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Horst, van der, J.W.

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The electronic and optical properties of conjugated polymers:

predictions from first-principles solid-state methods

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Chapter 1

Conjugated polymers: introduction

ABSTRACT

In this Chapter we give a short account of the chemistry and physics of the field of conjugated polymers, starting with the discovery of high conductivities in the late 1970s by Heeger, MacDiarmid and Shirakawa (for which they were awarded the 2000 Nobel prize in Chemistry) and ending with some potential and already realized applications. In spite of these commercially available applications, much of the physics of conjugated polymers is still ill-understood; we briefly sketch a number of problems, both technological and physical, and point out to which extent computational methods may be of use to resolve these issues.
FIGURE 1.1: Alan Heeger, Alan MacDiarmid and Hideki Shirakawa.

The 2000 Nobel prize in Chemistry was awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa "for the discovery and development of conductive polymers" [1]. Their discovery that polymers, commonly known as plastics, can be made electrically conductive [2], has created a new field, that of plastic electronics and optics.

1.1 The physics of conjugated polymers: in theory

We are used to the idea that polymers are insulators. And in fact, pristine polymers are: teflon has a room-temperature conductivity of $10^{-16}$ S/m, polyethylene (PE) of $10^{-12}$ S/m. The inorganic semiconductors silicon and germanium have conductivities of $10^{-2}$ and $10^{9}$ S/m, respectively, while true metals like lead, mercury, iron and copper have conductivities of $10^{4}$ to $10^{8}$ S/m. Undoped polyacetylene (PA), shown with some other polymers in Figure 1.2, has a conductivity of $10^{-9}$ S/m. Upon doping with $I_2$ or $AsF_5$ this can be increased by many orders of magnitude, to $10^{5}$ S/m.

Common to most conjugated polymers is the fact that a one-dimensional (1D) path of alternating short and long carbon-carbon bonds along the backbone of the polymer chain can be found. This is true even for ring-containing polymers like polythiophene (PT),

FIGURE 1.2: The repeat units of a number of conjugated polymers, from left to right: polyacetylene, polyphenylenevinylene, and polythiophene.
which looks like a deformed polyacetylene chain with intrachain sulphur-bridges, and polyphenylenevinylene (PPV), where the path along the chain has two branches on the ring, one going clockwise, the other counterclockwise.

It is this path of alternating long and short bonds, consisting of two and four electrons respectively, that creates the interesting properties of conjugated polymers. In PE, \((\text{CH}_2)_\infty\), each carbon atom in the chain has two hydrogen atoms bonded to it, and hence two electrons are left to form bonds with its carbon neighbors, so that all carbon-carbon bonds are single. This results in a very large one-particle band gap of \(\approx 9\) eV. If we remove one hydrogen atom per carbon, we get PA \((\text{CH})_\infty\), which then has only one hydrogen atom and two carbon atoms bound to it, and a free electron. Contrary to what might be expected due to the presence of a half-filled band, this structure is not metallic. Peierls [3] showed that this system is unstable with respect to a lattice dimerization. The polymer can lower its total energy by creating an alternating structure of short and long bonds, as shown in Figure 1.3. While this costs lattice energy, the gain in electronic energy makes up for this, creating a semiconducting polymer with an absorption gap of \(\approx 1.5\) eV. Most conjugated polymers have absorption gaps between 1.5 and 3.0 eV. We will come back to the question what the nature of this band gap is later in this Chapter.

The physical picture of the alternating long and short bonds is this: each carbon-carbon
FIGURE 1.4: Polymer LED. The (highly schematic) energy-level diagram on the right is rotated with respect to the schematic of the device over 90 degrees. The energies are in eV, without taking into account the applied bias of typically a few volts.

bond contains a σ-bond, located in the plane of the polymer backbone, and a π-bond, which is basically the overlap of the π-orbitals of the carbon atoms, extending perpendicular to the plane of the polymer (in Figure 1.3 this would be perpendicular to the paper; the hydrogen atoms would be in the plane of the paper). The overlap between the π-orbitals in the double, shorter, bonds is slightly larger than that in the single, longer, bonds. By doping this system, electrons (holes) can be inserted into the conduction (valence) band. This electron (hole) is then more or less free to move along the chain, by hopping from π-orbital to π-orbital, creating high conductivity. The fact that polymers can be made conducting or semiconducting means that they could be used, at least in principle, to replace traditional semiconductors in displays, integrated circuits and photovoltaic cells.

1.2 Applications

In this Section we will briefly discuss three applications of conjugated polymers, viz. light-emitting diodes, photovoltaic cells, and integrated circuits.

1.2.1 Light-emitting diodes and solar cells

With all due respect for the tremendous technological problems involved: the basic idea behind the polymer LED and the polymer solar cell (PVD, Photo-Voltaic Device) is the same, only the time-arrow is reversed. Put simply, in a LED electrons and holes are inserted, the electron and the holes form excitons, that decay and emit light. In a PVD,
FIGURE 1.5: Some applications of light-emitting conjugated polymers. From left to right: a polymer LED display (Philips Research, left) and a passive-matrix display of 180,000 pixels, each of which is a tiny polymer LED (CDT, right).

incoming light creates an electron-hole pair, and the electrons and holes are transported to separate electrodes, creating a current. Of course, things are far more complicated in realistic devices. First of all, in a LED a single emissive frequency is preferred, while in a PVD, a wide-band absorption, tuned to the solar spectrum, is preferred. Secondly, in a LED one would like the electron and the hole to recombine, while in a PVD, the opposite charges have to be transported to separate transport channels to prevent radiative decay.

A schematic lay-out of a polymer LED is given in Figure 1.4, together with a diagram of the electronic levels involved. Note that the picture on the right is rotated over 90 degrees with respect to the picture on the left. Electrons are injected by the calcium/aluminum electrode, holes by the transparent metal Indium-Tin-Oxide (ITO) and transported by a PEDOT-PSS (Polyethylenedioxythiophene-polystyrene sulfonic acid) layer. The electron and holes recombine in the poly-phenylene-vinylene (PPV) layer. By chemical modifications of the PPV layer, the emissive frequency can be tuned to the desired wavelength. As mentioned before, in a PVD the (time-)arrows are reversed.

Electroluminescence was first demonstrated in a conjugated polymer system in 1990 [4]. Since then, the first applications based on electroluminescent conjugated polymers have become available, as can be seen in Figure 1.5. The first successful polymeric PVDs were developed in the early 1990s as well [5], but commercially viable products have not been manufactured yet, as the solar-spectrum efficiency remains low (≈ 1%). Note that in the devices and schematics displayed in Figures 1.4 and 1.5, are not 'all-polymer', i.e., traditional metals are used for charge injection (retraction) in the LED (PVD), and the system is built on a glass substrate. The ideal of flexible displays, let alone one that can
FIGURE 1.6: Picture of flexible polyimide foil (top left) containing approximately 50 15-bit ICs (top right), each consisting of 326 transistors (bottom). See main text for details. Reproduced from Reference [7].

be rolled up, is not yet realized.

1.2.2 Integrated circuits

Much like conjugated polymers can replace traditional semiconductors in displays, as outlined in the preceding paragraphs, they can replace them in transistors, or arrays of transistors, integrated circuits (ICs), popularly known as 'chips'. A word of warning first. The minimum switching time of an electronic device is inversely proportional to the charge-carrier mobility; hence the operating, or clock, frequency of the device is proportional to the charge-carrier mobility. Therefore it is unlikely that conjugated polymers will replace single-crystalline silicon in central processing units. However, a clock frequency of up to $10^9$ Hz would suffice for low-end, high-volume applications: disposable (or more politically correct: recyclable) electronics for use in product tagging (no more waiting lines at supermarket check-out points) or identification (no more misplaced luggage at airports). For such applications, especially product tagging, a price of less than 10 euro cents, preferably less than 1 euro cent, is required.
Early demonstrations of conjugated polymers in logic gates date back to 1995 [6], but an all-polymer integrated circuit was first demonstrated in 1998 [7], shown in Figure 1.6. The device is built on a flexible polyimide foil, uses polyaniline (PANI) source and drain electrodes, a polythiophenevinylene (PTV) semiconductor, a polyvinylphenol insulator between PTV and top gate electrode (also PANI). The PANI electrodes in the second layer from the bottom are interdigitated; they do not short-circuit, as the PANI in between has been photochemically made insulating. As usual, the transistor can be switched between 'on' and 'off' by changing the gate voltage. The operating frequency of the displayed device is 30 Hz, which may be increased by using, for instance, a better polymeric semiconductor, or scaling down the size of the device.

1.3 The physics of conjugated polymers: in practice

Of course, reality is not as simple as sketched in the preceding Sections. Polyacetylene is virtually intractable experimentally and the samples degrade quite fast. Other polymers are not processable enough to be very useful in applications and have to be substituted with alkyl- (-C\textsubscript{n}H\textsubscript{2n+1}) or alkoxy- (-OC\textsubscript{n}H\textsubscript{2n+1}) sidegroups. Substituted or not, polymers do not form nice arrays of aligned 1D systems, but form a boiled-spaghetti structure, in which the chains are finite, but polydisperse, the rings are rotated around the connecting bonds and chemical defects are present. In other words, it is not quite clear if a certain effect that is measured is an intrinsic property of the chemical structure, or an extrinsic property, i.e., defect or disorder induced. Hence, a large number of properties of conjugated polymers and the devices based on them are still ill-understood also for that reason. To name just a few:

What are the effects of the substituents on the optical and electronic properties?

Alkyl chains are in fact short PE fragments, with a much larger electronic and optical gap than conjugated polymers. Therefore they do not alter the optical properties of the conjugated backbone directly. They can have large geometrical effects on the intra- and interchain order, hence influencing the electronic and optical properties, see below. In alkoxy-sidegroups, however, there is an oxygen atom directly attached to the chain, which is rather electro-negative and polarizable. This may be a contributing factor to the fact that the optical gap in alkoxy-substituted PPV is smaller by several tenths of an eV than that of alkyl-substituted, or non-substituted PPV [8, 9]. Similar effects occur in cyanosubstituted (-CN) PPV.

What are the effects of various levels of order on the electronic and optical properties?

Within each chain, the average angle between consecutive rings may vary. The angle depends heavily on the nature of the substituents on the ring, and on regularity of the substitution. Bulky substituents on consecutive rings will sterically hinder each other and
cause a larger average angle, limiting the effective conjugation length. This results in a shift of the excitation energies to higher energies, as the excitations involved are typically more localized, i.e., confined to a smaller volume. Moreover, the nature of the polymer chains and their substituents will also have an influence on the interchain order. Large substituents on twisted chains will prevent two polymer chains from being close together.

*If two, or more, conjugated backbones are close to each other, does this influence the electronic and optical properties?*

As two polymer chains come closer and closer together the wave functions will start to overlap, and hybridization will occur. This splits the energy levels of one- and two-particle excitations, changing the spectrum. This is a very important effect, since in general such hybridization results in a quenching of the luminescence, which is highly undesirable in LEDs.

*What factors contribute to electron/hole transport and trapping?*

It turns out that the mobility of electrons and holes in polymer devices is rather different: the hole mobility is in general several orders of magnitude larger. While this phenomenon has been attributed to trapping, the underlying mechanisms are not clear yet. An important second part of this question is: to what extent are measured mobilities intrinsic, and to what extent disorder or defect induced?

*Is a conjugated polymer a one-dimensional semiconductor or a molecular solid?*

Previously, we have described conjugated polymers as one-dimensional semiconductors. Alternatively, we might think of the polymer as a collection of molecules of varying conjugation length on which we have localized states, which couple only weakly to each other. In this molecular approach, the distribution of conjugation lengths leads to a distribution of excitation energies and hence the electronic and optical properties of conjugated polymers should be much like those of the associated oligomer compounds.

### 1.4 One-dimensional semiconductor or molecular solid

The two views mentioned in the last question in the previous paragraph, 1D semiconductor and molecular solid, lead to drastically different views of the elementary excitations in conjugated polymers, and fierce discussions are still ongoing [10, 11, 12]. The property in which all the discussion culminates is the exciton binding energy $E_b$, the binding energy of an electron-hole pair, created by either absorption or charge injection.

Three groups of scientists supporting different magnitudes of $E_b$ can be distinguished: the small binding energy group ($\sim 0.1$ eV or less; centered around the Santa Barbara group [13, 14]), the large binding energy group ($\sim 0.8$ eV or more; with the Utah group as the most prominent supporter [15]) and the intermediate binding energy group (0.4-0.5
eV; most European groups seem to belong to this group [8, 9]). All three groups have presented a large number of papers (see especially Reference [11] and references therein), both experimental and theoretical, to support their case, but even after more than ten years of discussion, no consensus has been reached. It is an elusive property; direct optical methods only sample the absorption gap $E_{\text{opt}}$, not the one-particle or band gap $E_g$. Hence the difference, $E_b = E_{\text{opt}} - E_g$ is not straightforwardly determined. A contributing factor to this continuing debate is that different magnitudes for $E_b$ are obtained using different methods, either experimental or theoretical.

