized as follows. Suppose we apply a scale transformation to the system by a factor \( s \), via grouping the sites in squares of \( sR_0 \). The site within each square that is best connected to sites in other squares is the one closest to the Fermi energy and we select this site to construct a new system with lattice constant \( sR_0 \). The density of states around the Fermi energy is equal to \( \rho' F = s^d \rho F \). However, the new system can also be viewed as a system with the original constant \( R_0 \), but with a scaled \( \alpha' = sa \). So, we have established a transformation \( \alpha \rightarrow \alpha' = sa \), \( \rho F \rightarrow \rho' F = s^d \rho F \) with the same current distribution. This transformation resembles very much a Migdal-Kadanoff transformation [197, 198] as used in statistical physics to illustrate scale invariance of a critical system. To investigate the latter transformation we apply it to a 200×200 lattice for \( \alpha = 2 \). We have plotted in Fig. 7.12 the distribution of the (electro-chemical) potential, which in the low-temperature limit is equal to \( \mu_i = kT p_i - eE \cdot R_i \) with \( p_i \equiv (n_i - n_i^0) /[n_i(1-n_i^0)] \) and \( n_i \) as defined in Chapter 5. Moreover we also plot in Fig. 7.12 the distribution of the potential in a 100×100 lattice for \( \alpha = 4 \) after the transformation prescribed above. From Fig. 7.12 we see that the large-scale
features in both potential distributions are equal and the same will hold for the current distributions. We observe a very specific character of the potential distribution. Terraces on which the potential is almost constant and cliffs where the potential varies rapidly. Apparently the large jumps at the cliffs change with temperature as does the resistance in order to produce a scaling function for the current distribution. Having established the fact that \( l \) is the only relevant parameter that determines the current distribution, we will now focus on the dependence on \( l \). The parameter \( l \) can be considered as a "space-energy" scale parameter, since form its definition we see that \( l \rightarrow s l \), if \( \alpha \rightarrow s \alpha \) and \( \beta \rightarrow s \beta \). Since \( l \) is the only relevant parameter that fixes the scale in space and energy of the hopping process, a plausible scaling form for the current distribution is

\[
I = \tilde{I}(l) f(\rho \equiv \alpha R/l, \epsilon \equiv \beta E/l),
\]  

(7.18)

with \( f(\rho, \epsilon) \) a universal function. We can read of typical conductances on the scale \( \alpha R = l \) and \( \beta E = l \) from Eq. (7.17) leading to values of the order \( \exp(-c l) \), with constants \( c \) of the order unity. These conductances determine the prefactor \( \tilde{I} \) in Eq. (7.18). Performing the integral over \( R \) and \( E \), without taking a special bound of the integral, in Eq. (7.18)

![FIGURE 7.12: Top: Schematic representation of the transformation \( \alpha \rightarrow \alpha' = s \alpha \), \( \varrho_F \rightarrow \varrho'_F = s^d \varrho_F \). Bottom left: the potential distribution of a 200×200 lattice for \( \alpha = 2 \) and \( \beta = 67.5 \). Bottom right: the same potential distribution of a 100×100 lattice after the transformation with \( s = 2 \). About 100 equipotential lines are drawn for a horizontal current.](image)
we straightforwardly find the Mott formula for the conductivity. From scaling arguments we can only conclude that the constant $c$ is of order unity, numerical simulations yield, as shown, the precise values.

### 7.8 Conclusions

To summarize, in $(R, \varepsilon)$ space the region of relevant Mott hops bounded by $\xi_M(\beta)$ is a scaling regime, in which the various possible hops self-organize into a distribution only determined by scaled variables. In this regime of relatively easy passages the effective hop probabilities are well below the corresponding single-hop Miller-Abrahams factors; this can be understood as being due to iterative hops before local escape. At the boundary there is a cross-over to a Miller-Abrahams-type single-bond hopping distribution, i.e. to an exponential cut-off. The boundary of the scaling regime shifts to higher values of $\xi_M$ with lower temperature and diverges at $\beta^{-1} = 0$. Most-frequent hops occur around the origin while there is a peak of dominant contributions well inside the scaling region. The position of the boundary is determined by the Mott percolation condition, which enables global escape and which introduces a first new scale above the nearest-neighbor regime. This is only the case if we use the variable $\xi = \alpha R_{ij} + \beta \varepsilon$. It is this position which is temperature-sensitive; due to the self-organized scaling up till the boundary, this temperature dependence enters the total mobility. In the above sense the critical bond for percolation, with its Miller-Abrahams form, does indeed determine the total mobility. Concerning our percolation calculations there seems to be a possibility to extend the ideas of Tyč and Halperin, who applied percolation theory to the problem of nearest-neighbor hopping, to the problem of variable-range hopping. They showed that for the problem of nearest-neighbor hopping the identification of the temperature dependence of the mobility to be given by the exponent of the percolation threshold is exact. However, in our approach the percolation argument does not need or even allow the omittance of less-favorable bonds as is done in the classical percolation approach. The latter operation would dramatically alter the properties of the network, as shown. In fact we have verified numerically that whereas integration of the distribution up till $\xi_M$ recovers the total mobility to within $O(\eta)$, the sequential introduction of decreasing conductances up till this point still gives a negligible $\mu^*$; further arguments beyond the percolation point are then required to arrive at the right level of mobility\[86]. The present scaling approach is free from such artificialities; while it gives new insight in the full distribution of hops and highlights the underlying scaling, it in fact remains closer to Mott’s original ideas.

Plotting the distribution function against the spatial and energy variables as used for the mapping to the random-resistor network results in similar scaling behavior, the only difference is that the peak position is shifted along the energy axis. In this picture it is not yet clear how to define a boundary of the scaling regime analogous to $\xi_M(\beta)$. Furthermore we provided an alternative scaling argument based on a ”Migdal-Kadanoff like” transformation.
Chapter 8

Density, temperature, and electric-field dependence of the mobility in a Gaussian DOS

ABSTRACT

Results of a study of the dependence of the mobility on temperature, charge-carrier density, and electric field are presented for disordered systems, modelled by a Gaussian density of states with a width \( \sigma \). We find that recently experimentally determined charge-carrier density dependence, ranging from densities that are typical for operating LEDs up to those found for operating FETs, can be fully reproduced. We compare our numerically exact results for the carrier-density dependence of the mobility with those obtained by recently developed semi-analytical approaches, in order to test the validity of the assumptions in these theories. Concerning the temperature dependence of the mobility we find for the low-temperature regime deviations from the generally accepted \( \mu \propto \exp[-\text{const.}(\sigma/k_B T)^2] \) behavior. As regards the electric-field dependence, we quantitatively show at which driving voltages of the polymer devices this dependence starts playing an important role. We perform a full device simulation of the current-voltage \( J - V \) characteristics in order to compare with the experimental characteristics. in the last section of this chapter we compare our results with a recently developed theory to describe field and density dependence of the mobility in a so-called mean medium approximation and show the importance of taking into account the changes of the electro-chemical potential.
8.1 Introduction

As discussed in Chapter 1, after the discovery of electroluminescence in the conjugated polymer PPV [19] and its derivatives, a lot of attention has been paid to the study of the (opto)electronic and electrical-transport properties. Understanding the charge-carrier transport properties in these polymeric materials is of crucial importance to design and synthesize better materials and further improve device performances. One of the most important parameters determining the performance of devices is the mobility of the charge carriers. In particular, the dependence of the mobility $\mu$ on temperature and electric field has been extensively addressed in literature [92, 98, 93, 94, 95, 96, 97] (where we have only mentioned a few references). It is by now common to assume a non-Arrhenius temperature dependence for the mobility, although there are examples where an Arrhenius-type behavior better describes the data [105, 106]. Concerning the electric-field dependence of the mobility, the consensus had converged to a Poole-Frenkel behavior $\mu \propto \exp[\gamma \sqrt{E}]$, see Eq. (1.18), as first pointed out by experiments of Gill [8]. Monte-Carlo simulations to study the temperature and electric-field dependence were first performed by Bässler et al. for the case of a Gaussian disorder model (GDM), showing $\mu \propto \exp[-\text{const.}(\sigma/kT)^2]$, with $\sigma$ the width of the Gaussian, while $\mu \propto \exp[\gamma \sqrt{E}]$ was found for the dependence on the electric field [92, 98], confirming the experiments by Gill and later by others [92, 93, 94, 95, 96, 97]. However, as pointed out by Gartstein and Conwell [100], a spatially correlated potential for the charge carriers is needed to explain the Poole-Frenkel behavior in the low-field region. The first theoretical foundation for this was given by Dunlap and co-workers [101, 102, 103], based on a charge-dipole model. Long-range spatial correlations of charge-carrier energies, coming from charge-dipole interactions, are the essential ingredient of this model. These authors also found a $\mu \propto \exp[-\text{const.}(\sigma/kT)^2]$ temperature dependence for the zero-field mobility, and the $\mu \propto \exp[\gamma \sqrt{E}]$ behavior was found over a wide range or electric fields. However, most conjugated polymers do not have a permanent dipole moment [96, 94]. Therefore, an alternative mechanism was needed to explain the Poole-Frenkel behavior of the mobility. Such an alternative mechanism has been given by the Los Alamos group [180, 181]. This mechanism is based on thermal fluctuations in the molecular geometry that modify the energy levels of the localized electronic states. Using this model this group also came up with a mobility $\mu \propto \exp[\gamma \sqrt{E}]$, but the zero field mobility was given by $\mu \propto \exp[-Q/kT]$, with $Q$ depending on microscopic system parameters. Many researchers have tried to extract microscopic parameters from the systems under consideration, e.g. pLEDs and pFETs, by fitting their experimental data for the electric-field and temperature dependence of the mobility to the above-given theories. However, recently it has been realized that the influence of one crucial parameter was fairly underestimated in the modelling of the devices, namely the charge-carrier density [165, 199, 200, 201, 202]. It followed from experiments for a hole-only diode and a FET, both fabricated from the same conjugated polymer, that the charge-carrier mobility could differ up to three orders of magnitude between densities present in the diode and the FET [165]. It was shown that
the only way to explain this huge difference is by taking into account a strong dependence of the mobility on the charge-carrier density.

In this chapter we will first focus on simulations of the density dependence of the charge-carrier mobility in a Gaussian DOS for a 3D model with realistic parameters taken from the experiments by Tanase et al. [165]. The obtained results will be compared with results obtained from percolation theory, with the generalized Mott theory discussed in Chapter 6, and with effective medium theory, presented in Chapter 5. Next, we will study the temperature dependence of the charge-carrier mobility for a system with Gaussian energy disorder. We will start looking at a 2D model system, for which the results can be extended to a realistic 3D system, as will be shown. The electric-field dependence will be discussed for the same 3D system. Next, we will address the interplay between all three parameters, temperature, electric field and charge-carrier density, and their combined effect on the mobility, which is investigated in a full device simulation, leading to $J-V$ characteristics that will be compared to experimental $J-V$ characteristics. Finally, we will compare our results for the dependence of the mobility on electric field and charge-carrier density with very recent results obtained by Roichman et al. [200, 201].

### 8.2 Results

In order to be able to investigate the combined effect of the electric-field and density dependence of the mobility, we will employ numerical simulations. We solve the nonlinear Master-equation, used to model the charge transport, by means of an iteration approach developed by Yu et al. [180, 181], as discussed in Chapter 5. For convenience we introduce units such that $e = R_0 = \nu_{ph} = 1$ for the particle charge $e$, the lattice constant $R_0$, and the intrinsic rate $\nu_{ph}$. For all simulations we use array sizes $L^d$, with $L = 200$ and $L = 130$ for $d = 2$ and $d = 3$, respectively. The number of sites to jump to is $N = 99$ and $N = 26$ for $d = 2$ and $d = 3$, respectively. We use a reduced energy-disorder parameter $\sigma/kT$ and consider values of this parameters between 1 and 10. The averaging procedure is always such that the error bars of the presented results are smaller than or equal to the symbol size.

#### 8.2.1 Charge-carrier density dependence

We will focus on the situation of 3D systems, with a realistic parameter set taken from the experiments by Tanase et al. [165], implying $\alpha = 20$, where $\alpha$ is the inverse localization length of the wave function in units $R_0^{-1}$. A typical result for a calculation of the mobility as a function of the charge-carrier density at different temperatures is presented in Fig. 8.1a, where $\sigma/kT = 4 - 5$ corresponds to realistic values for room temperature. In Fig. 8.1b we
show a typical result as obtained from experiment [165]. The global agreement is evident. Three clear features attract the attention: (1) the mobility stays roughly constant until a certain threshold value, after which (2) it starts to increase as function of carrier density, and (3) at very high temperatures $\sigma/kT = 1 - 2$ the mobility becomes almost density independent. The latter effect can be seen as a manifestation of the Meyer-Neldel rule [203]. Meyer and Neldel observed in 1937 that for processes of the form $X = X_0 \exp[-\Delta E/kT]$ the exponential prefactor $X_0$ and activation energy $\Delta E$ are related via $X = X_{00} \exp[\Delta E/E_{MN}]$, with $X_{00}$ and $E_{MN}$ positive constants. One observes for $T_{MN} = E_{MN}/k$ the process $X$ becomes independent of the activation energy. The general observation is that the density dependence becomes more pronounced at low temperatures. At $\sigma/kT = 5$ we see that the mobility increases about three orders of magnitude, which is in very good agreement with the experimental findings, as shown in Fig. 8.1b. The experimental data for the high-density regime can be fitted with a variable-range hopping model proposed by Vissenberg and Matters [166] (see straight lines in Fig. 8.1b). This model is based on percolation theory, as summarized in Chapter 1, in an exponential density of states. This yields an expression for the mobility as a function of temperature $T$ and charge-carrier density $n$ [166]

$$\mu(n, T) = \frac{\sigma_0}{e} \left( \frac{(T_0/T)^4 \sin(\pi T/T_0)}{(2\alpha)^3 B_c} \right)^{T_0/T} n^{T_0/T-1},$$

where $e$ is the elementary charge, $\sigma_0$ a prefactor for the conductivity, $\alpha^{-1}$ the effective overlap parameter between localized states, $T_0$ a measure for the width of the exponential density of states, and $B_c$ a critical number for the onset of percolation. This expression is derived for the field-effect regime where the density of states is often assumed to have an exponential form. It is clear from this expression that it does not account for a density-

Figure 8.1: (a) The calculated mobility as a function of charge-carrier density for different temperatures $\sigma/kT$. (b) Typical experimental results [165] (inset discussed in the original work).
independent mobility $\mu(0,T)$ at very low carrier densities. At low carrier densities we are not in the FET regime but in the LED regime, for which the density of states is often taken to be a Gaussian. So the natural question that has arisen (as stated in [165]) is the following: "Is the mobility description at low carrier density in a Gaussian DOS fundamentally different from the high carrier density regime with an exponential DOS?" From our results we can answer this question disaffirmatively. We used a Gaussian DOS for our simulations and we found a constant mobility at low-density regime, relevant for LED operation, and an increasing mobility at higher carrier densities, relevant for the FET operation. For the Gaussian density of states at low densities we are deep in the tail, with only very few sites available. This means that if the temperature is large enough, we are in the regime where the Fermi-Dirac distribution can be replaced by a Boltzmann distribution, which in its turn explains the absence of any density dependence of the mobility.

The fact that we are able to solve the problem in a numerically exact way opens the possibility to use our results as a reference for testing the outcomes of (semi-) analytical modelling. In the following, we will compare with recent results [204] based on the percolation model of Vissenberg and Matters for the case of a Gaussian density of states, and with the generalized Mott theory as developed in Chapter 6. In Fig. 8.2 we show the results of the different calculations. To obtain the results as presented in Fig. 8.2 we have

**Figure 8.2:** (a) Mobility as a function of charge carrier density for different values of $\sigma/kT$. The solid squares indicated with 'ME' are results obtained by the numerical solution of the Master-equation, the open squares represent results obtained by employing the approach developed in Chapter 6, and the open stars are the results obtained from application of percolation theory. (b) Magnification of the high density regime for high and low temperatures in order to better visualize the differences in this regime.

used the solution of the Master-equation as a reference. The results obtained either by percolation theory or by the theory as presented in Chapter 6 are rescaled by the same prefactor $\mu_0$. This rescaling of the mobility by the prefactor $\mu_0$ is necessary because both
theories are not capable to predict the temperature dependence of the prefactor. From Fig. 8.2a it is clearly observed that both analytical approaches produce the correct density and temperature dependence for the mobility. Only in the very high density regime, as shown in Fig. 8.2b, we observe differences in the density dependence of the mobility. This difference may be explained by the fact that in both cases the percolative character of the theories needs to be refined in order to account for the high density effects. It may also be that in our numerical simulations correlations between sites should be taken into account. These effects have not been investigated yet.

8.2.2 Temperature dependence

Sofar, we focused on the dependence on the charge-carrier density, but we already saw that the temperature plays an important role. In the following we will investigate the temperature dependence of the mobility in a 3D system with the same realistic parameters as given in the previous section. In Fig. 8.3 we present the temperature dependence of the mobility as found from our numerical simulations in the case of a low density of $10^{-5}$ (LED regime) and a relatively high density of 0.05 (FET regime). In Fig. 8.3 we show the results for the mobility as a function of temperature in the temperature range $\sigma/kT$ between 1
and 6. The linear dependence when the mobility is plotted logarithmically vs. $\sigma/kT$ is obvious. In case of the realistic parameter set taken from the experiments by Tanase et al. [165], the mobility is described by $\mu \propto \exp[-\text{const.}(\sigma/kT)]$ over a broader regime as compared to the small region of a $T^{-2}$-dependence. The insets of Fig. 8.3 show the mobility plotted logarithmically vs. $(\sigma/kT)^2$. This $(\sigma/kT)^2$ dependence for the mobility, first suggested by Bässler and coworkers [92, 98], is commonly taken in literature as the temperature dependence of the mobility in presence of a Gaussian energy disorder. Our results do not support this view. Only in the regime $(\sigma/kT)^2 < 15$ this dependence seems to be approximately obeyed, especially at low doping. So the conclusion to be drawn from Fig. 8.3 is that the mobility as a function of temperature for a highly doped system is not of the form $\mu \propto \exp[-\text{const.}(\sigma/kT)]$ for all temperatures. Only for $(\sigma/kT)^2 < 15$ such a behavior seems to be present. A thermally activated dependence of the mobility seems to describe the data over a more extended regime of temperatures. Note that from Fig. 8.3 we observe that the regime where the mobility is described by $\mu \propto \exp[-\text{const.}(\sigma/kT)]$ is extended upon increasing the charge-carrier density. We will come back to the $T^2$ versus activated temperature dependence at the end of this section.

We compare our results to results obtained from effective medium theory, as presented in Chapter 5, where we have to self-consistently solve the equations (5.32) and (5.33). The outcome is shown in Fig. 8.4 for the situation of high density $n = 5 \cdot 10^{-1}$. In this limit the equations are claimed to be exact within this mean-field approach [88]. The comparison shown in Fig. 8.4 indeed indicates good agreement between both methods.

As an intermezzo we will discuss the results for the temperature dependence of the mobility in a 2D model system, for which we take two different values of the inverse localization length of the wave function, $\alpha = 3$ and 10, in units $R_0^{-1}$. We have set the Fermi level in the middle of the Gaussian, meaning that we consider a highly-doped system with a density of 0.5 charge carriers per site. In Fig. 8.5 we show the results for the mobility as a function of temperature in the temperature range $\sigma/kT$ between 1 and 8. The results shown in Fig. 8.5 are in agreement with the trend we found for the 3D model system. Again the temperature dependence of the mobility is described by $\mu \propto \exp[-\text{const.}(\sigma/kT)]$ over a broader regime as compared to the small region of a $T^{-2}$-dependence (shown in the inset of Fig. 8.5). The linear dependence when the mobility is plotted logarithmically vs. $\sigma/kT$ is obvious both for $\alpha = 3$ and $\alpha = 10$. The first conclusion for a 2D model system can be drawn: the mobility for a highly doped system as a function of temperature is not of the form $\mu \propto \exp[-\text{const.}(\sigma/kT)^2]$ for all temperatures. Only for $(\sigma/kT)^2 < 15$ such a behavior seems to be present. A thermally activated dependence of the mobility seems to give the best results over a more extended regime of temperatures. In the case of $\alpha = 3$ we observe beyond $\sigma/kT \approx 6$ an upward curvature, whereas for $\alpha = 10$ this is not observed. Because the curvature for $\alpha = 3$ only appears at low temperatures we can suspect effects of Mott’s variable-range hopping to start playing a role. In order to examine this surmise, we have plotted in Fig. 8.6 the mobility as a function of $(\sigma/kT)^{1/3}$. From Fig. 8.6 we indeed see the appearance of a linear behavior when plotted in this way, for $\alpha = 3$. Apparently,
Figure 8.4: The results for the mobility as a function of $\sigma/kT$, with $\alpha = 20$ and a high density, $n = 5 \cdot 10^{-1}$, both from the Movaghar formula (as given in Chapter 5) and from the numerical solution of the Master-equation. We have rescaled the results obtained by the Movaghar formula such that they are on top of the numerical results for $\sigma/kT = 1$. The drawn line is a guide to the eye.

Figure 8.5: The mobility as a function of $\sigma/kT$ for $\alpha = 3$ and $\alpha = 10$. In the inset the same results are shown, but plotted vs. $(\sigma/kT)^2$. The drawn lines are a guide to the eye.

variable-range hopping effects have to be taken into account, as we have done. In the case of $\alpha = 10$ a much smaller range may be identified with a straight line when the mobility is plotted logarithmically versus $(\sigma/kT)^{1/3}$, but it is not really convincing. The reason is that
Figure 8.6: The mobility as a function of \((\sigma/kT)^{1/3}\) for \(\alpha = 3\) and \(\alpha = 10\). The straight lines are a guide to the eye.

with \(\alpha = 10\) the activated temperature dependence is still dominant at lower temperatures due to the stronger localization of the charge carriers.

Let us now summarize our findings concerning the temperature dependence of the mobility and put them in perspective with the commonly accepted dependence \(\mu \propto \exp[-\text{const.}(\sigma/kT)^2]\). We have found two parameters that determine the temperature dependence of the mobility: the inverse localization length \(\alpha\) and the charge-carrier density \(n\). The latter parameter is responsible for the activated temperature dependence. As soon as the density needs to be taken into account in the description of the mobility as compared to its constant low-density value, we observe the activated temperature dependence. This can be expounded with the help of Fig. 8.3 together with Fig. 8.1. From Fig. 8.3, for the case of a density \(n = 3 \cdot 10^{-5}\), we see a deviation of the \(\mu \propto \exp[-\text{const.}(\sigma/kT)^2]\) dependence around \(\sigma/kT = 4\). It is exactly this temperature where the dependence \(\mu \propto \exp[-\text{const.}(\sigma/kT)]\) starts. Furthermore, as is clear from Fig. 8.1, it is above this density and below this temperature that the becomes different from its constant low-density value. Hence, we can attribute the deviation of the \(T^{-2}\)-dependence as a charge-carrier density effect. At very low density, where Boltzmann statistics applies, one will find the commonly accepted dependence \(\mu \propto \exp[-\text{const.}(\sigma/kT)^2]\), whereas \(\mu \propto \exp[-\text{const.}(\sigma/kT)]\) will be observed when Fermi-Dirac statistics starts playing a role. Experimentally, the onset of density effects can thus be inferred from an upward curvature of the mobility at low temperatures when plotted logarithmically versus \((\sigma/kT)^2\). The second parameter, \(\alpha\), determines the crossover to variable-range hopping behavior, leading to a temperature dependence of the mobility \(\mu \propto \exp[-\text{const.}(\sigma/kT)^{1/(d+1)}]\), with \(d\) the dimensionality of the system.
8.2.3 Density, temperature, and field dependence

In this section we will address the interplay between the three different parameters determining the mobility: temperature, electric field and charge-carrier density. With the dependence of the mobility on these parameters as determined in the previous sections, we will calculate the current-voltage characteristics of hole-only diodes, which will be compared experiment. We will elaborate on the new insights obtained from this comparison and address the consequences for the interpretation of mobility measurements. Finally, we will pay attention to a recently developed theory by Roichman and Tessler [200, 201] and comment on their results.