$E_b$ is important from a fundamental point of view since if the exciton binding energy is small (less than 0.1 eV), the one-dimensional semiconductor picture applies and solid-state tight-binding models (like the Peierls model [3] for the bond-length dimerization in PA and the SSH model [16]) suffice to describe the electronic and optical excitations. In this case the Coulombic interaction can simply be neglected, and the absorption gap and the one-particle band gap coincide. If, on the other hand, $E_b$ is large (0.5 to 1.0 eV or more), a molecular exciton model, used to describe for instance excitations in molecular solids like anthracene, has to be used to describe the excitations, and the absorption gap is lower, by an amount $E_b$, than the one-particle gap $E_g$.

$E_b$ is important from a technological point of view since a small exciton binding energy would imply a small singlet-triplet splitting, which means triplet excitons require a relatively small spin-orbit coupling to be converted into singlet excitons. Since the singlet/triplet ratio for injected electrons and holes with random spin is 1/3, the theoretical maximum efficiency of polymer light-emitting devices in the low-binding-energy case would be 100%, rather than the 25% in the intermediate- or large-exciton-binding energy case, where efficient triplet-to-singlet conversion would be impossible. Moreover, in photovoltaic devices a small $E_b$ would facilitate the separation of charges.

It is interesting to note that there is one polymer, substituted poly-diacetylene (PDA, see Figure 1.2), for which there is no discussion about the magnitude of $E_b$. Estimates range from 0.45 to 0.55 eV, depending on the nature of the substituents [11, 17]. The reason that there is agreement for this polymer is that in this case, different experimental techniques do yield similar exciton binding energies. This in its turn is a result of the fact that high-quality crystals of PDA diluted in its monomer matrix can be made.

### 1.5 Modeling the electronic structure

In the preceding paragraphs, we have sketched a number of the problems related to the physics and technology of conjugated polymers and the devices based on them. The purpose of this thesis will be to model the intrinsic electronic and optical excitations of conjugated polymers using first-principles methods. Modeling of the electronic and optical properties of conjugated polymers is as old as the field itself. Since in PA, the Peierls di-
tortion [3] plays such a large role, the initial models, such as the SSH model [16], contain electron-lattice coupling and treat the electronic degrees of freedom itself by a (not self-consistent) tight-binding (in chemical terms: Hückel) approximation. More advanced ways to include electron-electron interactions are mainly based on quantum-chemistry methods, such as the Valence Effective Hamiltonian (VEH) [18], Möller-Plesset perturbation theory [19], and Configuration Interaction (CI) methods [20].

Some calculations have been carried out from first principles, but these become increasingly more expensive as the system size increases. While CI is a method that can in principle give exact results for all system properties, the reliability greatly depends on the input, the 'configurations'. Only if the energies of the configurations have been calculated from first principles, the results of the CI calculation can be considered ab-initio, which limits the system size to a few monomers. In fact, in most cases the system size is so limited, that a reliable extrapolation to the polymer is not possible. Our methods, originating from solid-state physics, are first-principles, or ab-initio methods. They are approximations of increasing complexity to the quantum-mechanical many-electron problem. They need no input from experiment and hence the results are not 'biased' to reproduce the experimental results.

The reason that methods from solid-state physics can deal with extended systems, while quantum-chemical methods cannot, is because of the different perspectives that solid-state physics and chemistry have. In solid-state physics, we look for the smallest possible repeating unit and apply periodic boundary conditions to it, thus creating an extended system. To study an extended system in quantum chemistry requires the consecutive adding of more and more of the repeat units, creating an ever larger system. Since the more advanced a method is, the worse its scaling in computer time as a function of the system size $N$, first-principles quantum-chemical calculations soon become computationally too demanding. In all fairness: when this project started four years ago, it was not quite clear to what extent the solid-state methods would be able to deal with the computational demand of these polymeric systems. It is interesting to note that while the essentials of the methods were developed in the 1960s, it took until the middle of the 1990s, before the first calculations for real systems were performed.

Another advantage of the solid-state based quantum-mechanical methods is that they do give good values, in a wide variety of systems, for the exciton binding energy, and the excitation energies. CI methods give good values for the excitation energies, even if the energies of one-particle excitations do not agree with experiment, e.g., if Hartree-Fock energies are used. Using 'bad' one-particle energies means that a one-particle gap is 'bad' in these calculations; since the exciton binding energy is the energy of the relevant excitation relative to the one-particle band gap, this binding energy is also 'bad'.

Our solid-state based methods, density-functional theory (DFT) for the ground-state atomic structure, the GW approximation for the one-particle (electron or hole) spectrum and the Bethe-Salpeter equation (BSE) for the two-particle (electron and hole) spectrum, have
been applied with great success to the electronic and optical properties of a wide variety of semiconducting and insulating systems of varying dimensionality: the Na$_4$ cluster [21], Li$_2$O [22], hydrogen-terminated Si clusters [23], Si [24, 25], diamond [24], Ge [24], LiF [26, 27], MgO [26], GaAs [24, 27], GaN [28], CaF$_2$ [28], Si surfaces [29], α-quartz [30], and Ge surfaces [31]. Conjugated polymers pose a new challenge to these methods, as the unit cells are relatively large and possess less symmetry than those of the systems mentioned before. This challenge is both computational, in terms of the amount of required resources, and conceptual, in terms of the straightforward applicability of the method.

This thesis can roughly be divided into two parts: part one, spanning Chapters 1 through 4, consists of this introduction and an extensive explanation of the theoretical methodology, including those methods that have been specifically developed to apply GW and the BSE to conjugated polymers; part two, consisting of Chapter 5 through 7, deals with application of these methods to the optical and electronic properties of conjugated polymers. Each Chapter in part two can be read independently, and also independent of the introductory part.

In Chapter 2 we will discuss the quantum-mechanical formalism used to describe the electronic and optical properties of conjugated polymers, as developed by Hohenberg and Kohn [32], Kohn and Sham [33], and Car and Parrinello [34] for the Density-Functional Formalism and ab-initio Molecular Dynamics; Hedin [35] for the GW formalism; Sham and Rice [36], and Strinati [37] for the Bethe-Salpeter equation.

Since conjugated polymer systems are quasi one-dimensional systems, i.e., they are extended in one direction only, a good and computationally affordable starting point for calculations is to study a single, isolated chain. As in this geometry the surroundings of the polymer, as present in the experiments that are performed on bulk samples, are not taken into account, we describe in Chapter 3 how the polarization effects of neighboring chains can be taken into account approximatively without having to perform calculations for a three-dimensional crystal.

A straightforward implementation of the formalism as outlined in Chapters 2 and 3 would not give a computationally feasible scheme, we explain the specifics of the implementation of the space-time formulation of the GW formalism (originally due to Rojas et al. [38], with adaptations by Rieger et al. [39]), our adaptations to it, and the implementation of the Bethe-Salpeter equation for conjugated polymers, in Chapter 4, a part of which appeared earlier [40].

In Chapter 5, parts of which appeared earlier [40, 41], we carefully study the effect of the surroundings of the polymer chain on its electronic and optical properties. First, three geometries of increasing computational complexity are studied for polythiophene: a single, isolated polythiophene chain in vacuum, a single chain embedded in a dielectric medium and a single-crystal. This latter calculation is repeated for polyphenylenevinylene.

The calculations in Chapter 5 show that while the GW calculation is necessary to obtain
the correct two-particle excitation energies, it is not required to obtain the correct two-particle binding energies for disordered polymer systems. Therefore we use only DFT and BSE calculations in Chapter 6, published earlier [42], skipping the time-consuming step of performing the GW calculations, to predict the exciton binding energies, polarizabilities and singlet-triplet splittings systematically for a large number of polymers, including polythiophene again, which yields good agreement with the calculations in Chapter 5, polyphenylenevinylene and polydiacetylene.

As we show in Chapters 5 that the polarization effects of the environment are dominant for quasi-one-dimensional systems, we can also use the method of Chapter 6 (i.e., the DFT and BSE calculations without the intermediate GW step) to study the properties of excitons on conjugated polymers chains in solution (specifically: the exciton polarizability and its lifetime) and compare them to experimental data obtained from flash-photolysis time-resolved microwave-conductivity and fluorescence decay measurements performed at the Interfaculty Reactor Institute of the Technische Universiteit Delft in Chapter 7, published in [43].

At the end a summary in English and een samenvatting in het Nederlands are included.
Chapter 2

Theoretical methods

ABSTRACT

The first-principles quantum-mechanical methods used in this work will be discussed. These are density-functional theory to calculate the ground-state geometry of the system, the GW approximation for the one-particle excitations (giving for instance the one-particle band gap) and the Bethe-Salpeter equation for the two-particle excitations (giving for instance the exciton binding energy). Two possible extensions of the present three-stage scheme, lattice relaxation and four-particle excitations (bi-excitons), and the magnitude of these effects in conjugated polymers, are briefly discussed.
The central question in the field of first-principles computational materials science is this: can we capture the essential physics of a system of \( \sim 6 \times 10^{23} \) interacting electrons and atomic nuclei in a computationally affordable scheme, and if so, how?

The answer to the first part of the question is, of course, 'yes'. Or rather, 'yes, with a proper definition of the essential physics'; in the past, much has been achieved in computational materials science by choosing the definition of 'essential physics' in such a way that it could indeed be captured. This is not a criticism; calculations that last more than a month are in practice not feasible and do not count as 'computationally affordable'. So, the size of the system studied is reduced and the complexity of the models used to describe it is reduced until the calculation takes a feasible amount of time, while retaining a maximum amount of essentiality: you do the best you can. Nowadays, we can describe larger systems with more complex equations than twenty years ago. New theories and algorithms have been developed, but just as importantly, computers are now a thousand times or more powerful than twenty years ago. Note that the 'essential physics' is not necessarily the same for all systems. For some systems, properties can be calculated on the back of an envelope; for other systems, or other properties, the 'essential physics' still has to be captured in a computationally affordable scheme.

The answer to the second part of the question is, in this thesis, 'by density-functional theory (DFT), by the GW approximation (GW or GWA), and by the Bethe-Salpeter equation (BSE)'. Since solving the latter also requires the former two to be done first, the method is in fact a three-stage rocket, which we will call DFT/GW/BSE. All three methods have in common that they map the quantum-mechanical many-electron problem, which is impossible to solve, onto effective one- or two-particle equations.

These three stages correspond to the following physical properties:

First, the precise ground-state structure of the polymer is calculated, using only a simple wireframe picture as input. That is: we give only the approximate bond lengths and angles as input. We perform this calculation within the local-density approximation (LDA) to DFT, which is known to give accurate bondlengths and -angles for covalent bonds.

Secondly, the one-particle, or quasi-particle spectrum, is calculated, i.e., the energies required to add or remove an electron (the latter being equivalent to adding a hole to the system) by solving the quasi-particle (QP) equation within the GW approximation.

As a third step, the interaction between an electron and a hole, present simultaneously, ignored in the previous step, is included by solving the Bethe-Salpeter equation for the two-particle (electron and hole) Green function, to obtain the two-particle, or optical, spectrum.

These theories are by no means the only, much less the ultimate methods of computational materials science. As we will see, for certain systems DFT/GW/BSE fails, and fails quite badly, missing energies of the order of 1 eV by 1 eV. Fortunately, this class of systems is well-defined, meaning that it can be predicted in advance whether the method will work or
not. Within the present, already quite strict definition of 'essential physics', these methods represent the state-of-the-art of the first-principles description of materials.

Of course, a myriad of quantum-chemical methods for the calculation of optical and electronic properties of molecules, clusters, and other finite systems exits. In many senses, these methods are more advanced than the ones presented here. However, the more advanced the scheme is, the smaller the system that can be considered due to very unfavorable scaling (often exponential) with the size of the system. As explained in the introduction, to be able to use these methods to describe larger system requires the use of semi-empirical methods, thus leaving the ab-initio path. We will not consider these methods in this Chapter, and only focus on DFT, GW, and the BSE and their history.