We will discuss the two limiting situations of low and high charge-carrier density ($3 \cdot 10^{-5}$ and $5 \cdot 10^{-2}$, respectively), representing the experimental conditions for a LED device and a FET device, respectively, and study the influence on the mobility of temperature and electric field. The results are shown in Fig. 8.7, where we plot $\mu$ as a function of the electric field $E$. We found that plotting against $E$ instead of $\sqrt{E}$ broadened the region over which a straight line could be observed. At low electric fields we have a $E^2$ dependence (as can be understood from electric-field reversal symmetry), which is followed by a rather large quasi-linear region. Some clear overall features can be observed. The effect of an applied electric field on the mobility depends on temperature and is strongly dependent on the density under consideration. At high carrier densities the mobility increases about 1.5 order of magnitude upon applying an electric field at the lowest temperature, whereas for low carrier densities an increase of about 4 orders of magnitude is achieved. An explanation for this behavior is that at low density the transport takes place deep in the tail.

![Figure 8.7: The mobility as a function of electric field for low and high charge-carrier densities ($3 \cdot 10^{-5}$ and $5 \cdot 10^{-2}$, respectively) and for different values of $\sigma/kT$.](image)
of the Gaussian, i.e. the density of sites is low. Application of an electric field decreases
the energy differences between the hopping sites in the direction of the applied field, in-
creasing the probability to find a suitable site to hop to. This effect of lowering the energy
differences is evidently more significant at low densities. Because for the high-density case
the density of sites at the Fermi level is initially already much larger, decreasing the en-
ergy differences plays a less important role than for the low-density case. The observation
that for decreasing temperatures in both cases the electric-field dependence becomes more
pronounced can be explained along the same way of reasoning, namely lowering the energy
differences. At high electric fields, the curves merge and decrease linearly with electric
field. This effect is due to a saturation of the velocity of the charge carriers, resulting from
the energy-independent downward hops. At high temperatures \( \sigma/kT = 1 - 2 \) the mobility
becomes almost field-independent and at very high temperatures (not shown) the mobility
decreases with increasing electric field (already at low electric fields). This latter behavior
is similar to the manifestation of the Meyer-Neldel rule for the density dependence (see
Section 8.2.1).

Now that we have established the different effects of charge-carrier density, temperature,
and electric field on the mobility, we are ready to tackle the problem of a full device
simulation. We will perform a calculation of current-voltage (\( J-V \)) characteristics from a
space-charge limited (SCL) current model for a real polymer hole-only diode, and compare
the calculated \( J-V \) characteristics with the experiment. Our special interest is in studying
the separate dependence vs. the combined dependence of the mobility on electric field and
charge-carrier density. Experimentally, it is very hard to disentangle the two contributions,
but in the calculations this is not a problem. Due to the space-charge limited character
of the device an increase of the applied bias voltage gives rise to an increase of both the
electric field and the charge-carrier density. For the understanding of charge transport in
polymeric devices it is of fundamental importance to know whether the current is governed
by the field or charge-carrier density dependence of the mobility. The equations for the
SCL current problem are:

\[
J = n(x) e \mu[n(x), E] E(x), \quad \frac{\epsilon_0 \varepsilon_r dE}{\varepsilon dx} = n(x),
\]

with \( n(x) \) the density at position \( x \). We take \( \varepsilon_r = 3 \), a typical value for the dielectric
constant of the involved polymers. Together with the dependence of \( \mu(n(x), E) \) obtained
from our calculations, this set of equations can be solved numerically to obtain the \( J-V \)
characteristics. In Fig. 8.8a we plot the \( J-V \) characteristics for different temperatures for
a 275 nm thick hole-only diode. In order to be able to disentangle the role of the charge-
carrier density and the electric-field dependence of the mobility we have calculated the \( J-V \)
characteristics for three different situations: (1) \( \mu(0,0) \): no dependence of the mobility on
carrier density \( n \) and electric field \( E \), (2) \( \mu(n,0) \): mobility depends only on the carrier
density \( n \), and (3) \( \mu(n, E) \): the mobility depends both on electric field \( E \) and carrier density
\( n \). Situation (1) describes the famous Mott-Gurney square law [205] \( J = \frac{9}{8} \mu V^2/L^3 \). As
can be seen from Fig. 8.8b, this situation is clearly far from what happens in the real device,
Figure 8.8: (a) The $J-V$ characteristics of a 275 nm thick hole-only device for different temperatures in the case that the mobility is taken to be (1) independent of density $n$ and electric field $E$ (dotted lines), (2) only dependent of the density $n$ (dashed lines), and (3) depending both on density and electric field (full lines). (b) The calculated $J-V$ characteristics as compared to the experimental characteristics obtained for the polymer OC$_1$C$_{10}$-PPV. We have used for the average intersite spacing $a = 1.6$ nm and for the width of the Gaussian DOS $\sigma = 140$ meV.

with the polymer OC$_1$C$_{10}$-PPV as active material. The situations (2) and (3) turn out to be almost identical in the studied voltage range. Hence, from this result we have to draw the conclusion that apparently the field dependence of the mobility only plays a minor role. It is the charge-carrier density that matters. However, we have to be careful with drawing too premature conclusions. In Fig. 8.9 we compare our calculated $J-V$ characteristics for the two different situations $\mu(n,0)$ and $\mu(n,E)$ with the experimental characteristics of a thicker hole-only diode for a different polymer, NRS-PPV. NRS-PPV is a co-polymer of PPV with a more disordered morphology. Fig. 8.9 clearly shows an excellent agreement with experiment only when taking into account the dependence of the mobility both on electric field and charge-carrier density. A neglect of the field dependence leads to wrong results for electric fields larger than 10 Volts. The onset of the electric-field dependence is determined by the value of $eEa/\sigma$ and does not depend on temperature, whereas the strength of the electric-field dependence is dependent on temperature. These conclusions have a large impact on the interpretation of $J-V$ characteristics in literature in the past. What has been attributed to an electric-field dependence of the mobility is actually (to a large extent) a charge-carrier density effect, as has already been suggested by Tanase et al. [165]. We can now sharpen this conclusion: the electric-field dependence of the mobility must be taken into account only for high applied voltages. This also means that arguments to include some kind of long-range spatial correlations of charge-carrier energies, either coming from charge-dipole interactions or from thermal fluctuations in the molecular geometry [100, 101, 102, 103, 180, 181], are not needed. The onset at low voltages of what
Figure 8.9: (a) The calculated $J$-$V$ characteristics as compared to the experimental characteristics of a hole-only diode with a 560 nm thick layer of NRS-PPV. We have used $a = 1.8$ nm, and $\sigma = 140$ meV. The dashed lines are the results of the calculations with $\mu(n,0)$ and the solid lines are obtained with $\mu(n,E)$

seemed to be an electric-field effect is actually caused by the carrier-density dependence of the mobility. This can be concluded from Fig. 8.1, where we already observed an increase of the mobility starting at very low densities.

Finally, let us briefly discuss a recently developed theory to describe the field and density dependence of the mobility as developed by Roichman and Tessler [200, 201]. They assume the total current to be the integral of the current between each two sites while applying a so-called mean medium approximation (MMA). In this approximation it is assumed that in each point all possible energy states are realized with a relative weight determined by the DOS. Within this approximation, the current becomes

$$J = \int dR_{ij} \int d\varepsilon_i \int d\varepsilon_j W_{ij}(R_{ij}, \varepsilon_i, \varepsilon_j) g(\varepsilon_i) f(\varepsilon_i, \eta) g(\varepsilon_j - R_{ij} \cdot \mathbf{E}) [1 - f(\varepsilon_j - R_{ij} \cdot \mathbf{E}, \eta)] R_{ij} \cdot \hat{\mathbf{E}},$$

(8.3)

with $\hat{\mathbf{E}}$ the unit vector of the electric field. In their expression for the current the authors do not take into account the changes of the local electro-chemical potential $\mu_i$. This gives rise to an overestimation of the mobility and especially at low temperatures this overestimation can easily exceed two orders of magnitude. This effect was already realized by Ambegaokar et al. [84]. In Fig. 8.10 we visualize, for the case of a low temperature ($\sigma/kT = 6$), the electro-chemical potentials, defined as $\mu_i = -kT \delta n_i/[n^0_i(1 - n^0_i)] - e\mathbf{E} \cdot \mathbf{R}_i$, with $n^0_i$ the equilibrium Fermi-Dirac distribution and $\delta n_i$ obtained from the solution of the Master-equation. Fig. 8.10 clearly confirms our doubts. This figure shows an intricate spatial structure of the electro-chemical potential. We can clearly see terraces on which the potential is almost constant, separated by cliffs where the potential
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Figure 8.10: Electro-chemical potential in a plane of a 100x100x100 array with $\sigma/kT = 6$, in the linear-response regime at low voltages, for a particular disorder configuration. About 150 equipotential lines are shown.

varies quickly. This peculiar self-structuring of the potential is a subtlety inherent in the exact stationary solution of the Master-equation and cannot be obtained by simplified approaches. One of the consequences of this very inhomogeneous potential landscape is that the current distribution will also be inhomogeneous, leading to "hot spots". Another consequence is an inhomogeneous production of electron-hole pairs in polymer LEDs. Both consequences are of great relevance for a better understanding and further improvement of polymer opto-electronic devices.

8.3 Conclusions

By a numerically exact approach we have solved the Pauli Master equation corresponding to variable-range hopping on a regular array in 3D for a system with a Gaussian DOS, in contrast to Chapter 7, where we dealt with a constant DOS. Concerning the charge-carrier density dependence of the mobility, we have shown that the recently experimentally observed density dependence of the mobility $\mu$ in conjugated polymers can be fully understood from the single assumption of uncorrelated Gaussian energy disorder. For the temperature dependence of the mobility we have shown that the commonly used
description $\mu \propto \exp[-\text{const.}(\sigma/kT)^2]$ is only valid in the low-density regime where Boltzmann statistics applies. As soon as the density dependence must be taken into account the temperature dependence of the mobility is described by $\mu \propto \exp[-\text{const.}\sigma/kT]$. Moreover, with decreasing temperature a crossover to variable-range hopping will take place, leading to a temperature dependence $\mu \propto \exp[-\text{const.}(\sigma/kT)^{1/(d+1)}]$, where the crossover temperature is dependent on $\alpha$. Finally, we have shown quantitatively that the electric-field dependence of the mobility starts playing an important role only for high voltages. This has been verified by comparison with experimental $J-V$ characteristics for different polymeric devices. We have shown that the electro-chemical potential has a very interesting inhomogeneous character, which seems to be a subtlety inherent in the exact solution of the Master-equation. Better insight in this "terraces-cliffs" pattern may have important consequences for the understanding of polymer opto-electronic devices. It would be very interesting to experimentally observe this pattern, e.g. by scanning-probe measurements.
In this chapter the frequency dependent mobility for a disordered material, e.g. a conjugated polymer system, is studied. We start with an overview of the field of AC conductivity in disordered materials. Subsequently, we show the results for the frequency-dependent conductivity of fermions for a wide range of temperatures, analyzed on a two-dimensional lattice. In our model the charge carriers are allowed to hop over a variable range in an energy landscape with site-energy disorder. Within this model we show the existence of scaling properties for the AC conductivity, ultimately leading to the construction of a Master-curve. We show that the resulting Master-curve agrees well with the one obtained by Schröder and Dyre for a simpler model, namely that of a random barrier model. These two conclusions answer the longstanding question of the existence of AC universality in case of variable-range hopping of fermions in the presence of site-energy disorder, and how this compares to the AC universality curve obtained by the random-barrier model. The last section of this chapter deals with a coarse-grained analytical argument to derive the temperature dependence of the slope of the AC curves when plotted as a function of frequency.
9.1 General characteristics

For a large class of different disordered solids [206] data on the frequency-dependent conductivity exhibit remarkable similarities. The real part $\sigma'(\omega)$ of the complex conductivity $\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega)$ is found to be constant below a critical frequency $\omega_s$, $\sigma'(\omega) \approx \sigma(0) = \sigma_{dc}$ for $\omega < \omega_s$, while for $\omega > \omega_s$, $\sigma'(\omega)$ increases monotonously with $\omega$ until typical phonon frequencies $\nu_{ph} \approx 10^{12} \text{s}^{-1}$, above which vibrational contributions become dominant. Throughout this chapter we will denote $\sigma'(0) = \sigma_{dc} = \sigma(0)$. A schematic illustration is given in Fig. 9.1. We will elaborate on the three different regimes shown in this figure in a later section.