2.1 Before Density-Functional Theory

It all starts with the Hamiltonian for a many-electron (say $N$) system given by (in atomic units; $\hbar = e^2/(4\pi\varepsilon_0) = m_e = 1$):

$$
H = \sum_i \left[ -\frac{1}{2} \nabla_i^2 + V_{\text{ext}}(r_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \\
= T + V + U,
$$

(2.1)

where $T$, the kinetic energy, and $V_i$, the external potential (the potential of the nuclei, which we assume fixed to begin with, and possibly an electric field; it is assumed to be time-independent here) are the 'easy' parts, and $U$, the electron-electron interaction, the 'hard' part. The corresponding Schrödinger equation is:

$$
H \Phi = E\Phi,
$$

(2.2)

where $\Phi = \Phi(r_1, r_2, \ldots, r_N)$ with $r_i$ labeling both position and spin. The first approximation to solve this problem was made by Hartree, who proposed to write $\Phi$ as:

$$
\Phi(r_1, r_2, \ldots, r_N) = \phi_1(r_1)\phi_2(r_2)\ldots\phi_N(r_N),
$$

(2.3)

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

$$
\left[ -\frac{1}{2} \nabla_i^2 + V_{\text{ext}}(r_i) + V_{\text{H}}(r_i) \right] \phi_i(r_i) = \epsilon_i \phi(r_i),
$$

(2.4)

with $V_{\text{H}}$ the Hartree potential, given by:

$$
V_{\text{H}}(r_i) = \sum_j \int d r_j \frac{\phi_j(r_j)^2}{|r_i - r_j|}.
$$

(2.5)
Thus, the Hartree potential is the electrostatic field created by all electrons \( j \) acting on electron \( i \). By writing the wave functions as in equation (2.3), the many-electron problem formulated in Equation (2.1) and (2.2) has become an effective one-particle problem. An obvious deficiency of the approximation (2.3) is that it does not take the fermionic nature of the electrons, i.e., the fact that their wave function should be anti-symmetric with respect to exchanging two electrons, into account. This can be achieved by replacing the single wave function in (2.3) by a Slater-determinant:

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

(2.6)

By using this Ansatz for the many-body wavefunction and using the variational principle with the single electron wave functions \( \{\phi_i(r)\} \) as variational parameters, an extra, non-local term \( V_f \), the exchange interaction, is introduced in the Hartree-equation (2.4). The resulting set of equations is referred to as the Hartree-Fock equations. Since the Hartree-Fock equations for the wave functions contain potential terms that depend on these same wavefunctions, these equations have to be solved self-consistently, hence the name self-consistent-field (SCF), which is often used.

Hartree-Fock calculations for ground-state properties of molecules usually give fairly accurate results, in spite of the fact that no electron-electron correlation effects are taken into account. For extended systems the ground-state properties are also described fairly well, but the lack of correlation results in one-particle band gaps which are too large by a factor of two or more. Two major ways to include correlation effects beyond Hartree-Fock, without turning to a different schemes such as density functional theory, exist. The first is by Möller-Plesset perturbation theory (MP\(_n\), with \( n \) the order of the perturbation theory [19]), the second by taking more than one Slater determinant, called 'configuration', of the form (2.6) into account, resulting in a better approximation of the many-body wave function \( \Phi(r_1, r_2, \ldots, r_N) \). With this latter method, Configuration Interaction (CI) [20], the exact wave functions, of both ground and excited states, and from that all system properties, can in principle be obtained, but the amount of work involved for larger, or periodic, systems is prohibitive.

## 2.2 Structure: Density Functional Theory

At this point, it is fair to mention that before the basic equations of DFT, and the related one-particle equations, were derived by Hohenberg and Kohn [32], and Kohn and Sham [33], a simpler form of density-functional theory existed, the Thomas-Fermi approximation [44]. Not formally derived like DFT itself, it suffered from a number of serious drawbacks, and it has been superseded by DFT as it is known today. In the following, we will follow
the original formulation of Hohenberg and Kohn, which applies to a non-degenerate ground state only. Their formulation was later generalized by Levy [45] for the case of a degenerate ground state.\footnote{By following the Hohenberg and Kohn formulation, we restrict ourselves to $V$-representable densities, i.e., those densities that can be realized by some external potential. In the Levy formulation, all $N$-representable densities are allowed, i.e., all densities that can be realized by a certain anti-symmetric many-electron wave function. Note that, intuitively, for realistic systems only $V$-representable densities are relevant. Side note: the class of all $V$-representable densities is a subclass of the class of $N$-representable densities.} We will assume a non-spin-polarized electron gas only.

### 2.2.1 Formulation of one-particle equations

The problem at hand is the same as in the previous section, i.e., to solve the many-electron equations (2.1) and (2.2) for the ground state, with a fixed nuclei geometry. The density is given by:

$$n(r) = N \int d \mathbf{r}_2 \ldots \int d \mathbf{r}_N \Phi'(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \Phi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

(2.7)

It is clear, that once the external potential $V_{\text{ext}}(\mathbf{r})$ is given, the ground-state wave function $\Phi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is uniquely determined and hence also the ground-state density $n_0(\mathbf{r})$. The first theorem of Hohenberg and Kohn now states that the inverse is also true: given a certain $n_0(\mathbf{r})$, there is only one possible $V_{\text{ext}}(\mathbf{r})$ that can realize this ground-state density. The proof proceeds as follows: suppose we have two potentials $V_{\text{ext}}(\mathbf{r})$ and $V'_{\text{ext}}(\mathbf{r})$ that result in the same ground-state density $n_0(\mathbf{r})$ but different $\Phi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and $\Phi'_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$. Using bra- and -ket notation, we have because of the variational principle:

$$\langle \Phi_0 | H | \Phi_0 \rangle < \langle \Phi'_0 | H | \Phi'_0 \rangle = \langle \Phi'_0 | H' + V_{\text{ext}} - V'_{\text{ext}} | \Phi'_0 \rangle$$

$$E_0 < E'_0 + \int d \mathbf{r} [V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})] n_0(\mathbf{r})$$

(2.8)

But by interchanging the potentials, we also have:

$$E'_0 < E_0 + \int d \mathbf{r} [V'_{\text{ext}}(\mathbf{r}) - V_{\text{ext}}(\mathbf{r})] n_0(\mathbf{r})$$

(2.9)

Adding equations (2.8) and (2.9) we have:

$$E_0 + E'_0 < E'_0 + E_0$$

(2.10)

which is clearly absurd. The only way out is to assume that $\Phi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and $\Phi'_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, and $V_{\text{ext}}(\mathbf{r})$ and $V'_{\text{ext}}(\mathbf{r})$ are the same. Rephrasing, we have proved 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.

Note that this also implies that the ground-state wave function is also a functional of the ground-state density. To find this ground-state density, we write the expectation values of the kinetic $T$ and Coulomb terms $U$ in equation (2.1):

$$\langle \Phi | T + U | \Phi \rangle = F[n(r)],$$

where the square brackets have been used to indicate functional dependence, and $n(r)$ is some density, not necessarily the ground-state density, and $\Phi$ the corresponding wave function. We now introduce the functional:

$$E[n(r)] = F[n(r)] + \int dV_{\text{ext}}(r)n(r).$$

(2.12)

In Equation (2.12), $F[n(r)]$ is a universal functional of the density, as it does not depend on the external potential; the second term on the right-hand side of Equation (2.12) is, obviously, non-universal. If we now introduce a functional of the wave function:

$$\tilde{E}[\Phi] = \langle \Phi | H | \Phi \rangle = \langle \Phi | V | \Phi \rangle + \langle \Phi | T + U | \Phi \rangle = \int dV_{\text{ext}}(r)n(r) + \langle \Phi | T + U | \Phi \rangle.$$ 

(2.13)

According to the variational principle, $\tilde{E}[\Phi]$ is minimized for the ground-state wave function $\Phi_0$. Of course, $\Phi$ is the ground-state wave function corresponding to some external potential. With Equation 2.11, we then get:

$$\tilde{E}[\Phi] = \langle \Phi | H | \Phi \rangle = \int dV_{\text{ext}}(r)n(r) + F[n(r)].$$

(2.14)

For $\Phi = \Phi_0$ we have:

$$\tilde{E}[\Phi_0] = \langle \Phi_0 | H | \Phi_0 \rangle = \int dV_{\text{ext}}(r)n_0(r) + F[n_0(r)].$$

(2.15)

But because of definition (2.12) we have $\tilde{E}[\Phi] = E[n(r)]$ and $\tilde{E}[\Phi_0] = E[n_0(r)]$. Since $\tilde{E}[\Phi] > \tilde{E}[\Phi_0]$, we also have $E[n(r)] > E[n_0(r)]$. This is Hohenberg and Kohn's second theorem:

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

The considerations in the previous paragraphs are very nice, but have not yielded a practical computational scheme. The idea of Kohn and Sham is to rewrite the energy functional
of the interacting electron system in a certain potential as that of a non-interacting electron system in another, effective, potential:

\[
E[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) n(\mathbf{r}') + E_{\text{sc}}[n(\mathbf{r})]
\]

\[
= T_0[n(\mathbf{r})] + E_{\text{ext}}[n(\mathbf{r})] + E_{\text{H}}[n(\mathbf{r})] + E_{\text{sc}}[n(\mathbf{r})]
\]

(2.16)

where \(T_0[n(\mathbf{r})]\) is the kinetic energy of a non-interacting electron gas with density \(n(\mathbf{r})\), \(E_{\text{ext}}[n(\mathbf{r})]\) the interaction energy with external field, \(E_{\text{H}}[n(\mathbf{r})]\) the classical Coulomb interaction or Hartree energy, and \(E_{\text{sc}}[n(\mathbf{r})]\) the exchange-correlation (XC) energy. \(E_{\text{sc}}[n(\mathbf{r})]\) is basically the quantity in which we have gathered all the unknowns. Functional minimization with respect to \(n(\mathbf{r})\) yields:

\[
\frac{\delta E}{\delta n(\mathbf{r})} = \frac{\delta T_0}{\delta n(\mathbf{r})} + V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') + \frac{\delta E_{\text{sc}}}{\delta n(\mathbf{r})}
\]

(2.17)

By now defining:

\[
V_{\text{H}}(\mathbf{r}) = \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}')
\]

(2.18)

\[
V_{\text{sc}}(\mathbf{r}) = \frac{\delta E_{\text{sc}}}{\delta n(\mathbf{r})}
\]

(2.19)

\[
V_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{sc}}(\mathbf{r})
\]

(2.20)

equation (2.17) reduces to:

\[
\frac{\delta E}{\delta n(\mathbf{r})} = \frac{\delta T_0}{\delta n(\mathbf{r})} + V_{\text{eff}}(\mathbf{r})
\]

(2.21)

As we are now studying a (fictitious) system of non-interacting electrons, we can obtain the single-particle wave functions from the Kohn-Sham equations:

\[
\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}),
\]

(2.22)

with:

\[
n_0(\mathbf{r}) = \sum_i f_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}),
\]

(2.23)

where \(f_i\) is the occupation number of the one-electron state \(i\). The ground-state wave function is then obtained by taking Slater determinants of the one-electron wave functions \(\phi_i(\mathbf{r})\). We can now write the ground-state energy \(E_0\) as:

\[
E_0 = \sum_i \epsilon_i - \frac{1}{2} \int d\mathbf{r} V_{\text{H}}(\mathbf{r}) n_0(\mathbf{r}) - \int d\mathbf{r} V_{\text{sc}}(\mathbf{r}) n_0(\mathbf{r}) + E_{\text{sc}}[n_0(\mathbf{r})]
\]

(2.24)

\[
= E_{\text{KS}},
\]

(2.25)
where subscript KS stands for Kohn-Sham. Note that the problem is by no means solved now. We have of course come a long way by rewriting the single many-particle equation to many single-particle equations, but we have hidden the many-body interactions in the XC functional \( E_{xc}[n(r)] \). Just how useful this reformulation is, depends on the reliability and computational efficiency of approximations for \( E_{xc}[n(r)] \).

Rather than focusing on what we do not know, a good idea is to approximate \( E_{xc}[n(r)] \) by something that we do know: the exchange-correlation energy of the homogeneous electron gas. Of course, it is by no means clear that this approximation will yield reliable results for realistic systems, where regions with high and low density, often with large density gradients, are present. As a first approximation, we choose:

\[
E_{xc}^{\text{LDA}}[n(r)] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r})],
\]

(2.26)

where the superscript LDA refers to the name for this approximation, the local-density approximation, and \( \varepsilon_{xc}[n(r)] \) is the XC energy per electron of a homogeneous electron gas of density \( n(r) \), for which very precise quantum Monte Carlo results are available. It turns out that with this approximation, we can predict covalent and ionic bond length and angles with an accuracy of \( \approx 1\% \). In the present work, the Perdew-Zunger parameterization [46] of the Ceperley-Alder [47] Quantum Monte Carlo LDA will be used, unless mentioned otherwise.

A natural way to extend the approximation (2.26) is to include also a term which depends on the density gradient:

\[
E_{xc}^{\text{GGA}}[n(r)] = E_{xc}^{\text{LDA}}[n(r)] + E_{xc}^{\text{Correction}}[n(r), \nabla n(r)],
\]

(2.27)

Nowadays a myriad of different GGAs (Generalized Gradient Approximations), or equivalently GCs (Gradient Corrections) are available [48, 49, 50, 51, 52]. It turns out that by using these GGAs, the accuracy of DFT for describing bond lengths and angles, and cohesive energies is generally increased, giving the method the required precision to be used for the study of, e.g., chemical reactions and hydrogen-bonded systems.

Now that we have a reasonable to good approximation for the XC energy, we can perform calculations with the DFT scheme, that is, we can solve the Kohn-Sham equations (2.22) self-consistently, which in the end gives us a set of Kohn-Sham eigenvalues \( \epsilon_i \) and eigenfunctions \( \phi_i \). The physical meaning of these quantities is unclear: Hohenberg and Kohn, and Kohn and Sham, derived DFT and the Kohn-Sham equations, which are in principle exact, making statements about the total energy and the ground-state density only. Formally, this means that \( \epsilon_i \) and \( \phi_i \), which are the one-particle energies and wave functions of the fictitious non-interacting system, have no direct physical interpretation. It turns out that interpreting them as real one-particle energies and wave functions gives very good agreement with experiment for many systems, especially when only the occupied states, or valence states, are considered. Moreover, it turns out that in semiconductors and insulators the unoccupied states, or conduction states, are separated from the valence states
by a gap which is typically 30 to 50% too small, but the shape of the conduction bands is more or less correct [53]. Equivalently, we could say that the 'real' conduction bands can be obtained from the Kohn-Sham bands by performing a rigid shift of the conduction bands. To obtain real understanding and quantitatively correct one-particle energies, more advanced many-body calculations have to be performed.

It is worth mentioning at this point that a time-dependent formulation of DFT exists (TDDFT), which is successful, to a certain extent, in the calculation of excitation energies. The excitation energies are still underestimated, but by a different, smaller, energy value. Since TDDFT, like the construction of XC functionals, is a field in its own right, we only mention reference [54], in which a detailed account of the present state of the art in this field is given.

2.2.2 Moving the nuclei

In the previous subsections, we have assumed the nuclei to be fixed. In principle, the exact structure of the system under consideration is not necessarily known and this structure has to be calculated as well. Assuming the nuclei to behave classically, we have for the k-th nucleus with mass $M_k$:

$$M_k \ddot{R}_k = -\nabla_{\mathbf{R}_k} V_{\text{tot}},$$

where

$$V_{\text{tot}} = \sum_{j \neq k} \frac{Z_j Z_k}{|\mathbf{R}_k - \mathbf{R}_j|} + E_{\text{KS}}(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_M),$$

where we have explicitly indicated the dependence of the Kohn-Sham energy on the nucleonic coordinates. This means that the force $\mathbf{F}_k$ acting on nucleus $k$ is given by:

$$\mathbf{F}_k = \sum_{j \neq k} \frac{Z_j Z_k (\mathbf{R}_k - \mathbf{R}_j)}{|\mathbf{R}_k - \mathbf{R}_j|^3} - \frac{\partial E_{\text{KS}}}{\partial \mathbf{R}_k}.$$  

(2.30)

where we have used the Hellman-Feynman theorem to eliminate the implicit dependence (through the electron density) of the KS energy on the positions of the nuclei; the derivative $\frac{\partial E_{\text{KS}}}{\partial \mathbf{R}_k}$ is the explicit dependence of the Kohn-Sham energy on the nucleonic coordinates via the external potential. We then obtain the time-discretized equations of motion for the nuclei:

$$\mathbf{R}_k(t + \Delta t) = \mathbf{R}_k(t) + \Delta t \dot{\mathbf{R}}_k(t) + \frac{\Delta t^2}{2 M_k} \mathbf{F}_k(t) + \ldots$$

(2.31)

$$\ddot{\mathbf{R}}_k(t + \Delta t) = \dot{\mathbf{R}}_k(t) + \frac{\Delta t}{2 M_k} [\mathbf{F}_k(t) + \mathbf{F}_k(t + \Delta t)] + \ldots$$

(2.32)

After each step of the nuclei, we have to calculate the electronic structure again; the nuclei have been moved, and hence the external potential $V_{\text{ext}}(\mathbf{r})$ acting on the electrons has
changed. Using the old electronic configuration as initial configuration this recalculation usually does not take much time. We can either perform true Molecular Dynamics, i.e., look at the behavior of the system as a function of time, and study for instance chemical reactions or crystal growth, or we can extract energy from the system to obtain the ground state nucleonic structure of the system.

Most methods for solving the Kohn-Sham equations (2.22) rely upon the repeated diagonalization of very large matrices, an operation which scales as $N^{3}$, with $N$ the size of the system. For larger, more complex systems, this diagonalization becomes too expensive. Moreover, having to recalculate the electronic structure after each nucleonic step becomes a costly affair. Therefore Car and Parrinello (CP) [34] suggested to use one Lagrangian not only for the nuclei, but also for the electronic and lattice degrees of freedom. This means that by solving the corresponding Euler-Lagrange equations we get a set of equations which give us not only the nucleonic, but also the electronic ground state and the size and shape of the unit cell. Their Lagrangian is:

$$\mathcal{L}_{\text{CP}} = \frac{1}{2} \sum_{k} M_{k} |\mathbf{\dot{R}}_{k}|^{2} + \frac{1}{2} \mu \sum_{i} \int d\mathbf{r} |\mathbf{\dot{\phi}}_{i}(\mathbf{r})|^{2} + \beta \sum_{\nu} \mathbf{\ddot{a}}_{\nu}^{2} - E_{\text{tot}}(\{\phi_{i}\}, \{\mathbf{R}_{k}\}, \{\alpha_{\nu}\}), \quad (2.33)$$

where $\mu$ is the fictitious mass of the electronic degrees of freedom $\{\phi_{i}\}$, $\beta$ that of the lattice degrees of freedom $\{\alpha_{\nu}\}$, and $E_{\text{tot}}(\{\phi_{i}\}, \{\mathbf{R}_{k}\}, \{\alpha_{\nu}\})$ contains all the potential terms:

$$E_{\text{tot}}(\{\phi_{i}\}, \{\mathbf{R}_{k}\}, \{\alpha_{\nu}\}) = E_{\text{KS}} + V_{\text{nn}} + V_{\text{lat}}, \quad (2.34)$$

where $V_{\text{nn}}$ is the sum all nucleus-nucleus potentials [see Equation (2.29)] and $V_{\text{lat}}$ the potential derived from the lattice stress tensor.

Normal diagonalization techniques automatically ensure orthonormality, the bare CP Lagrangian and its Euler-Lagrange equations do not. In order to ensure orthonormality, we add the following term:

$$\sum_{ij} \Lambda_{ij} \left[ \int d\mathbf{r} \mathbf{\phi}_{i}^{\dagger}(\mathbf{r})\mathbf{\phi}_{j}(\mathbf{r}) - \delta_{ij} \right] \quad (2.35)$$

This gives us the following Euler-Lagrange equations:

$$\mu \mathbf{\dddot{\phi}}_{i} = -\frac{\delta E_{\text{tot}}}{\delta \mathbf{\phi}_{i}^{\dagger}} + \sum_{j} \Lambda_{ij} \mathbf{\dot{\phi}}_{j}, \quad (2.36)$$

$$M_{k} \mathbf{\dddot{R}}_{k} = -\nabla_{k} [E_{\text{KS}} + V_{\text{nn}}], \quad (2.37)$$

$$\beta \mathbf{\dddot{a}}_{\nu} = -\frac{\partial E_{\text{tot}}}{\partial \alpha_{\nu}}, \quad (2.38)$$

where

$$\frac{\delta E_{\text{tot}}}{\delta \mathbf{\phi}_{i}^{\dagger}} = H \mathbf{\phi}_{i}, \quad (2.39)$$

where $H$ is the Kohn-Sham Hamiltonian and the Lagrange multipliers $\Lambda_{ij}$ have to be determined such that orthonormality is ensured. In principle these equations can simultaneously
be integrated with equations like (2.31) and (2.32). Performing the CP calculations using these equation leads to difficulties associated with the transfer of 'kinetic' energy between the lattice degrees of freedom, those of the atoms, and those of the electrons. These complications can be avoided by performing a number of electronic integration steps before performing a nucloonic step, as is done in the Car-Parrinello implementations used in this work, the fh195cp [55] and fh196md [56] codes of the Fritz-Haber Institut, and leaving out the automatic optimization of the lattice.

2.2.3 Additional approximations

In spite of all the approximations made already (though they do not severely comprise the reliability of the methods), we still do not have a workable scheme for the prediction of the structure of bulk solids. To mention the most important:

- It is impossible to study a macroscopic, bulk system such as a crystal by looking at the full crystal. Since a crystalline system is invariant under translations, we can apply periodic boundary conditions to a small part of the system (the unit cell) and hence predict the properties of the full crystal. Due to these boundary conditions, we introduce a new quantum number, \( k \), crystal momentum, on which both wave-functions and -energies depend [57]. Since polymers are also translationally invariant along the chain direction, applying periodic boundary conditions is a suitable way to study polymers. The use of periodic boundary conditions and its consequences are dealt with in Section 4.1.

- The one-particle wave functions \( \phi_n(\mathbf{r}) \) have to be expanded in a basis. For the study of finite systems (atoms, molecules, clusters) a basis set which has orbitals localized on each atom is the most convenient. In the popular quantum-chemical package Gaussian [58], gaussian orbitals are chosen, in ADF (Amsterdam Density Functional program; [59]) Slater-type orbitals. For infinite (periodic) systems, a plane-wave basis set is most convenient [60]. Since we will study periodically repeated systems, we use the latter basis set in the CP calculations. In either case, this basis set has to be truncated in such a way that the calculations remain computationally feasible and yet give reliable results.

- When we move an atom to another chemical environment, only the properties of the valence electrons will change notably. Only these electrons will contribute to chemical bonding and determine the optical and electronic properties on the \(< 10\, \text{eV} \) scale. Since the core electrons are much more localized than the valence electrons, their wave functions are very hard to expand in a plane-wave basis set. It is therefore a good idea to replace the potential of the core electrons by a pseudo-potential, which reproduces the same valence eigenvalues and scattering properties (up to a certain energy) as the full potential. Not only is this potential much 'softer' than
the full potential, making the wave functions easier to expand in a plane wave basis, it also reduces the number of electrons and hence the size of the problem. Even with more strict, mathematical, constraints than the loosely formulated 'reproduce the valence eigenvalues and scattering properties', an enormous amount of freedom remains in the construction of the pseudo-potential. This freedom has been exploited [61, 62, 63, 64, 65, 66] in a search for pseudo-potentials that minimizes the size of the basis set. In this work, we will use the Troullier-Martins pseudo-potentials [65].

2.3 One-particle excitations

The considerations in the previous Section have given us a way to describe the electronic and atomic ground state structure of an arbitrary system of atoms and electrons. In this Section we will derive the Green-function techniques needed to correctly describe the one-particle excitations. Many of the many-body techniques used here may be found in, e.g., Reference [67]; the original derivation of the GW scheme is due to Hedin [35].

2.3.1 Green functions and the self-energy

The central object in the description of the quasi-particles and the associated self-energy is the one-particle Green function, or propagator, \( G(\mathbf{r}, \mathbf{r}', t, t') \) which is the probability amplitude for annihilating an electron at position \( \mathbf{r} \) at time \( t \) and creating an electron at position \( \mathbf{r}' \) at time \( t' \). Equivalently, it can be said that it is the probability amplitude for the propagation of an electron from position \( \mathbf{r} \) at time \( t \) to position \( \mathbf{r}' \) at time \( t' \).