![Figure 9.1](image)

**Figure 9.1:** A schematic plot of the AC conductivity in disordered media. There are three different regimes: I denotes the low-frequency regime, II the regime where a power-law like dependence is observed, and III the high-frequency regime bounded by the vibrational frequency $\omega_0 = 2\pi \nu_{ph}$.

For $\omega_0 \gg \omega \gg \omega_s$, $\sigma'(\omega)$ exhibits an approximate power-law behavior $\sigma'(\omega) \sim \omega^n$, with $n < 1$. A more detailed analysis shows a weak temperature and frequency dependence for $n$. A final ubiquity is the Barton-Nakajima-Namikawa (BNN) relation [218, 219, 220]. This relation connects the frequency $\omega_s$ of the dielectric-loss peak, the dielectric-loss strength $\Delta \epsilon$, and the DC conductivity: by $\sigma(0) = p\Delta \epsilon \epsilon_0 \omega_s$, where $\epsilon_0$ is the permittivity of vacuum, and $p$ is a material-dependent constant of order unity. The dielectric-loss peak shows up when we plot $(\sigma'(\omega) - \sigma(0))/\omega$ vs. $\omega$ and $\omega_s$ is defined as the frequency around which AC conduction takes place. The dielectric-loss strength is defined as: $\Delta \epsilon = \epsilon(0) - \epsilon(\infty) = -\epsilon_0^{-1}\lim_{\omega \to 0} \sigma''(\omega)/\omega$.

Because of this (quasi-)"AC universality" property it is usually possible to construct a Master-curve, consisting of the scaled AC conductivity $\Sigma(\omega) = \sigma(\omega)/\sigma(0)$ as a function of a dimensionless frequency $\Omega \equiv \omega/\omega_s$, with $\omega_s$ the scaling frequency. The fact that the
shape of this Master-curve does not depend on temperature anymore means that the AC conductivity obeys the "time-temperature superposition principle" [207].

9.2 Prior understanding

The construction of a Master-curve has been discussed quite extensively in literature [208, 209, 210, 211, 212, 213] and basically starts from the following expression, which is often called the Taylor-Isard scaling relation [214, 215]

\[ \Sigma(\omega) = F\left(\frac{C \omega}{\sigma(0)}\right), \]  

(9.1)

with F a universal function. From the above definition for the scaled frequency \( \Omega \) it follows that Taylor-Isard scaling implies \( \omega_s = \sigma(0)/C \). Via the BNN relation, which relates \( \omega_s \) and \( \sigma(0) \), the constant \( C \) can be identified: \( C = p\Delta\epsilon\epsilon_0 \). The first proof of the BNN relation is by Sidebottom in [217], where he supported his arguments by considering the hopping motion within a Debye model for the rotation of permanent dipoles. If we consider \( n \) mobile carriers of charge \( q \) that traverse a distance \( d \) in a single hop with a jump rate \( \omega_H \), then it follows that \( \sigma(0) \propto nq^2d^2\omega_H/kT \). The permittivity change \( \Delta\epsilon \) resulting from the rotation of permanent dipoles is given by \( \Delta\epsilon \propto nq^2d^2/(kT\epsilon_0) \), and hence a combination of these formulas gives a relation for the characteristic jump rate \( \omega_H \propto \sigma(0)/(\epsilon_0\Delta\epsilon) \). This characteristic jump rate \( \omega_H \) has to be identified with the scaling frequency \( \omega_s \). This proves the BNN relation. Later, the relation \( C = \Delta\epsilon\epsilon_0 \) has been proven mathematically [216].

That the issue about how to scale correctly is a subtle one is clear from literature. Sometimes it is found that \( \Omega \propto \omega/\sigma(0) \) [221, 222, 223] drastically increases the quality of the scaling curve as compared to \( \Omega \propto \omega/\sigma(0)T \) [208, 210]. The latter finding, \( \Omega \propto \omega/\sigma(0)T \), can be interpreted as a manifestation of the 'Curie-law' with \( C = \Delta\epsilon \sim 1/T \) [206]. However, it has been shown that \( \Delta\epsilon \) can decline with temperature much more rapidly than \( 1/T \) [224].

Arguments to understand the increase of the AC conductivity in disordered solids as a function of frequency generally run along the following line of reasoning. The hopping process involves forward and backward hopping of the charge carriers. As we know, the DC conductivity is determined only by those charge carriers that are able to find a percolating path from one electrode to the other. This percolating path contains difficult hops with small jump probabilities, and charge carriers that can only move on isolated clusters do not contribute to the DC conductivity. However, if the frequency of the applied electric field is increased, regions of charge carriers with higher jump probabilities, e.g. isolated clusters, start to contribute to the AC conductivity, and less difficult hops will be experienced by the charge carriers. We can thus conclude that the AC conductivity increases with increasing frequency of the electric field.
9.3 Quantitative models

In order to describe the frequency-dependent conductivity with quantitative models, processes governing the response to an AC field are distinguished in three different frequency regimes. These three frequency regimes are illustrated in Fig. 9.1.

*Regime I* is the low-frequency regime which approaches the DC regime, $0 < \omega < \omega_s$; conduction takes place in large clusters consisting of up to an infinite amount of sites.

*Regime II* is the multiple-hopping regime, $\omega_s < \omega < \omega_0$; conduction occurs in isolated clusters of many sites.

*Regime III* is the high-frequency pair-hopping regime, $\omega_0 < \omega < 2\pi\nu_{ph}$, where conduction is between isolated pairs of sites.

The reason why it is possible to distinguish three different regimes is as follows. By considering frequencies $\omega > \omega_0$ such that only hopping between pairs of isolated sites needs to be considered, one immediately arrives at the so-called pair-hopping approximation. This approximation logically breaks down if the transition rates are such that a charge carrier can hop across more than two sites during a period of the applied field, which happens at lower frequencies. In this frequency regime the carrier can thus make multiple hops, which explains the name of this so-called multiple-hopping regime. Finally, if the frequency is so low that infinite clusters start to appear regime I is encountered.

The first who developed a theory to deal with the frequency-dependent conductivity, using the pair-hopping approximation, were Pollak and Geballe in 1961 [225]. In their approach they assumed thermally activated hopping between pairs of sites with a random distribution of pair spacings to describe impurity conduction at high temperatures. As a result they found a frequency-dependent conductivity independent of temperature. Later (1969), Austin and Mott [226] addressed the same approximation but by considering hopping between pairs of sites separated by variable distances and energy differences $\sim kT$ or less from the Fermi energy. Thus, only a fraction proportional to $kT$ of the available electrons can take part in the hopping process. As a result they found the following formula for the temperature-dependent AC conductivity:

$$\sigma'(\omega) = [kT N(\varepsilon_F)]^2(e^2/kT)\omega \alpha^{-(d+2)}\ln(\nu_{ph}/\omega)^{d+1},$$

(9.2)

with $N(\varepsilon_F)$ the density of states at the Fermi level, $\alpha$ the inverse localization length of the wave function, and $d$ the dimensionality. The link between this Austin-Mott relation and the one found by Pollak and Geballe "is simple", as Mott stated [227], "this equation should be multiplied by $E_F/kT$ in order to have the conductivity independent of temperature as described by Pollak and Geballe". Now, when writing $\sigma'(\omega) \propto \omega^n$, one can take the logarithmic derivative, under the assumption that $n$ is approximately constant, to arrive at the following expression for the slope $n(\omega)$ in regime III as sketched in Fig. 9.1:

$$n(\omega) = 1 - (d + 1)/\ln(\nu_0/\omega).$$

(9.3)

From this equation we see that the slope is a decreasing function of frequency. However, as pointed out first by Jonscher in 1977 [228], the slope of the AC conductivity tends
Scaling of AC conductivity

to increase with increasing frequency if monitored from the onset $\omega_s$ till the frequency $\omega_0$ from whereon the pair-limit is valid, see Fig. 9.1. Because such an increasing slope as a function of frequency cannot be understood within the pair-hopping approximation, another theory, for frequencies $\omega_s < \omega < \omega_0$, the 'multiple hopping' regime (regime II in Fig. 9.1), is required. In this regime, from the work by Hunt [229], the value $n$ of the slope of the conductivity as a function of frequency is known to develop with temperature, in case of variable-range hopping, as $1 - n \propto (T/T_0)^{1/(d+1)}$. Here $d = 0$ means only energy disorder without the possibility to hop over a variable range [234].

In the low-frequency regime (regime I in Fig. 9.1) the conductivity shows a flattening, which at first appearance might look uninteresting. Nevertheless, it is in this regime where differences between theoretical predictions from effective-medium theories by Ganter and Schirmacher [235], $\sigma(\omega) = \sigma(0)(1 + \Omega^{d/2})$, and from percolation-based theories by Hunt [236], $\sigma(\omega) = \sigma(0)(1 + \Omega^{(d-1)/2} + \Omega^{d/2})$ can be extracted, with $d$ the dimensionality of the system. In this regime there is the ongoing discussion about the issue whether the conductivity should have the term with the power $(d - 1)/2$, as predicted by the latter theory, or not [229].

The percolation theory as applied to this problem is based on the use of cluster statistics, where the disordered medium is considered as a network of random impedances. The rationale behind the approach is that large clusters of resistances that are not connected to the infinite percolation cluster are effectively in parallel with the infinite cluster. As a result the total conductivity is identified to be a sum of two terms: one is the DC conductivity of the infinite percolation clusters and the other is the AC conductivity of the large clusters. For more details the reader is referred to [236, 237, 238].

The effective-medium approximation calculations [235] are based on the following ingredients. As has been shown by Movaghar and Schirmacher (see Chapter 6), it is of crucial importance to take into account repeated forward and backward hopping of charge carriers. However, in their work they did not include revisiting of the same site via recurrent walks, which are often called "closed loops". It is exactly this behavior that has been pointed out to be responsible for important low-frequency characteristics [239, 240]. In order to systematically incorporate these effects in a self-consistent manner, a so-called closure relation has to be used. In technical terms the method of Ganter and Schirmacher combines the method of resummation of all paths involving a particular index. Repeated indices are effectively removed (renormalized perturbation expansion [241], accounting for the backward and forward hopping) with the path summation technique [242, 243, 244], developed to treat the closed paths in a systematic way via a decoupling approximation [88].

To study all the above-mentioned dependencies and especially the discussion about the universal behavior of the AC conductivity, computer simulations have been carried out in the past, of which we mention in particular those by Dyre and Schröder [216, 206]. They have investigated the AC conductivity for a model with only energy disorder and symmetric transition rates, the so-called symmetric hopping model or random-barrier model. These
authors studied the very low temperature limit, which is equivalent to the extreme-disorder limit. Their results clearly point to the existence of a universal Master-curve [216]. However, it would be more realistic to take into account the Pauli exclusion principle for the charge carriers, and to allow the carriers to hop over variable distances and with asymmetric transition rates, instead of considering only nearest-neighbor hopping with symmetric transition rates. A logical question is then: does a model of fermions with asymmetric transition rates show AC universality? First attempts to a more realistic model have been by Baranovskii and Cordes, and Porto et al., who included Fermi statistics and site-energy disorder, but at relatively high temperatures and taking nearest-neighbor hopping only [245, 246]. Another question is: how does this AC Master-curve (if it exists) compare with the one obtained for the symmetric hopping model? It is exactly this issue that we like to focus on. In Fig. 9.2 we have drawn a schematic picture indicating the difference between the random-barrier model and the site-energy disorder model. In this chapter

![Figure 9.2: A schematic view of the random-barrier model and the site-energy disorder model. (a) The random-barrier model: only nearest-neighbor jumps are allowed, and it is clear that the transition rates of the particle are symmetric. (b) The site-energy disorder model: jumps over variable distances are allowed, and the transition rates are clearly asymmetric (we have to distinguish between jumps upward and downward in energy).](image)

we make a first attempt to study the AC conductivity in the more realistic situation, as already suggested in [247, 206], considering hopping of fermions, which we allow to hop over a variable range with the more general assumption of an asymmetric transition rate, i.e. with lattice sites of differing energies. The focus will be on the open question [247, 206] of the existence of AC universality for this model system. We will examine the case of a two-dimensional system, because a calculations for a three-dimensional system was not feasible from a computational point of view. Unfortunately, a only problem is that there is not much known about two-dimensional systems, and especially the scaling properties have not been analyzed [250]. However, we will give a reasoning why a comparison with results for a two-dimensional system is still interesting. Finally, we will make a comparison with the results obtained for the symmetric hopping model. The numerical methods we apply are described in Chapter 6, where the frequency-dependent conductivity is calculated from the current between all sites \((i, j)\), summed over the lattice.
9.4 Numerical results

Figure 9.3: Temperature dependence of the DC conductivity $\sigma(0)$ and $\lim_{\omega \to 0} \sigma'(\omega)$ from the DC and AC calculations, respectively.