In the second-quantization formalism, we use creation and annihilation operators, which are indicated by \( \psi^\dagger(\mathbf{r}, t) \) and \( \psi(\mathbf{r}, t) \), and obey:

\[
[\psi^\dagger(\mathbf{r}, t), \psi^\dagger(\mathbf{r}', t)]_+ = [\psi(\mathbf{r}, t), \psi(\mathbf{r}', t)]_+ = 0, 
\]

\[
[\psi(\mathbf{r}, t), \psi^\dagger(\mathbf{r}', t)]_+ = \delta(\mathbf{r} - \mathbf{r}'), 
\]

where \( [A, B]_+ = AB + BA \). We will indicate the five coordinates of the \( i \)-th electron (or hole) as \( i = (\mathbf{r}_i, t_i, \sigma_i) \), where \( \sigma_i \) is the spin of the electron, -1/2 or 1/2. We will ignore spin in the following derivations. The superscript + in \( t_i^+ \) (or \( i^+ \)) will be used to indicate the limit \( \lim_{\delta \to 0} t_i + \delta \). We can write the Green function \( G(\mathbf{r}, \mathbf{r}', t, t') \) as:

\[
G(1, 2) = -i \left< N \left| \mathcal{T}[\psi(1), \psi^\dagger(2)] \right| N \right>, 
\]

where \( \mathcal{T} \) is Wick's time-ordering operator:

\[
\mathcal{T}[\psi(1)\psi^\dagger(2)] = \begin{cases} 
\psi(1)\psi^\dagger(2) & \text{if } t_1 > t_2, \\
-\psi(2)\psi^\dagger(1) & \text{if } t_1 < t_2,
\end{cases} 
\]

(2.43)
and $|N\rangle$ the ground state of the interacting $N$ electron system. The Hamiltonian from Equation (2.1) then becomes:

$$\hat{H} = \hat{T} + \hat{V} + \hat{U},$$

(2.44)

with:

$$\hat{T} = - \int d\mathbf{r} \psi^\dagger(\mathbf{r}) \frac{1}{2} \nabla^2 \psi(\mathbf{r}),$$

(2.45)

$$\hat{V} = \int d\mathbf{r} \psi^\dagger(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) \psi(\mathbf{r}),$$

(2.46)

$$\hat{U} = \int d\mathbf{r} d\mathbf{r}' \psi^\dagger(\mathbf{r}) \psi^\dagger(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}) \psi(\mathbf{r}'),$$

(2.47)

where $\hat{T}$ is the kinetic term, $\hat{V}$ the interaction with an external field, and $\hat{U}$ the mutual interaction of the electrons through the Coulomb interaction $v(\mathbf{r} - \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$. Similarly, we can write down the Hamiltonian for a fictitious non-interacting system:

$$\hat{H}_0 = \hat{T} + \hat{V}_0,$$

(2.48)

with $\hat{V}_0$ defined analogously to $\hat{V}$, but with the external potential $V_{\text{ext}}$ replaced by some effective potential $V_{\text{eff}}$, including for instance also the electrostatic electron-electron interaction or the exchange-correlation potential. Using the Heisenberg equations of motion for the field-operators $\psi^\dagger(\mathbf{r}, t)$ and $\psi(\mathbf{r}, t)$:

$$i \frac{\partial \psi^\dagger(\mathbf{r}, t)}{\partial t} = [\psi^\dagger(\mathbf{r}, t), \hat{H}],$$

(2.49)

$$i \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = [\psi(\mathbf{r}, t), \hat{H}],$$

(2.50)

where $[A, B] = AB - BA$, we can derive the equation of motion for the non-interacting Green function $G_0(1, 2)$:

$$\left[ i \frac{\partial}{\partial t_1} + \frac{1}{2} \nabla_1^2 - V_{\text{eff}}(1) \right] G_0(1, 2) = \delta(1, 2).$$

(2.51)

A similar derivation gives for the interacting Green function $G(1, 2)$:

$$\left[ i \frac{\partial}{\partial t_1} + \frac{1}{2} \nabla_1^2 - V_{\text{eff}}(1) \right] G(1, 2) - \int d3\Sigma(1, 3) G(3, 2) = \delta(1, 2),$$

(2.52)

with the self-energy $\Sigma(1, 3)$ implicitly defined by:

$$\int d3\Sigma(1, 3) G(3, 2) = \langle N | \mathcal{T} \left[ \psi^\dagger(1), \hat{U} + \hat{V} - \hat{V}_0, \psi^\dagger(2) \right] | N \rangle,$$

(2.53)

Combining Equation (2.51) and (2.52) we arrive at Dyson’s equation:

$$G(1, 2) = G_0(1, 2) + \int d3d4G_0(1, 3) \Sigma(3, 4) G(4, 2).$$

(2.54)
In principle, this gives us a recipe to construct the one-particle Green function and, from it, all the one-particle excitations. Equivalently, we may give the quasi-particle equation, which is in fact a Dyson equation in disguise:
\[
\left[-\frac{\nabla^2}{2} + V_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r})\right] \phi_{nk}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', E_{nk}) \phi_{nk}(\mathbf{r}') = E_{nk} \phi_{nk}(\mathbf{r}),
\]
(2.55)

Note that the Kohn-Sham equations (2.22) are a special case of the quasi-particle equation with:
\[
\Sigma(\mathbf{r}, \mathbf{r}', \omega) = V_{\text{xc}}[n(\mathbf{r})] \delta(\mathbf{r} - \mathbf{r}')
\]
(2.56)

2.3.2 The Hedin equations

A systematic way to calculate the self-energy \(\Sigma\) was developed by Hedin [35] using linear response theory. He derived a set of four coupled integral equations, for the self-energy \(\Sigma\), the screened interaction \(W\), the polarizability \(P\), and the vertex function \(\Gamma\):
\[
\Sigma(1, 2) = i \int d^3d^4 G(1, 3) W(1^+, 4) \Gamma(3, 2, 4)
\]
(2.57)
\[
W(1, 2) = v(1, 2) + \int d^3d^4 v(1^+, 3) P(3, 4) W(4, 2)
\]
(2.58)
\[
P(1, 2) = -2i \int d^3d^4 G(1, 3) G(4, 1^+) \Gamma(3, 4, 2)
\]
(2.59)
\[
\Gamma(1, 2, 3) = \delta(1, 2) \delta(1, 3) + \int d^4d^5 \delta(1, 2) \delta G(4, 5) G(4, 6) G(7, 5) \Gamma(6, 7, 3)
\]
(2.60)

We can write these equations, including the Dyson equation (2.54) symbolically:
\[
G = G_0 + G_0 \Sigma G
\]
(2.61)
\[
\Sigma = GWG
\]
(2.62)
\[
W = v + vPW
\]
(2.63)
\[
P = GG\Gamma
\]
(2.64)
\[
\Gamma = 1 + \frac{\delta \Sigma}{\delta G} G\Gamma
\]
(2.65)

While definitely shorter than the previous four equations, it is questionable whether or not this formulation offers more insight. We can use Feynman diagrams, however, to give the schematic as displayed in Figure 2.1. The diagrams should be read in the following way: a single directed line is the non-interacting Green function \(G_0\), a double directed line is the interacting Green function \(G\), the dotted line is the screened interaction \(W\), the dashed line is the bare Coulomb interaction \(v\), and the black dot a double delta-function. The (non-rotated) filled square is the functional derivative \(\frac{\delta \Sigma}{\delta G}\). Every node represents a space-time point \((\mathbf{r}, t)\); internal space points are integrated over.
\[ G = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array} = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array} + \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array}\]

\[ \Sigma = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array} = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array}\]

\[ W = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array} = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array} + \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array}\]

\[ P = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array} = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array}\]

\[ \Gamma = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array} = \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array} + \begin{array}{c}
\hline
\hline
\hline
\hline
\end{array}\]

**FIGURE 2.1:** Diagrammatic notation of the Dyson (2.54) and Hedin Equations (2.57)-(2.60).

### 2.3.3 The GW approximation

The GW approximation boils down to approximating the vertex function \( \Gamma(1, 2, 3) \) by \( \delta(1, 2) \delta(1, 3) \). Hedin’s equations (plus the Dyson equation) then reduce to:

\[
P(1, 2) = -2iG(1, 2)G(2, 1^+) \tag{2.66}
\]

\[
W(1, 2) = \nu(1, 2) + \int d^3d^4\nu(1^+, 3) P(3, 4) W(4, 2) \tag{2.67}
\]

\[
\Sigma(1, 2) = iG(1, 2) W(1^+, 2) \tag{2.68}
\]

\[
G(1, 2) = G_0(1, 2) + \int d^3d^4G_0(1, 3) \Sigma(3, 4) G(4, 2) \tag{2.69}
\]

By choosing a proper starting point, i.e. a proper choice of \( G_0 \) (in our case the DFT-LDA \( G_0 \)), we can first calculate the polarizability \( P \) (the response of the system to a change of the
external potential plus the Hartree potential), the screened interaction \( W \) (the interaction between the quasi-particles, which is weaker than the bare Coulomb interaction) and the self-energy \( \Sigma \). With this self-energy, we can calculate the quasi-particle energies by inserting it in the quasi-particle equation (2.55). By performing the calculations in this manner, very good quasi-particle gaps have been obtained for a variety of semiconductor systems, as is shown in Figure 2.2. We can then also calculate the quasi-particle wave functions (and interacting Green functions \( G \)), but it turns out that [68]:

\[
\langle \phi^{\text{QP}} | \phi^{\text{DFT}} \rangle > 0.999.
\]  

Note that in principle the set of Equations (2.66)-(2.69) has to be iterated to obtain a self-consistent set of \( G, P, W \), and \( \Sigma \), as displayed in Figure 2.3. Apart from the fact that this is computationally much more demanding than 'standard' \( GW \) calculations, it turns out that the quality of the results obtained with self-consistent \( GW \) is not as good as 'standard' \( GW \) results, giving too large band gaps for instance [69]. This has been attributed to the fact that self-consistency and vertex corrections [i.e. corrections to approximating \( \Gamma \) by \( \delta(1,2)\delta(1,3) \)] should be included simultaneously for a consistent description, where consistent is meant in the sense of 'consistent with respect to what order of approximation of the full Hedin equations (2.57) - (2.60) we make'. If both are included, these corrections cancel to a large extent, but not completely [70, 71]. The only kind of self-consistency in first-order, i.e., in 'standard' \( GW \), that works in practice is to update the DFT-LDA eigenvalues that are used to construct the Green functions and perform one extra iteration [68]. Therefore, the success of the GWA, as displayed in Figure 2.2, is still largely unexplained.

### 2.4 Two-particle excitations

In the previous Section, we have described excitations that change the number of particles in the system, \( N \rightarrow N \pm 1 \), adding (removing) an electron. However, absorption, reflectivity, fluorescence spectroscopy and other optical techniques, do not add or remove an electron, but create charge-neutral excitations. Absorption, for instance, removes an electron from an orbital or band, *leaving a hole*, and puts it in another orbital or band, creating an effective two-particle excitation. In systems where the interaction between the electron and the hole is weak, a one-particle description, as outlined in the previous Section, may suffice to calculate the optical gap; in systems where excitations are much more localized or in systems of reduced dimensionality, this interaction becomes increasingly important. Moreover, even for systems where the interaction is weak, including this interaction will result in a redistribution of oscillator strength, hence modifying the absorption spectra.

In this Section, we will derive how to map the many-body problem onto an effective two-particle, Schrödinger-like equation for the electron and the hole, as originally done by Sham and Rice [36] and Strinati [37]. The first modern day applications are due to Onida *et al.*
**FIGURE 2.2:** The errors in one-particle band gaps $E_g$ within DFT-LDA (×) and GWA (+) as a function of the experimental values for a large number of semiconductors and insulators. After Reference [72]. Note that DFT-LDA incorrectly predicts some small band gap semiconductors to be metals.

**FIGURE 2.3:** Schematic of the GW self-consistency loop. In practice no more than two iterations are performed. As a starting point, the DFT-LDA Green functions are inserted in the lower left rectangle. 'Standard' GW stops in the lower right rectangle.
[21], Albrecht et al. [22], Rohlfing and Louie [23], and Benedict et al. [24]. We will roughly
follow the derivation of Rohlfing and Louie [73].

2.4.1 The Bethe-Salpeter equation

Analogously to the one-particle Green function, defined earlier in Equation (2.42):
\[ G_1(1, 2) = -i \langle N \left| \mathcal{T}[\psi(1), \psi^\dagger(2)] \right| N \rangle, \tag{2.71} \]
(note the subscript 1, used to indicate the fact that this is the one-particle Green function),
we can define the two-particle Green function:
\[ G_2(1, 2, 1', 2') = -\langle N \left| \mathcal{T}[\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1') \right| N \rangle. \tag{2.72} \]

It is convenient to introduce the two-particle correlation function:
\[ L(1, 2, 1' , 2') = G_1(1, 1')G_1(2, 2') - G_2(1, 2, 1', 2'), \tag{2.73} \]
\[ = L_0(1, 2, 2', 1') - G_2(1, 2, 1', 2'), \tag{2.74} \]
where \( L_0 \) is the propagator for the free electron-hole pair. \( L \) then satisfies a Dyson-type
equation of motion [cf. Equation (2.54)], known as the Bethe-Salpeter equation (BSE):
\[ L(1, 2, 1', 2') = L_0(1, 2, 1', 2') + \int d3d4d5d6 L_0(1, 4, 1', 3)\Xi(3, 5, 4, 6)L(6, 2, 5, 2'), \tag{2.75} \]

where the interaction kernel \( \Xi \) is the effective two-particle interaction, given by:
\[ \Xi(3, 5, 4, 6) = \frac{\delta \Sigma(3, 4)}{\delta G_1(6, 5)}. \tag{2.76} \]

If we use the \( GW \) approximation for the self-energy again and neglect the dependence of
the screened interaction \( W \) on the one-particle Green function, we obtain:
\[ \Xi(3, 5, 4, 6) = -i\delta(3, 4)\delta(5, 6)c(3, 6) + i\delta(3, 6)\delta(4, 5)W(3, 4) \tag{2.77} \]
\[ \equiv V^x(3, 5, 4, 6) + W(3, 5, 4, 6), \tag{2.78} \]
where \( V^x \) is the exchange part of the interaction and \( W \) the screened part.

2.4.2 Generalized eigenvalue problem

Note that \( L(1, 2, 1', 2') \) depends on four time variables. Restricting ourselves to simultaneous
creation and annihilation, this reduces to two; by further taking the translational invariance in time into account, this reduces to one, which means we can also look at the
Fourier transform \( L(1, 2, 1', 2', \omega) \), where \( i \) now indicates the spin and position coordinates of the particle only.

If we expand the one-particle Green functions in the quasi-particle wave functions, we get for \( L_0 \):

\[
L_0(1, 2, 1', 2', \omega) = i \sum_{\nu, c} \left[ \frac{\phi_c(r_1) \phi^*_c(r_1') \phi_{\nu}(r_2) \phi^*_{\nu}(r_2')}{\omega - (E_c - E_{\nu}) + i0^+} - \frac{\phi_c(r_1) \phi^*_{\nu}(r_1') \phi_{\nu}(r_2) \phi^*_c(r_2')}{\omega + (E_c - E_{\nu}) - i0^+} \right],
\]

(2.79)

where \( c \) and \( \nu \) indicate conduction (unoccupied) and valence (occupied) states respectively. \( E_c \) and \( E_{\nu} \) are the (real parts of the) valence and conduction state one-particle excitation energies. A similar expansion for \( L \) gives:

\[
L(1, 2, 1', 2', \omega) = i \sum_{\nu, c} \left[ \frac{\chi_i(r_1, r_1') \chi^*_i(r_2, r_2')}{\omega - E^i + i0^+} - \frac{\chi_i(r_2, r_2') \chi^*_i(r_1, r_1')}{\omega + E^i - i0^+} \right],
\]

(2.80)

where \( i \) runs over all two-particle excitations (with excitation energy \( E^i \)), and \( \chi_i(r, r') \) are the electron-hole amplitudes, given by:

\[
\chi_i(r, r') = \langle N, 0 | \psi^i(r') \psi(r) | N, i \rangle,
\]

(2.81)

with \( |N, 0\rangle \) the ground state of the \( N \)-particle system (called \( \langle N \rangle \) in Section 2.3) and \( |N, i\rangle \) the \( N \)-particle system with a specific excitation \( i \). Equivalently, \( \chi_i(r, r') \) is expressed by:

\[
\chi_i(r, r') = \sum_{\nu, c} \left[ A^i_{\nu c} \phi_{\nu}(r) \phi^*_c(r') + B^i_{\nu c} \phi_c(r) \phi^*_\nu(r') \right].
\]

(2.82)

Using Equations (2.79), (2.80) and (2.82) we can turn the BSE (2.75) into a generalized eigenvalue problem:

\[
(E_c - E_{\nu}) A^i_{\nu c} + \sum_{\nu', c'} \Xi^{AA}_{\nu c, \nu' c'}(E^i) A^i_{\nu' c'} = E^i A^i_{\nu c},
\]

(2.83)

with

\[
\Xi^{AA}_{\nu c, \nu' c'}(E^i) = V^{AA}_{\nu c, \nu' c'} + W^{AA}_{\nu c, \nu' c'}(E^i).
\]

(2.84)

In Equation (2.83), we have used the fact that in practice the coupling between the \( A \)- and \( B \)-blocks is weak, i.e., the matrix elements \( \Xi^{AB}_{\nu c, \nu' c'} \) and \( \Xi^{BA}_{\nu c, \nu' c'} \) are small [25, 73], and identical equations for \( A^i_{\nu c} \) and \( B^i_{\nu c} \) result [apart from a minus sign on the right hand side of Equation (2.83) for the \( B \)-block]. The preceding mathematical manipulations have mapped the problem onto an effective two-particle equation, which is still hard to solve, because the screened-interaction parts of the matrix elements \( \Xi^{AA}_{\nu c, \nu' c'}(E^i) \) contain an energy convolution, depending on the two-particle excitation energy \( E^i \):

\[
W^{AA}_{\nu c, \nu' c'}(E^i) = \frac{i}{2\pi} \int d\omega d\omega' \phi^*_c(r) \phi_{\nu}(r) \phi_{\nu'}(r') \phi^*_\nu(r') \int d\omega e^{i\omega\sigma} W(r, r', \omega)
\]

\[\times \left[ \frac{1}{E^i - \omega - (E_{\nu'} - E_{\nu}) + i0^+} + \frac{1}{E^i + \omega - (E_c - E_{\nu}) - i0^+} \right].
\]

(2.85)
If $E^i \approx E_c - E_v$, i.e., if the exciton binding energy, $E_b = E_g - E^i$, is small compared to the one-particle gap $E_g$, we can approximate the energy convolution in Equation (2.85) by $W(\mathbf{r}, \mathbf{r}', \omega = 0)$, the static part of the screened interaction, which greatly simplifies solving Equation (2.83). In practice, this approximation is also used when $E_b \ll E_g$ does not strictly hold, resulting in only a $\approx 5\%$ change of binding energies [73]. Formally, this approximation is validated by the cancellation of dynamical effects in the one-particle Green function and the screened interaction [74]. An expression similar to Equation (2.85), without the energy convolution, holds for $V_{cv,c'v'}^{x\tau_A}(E^i)$, thus completely determining the interaction $\Xi_{cv,c'v'}(E^i)$.

Assuming negligible spin-orbit interaction (which is well-justified for first and second row elements), we can classify the one-particle states $c$ and $v$ as either spin up ($\uparrow$) or spin down ($\downarrow$). This means we have four possible combinations for each set of $v$ and $c$: $v \uparrow c \uparrow$, $v \downarrow c \uparrow$, $v \uparrow c \downarrow$, and $v \downarrow c \downarrow$. The Hamiltonian of the total eigenvalue problem, written symbolically, then becomes:

$$
\begin{pmatrix}
E + W + V^x & 0 & 0 & V^x \\
0 & E + W & 0 & 0 \\
0 & 0 & E + W & 0 \\
V^x & 0 & 0 & E + W + V^x
\end{pmatrix}, \quad (2.86)
$$

where $E = E_c - E_v$. Making the distinction between spin triplet ($T$) and singlet ($S$) excitations, the former containing $v \uparrow c \downarrow$, $v \downarrow c \uparrow$ and $1/\sqrt{2}(v \uparrow c \uparrow + v \downarrow c \downarrow)$, the latter only $1/\sqrt{2}(v \uparrow c \downarrow - v \downarrow c \uparrow)$, the Hamiltonian (2.86) decouples into one for the $T$ and one for the $S$ manifold, $E + W$ and $E + W + 2V^x$, respectively. This means that we have to solve the BSE (2.83) twice, with different interaction kernels for $T$ and $S$ manifold. Of course, for absorption or fluorescence spectra, only the latter are relevant.

In Figure 2.4 we have given a number of spectra calculated using the DFT/GW/BSE formalism, as an example of what the method can do. Note that even for systems where the exciton binding energy is small, such as Si, inclusion of exciton effects by solving the BSE, results in a drastic change of the optical spectra. Even though the agreement with the experimental spectra is remarkably good, some discrepancies remain. In fact, for Si and GaAs various groups have performed DFT/GW/BSE calculations, and the agreement between the various calculations among each other is better than the agreement with experiment, indicating that the description of optical excitations by the present formalism is very accurate, but not yet fully complete.

## 2.5 Not included in the present formalism

In the preceding Sections we have shown how to calculate the geometry and one- and two-particle excitation energies of in principle any material, starting from a wireframe model...
FIGURE 2.4: The calculated absorption spectrum of Si [25], GaAs [24], SiO₂ [30] and the differential reflectivity spectrum of the Ge(111) surface in the (2x1) reconstruction [31]. The solid lines are DFT/GW/BSE calculations, taking electron-hole interaction into account, the dashed DFT/GW calculations, not taking electron-hole interactions into account, and the squares are experimental results.

of the geometry only. In this Section we will briefly discuss two effects that have not been included, and might play a role in conjugated polymers: lattice relaxation of the excited state and four-particle excitations.

2.5.1 Lattice relaxation in the excited state

We calculate the geometry of the polymer chain in its electronic ground state (by definition since we are using DFT to do so). It is not a priori clear that creating a one- or two-particle excitation, which changes the electron density, does not affect the geometry. An excited electron (hole) might lower its energy by creating a lattice distortion around it. The complex, the electron (hole) with the associated lattice deformation, is called an electron (hole) polaron, abbreviated as $P^{-}$ ($P^{+}$). Effectively, this lowers its excitation energy below
the value calculated assuming a fixed geometry, by the relaxation energy $E_{r,p^\pm} - (E_{r,p^\mp})$. Moreover, moving the polaron around should in general be harder than moving an electron (hole) around, since the lattice deformation would have to move as well; the electron (hole) has become self-trapped or self-localized. Two polarons, even like-charged polarons, might form a bound state (cf. Cooper pairs in the BCS theory of superconductivity), referred to as a bipolaron. The requirement for the stability of the bipolaron is $E_{r,p^\pm} > 2E_{r,p^\pm}$. In other words, the occurrence of two polarons on a polymer chain is only a bipolaron if it gains extra relaxation energy compared to two separate polarons. In this terminology, the relevant two-particle excitation, the bound electron-hole pair or exciton, is a bound state of two oppositely charged polarons, with its own associated lattice relaxation energy $E_{r,p^+p^-}$, of which it is a priori not clear whether $E_{r,p^+p^-} < E_{r,p^+} + E_{r,p^-}$ or $E_{r,p^+p^-} > E_{r,p^+} + E_{r,p^-}$.

In Figure 2.5, we have given a number of energy levels, corresponding to different scenarios for the relative magnitude of the lattice relaxation energies $E_{r,p^\pm}$, $E_{r,p^\mp}$, $E_{r,p^+p^-}$ and electron-hole binding energy $E_b$. Situation 1 corresponds to the creation of a fully separated (unbound) electron-hole pair, which costs an energy equal to the one-particle (or band) gap. Hence, the lowest possible excitation energy in an absorption experiment $E_{\text{abs}}$ is equal to the band gap $E_g$. In this situation, both the lattice relaxation energy and the exciton binding energy are small. In Situation 2, the one-particle gap $E_g$ is reduced to $E_{g,\text{rel}} =$
\( E_g - E_{r,p^{-}} - E_{r,p^{+}} \), because both the electron and the hole create a lattice distortion around them. In Situation 3 we have the creation of a bound electron-hole pair with a binding energy \( E_b \), where the electron-lattice, or electron-phonon coupling is ignored. The exciton binding energy results in a reduction of the excitation energy to \( E_{\text{exc}} = E_{\text{exc}} = E_g - E_b \), with \( E_{\text{exc}} \) the absolute exciton energy. Both the electron-phonon coupling and the concomitant lattice relaxation and the electron-hole interaction are included in Situation 4, where both the one-particle band gap \( E_g \) and the exciton energy \( E_{\text{exc}} \) are reduced to \( E_{\text{g,rel}} \) and \( E_{\text{exc,rel}} \), respectively.

The calculations as outlined before are performed for Situation 3, i.e., no lattice relaxation is included, but the electron-hole interaction is included. This means that we make an error \( E_{r,p^{+}} + E_{r,p^{-}} \) for our prediction for the band gap \( E_g \), \( E_{r,p^{+}} + E_{r,p^{-}} \) for the absolute exciton energy \( E_{\text{exc}} \), and an error \( E_{r,p^{+}} + E_{r,p^{-}} - E_{r,p^{+}} + E_{r,p^{-}} \) for the exciton binding energy. Is neglecting lattice relaxation justified?

On the theoretical side, strong evidence for the fact that \( E_{r,p^{+}} \) and \( E_{r,p^{-}} \) are small for pristine polymers has been presented. DFT studies of thiophene-oligomer cations \([75, 76, 77]\) of increasing length have yielded a very small polaron relaxation energy, \( \sim 0.05 \text{ eV} \), for the extrapolation to infinity, i.e., the polymer. Correlated quantum-chemical MP2 calculations yield similar results \([77, 78]\).

On the experimental side, polarons and bipolarons have been shown to exist in conjugated polymers, but since the observations are material and sample dependent \([79, 80]\), it is not clear to which extent the observations are intrinsic (in which case polarons do self-localize in a perfect chain) or extrinsic (polarons do localize, but only because of disorder and chemical impurities). Given the fact that two rather different computational procedures (DFT and MP2) indicate that the relaxation energy related to polarons in perfect polymers is small, it is allowed to neglect this relaxation in our calculation.

In simple tight-binding models, such as the SSH model \([16]\), polarons are found to have a large relaxation energy. Given the fact that the electron-electron interactions are not taken into account self-consistently in these methods and the parameters in these models are often fit to experiment, the predictive power of these methods should be considered of a lesser order than that of DFT or MP2.