To show the numerical results for the temperature dependence of the conductivity we introduce units such that $e = R_0 = \nu_{ph} = \varepsilon_0 = 1$ for the particle charge $e$, the lattice constant $R_0$, the intrinsic rate $\nu_{ph}$, and the width of the DOS $\varepsilon_0$. Note that $\varepsilon_0$ should not be confused with the vacuum permittivity $\varepsilon_0$. For all our simulations we use a 200x200 array, and the numbers of neighbors taken into account is $N = 143$. In the case of a constant DOS we sample the energies $\varepsilon$ from an interval $|\varepsilon| \leq \varepsilon_0/2 \equiv (2R_0\rho_F)^{-1}$, and charge is introduced by setting the chemical potential in the Fermi-Dirac distribution equal to zero. In case of a Gaussian DOS we sample from a normalized Gaussian distribution with a width $\sigma$, and charges are introduced by putting the chemical potential equal to a desired value. The averaging procedure over different realizations of disorder is always such that the error bars are smaller than or equal to the symbol size in the figures presented below. For the inverse localization length we take $\alpha = 7/R_0$. Before we investigate the AC conductivity of our hopping model, let us start to consider the temperature dependence of the conductivity $\sigma(\omega)$ in the case $\lim_{\omega \to 0} \sigma'(\omega)$. In this limit the resulting dependence should correspond to that of the DC conductivity discussed in Chapter 7. This comparison is a useful possibility to check the compatibility of the computer programs for the AC and DC calculations. Additionally, it turned out that with the AC program we could extrapolate the DC conductivity, determined as $\lim_{\omega \to 0} \sigma'(\omega)$, to much lower temperatures than obtained from the DC program (for reasons of computational time). The results for the DC conductivity as a function of temperature are shown in Fig. 9.3, and it is clear that Mott’s variable-range hopping conduction is retrieved. The compatibility between the results for the DC conductivity obtained from the frequency dependent and from the DC computer program turns out to be excellent. The fact that the conductivity for the
values $\beta = 200$ and $\beta = 350$ in Fig. 9.3 is not on the straight line is due to the inability of the AC program to compute the limit $\omega \to 0$. In Fig. 9.4 we give a typical example of

![Figure 9.4: Results for the frequency dependence of the AC conductivity, without any scaling procedures involved.](image)

the 'raw' data for the real part of the AC conductivity, in the case of a constant DOS, as a function of frequency for different temperatures. The overall behavior of the complex conductivity $\sigma(\omega)$ compares fairly well with the universal trend as found in experiments. There is a crossover regime for $\sigma'(\omega)$ from $\sigma'(\omega) \simeq \sigma(0)$ to a regime where $\sigma'(\omega)$ increases monotonously as a function of frequency, showing an approximate power-law with slope $n$. One can clearly see that $n$ is a function of temperature. Hunt indicated [229] that in case of two-dimensional VRH a temperature dependence of $n$ will develop, with $1 - n \propto \beta^{-1/3}$, provided that we consider a fixed frequency range. In Fig. 9.5 we check this, and it is seen to be well obeyed. In the inset we show an extrapolation to zero temperature and, as can be seen, the value of $n$ approaches 1, as it should in the $T = 0$ limit [206].

As an intermezzo, let us now make a comparison with effective-medium theory as discussed in Chapter 6, and in particular with the analytical derivations by Movaghar and Schirmacher [88]. Considering the limit of low-temperature hopping near the Fermi level, and assuming a constant density of states, they obtain the following result for the frequency-dependent conductivity in the symmetric energy-dependent case [230]:

$$\sigma(\omega) = \frac{\langle R^2 \rangle}{6} \frac{e^2}{k_B T} \left[ n N(E_F) k_B T \nu_0 \sigma_1(\omega) \right], \quad (9.4)$$

where $\sigma_1(\omega)$ has to be determined via the self-consistent equation

$$\sigma_1(\omega) = \frac{4T a_p}{T_0} \left[ i\omega + \sigma_1(\omega) \right] \int_0^\infty \frac{x^3 \exp[-x]}{i\omega + \sigma_1(\omega)} dx, \quad (9.5)$$
with \( \langle R^2 \rangle \) defined in Eq. (5.31). As a result of their numerical calculation they found the real part of the conductivity to behave as

\[
\text{Re}[\sigma(\omega)] \sim \omega^x,
\]

(9.6)

with \( x = a_1 - a_2 T \) and \( a_1 \) and \( a_2 \) some constants. So indeed these authors find a temperature-dependent exponent \( x \), where \( a_1 \) and \( a_2 \) are some constants. The linear temperature dependence of \( x \), instead of the inverse Mott-type dependence as we observe in Fig. 9.5, is probably due to the fact that the temperatures they considered were not low enough.

As stated in the introduction, in literature there has been some debate about how to scale the frequency in order to find the proper Master-curve. Sometimes it is found that \( \Omega \propto \omega / \sigma(0) \) [221, 222, 223] gives better results, but in other cases \( \Omega \propto \omega / \sigma(0) T \) [208, 210] does. To obtain the scaled AC conductivity \( \Sigma \) we can use the extrapolations for the DC conductivity at very low temperatures, as shown in Fig. 9.3, in order to arrive at the real part of the scaled AC conductivity \( \Sigma' \). We show in Fig. 9.6 the effect of scaling the frequency with \( \sigma(0) \) only. The result is unambiguous: we do not find a proper Master-curve, but it is evident that the common point for the onset of AC conductivity (as needed for a proper Master-curve) is mainly due to scaling of the horizontal axis with \( \sigma(0) \).

We will now discuss how to obtain the dimensionless frequency \( \Omega \). For this we have to determine \( \omega_s \), which needs some clarification. As mentioned before we are not able to make a full frequency sweep into the DC regime for the lowest temperatures, so we cannot use the method for scaling the frequency as described in [216], which makes use of results at very low frequencies. Instead, we use an alternative method, discussed in [248]: \( \omega_s \) is chosen to
be the characteristic frequency defined by $\sigma(\omega_s)/\sigma(0) = \sqrt{10}$ [248], where the value $\sqrt{10}$ is rather arbitrary. In Fig. 9.7 we show the results for both the real and imaginary part

Figure 9.6: Results for the frequency dependence of the AC conductivity where the frequency is scaled only with $\sigma(0)$.

Figure 9.7: Results for the scaled complex frequency dependent conductivity $\Sigma$. (a) The real part of the scaled conductivity $\Sigma'$ as a function of the dimensionless frequency $\Omega$. The drawn line through the data represents the scaled conductivity $\Sigma'$ for the case of a Gaussian energy disorder The inset shows the scaling parameter $\omega_s$ divided by $\sigma(0)$ as a function of $\beta$. The drawn line is a fit to a power-law. (b) The imaginary part of the scaled conductivity $\Sigma''$ as a function of $\Omega$.

of the scaled conductivity $\Sigma'$ and $\Sigma''$ at low temperatures, obtained with this definition of
\( \omega_s \). The results show that both the real and imaginary part of the conductivity exhibit unequivocal scaling behavior, and they tend to follow a so-called universal function, or Master-curve. Besides, the drawn line through the data represents the real part of the scaled conductivity, but now for the case of a Gaussian energy disorder. The temperature under consideration is such that \( \sigma/kT = 9 \), with \( \sigma \) the width of the Gaussian, and the Fermi energy is at \(-2\sigma\). If the behavior is really universal there should be no difference if another energy distribution is taken. The fact that this is indeed the case demonstrates the validity of the concept of universality. The inset in Fig. 9.7a shows the dependence of \( \omega_s \) on temperature; \( \omega_s \) is proportional to \( \sigma(0) \) including a weak \( \beta \) dependence (analogous to the dielectric loss strength \( \Delta \epsilon \) [206]). The first question mentioned in the introduction, the question about the existence of AC universality in the case of Fermi hopping, site-energy disorder and variable range hopping, has thus been answered: we do find scaling behavior and a tendency to AC universality.

Another very sensitive way of studying universality is by plotting \( n = d \log_{10}(\Sigma')/d \log_{10}(\Omega) \) as a function of \( \Sigma' \). The result is shown in Fig. 9.8. Again we see a tendency to universal behavior when lowering the temperature. However, some structure seems to develop. This structure can be attributed to a crossover to resonant pair hopping, introduced by the discreteness of the lattice, comparable to the crossover to pair hopping at high frequencies.

We will now address the interesting issue of how the concept of universality enters in the very low frequency regime. One might be tempted to conclude that it is just the DC conductivity that matters in this regime. To get more insight into the structure of \( \Sigma(\Omega) \) at low frequencies, one should plot \( |\sigma'(\omega) - \sigma(0)|/\sigma(0) \) as a function of \( \Omega \), as is done in Fig. 9.9. In this way it is possible to disentangle the DC conductivity from the contributions to the AC conductivity due to the very small but nonzero frequency. The universality is seen to hold very well at the low frequencies. This clearly demonstrates that universality at

\[ \text{Figure 9.8: } n = d \log_{10}(\Sigma)/d \log_{10}(\Omega) \text{ as a function of } \Sigma'. \]
Figure 9.9: $[\sigma'(\omega) - \sigma(0)]/\sigma(0)$ as a function of $\Omega$. The numerical data are very well approximated by $\sigma(\omega) = \sigma(0)(1 + \Omega^{d/2})$, derived from an effective-medium theory approach, where $d$ is the dimensionality of the system. The drawn line indicates a slope 1 as obtained from effective-medium theory for $d = 2$ [235].

low frequencies is not just an effect dominated by the DC conductivity. Actually, a recent derivation for the conductivity based on effective-medium theory [235] generates precisely the exponent 1 for $\Omega$, namely $d/2$ with $d = 2$, in agreement with our observations. We also conclude that from our results we do not appear to find any $\Omega^{(d-1)/2}$ dependence, as predicted from percolation-based theories [236]. However, we still should be very careful with excluding a possible $\Omega^{(d-1)/2}$ term. It would not be easily visible in VRH systems, and one would have to attain very low frequencies in real systems, or very large systems in simulations [251].

9.5 Comparison with the symmetric hopping model

Nowadays, the standard work in literature to refer to when discussing AC universality is that of Schröder and Dyre [206, 216]. They performed computer simulations of the AC conductivity for a random-barrier model and showed universal curves for the AC conductivity in $d = 3$. So, a natural question would be to see how the results for our model compare with those obtained for the random-barrier model. It is exactly this question we put forward in the introduction and which has remained an open question in literature. In Fig. 9.10 we show the comparison. The AC conductivity results for the 2D simulations of a random-barrier model are taken from [249]. It is found that in the regime up to $\omega/\omega_s = 10^4$ the comparison is very good. Only for the higher frequencies the correspondence becomes worse, because our curve has a smaller slope. However, from the data plotted in Fig. 9.3 we
see that for lower temperatures our slope would extrapolate to larger values. This means that at even lower temperatures we tend to retrieve the same universal curve as found for the random-barrier model. Because we are not aware of detailed experiments concerning AC universality in two-dimensional systems, it is not possible to compare our data with existing experimental data.

An interesting experimental finding, reproduced by simulations for the random-barrier model, is that the AC conductivity in 2D is slightly less frequency dependent than in 3D [249, 250]. Obviously, the same holds for the corresponding Master-curves. We have just shown that there is no difference between our Master-curve and the one obtained for the random-barrier model in the regime $\omega/\omega_s < 10^4$. This means, keeping in mind the small difference between the 2D and the 3D Master-curve for the random-barrier model, that within this range we are able to compare with the 3D results as presented in [216]. In that work a comparison is made between a 3D Master-curve obtained for a random-barrier model and experiments, showing a good correspondence. If the same step from 2D to 3D can be made for our model, it would mean that our results also compare fairly well with experiment.

### 9.6 DC to AC cross-over: an analytical argument

In the introduction we already mentioned that, as stated by Hunt in [229], in regime II the value of the slope is known to increase as a function of decreasing temperature, $1 - n \propto (T/T_0)^{1/(d+1)}$ [229], where $d = 0$ means that only energy disorder is taken into
account [234]. However, no explicit proof of why this should happen is given. In this section we will present a coarse-grained argument to derive this dependence in the case of energy disorder and VRH. For the frequency-dependent conductivity in the regime $\omega > \omega_s$ we postulate a power-law dependence (as often discussed in literature):

$$\sigma(\beta, \omega) = \sigma(\beta, 0) \left[ 1 + \left( \frac{\omega}{\omega_s} \right)^n \right]. \quad (9.7)$$

The rationale behind this expression is as follows. For DC conductivity there is a largest length scale (or time scale) $\xi_{dc}(\beta)$, such that carriers can percolate through the system. This length scale $\xi_{dc}(\beta)$ will determine the DC conductivity as

$$\sigma(\beta, 0) \sim \exp\left[ -\xi_{dc}(\beta) \right] = \exp\left[ -\frac{T_0}{T} \frac{1}{d+1} \right].$$

The latter step implies the assumption of variable-range hopping, the case we will focus on. Additionally, the length-scale $\xi_{dc}(\beta)$ determines the onset frequency $\omega_s \sim \exp\left[ -\xi_{dc}(\beta) \right]$. For AC conductivity there will be an analogous largest length scale $\xi_{ac}(\beta, \omega)$, which through the single-hop rate is determined by the applied frequency $\omega$ of the electric field. So, in order to have an AC conductivity we need a frequency such that $\xi_{ac}(\beta, \omega) < \xi_{dc}(\beta)$, i.e. $\omega > \omega_s$. If we claim that we are in the ’multiple hopping’ regime, we can rewrite Eq. (9.7) as

$$\sigma(\beta, \omega) \sim \left[ \sigma(\beta, 0) \right]^{1-n} \omega^n \sim \exp\left[ -(1-n)(T_0/T)^{1/(d+1)} \right] \omega^n. \quad (9.8)$$

Realizing that for $\omega > \omega_s$, $\sigma(\beta, \omega)$ should be finite if $T \to 0$ and that the coefficient of $\omega^n$ does not dependent on temperature, we find $1-n \propto (T_0/T)^{1/(d+1)}$, as stated by Hunt [229]. So, in fact the vanishing of $\sigma(\beta, 0)$ and $\omega_s$ cancel each other in Eq. (9.7), which leads to the expression for $n$.

Arguments reminiscent of the derivation of an expression with a similar structure as Eq. (9.7) have been first used by Straley [231], Efros and Shklovskii [232], and Bergman and Imry [233] in the case of a mixture of a conductor and a dielectric. They find for the effective bulk conductivity of the heterogenous mixture:

$$\sigma(\phi, \omega) = \sigma_2 |\phi - \phi_c|^t \mathcal{F}\left( \frac{i \omega \epsilon_1}{\sigma_2 |\phi - \phi_c|^{s+t}} \right), \quad (9.9)$$

with $\mathcal{F}$ a homogeneous scaling function, $\phi$ the volume fraction of the conductor and $\phi_c$ the percolation threshold, and both $\epsilon_1$ and $\sigma_i$ some pre-factors. The expression in front of the homogeneous scaling function $\mathcal{F}$ is to be identified as the DC conductivity of the heterogeneous mixture $\sigma(\phi, 0)$. From this expression they prove that at the singular point $\phi = \phi_c$ the effective conductivity behaves like

$$\sigma(\phi, \omega) \sim \mathcal{G}(0) \sigma_2 \left( \frac{i \epsilon_1 \omega}{\sigma_2} \right)^u, \quad (9.10)$$

with $u = \frac{1}{s+t}$ and $\mathcal{G}(x) = x^s \mathcal{F}(x^{t-s})$. The argument is the following. The effective conductivity must be finite at $\phi = \phi_c$ and exhibit a power-law dependence on $\omega$. As such
it should be independent on $|\phi - \phi_c|$, leaving the only possibility for the power of $\omega$ to be $u = \frac{t}{s+t}$.

If we now once more analyze both approaches we observe a striking similarity. By replacing the expression for the singular point $\phi \to \phi_c$ with $T \to 0$ we note that the way of reasoning is equivalent. A pre-factor to be identified with the DC conductivity and a certain length-scale (or time-scale) in order to have AC conductivity must cancel each other from the dependence of the singular point.

## 9.7 Conclusions

We have investigated the existence of scaling for the AC conductivity in a two-dimensional system consisting of fermions that are allowed to hop variable range and experience asymmetric transition rates. The trend to a universal AC conductivity curve is observed and is compared with the universal curve obtained by simulations of a random barrier model by Schröder and Dyre. The comparison is very good up to $\Omega \equiv \omega/\omega_s = 10^4$, for larger values of $\Omega$ we find a smaller slope. But on the basis of Fig. 9.5, where we show the temperature dependence of the slope, we may conclude from the extrapolations to lower temperatures that the same Master-curve as for the random barrier model will be recovered. Moreover, we have derived an expression for the temperature dependence of the slope from analytical arguments.
Chapter 10

Exciton dynamics in a dye-doped polymer system

ABSTRACT

A promising way to fabricate full-color polymer displays is the use of polymer-dye blends as emissive layers, wherein the electronic excitations are created on the polymer and transferred to the dye, resulting in the specific emission properties of the latter. The transfer of photoexcitations to the dye, when dye-doping a polymer, has been studied by means of Monte-Carlo simulations. The polymer-dye blend is modelled as an energetically disordered system with a Gaussian density of states representing the polymer, and randomly distributed traps representing the dye molecules. The excitation-energy transfer is assumed to be Förster-type. We study the influence of the dye molecules on the time-dependent rest-emission spectrum of the polymer. The spectrum is found to become asymmetric and red-shifted with increasing dye concentration, in agreement with experiment. The implications for the efficiency of these blends in electroluminescent devices are discussed.
10.1 Introduction

The discovery of electroluminescence in conjugated polymers [19] has initiated a lot of activity in the field of conjugated polymers both in academia and industry, because of the possible application in display technology. Nowadays, the first commercial applications of monochrome polymer light-emitting displays (pLEDs) are a fact, and research focuses on the development of full-color polymer displays. However, the fabrication and processing of three different polymers for the three principal colors is rather difficult and costly. To circumvent these problems a substantial research effort is put into the incorporation of dye molecules in the polymer layer [45, 46, 47, 48, 49, 50, 51, 52]. Other benefits of using dye molecules as emission centers are their narrow emission bandwidth, leading to a high color purity, and the possibility to fine-tune their emission wavelength by attaching different sidegroups [107]. Put together, all these properties make these blends excellent candidates for full-color pLEDs.

The functionality of a dye-doped polymer is based on the transfer of electronic excitations from the polymer to the dye. Depending on the alignment of the Highest Occupied/Lowest Unoccupied Molecular Orbital (HOMO/LUMO) between polymer and dye, charged excitations (holes/electrons) may be trapped by the dye [107]. Although this can be an additional mechanism for the transfer of excitation energy from polymer to dye, we will focus in this paper on the transfer of photoexcitations (excitons) [50]. The latter transfer occurs quite effectively via the long-range Förster mechanism [108], whereas charge transfer occurs via a short-range hopping mechanism.

Polymers are highly disordered molecular solids and due to the more or less random positions of the chemical and conformational defects there is a broad distribution of effective conjugation lengths of the chain segments. This distribution of conjugation lengths translates into an inhomogeneously broadened density of states (DOS) for the excitons, which is generally taken to be a Gaussian. Once an exciton is formed within this DOS it will relax by Förster transfer towards states with lower energies [115, 111]. As a result, after each relaxation step the energy of the exciton is on average lower and hence the probability to again find a state with a lower energy decreases, because of the lower density of these states. Accordingly, the diffusion constant of the excitons is time-dependent, leading to what is called “dispersive transport” [116, 117, 113, 114, 87].

Generally, energy transport in an energetically disordered landscape is modelled as incoherent hopping between localized states [113, 114]. In recent studies [111, 253, 254, 255, 256] dispersive relaxation dynamics of excitons in a disordered polymer was studied. In [111] this was done by Monte-Carlo simulations, where, in particular, the average and the width of the energy distribution of the excitons as a function of time was investigated and good agreement with time-resolved fluorescent spectroscopy experiments was obtained. In the present study we will employ similar simulation techniques to study the dynamics of excitons in a polymer system, but doped with dye molecules. We will study how the presence
of the dye molecules influences the energy distribution of excitons and discuss the efficiency of photoexcitation transfer from polymer to dye.

## 10.2 Computational details

In our Monte-Carlo simulations the disordered polymer-dye system is modelled by a regular cubic lattice consisting of 100x100x100 sites with a lattice constant $a$ and periodic boundary conditions. The excited-state energies $\varepsilon$ of the sites are statistically distributed according to a Gaussian probability density with standard deviation $\sigma$:

$$g(\varepsilon) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left(-\frac{\varepsilon^2}{2\sigma^2}\right).$$

(10.1)

Like in Ref. [111] we take $\sigma = 70$ meV. The sites for the dyes are chosen randomly with a total number determined by an imposed dye fraction. These sites are given a fixed large negative energy, meaning that it is favorable for the exciton to jump from the polymer to the dye, but that the reverse process is blocked. It has been shown that this situation corresponds to the optimal condition for energy transfer, despite the fact that the spectral overlap of the emission spectrum of the polymer and the absorption spectrum of the dye might not be optimal [50]. Förster-type energy transfer via dipole-dipole coupling between a donor and an acceptor [108] is assumed to be responsible for the transport of the excitation. The transfer rate $W_{ij}$ for hopping from a site $i$ to $j$ is then supposed to be of the form

$$W_{ij} = \begin{cases} 
  k_0 \left(\frac{R_0}{R}\right)^6 \exp \left[-\frac{\varepsilon_j - \varepsilon_i}{kT}\right], & \varepsilon_j > \varepsilon_i \\
  k_0 \left(\frac{R_0}{R}\right)^6, & \varepsilon_i > \varepsilon_j
\end{cases}$$

(10.2)

where $k_0$ is the inverse lifetime of the excitons and $R_0$ is the so-called Förster radius. The latter is a characteristic property of a donor-acceptor system and depends on the refractive index $n$ of the medium, $\kappa$ the relative orientation of the donor and acceptor dipoles with respect to each other, the fluorescence quantum yield $\phi_D$ in the absence of an acceptor, the spectral-overlap integral $I$ (degree of spectral overlap between the molar absorption spectrum of acceptor and emission spectrum of donor), and Avogadro’s constant $N_A$ [108, 252]:

$$R_0^6 = \frac{9000(\ln 10)\kappa^2 \phi_D I}{128\pi^3 N_A n^4}.$$ 

(10.3)

In our simulations for intra-polymer hopping we set $R_0 = 2a$, which roughly corresponds to the experimental situation [111]. $a$ is then to be interpreted as the average distance between two neighboring chain segments. Like in Ref. [111] we take $R_0$ constant, meaning that all sites within the polymer are equivalent. For reasons of simplicity we take the same value $R_0 = 2a$ for the transition from polymer to dye. In real polymer-dye blends the Förster radius $R_0$ for transfer within the polymer is indeed comparable to that for transfer
from polymer to dye [50]. However, a small change in $R_0$ will have a large effect on the transfer rate $W_{ij}$, in view of its proportionality to $R_0^6$, Eq. (10.2). In particular this means that our predictions have in the first place a qualitative meaning and care should be taken when making a comparison with a specific polymer-dye blend.

At the start of a simulation the exciton is given a certain initial energy and is placed on a polymer site corresponding to that energy. During the simulation a subcell of 15x15x15 sites around the exciton at site $i$ is defined and for each site within the subcell the probability for hopping from site $i$ to site $j$ given by Eq. (10.2) is calculated. The normalized probability that an exciton jumps from site $i$ to any site $j$ within the subcell is

$$P_{ij} = \frac{W_{ij}}{\sum_{i \neq j} W_{ij}} \equiv W_{ij} \tau,$$  \hspace{1cm} (10.4)

with $1/\tau$ the total transition rate for the exciton to jump from away from $i$. The possible hop to each site $j$ in the subcell is given a length $P_{ij}$ on the interval $(0,1)$. To decide for a particular hop we take a random number $x$ from a uniform distribution on the interval $(0,1)$, which specifies to which site $j$ the exciton jumps. The waiting time $t$ between the consecutive hops is drawn from the exponential distribution

$$P(t) = \frac{1}{\tau} e^{-t/\tau}. \hspace{1cm} (10.5)$$

We stop the simulation when the exciton reaches a dye site.