As for \( E_{r,p^{+},p^{-}} \): the relaxation energy of the lowest triplet exciton polythiophene oligomers, calculated within DFT\(^2\) \([81]\), extrapolates to 0.15 eV for the polymer. Experimentally, \( E_{r,p^{+},p^{-}} \) can be estimated from experimental absorption and fluorescence spectra, which (for high-quality samples) show, for each optically active exciton, a number of peaks called vibronic sidebands, which are related to the creation (or annihilation) of a number of lattice phonons in the absorption (emission) process. The relative intensity \( I_n \) of the peak related

\(^2\)Even though the lowest triplet state is not the ground state of the system, it is the ground state within that symmetry manifold and hence can be calculated using DFT.
to the creation of $n$ phonons give the Huang-Rhys factor $S$ [82]:

$$I_n = S^n e^{-S} / n!.$$  \hspace{1cm} (2.87)

Since most polymers have one dominant phonon mode of $\hbar \omega_{\text{ph}} = 0.15-0.18$ eV, related to either C=C stretching or ring 'breathing' modes, and the relaxation energy upon excitation is given by [83]:

$$E_{r,p^+p^-} = S\hbar \omega,$$  \hspace{1cm} (2.88)

we can use $S$ to estimate $E_{r,p^+p^-}$. For high-quality samples $S = 0.5-1.0$, implying that $E_{r,p^+p^-} \approx 0.1$ eV, consistent with the theoretical value of 0.15 eV quoted above. Note that the effect may be larger for other excitons, for which an analysis of the vibronic sidebands is not possible.

### 2.5.2 Four-particle excitations

We have described how to include excitations involving an increasing number of particles. In Section 2.3 one-particle excitations were described; then these initially non-interacting particles (electrons and holes) were allowed to interact in Section 2.4. Experimental evidence [17, 84], as well as CI modelling [85, 86], on the non-luminescent polymers polyacetylene (PA) and polydiacetylene (PDA) suggest that in these systems four-particle excitations are required for a correct description of what are referred to as two-photon states. These two-photon states are suggested to be a mixture of two- and four-particle excitations. While in principle these four-particle excitations have to be taken into account for all polymers, in the general case the electron-electron correlation is weak or moderate, so that the amount of mixing is small and a two-particle excitation description suffices.

In Chapter 6 we will see that these four-particle excitations are required for a correct description of these two-photon states in PA and PDA, by comparing the results of our two-particle excitation formalism with the experimental results. Including the four-particle excitations into the formalism as presented here would involve writing down the equation of motion for the four-particle Green function:

$$G_4(1, 2, 3, 4, 1', 2', 3', 4') = - \left\langle N \left| \mathcal{T}[\psi(1)\psi(2)\psi(3)\psi(4)\psi^+(4')\psi^+(3')\psi^+(2')\psi^+(1')]] N \right\rangle, \hspace{1cm} (2.89)$$

to construct a Dyson equation of the type of Equation (2.75). Performing calculations with it would be a formidable task. Within CI-based methods, including these four-particle excitations is relatively easy. It can be achieved by incorporating configurations with two holes and two electrons. In such calculations, substantial four-particle character of some excited states is found. A more extensive discussion of this can be found in Chapter 6.
Chapter 3

Screening in conjugated polymer systems

ABSTRACT

The easiest geometry to perform calculations for conjugated polymers is an isolated, single chain, rather than an amorphous or crystalline situation. Unfortunately, an isolated chain is a quasi-one-dimensional system, in which the Coulomb interaction is not screened for large distances, which greatly affects the spectra, but is not realistic for the comparison with experiment. In this Chapter we outline a method to construct a more realistic screening for the Coulomb interaction based on calculations for a single chain only. Starting from the single-chain polarizability and the polarizability tensor, we calculate the dielectric tensor within a line-dipole model, and use this dielectric tensor to provide long-range screening for the Coulomb interaction.

3.1 Quasi one-dimensional versus three-dimensional approach

The first-principles methods in the preceding Chapter have been described in the most general terms, not focusing on an application to a specific system. In describing the electronic and optical properties of conjugated polymers, we are faced with the problem of exactly what system to study: polymers are not well-ordered materials, so assuming a certain ordering of one chain relative to another is not necessarily a good approach. While the crystal structure of a number of unsubstituted conjugated polymers has been determined [87, 88, 89, 90], even the most crystalline areas in these samples are still rather disordered [88]. Moreover, when this project started the computational demands of performing a calculation for crystalline polythiophene or polyphenylenevinylene were just too high. Since a single polymer chain has a higher symmetry than a crystal, performing a calculation for a single chain is substantially less expensive computationally.

Apart from the computational reason to choose a single isolated chain in vacuum to be studied first, density-functional calculations for conjugated polymers showed that the electronic structure of a single chain is not much different from that of the crystal in this theory [91, 92, 93, 94]. In the GW and Bethe-Salpeter approaches, treating a single isolated chain, a quasi-one-dimensional (quasi-1D; infinite in one, finite in the two other spatial dimensions system), presents a problem, since in a quasi-1D system the Coulomb interaction is not screened for long ranges [69, 95, 96], i.e., for large separation $r$ along the chain. This means that for large $r$ the Coulomb interaction $v$ and the screened interaction $W$ are the same. A way to understand this lack of long-range screening is to realize that if we have two charges on a polymer chain with a separation larger than the width of the chain ($\sim 7$ a.u.), most field lines connecting the charges will be outside the chain, in vacuum.

Note that the problem sketched here is not a methodological problem. The problem is: what should we compare the one- and two-particle spectrum calculated for the isolated chain with? In all experimental situations, the chain is embedded in a medium, (possibly, but not necessarily, consisting of similar chains). This medium provides a long-range screening of the Coulomb interaction, substantially altering both the one- and two-particle spectra. Performing the calculations for a single, isolated chain results in unrealistically large one-particle band gaps, and unrealistically large exciton binding energies compared to experiment.

As a compromise between on the one hand computational feasibility and on the other hand physical realism we first chose to perform calculations for an intermediate between the isolated chain and the crystal: we calculate the dielectric tensor of a crystal, starting from the single-chain polarizability $\gamma$. Next, we embed the chain in a medium with this dielectric tensor, thus providing long-range screening for the Coulomb interaction, which reduces the one-particle gaps, and the exciton binding energies. An additional advantage is that most polymer samples are rather disorder systems, so we expect the average surroundings of the
chain, represented by the dielectric tensor, to be more important than the details of the screening, represented by the full dielectric function \( \varepsilon(\mathbf{r}, \mathbf{r'}, \omega) \).

As more powerful computers have become available, it is now also possible to perform calculations for the crystalline situation, in which case no additional considerations for the screened interaction \( W \) are required.

### 3.1.1 The screening in an anisotropic homogeneous dielectric

Assume that the bulk polymer is an anisotropic homogeneous dielectric, with a dielectric constant \( \varepsilon_{\parallel}(i\omega) \) along the chain, and a dielectric constant \( \varepsilon_{\perp}(i\omega) \) in the perpendicular directions. The screened interaction \( W \) of a charge \( q \) can be obtained from solving the Poisson equation (assuming the chain is along the \( x \)-axis) [97]:

\[
\varepsilon_{\parallel} \frac{\partial^2 W}{\partial x^2} + \varepsilon_{\perp} \frac{\partial^2 W}{\partial y^2} + \varepsilon_{\perp} \frac{\partial^2 W}{\partial z^2} = q \delta(\mathbf{r}) \tag{3.1}
\]

Substituting \( \sqrt{\varepsilon_{\parallel}} u = x, \sqrt{\varepsilon_{\perp}} v = y \) and \( \sqrt{\varepsilon_{\perp}} w = z \) and solving for \( \tilde{W}(\mathbf{s}) \) [where the tilde is used to indicate the change of variables and with \( \mathbf{s} = (u, v, w) \)] we find:

\[
\tilde{W}(\mathbf{s}) = \frac{q}{\sqrt{\varepsilon_{\parallel}^2 u^2 + \varepsilon_{\perp}^2 v^2 + w^2}} \tag{3.2}
\]

Substituting \( u = x/\sqrt{\varepsilon_{\parallel}}, v = u/\sqrt{\varepsilon_{\perp}} \) and \( w = z/\sqrt{\varepsilon_{\perp}} \) we find for \( W(\mathbf{r}) \):

\[
W(\mathbf{r}) = \frac{q}{\sqrt{\varepsilon_{\parallel}^2 x^2 + \varepsilon_{\perp}^2 (y^2 + z^2)}} \tag{3.3}
\]

This screening will be called the interchain screening.

### 3.1.2 Intrachain and interchain screening

At this point it is convenient to introduce the screening interaction \( W^{scr} \) related to the screened interaction \( W \) by:

\[
W^{scr} \equiv W - v \tag{3.4}
\]

This means we can split the self-energy from Equation (2.68) as well:

\[
\Sigma = G W^{scr} + G v \tag{3.5}
\]

\[
= \Sigma^e + \Sigma^r, \tag{3.6}
\]

\footnote{We are anticipating the fact that in the space-time formalism for the \( GW \) approximation as used in thesis, and explained in Chapter 4, we calculate all functions \( G, P, W \) and \( \Sigma_\alpha \), along the imaginary frequency or time axis.}
where the superscripts \( c \) and \( x \) refer to the correlation and exchange part of the self-energy respectively. Note that only the former is time (or frequency) dependent, with \( \Sigma^c \to 0 \) when \( \omega \to \infty \).

Assuming we have the dielectric constants \( \varepsilon_\parallel \) and \( \varepsilon_\perp \) for a number of frequencies \( i\omega \) (these will be calculated in the next Section), we have two screening interactions. The single-chain or isolated-chain interaction, which contains intrachain interaction only: \( W^{\text{scr}}_{\text{intra}} \), and the screening resulting from embedding the chain in the medium, which contains the interchain interaction: \( W^{\text{scr}}_{\text{inter}} \). Both interactions give physically realistic screening interactions for only one of the two limiting cases \( |\mathbf{r} - \mathbf{r}'| \to 0 \) and \( |\mathbf{r} - \mathbf{r}'| \to \infty \). \( W^{\text{scr}}_{\text{intra}} \), being a quasi-1D screening, gives a correct short range behavior only, while it vanishes for large distances. \( W^{\text{scr}}_{\text{inter}} \), being an average interaction, is correct by construction for large distances, but also gives a screening for short distances, which is not realistic; for short distances not enough screening charge can be built up. If we add the two interactions in the following way:

\[
W_{\text{total}}(\mathbf{r}, \mathbf{r}', \omega) = W^{\text{scr}}_{\text{intra}}(\mathbf{r}, \mathbf{r}', i\omega) + \left[ 1 - e^{-|\mathbf{r} - \mathbf{r}'|/r_{\text{inter}}} \right] W^{\text{scr}}_{\text{inter}}(\mathbf{r} - \mathbf{r}', \omega) + \nu(\mathbf{r} - \mathbf{r}'), \tag{3.7}
\]

where \( r_{\text{inter}} \) is the interchain distance (typically 10 a.u. in PT), we have constructed an interaction for a single isolated chain embedded in a bulk medium which is composed of similar chains. This interaction is correct for short ranges, due to the cut-off that is applied to the short-range part of \( W^{\text{scr}}_{\text{inter}} \) and correct for long ranges, because \( W^{\text{scr}}_{\text{intra}} \) vanishes due to its quasi-1D nature. Of course, the screening interactions are, strictly speaking, not additive. However, the screened interaction \( W_{\text{total}} \) is correct at short range \((|\mathbf{r}| \ll r_{\text{inter}})\), where the cut-off interchain screening is vanishingly small compared to the \( 1/|\mathbf{r}| \) divergence of the intrachain screening, and at long range \((|\mathbf{r}| \gg r_{\text{inter}})\), where the intrachain screening vanishes due to its quasi-1D nature. For intermediate ranges, we expect Equation (3.7) to give a reasonable interpolation. The total self-energy can be expressed as:

\[
\Sigma_{\text{total}} = \Sigma^{\text{c}}_{\text{intra}} + \Sigma^{\text{c}}_{\text{inter}} + \Sigma^{x}.
\tag{3.8}
\]

Because the self-energies in this equation are additive, we can calculate the self-energies \( \Sigma^{\text{c}}_{\text{intra}} \) and \( \Sigma^{x} \) for the isolated chain separately.