## 10.3 Results and Discussion

The outline of this section is as follows. First, in subsection A, we examine the influence of dyes in a polymer on the time dependence of the energy distribution of the excitons, which is related to the rest-emission of the polymer. Next, in subsection B, the capture rate for excitons by the dye molecules will be calculated and the efficiency of electroluminescent devices of polymer-dye blends as a function of the dye concentration will be discussed.

### 10.3.1 Time dependence of the exciton energy distribution

In Figure 10.1 we plot the fraction of excitons left in the polymer as a function of time for different dye concentrations. We did not take into account the effect of the finite lifetime $\tau$ of the excitons, which would lead to a trivial multiplication by $\exp(-t/\tau)$. We started the simulations with all excitons at an energy $E = 0$ at $t = 0$. In Figure 10.2 the average energy of the excitons left in the polymer, $\langle E \rangle$, is shown as a function of time for various dye fractions in the polymer matrix. For low dye concentrations (0.05%) the relaxation process does not differ much from the relaxation of an all-polymer system (i.e. no dyes).
A red shift in time is observed because of the relaxation of the excitons to lower energy states, as shown in literature [115, 111]. With increasing dye concentration one observes an additional red shift after approximately 20 ps towards lower energies. The reason for this is that high-energy excitons (i.e. excitons at the high-energy tail of the Gaussian distribution) move faster than the low-energy excitons, because the high-energy excitons have more states available to hop to than the low-energy excitons. Hence, mainly the
high-energy excitons are captured by the dye molecules, leaving the low-energy excitons in the polymer. In the inset of Figure 10.2 we have drawn the standard deviation $\sigma_E$ of the energy distribution, which shows no significant dye-concentration dependence.

![Graph showing energy spectra](image)

**FIGURE 10.3:** Evolution of the energy spectrum of the excitons left on the polymer in a dye-doped system after two different times for different dye concentrations. The intensities of the spectra are normalized according to the number of excitons still present in the polymer. Average over 10,000 runs.

In Figure 10.3 we show energy spectra for three different dye concentrations at two distinct times $t = 50$ ps and $t = 400$ ps. The spectra have been normalized with respect to the number of excitons still present in the polymer. The absolute spectra can be obtained by combining the results in this figure with those of Figure 10.1. At $t = 50$ ps the shape of the spectra is the same for all dye concentrations, but the intensities are different. On the other hand, at $t = 400$ ps the spectra have become asymmetric, and different red shifts are observed for different dye concentrations. The asymmetry of the spectra apparently does not affect the standard deviation of the energy, see inset in Figure 10.2.

### 10.3.2 Comparison with experiment

In this section we will compare the above-mentioned observations for our simulations with experimental results. The experiments have been performed on polymer-dye blends consisting of dye molecules, synthesized at TNO Industrial Technology, and a yellow-PPV host matrix [50, 257]. The structures of the polymer and the dye are shown in Figure 10.4. In Figure 10.5 we show the results of a typical time-resolved photoluminescence experiment for different dye concentrations at two different times $t = 50$ ps and $t = 550$ ps. Like we found in the simulations, all graphs overlap at $t = 50$ ps, while at $t = 550$ ps we find a red shift. In order to clarify the differences and similarities in the spectra we have given them an offset. To further analyze the red shift resulting from the bare polymer system.
FIGURE 10.4: The structural formula of the yellow emitting PPV-based host (yellow-PPV) polymer (I), and of the 3,5-diaryl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene-based dye (II).

FIGURE 10.5: Experimental time-resolved electroluminescence spectra for a dye-doped system after two different times $t = 50$ ps (left) and $t = 550$ ps (right) for different dye concentrations. The intensities of the spectra are normalized according to the rest-emission of the polymer. All spectra have been given an offset to better indicate the differences and similarities. In the right figure we included the spectrum for zero dye concentration at $t = 50$ ps in order to visualize the red shift for the bare polymer system.

and from the dyes present in the system, we have also plotted in Figure 10.5 for the graph representing $t = 550$ ps, the the spectrum for zero dye concentration at $t = 50$ ps for the bare polymer system. The red shift of the bare polymer system can now be obtained by comparing the two graphs for zero dye concentration at $t = 50$ ps and at $t = 550$ ps. A clear red shift due to the relaxation of the excitons to the lower-energy states is observed. Furthermore, we find an additional red shift as a function of the increasing dye concentration of about 0.2 eV. This value is smaller than the value of 0.5 eV we find in our
simulations; we will elaborate on this finding later. We have checked that the observed red
shift due to increasing dye concentration is not resulting from the growing peak at the red
part of the spectrum, which shows the increase in the emission of the dye molecule. The
emission spectrum of the bare dye does not show significant luminescence below 600 nm.

10.3.3 Efficiency of polymer-dye systems

To define the efficiency of a polymer-dye system one has to realize that two different mech-
anisms can be operative in the decay of an exciton. First, capture by a dye molecule may
happen. This process has been discussed in the previous section. Second, natural radia-
tive and non-radiative decay of an exciton may occur before it reaches a dye molecule.
Our interest is in the amount of excitons captured by the dye molecules before radiative
decay on the polymer happens, since this leads to emission of photons with the desired
wavelength. This brings us to a question of practical importance, namely residual polymer
emission. As a result of the variable color sensitivity of the human eye, any small amount
of green emission in a primarily red-emitting environment will lead to the perception of
an orange color. Hence, it is important that if such a combination is used in a pLED
the residual green emission is heavily suppressed. In this section we will discuss the effi-
ciency of exciton capture by the dye molecules for two situations: photoluminescence and
electroluminescence.

The simulations are performed in the same way as described in Section II, apart from the
fact that the simulation time, $t$, is now chosen from an exponential distribution

$$P(t) = e^{-t/\tau_{lff_e}}$$

with $\tau_{lff_e} = 300$ ps. The maximum simulation time is set to 2 ns. Furthermore, the
simulations are stopped if either the exciton is captured by a dye molecule or decays
at time $t$. The efficiency is defined by the fraction of excitons that is captured by the
dye molecules. To simulate electroluminescence, the starting energies of the excitons are
chosen to be distributed according to the Gaussian DOS. In the case of photoluminescence
experiments we are left with one more degree of freedom, namely the starting energy $E_{start}$
representing in experiments the laser excitation frequency. In our simulation we mimic
this by putting all excitons in the polymer at a single energy (denoted as $E_{start}$). Note
that both in the case of electroluminescence and of photoluminescence we assume eventual
decay of the exciton on the dye molecule.

Photoluminescence

The basic parameters that determine the exciton dynamics in a polymer-dye system in
the case of photoluminescence are: the disorder parameter $\sigma/k_BT$, the starting energy of
the excitons $E_{start}$, and the concentration of dye molecules. In Figure 10.6 the influence


of all three different parameters on the efficiency is shown for dye concentrations 0.5% and 1.0%. From the data with dye concentration of 0.5% it is clear that for low starting energies \((E_{\text{start}} \leq -3\sigma)\) there is a higher threshold temperature \((\approx 300 \, \text{K})\) at which the efficiency starts to increase than for the higher starting energies. The reason is that there is not enough thermal energy available for the exciton to make an upward jump in energy to escape from a low energy position. This results in a low (more or less constant) mobility of the excitons, which in its turn accounts for the low efficiency. As a result the threshold temperature increases as a function of decreasing starting energy. For \(E_{\text{start}} > -3\sigma\) all curves have a threshold temperature \(\approx 100 \, \text{K}\) after which the efficiency starts to rise. All efficiency differences disappear at the highest temperature. For low concentrations (0.1%) the efficiency difference between low and high starting energy more or less disappears and the dependence of the threshold temperature on \(E_{\text{start}}\) is less pronounced. Apparently the temperature is the most important parameter at low concentrations.

**Electroluminescence**

For electroluminescence there are only two parameters that determine the dynamics of the excitons, namely the disorder parameter \(\sigma/k_BT\) and the concentration of dye molecules. In Figure 10.7 we have shown the influence of these two parameters on the efficiency. It is observed that the trends in the electroluminescence efficiencies are very similar to those of photoluminescence efficiencies for \(E_{\text{start}} = 0\). Again there is a threshold temperature of about 100 K after which the efficiency shows a considerable increase as a function of temperature. At room temperature an efficiency of 45% is obtained for 0.5% dye concentration. This efficiency is lower than found in the specific blends studied in Ref. [50], which...
has to do with the fact that we have assumed the spectral overlap for polymer-to-polymer and polymer-to-dye Förster transfer to be equal, see the discussion after Eq. (3).

### 10.4 Summary and Conclusions

By means of Monte-Carlo simulations we have studied the influence of dye-doping a polymer on the transport of excitons in the polymer and their capture by the dye molecules. We have assumed that the excitation transfer is Förster-type, with an equal Förster radius for transfer within the polymer and from polymer to dye. First, we addressed the influence of the dye concentration on the time-dependent rest-emission spectrum of the polymer. The spectrum was found to become asymmetric and red shifted with increasing dye concentration, which is in agreement with experiment. Next, we studied the efficiencies of transfer of the excitons from the polymer to the dye in photoluminescence and electroluminescence. For a dye concentration of 0.5 % we found an electroluminescence efficiency of 45 % at room temperature. When comparing this value to experiments, one should realize that the efficiency depends very much on the specific ratio of the Förster radii for intra-polymer and polymer-dye transfer. The same same holds for the comparison of the experimental red shift observed in Figure 10.4 and the calculated red shift as given in Figure 10.3. Therefore, the present study should be considered as a first step. With specific information about the ratio of the Förster radii more realistic simulations can in principle be performed.
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Summary and conclusions

The goal of this thesis was to present a unified picture of the charge and energy transport properties in disordered π-conjugated systems. The approach was both on the level of the electronic properties and on the level of the disorder.

On the level of the calculations of the electronic properties, we have used ground-state density-functional theory (DFT) calculations for polymer-dye blends to study the effect on the HOMO and LUMO energies when substituting different sidegroups of specific dye molecules. The results compare very well with the outcomes from cyclic-voltammetry measurements. Moreover, we show that by calculating the HOMO and LUMO energies of two polymers we can make predictions about the occurrence of charge and/or energy transport between the two polymers and the dye molecules by comparing the calculated HOMO/LUMO energies of the polymers with those of the different dye molecules. We have also calculated optical gaps of these dye molecules using time-dependent (current) density-functional theory TD(C)DFT, in order to see how the results of the different theories and the experimental data compare with each other. The issue of the comparison between the two theories was one of the main reasons to do these calculations. TDCDFT is a new method and its applicability to the large systems we have investigated has never been tested. The results of our calculations are not always satisfactory, from which we conclude that certain improvements are needed.

On the level of the disorder involved in π-conjugated systems, the focus has been especially on the influence on the charge-carrier mobility of the following parameters: the charge-carrier density (or doping), the temperature, the electric-field strength, and the frequency of an applied electric field. The current state-of-the-art regarding the temperature and electric-field dependence of the mobility is the work of Bässler and coworkers, whereas regarding the frequency dependence it is the work of Dyre and Schrøder. One of the puzzling features about the temperature dependence of the mobility was the fact that in the same polymer different dependencies were observed. These dependencies were interpreted in terms of models based on different types of energy disorder, which is of course not a satisfying idea. One of the major problems was that it was not possible to study the combined effects of changing charge-carrier density, temperature, and electric-field strength in a large parameter range. The present work has changed this situation. From our newly developed method to analyze the mobility, based on a numerically exact solution of the
Summary

Pauli Master-equation, we are able to cover a large parameter space. In our description we take into account variable-range hopping, site energy disorder, and the Pauli principle. With our method we can now study and distinguish all the effects due to charge-carrier density, temperature, electric-field strength, and frequency of the applied electric field. In addition to the numerical work, we have developed a couple of new analytical theories. We will now summarize our most important results on charge transport:

• We have developed an analytical generalization of Mott’s theory for variable-range hopping, in order to describe the temperature and (chemical) doping dependence of the conductivity. When applied to experimental data this theory gives an excellent description of the data. With the help of this theory it is possible to obtain insight into the strong doping dependence of the conductivity, as observed in experiments, by relating it to two dominant effects: an increasing density of states at higher doping concentrations and a growth of the regions in which the carriers are localized.

• With the Pauli Master-equation approach we have been able to describe the temperature, charge-carrier density, and electric-field dependence as observed in experiments. We are now able to identify the regime where earlier found results by Bässler and coworkers for the temperature dependence are valid. Even more importantly, we can predict where, why, and how deviations will start to appear, which turns out to depend strongly on the charge-carrier density under consideration. As a final test, we have used our results to model the experimentally determined current-voltage characteristics of hole-only devices. From the comparison it follows that our results excellently describe the experimental data, but only if we take into account the full carrier-density, temperature, and electric field dependence of the mobility.

• From the numerical solution of the Pauli Master-equation we can perform a detailed analysis of the microscopic origin behind variable-range hopping. The most important aspect is that the data reveal a hitherto never reported scaling of the temperature-dependent mobility in \((R, \varepsilon)\) space, where \(R\) is the hopping distance and \(\varepsilon\) the hop energy. The numerical findings are rationalized and we postulate a new analytical scaling theory of variable-range hopping. Another important outcome is that from a comparison with a theory based on percolation arguments for random-resistor networks, which is regarded to be the formal foundation of variable-range hopping theory, it was shown that the identification of the temperature dependence of the mobility with that of the conductivity of the resistances at the percolation threshold is not correct.

• We show a scaling behavior for the AC conductivity in the extreme-disorder limit when variable-range hopping, asymmetric transition rates and the fermionic character of the charge carriers are included. The obtained Master-curve for the AC conductivity is compared to the one obtained by Dyre and Schroder within a random-barrier model (only symmetric transition rates and nearest-neighbor hopping taken into account), and we conclude that the two curves seem to be the same. The issue about the existence of a master curve for our model and (if it exists) how it compares to that of the random-barrier model has been an open question in literature that has been settled by the our work.

Concerning energy transport in disordered \(\pi\)-conjugated systems, we present results that
should be considered as a first step towards simulating the operation of a device in the case of a polymer-dye blend. The influence on the exciton dynamics due to the presence of dye molecules in a polymer matrix was studied by Monte-Carlo simulations. The trends in the efficiencies of electro- and photoluminescence as a function of temperature and dye concentration are found to be in qualitative agreement with experiment.
Samenvatting

Het doel van dit proefschrift was om te komen tot een universeel beeld aangaande de eigenschappen van het lading- en energietransport in wanordelijke π-geconjugeerde systemen. De gevolgde aanpak was zowel op het niveau van de elektronische eigenschappen als op het niveau van de wanorde.

Om berekeningen te doen op het gebied van de elektronische eigenschappen is gebruik gemaakt van dichtheidsfunctionaal theorie berekeningen. Voor polymeer-kleurstof mengsels is het effect op de energieniveaus van de hoogste bezette moleculaire orbitaal (HOMO) en laagste onbezette moleculaire orbitaal (LUMO) bestudeerd wanneer van een specifiek kleurstof-molecuul verschillende zijgroepen worden gesubstitueerd. De berekende resultaten komen zeer goed overeen met de uitkomsten van cyclische-voltammetrie metingen. Bovendien zijn we in staat door de HOMO en LUMO energieniveaus van polymeer en kleurstof met elkaar te vergelijken. Verder hebben we ook de optische bandkloof van deze kleurstof-moleculen berekend door gebruik te maken van tijdsafhankelijke (stroom)-dichtheidsfunctionaal theorie berekeningen. Deze berekeningen zijn uitgevoerd om inzicht te krijgen in hoe de twee theorieën zich met elkaar en met experimentele data vergelijken. Inzicht in hoe de twee theorieën zich met elkaar laten vergelijken was één van de belangrijkste redenen om deze berekeningen uit te voeren. Tijdsafhankelijke stroom-dichtheidsfunctionaal theorie is namelijk een nieuwe methode en de toepasbaarheid op systeemgroottes zoals door ons bekeken is nog niet eerder onderzocht. De resultaten van de berekeningen zijn niet altijd bevreidelijk, waaruit geconcludeerd wordt dat verbeteringen noodzakelijk zijn.

Op het niveau van de wanorde aanwezig in π-geconjugeerde systemen is gefocusséerd op de invloed op de mobiliteit van de ladingstragers als functie van de volgende parameters: de dichtheid van ladingstragers (of de hoeveelheid dotering), de temperatuur, de sterkte van het elektrische veld en de frequentie van het aangelegde elektrische veld. De huidige state-of-the-art wat betreft de temperatuur en elektrisch veld afhankelijkheid is het werk van Bässler en collega’s. Wat betreft de frequentie afhankelijkheid van het elektrische veld zijn dit de berekeningen gedaan door Dyre en Schröder. Aangaande de temperatuur-afhankelijkheid was één van de problemen waarom voor hetzelfde polymeer verschillende
afhankelijkheden gemeten worden. De uitkomsten konden verklaard worden door verschillende typen van wanorde in energie aan te nemen. Echter, dit stemt natuurlijk niet tot tevredenheid. Eén van de grootste problemen was dat het niet mogelijk was om in een voldoend groot parametergebied het gecombineerde effect van ladingsdichtheid, temperatuur en elektrisch veld op de mobiliteit te bestuderen. Het werk beschreven in dit proefschrift heeft hier verandering in gebracht. Met behulp van een nieuwe door ons ontwikkelde methode, gebaseerd op een numeriek exacte oplossing van de Pauli Master-vergelijking, is het mogelijk de mobiliteit te bestuderen over een groot parametergebied. In onze be-schrijving worden effecten meegenomen van sprongen over variabele afstanden (variable-range hopping), wanorde in de site energieën en er wordt ook rekening gehouden met het Pauli principe. Met deze methode is het nu mogelijk om de gecombineerde effecten van ladingsdichtheid, temperatuur, sterkte en frequentie van het elektrische veld te bestuderen, maar ook om ze te onderscheiden. Naast het numerieke werk hebben we ook enige nieuwe analytische theorieën ontwikkeld. De belangrijkste uitkomsten wat betreft het ladingstransport zijn:

- We hebben een analytische theorie ontwikkeld die een generalisatie is van de standaard Mott-theorie voor variable-range hopping. Deze theorie wordt toegepast om de experimenteel gevonden afhankelijkheid voor de geleidbaarheid als functie van temperatuur en chemische dotering te beschrijven. Het blijkt dat de theorie de data uitstekend beschrijft. Met behulp van de theorie is het mede mogelijk te begrijpen waarom een sterke doteringsafhankelijkheid voor de geleidbaarheid gevonden wordt. Deze afhankelijkheid is te relateren aan twee dominante effecten: een toenemende toestandsdichtheid voor de hogere doteringsconcentraties en een toename van het gebied waarover de ladingsdragers gelokaliseerd zijn.

- Met behulp van de numerieke methode om de Pauli Master-vergelijking op te lossen, is het mogelijk de ladingsdichtheids-, temperatuurs- en elektrisch-veld-afhankelijkheid van de mobiliteit te beschrijven zoals deze ook in experimenten gezien wordt. Op basis van onze resultaten zijn we in staat om het gebied waar de eerder gevonden resultaten van Bässler en collega’s geldig zijn, te identificeren. Bovendien kunnen we voorspellen waar, waarom en hoe afwijkingen zich zullen ontwikkelen. Dit blijkt zeer sterk afhankelijk te zijn van de ladingsdichtheid in kwestie. Als een laatste test voor de toepasbaarheid van de uitkomsten hebben we de resultaten gebruikt om de stroom-spanningskarakteristieken van een hole-only device te modelleren. Uit de vergelijking met de experimentele karakteristieken volgt dat we de experimenten uitstekend kunnen beschrijven. Echter, dit is slechts het geval wanneer de volledige ladingsdichtheids-, temperatuurs- en elektrisch veld afhankelijkheid van de mobiliteit wordt meegenomen.

- De numerieke oplossing van de Pauli Master-vergelijking geeft de mogelijkheid de achtergrond van variable-range hopping op een meer gedetailleerde manier te analyseren. De belangrijkste uitkomst van deze analyse is het feit dat er een nog nooit eerder gerapporteerd schalingsgedrag gevonden wordt van de mobiliteit in de $(R, \varepsilon)$ ruimte, waarbij $R$ de hop afstand en $\varepsilon$ de hop energie is. De numeriek gevonden resultaten worden beargumenteerd en een nieuwe analytische schalingstheorie voor variable-range hopping wordt gepostuleerd. Een ander belangrijk resultaat volgt uit de vergelijking met een theorie gebaseerd op perco-
latie argumenten voor een netwerk van random weerstanden. Deze theorie wordt gezien als de formele basis van de theorie van variable-range hopping. Uit deze vergelijking volgt dat het identificeren van de temperatuurafhankelijkheid van de mobiliteit met de temperatuurafhankelijkheid van mobiliteit van de weerstanden op de percolatie-drempel niet correct is.

- Er wordt schalingsgedrag aangetoond voor de AC geleidbaarheid in de limiet van extreme wanorde, waarbij we rekening houden met: variable-range hopping, een asymmetrische overgangswaarschijnlijkheid en het fermionische karakter van de ladingsdragers. De Master-curve die gevonden is voor de AC geleidbaarheid wordt vergeleken met de Master-curve gevonden door Dyre en Schröder voor een model (random-barrier model) waar alleen rekening gehouden is met sprongen naar naaste buren en symmetrische overgangswaarschijnlijkheden. De conclusie die wordt getrokken luidt dat de twee curves dezelfde lijken te zijn. De kwestie of er een Master-curve bestaat voor ons model en (als deze bestaat) hoe de vergelijking is met de curve voor het random-barrier model is een open vraag in de literatuur geweest die met ons werk beantwoord is.

Wat betreft het energietransport in wanordelijke π-conjugeerde materialen worden er resultaten getoond die dienen gezien te worden als een eerste stap tot een volledige simulatie van de werking van een polymeer-kleurstof device. De invloed van de kleurstof-moleculen, aanwezig in de polymere matrix, op de dynamica van de excitonen is bestudeerd met behulp van Monte-Carlo simulaties. De trends die gevonden worden in resultaten voor de efficiëntie van electro- en fotoluminiscents als functie van de temperatuur en de concentratie kleurstof-moleculen zijn in kwantitatieve overeenstemming met de experimenten.
List of Publications

*Crossover from space-charged-limited to recombination-limited transport in polymer light-emitting diodes*
H.C.F. Martens, W.F. Pasveer, H.B. Brom, J.N. Huiberts, and P.W.M. Blom

*Hopping transport in polythiophene versus poly(phenylene vinylene)*

*Excitons in conjugated polymers from first principles*
Comp. Phys. Comm. 147, 331 (2002)

*Understanding the doping dependence of the conductivity of conjugated polymers: Dominant role of the increasing density of states and growing delocalization*

*Relating substitution to single-chain conformation and aggregation in poly(p-phenylene vinylene) films*
Ab initio study of energy-level alignments in polymer-dye blends

Charge carrier properties below and above the metal-insulator transition in conjugated polymers - recent results

Temperature and field dependence of the mobility in 1D for a gaussian density of states
W.F. Pasveer, P.A. Bobbert, and M.A.J. Michels

Scaling in variable-range hopping
W.F. Pasveer, P.A. Bobbert, H.P. Huinink, and M.A.J. Michels

Monte-Carlo simulation of exciton dynamics in a polymer-dye blend
submitted to J. Phys. Chem. B

Scaling of ac conductivity: allowing Fermions to hop variable range in presence of site-energy disorder
W.F. Pasveer, P.A. Bobbert, and M.A.J. Michels
to be submitted to Phys. Rev. B

Temperature-, field and density-dependence of the mobility in disordered conjugated polymers: simulation versus experiment
W.F. Pasveer, J. Cottaar, P.A. Bobbert, and M.A.J. Michels
submitted to Synth. Met.
Energy-level alignments in polymer-dye blends
submitted to Synth. Met.

Calculation of excitation energies of complex dye molecules: TDDFT vs. TDCDFT
W.F. Pasveer, P.A. Bobbert, M.A.J. Michels, and P.L. de Boeij
to be submitted to J. Chem. Phys.

Modelling the temperature-, field and density-dependence of the mobility in devices based on disordered conjugated polymers
to be submitted to Phys. Rev. Lett.

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van Willem Franke Pasveer, geboren te Zwijndrecht op 6 november 1975.