### 3.2 Dielectric tensor of a crystalline polymer

In order to construct the screening interaction of Equation (3.3), we have to calculate the dielectric tensor of the bulk polymer. We do this for polythiophene (PT) for the crystalline structure of Reference \[89\], which is reproduced in Figure 3.1. We use a model in which the chains are replaced by polarizable line objects with a polarizability tensor obtained from the single-chain polarizability function. The principal axes of the chain are the following:

\[
\hat{x}_1 = \hat{x}, \quad \hat{x}_2 = \frac{1}{\sqrt{2}}(\hat{z} + \hat{y}), \quad \hat{x}_3 = \frac{1}{\sqrt{2}}(\hat{z} - \hat{y}).
\tag{3.9}
\]
3.2.1 Calculation of the crystal dielectric tensor within a line-dipole model

To calculate the dielectric constants $\varepsilon_i$, we apply an electric field $\mathbf{E}_{\text{appl}}(\mathbf{r}) = \mathbf{E}_0 e^{\mathbf{k} \cdot \mathbf{r}}$ (and we will take the limit $k \to 0$), where $\mathbf{E}_0$ and $\mathbf{k}$ are parallel to the $a$, $b$ or $c$-axis of the crystal (see Figure 3.1) for the calculation of $\varepsilon_a$, $\varepsilon_b$ and $\varepsilon_c$, respectively. The applied field $\mathbf{E}_{\text{appl}}$ leads to an induced field $\mathbf{E}_{\text{ind}}(\mathbf{r})$; the total microscopic field $\mathbf{E}_{\text{micr}}(\mathbf{r})$ is then given by:

$$\mathbf{E}_{\text{micr}}(\mathbf{r}) = \mathbf{E}_{\text{appl}}(\mathbf{r}) + \mathbf{E}_{\text{ind}}(\mathbf{r}).$$

(3.10)
We define $\vec{\rho} = u\hat{a} + v\hat{b}$ with $\rho^2 = u^2 + v^2$. Note that there are two different chains: the $A$ type, at the corners of the unit cell, and the $B$ type at the center of the unit cell. For the $A$ and $B$ chain we have:

$$\mathbf{p}_A(x) = \chi_A \cdot \mathbf{E}_{\text{micr}}(x, \vec{\rho} = 0)$$

$$\mathbf{p}_B(x) = \chi_B \cdot \mathbf{E}_{\text{micr}}(x, \vec{\rho} = \frac{1}{2} \hat{a} + \frac{1}{2} \hat{b})$$

with $\mathbf{p}_A(x)$ ($\mathbf{p}_B(x)$) the long-wavelength dipole moment per unit length of the $A$ ($B$) chain and $\chi_A$ ($\chi_B$) the polarizability tensor of the $A$ ($B$) chain calculated from the single-chain polarizability tensor $\chi$ (to be calculated below) by using the relations:

$$\chi_A = U_A^{-1} \cdot \chi \cdot U_A, \quad \chi_B = U_B^{-1} \cdot \chi \cdot U_B,$$

where $U_A$ and $U_B$ are the rotation matrices relating the $(x_2,x_3)$ coordinate system to the $(a,b)$ coordinate system ($\hat{c} = \hat{x}_1$):

$$U_A = \begin{pmatrix}
\cos(\frac{\pi}{4} - \alpha) & -\sin(\frac{\pi}{4} - \alpha) \\
\sin(\frac{\pi}{4} - \alpha) & \cos(\frac{\pi}{4} - \alpha)
\end{pmatrix},$$

$$U_B = \begin{pmatrix}
\cos(\frac{3\pi}{4} - \alpha) & \sin(\frac{3\pi}{4} - \alpha) \\
-\sin(\frac{3\pi}{4} - \alpha) & \cos(\frac{3\pi}{4} - \alpha)
\end{pmatrix}.$$ (3.14)  

(3.15)

The prime in Equations (3.11) and (3.12) indicates that the field caused by the chain itself is excluded. We will refer to our model, in which a PT chain is represented by a homogeneous line with a certain dipole moment per unit length $\mathbf{p}$, as a ‘line dipole’.

In CGS units the dielectric tensor $\varepsilon$ is defined as:

$$\mathbf{E}(r) + 4\pi\mathbf{P}(r) = \varepsilon \cdot \mathbf{E}(r).$$

(3.16)

where $\mathbf{E}(r)$ is the macroscopic field, and $\mathbf{P}(r)$ is the macroscopic polarization. For each direction of the applied field, we will calculate $\mathbf{E}_{\text{micr}}(r)$, evaluate the macroscopic fields $\mathbf{E}(r)$ and $\mathbf{P}(r)$ by averaging, and solve Equation (3.16) to obtain the dielectric tensor $\varepsilon$.

### 3.2.2 The polarizability tensor

The full polarizability function $X(r, r', i\omega)$ of a single chain is given by:

$$X(r, r', i\omega) = P(r, r', i\omega)$$

$$+ \int \int d\mathbf{r}'' d\mathbf{r}''' P(r, r'', i\omega) W_{\text{intra}}(r'', r'''', i\omega) P(r''', r', i\omega)$$

$$\equiv X^{(0)}(r, r', i\omega) + X^{(1)}(r, r', i\omega).$$

(3.17)  

(3.18)
The long-wavelength \((q \to 0)\) polarizability tensor \(\chi\) per unit of chain length of a single chain in the \((x_1, x_2, x_3)\) coordinate system is diagonal and has diagonal elements given by:

\[
\chi_i(i\omega) = \lim_{q \to 0} \left[ \frac{1}{q^2} \int d\mathbf{r} d\mathbf{r}' e^{-iq(x_1-x_1')}X(\mathbf{r}, \mathbf{r}', i\omega) \right],
\]  

(3.19)

and for \(j = 2, 3\):

\[
\chi_j(i\omega) = \int d\mathbf{r} d\mathbf{r}' x_j X(\mathbf{r}, \mathbf{r}', i\omega) x_j'.
\]  

(3.20)

### 3.3 Mathematical details

#### 3.3.1 Calculation of \(\varepsilon_c\)

For \(\mathbf{E}_{\text{appl}}\) and \(\mathbf{k}\) parallel to \(\dot{x}\) (and hence to \(\dot{c}\) and also \(\dot{x}_1\)), we have for both the \(\mathcal{A}\) and \(\mathcal{B}\) chain from Equations (3.11) and (3.12):

\[
p_x(x) = \chi_i E'_x(x)
\]  

(3.21)

The field induced by a line-dipole on the \(x\)-axis is given by:

\[
\mathbf{E}_{\text{ind}}(\mathbf{r}) = -\nabla \Phi(\mathbf{r}) = -\nabla \int \frac{p_x e^{ikx'}(x - x')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}',
\]  

(3.22)

where \(\Phi\) is the electrostatic potential and we have used the fact that \(p_x(x') = p_x e^{ikx'}\). Evaluation of Equation (3.22) yields:

\[
E_{\text{ind},x}(\mathbf{r}) = -2k^2 p_x K_0(\rho k) e^{ikx},
\]  

(3.23)

where \(K_0\) is a zeroth-order Bessel function of the third kind. From here on, we omit the factor \(e^{ikx}\). We can calculate the total microscopic field at the \(x\)-axis, due to both applied and induced fields, for a crystal of line dipoles, by summing over all line dipoles but the one at the origin:

\[
E'_{\text{mcr},x}(\bar{\rho} = 0) = E_{\text{appl},x}(\bar{\rho} = 0) + \sum_{\bar{\rho}_i \neq 0} E_{\text{ind},x}(-\bar{\rho}_i)
\]  

(3.24)

where the positions of the other chains are given by \(\bar{\rho}_i\). In the limit \(k \to 0\), we can replace the sum by an integral:

\[
\lim_{k \to 0} \sum_{\bar{\rho}_i \neq 0} E_{\text{ind},x}(\bar{\rho}_i) = \frac{2\pi p_x}{\mathcal{A}} \int_0^\infty \rho' d\rho' K_0(\rho') = \frac{4\pi}{\mathcal{A}} p_x,
\]  

(3.25)

(3.26)
where $\rho' = \rho k$ and $A = ab/2$ is the area of the two-dimensional unit cell per chain. Substitution of Equation (3.26) and (3.24) in Equation (3.21) yields:

$$
p_x = \frac{\chi_1 A}{A + 4\pi \chi_1} E_{\text{appl}, x}.
$$

(3.27)

Since $P_x = p_x / A$, we have:

$$
P_x = \frac{\chi_1}{A + 4\pi \chi_1} E_{\text{appl}, x}.
$$

(3.28)

The macroscopic field $E_x$ is the average over the two-dimensional unit cell of the microscopic field as given by Equation (3.24) for general $\rho'$, but now including the chain at $\rho'_k = 0$ in the sum:

$$
E_x = E_{\text{appl}, x} + \lim_{k \to 0} \frac{1}{2A} \int_{\text{unit cell}} d^2\rho \sum_{\rho'_k} E_{\text{ind}, x}(\rho' - \rho'_k)
$$

(3.29)

$$
= E_{\text{appl}, x} + \lim_{k \to 0} \frac{2\pi}{A} \int d\rho \sum_{\rho'_k} E_{\text{ind}, x}(\rho' - \rho'_k)
$$

(3.30)

$$
= E_{\text{appl}, x} - \frac{4\pi p_x}{A}
$$

(3.31)

Combining this with Equations (3.16) and (3.28) we obtain:

$$
\varepsilon_c = 1 + \frac{4\pi \chi_1}{A}.
$$

(3.32)

### 3.3.2 Calculation of $\varepsilon_a$ and $\varepsilon_b$

We now take $E_{\text{appl}}(r)$ and $k$ parallel to $\hat{a}$. The derivation for $E_{\text{appl}}(r)$ and $k$ parallel to $\hat{b}$ is equivalent. The dipole moments of the chains must satisfy Equations (3.11) and (3.12). The field induced by the chain at the origin is given by:

$$
E_{\text{ind}}(r) = -\nabla \Phi(r) = -\nabla \int \frac{P_A \cdot r}{|r - r'|^3} dx'
$$

(3.33)

$$
= \frac{M(\rho)}{P_A} \cdot P_A,
$$

(3.34)

where

$$
M(\rho) \equiv \begin{pmatrix}
\frac{4\mu^2}{\rho^2} & -\frac{2}{\rho^3} & \frac{4\mu \omega}{\rho^2} \\
-\frac{2}{\rho^3} & \frac{4\mu^2}{\rho^4} & \frac{4\mu \omega}{\rho^2} \\
\frac{4\mu \omega}{\rho^2} & \frac{4\mu \omega}{\rho^2} & \frac{4\mu^2}{\rho^4} - \frac{2}{\rho^5}
\end{pmatrix}
$$

(3.35)

in the two-dimensional $(a,b)$ coordinate system (the dipole moment in the $c$-direction is zero and hence we work with $2 \times 2$ instead of $3 \times 3$ matrices). The microscopic electric field $E_{\text{micr}}'$ at the origin, excluding the field induced by chain at the origin itself, is given by:

$$
E_{\text{micr}}'(\rho = 0) = E_{\text{appl}}(\rho = 0) + \frac{M_A \cdot P_A + M_B \cdot P_B}{M_A + M_B},
$$

(3.36)
where
\[
\begin{align*}
M_A & \equiv \lim_{k \to 0} \sum_{\vec{\rho}_i \in A, \vec{\rho}_j \neq 0} M(\vec{\rho}_i) \cos k u_i, \\
M_B & \equiv \lim_{k \to 0} \sum_{\vec{\rho}_j \in B} M(\vec{\rho}_j) \cos k u_j,
\end{align*}
\]  
(3.37)  
(3.38)

These sums are evaluated below. Substitution of Equation (3.36) in Equation (3.11) and solving yields:
\[
\hat{x}_a \equiv p_{A,a}/E_{\text{appl},a} = \left( \chi_A \left[ 1 - \chi_A \cdot M_A - \chi_B \cdot M_B \right]^{-1} \right)_{aa},
\]  
(3.39)

with $\chi_A$ and $\chi_B$ as defined in Equation (3.13) and the tilde is used to indicate that we are dealing and effective polarizability tensor here. Analogous to the derivation given by Jackson [98] for a point dipole, we can derive the electric field of a line dipole at $\vec{\rho} = 0$ [99]:
\[
\mathbf{E}(\vec{\rho}) = (M(\vec{\rho}) - 2\pi \delta(\vec{\rho}) \mathbb{I}) \cdot \mathbf{p}
\]  
(3.40)

where the convention in Equation (3.40) is that the field within the line-dipole at $\vec{\rho} = 0$ is given by the term $-2\pi \delta(\vec{\rho})\mathbf{p}$ and the Cauchy principal value of the integral should be taken in integrals across the $1/\rho^2$ singularity at $\vec{\rho} = 0$. The macroscopic field is given by the average over the microscopic field of Equation (3.36) for general $\vec{\rho}$ including the chain at the origin. Note that, by symmetry, $p_{A,b} = -p_{B,b}$, the $b$ components do not contribute to the macroscopic field. Also by symmetry, we have $p_{A,a} = p_{B,a} = p_a$. We then have for the macroscopic field $E_a(\vec{\rho})$:
\[
E_a(\vec{\rho}) = E_{\text{appl},a} + \lim_{k \to 0} \frac{1}{2\pi A} P \int_{\text{unit cell}} d^{2}\rho \sum_{\rho^2} M_{aa}(\vec{\rho} - \vec{\rho}_k) \cos(k u_k) p_a - \frac{2\pi}{A} p_a
\]  
(3.41)
\[
= E_{\text{appl},a} + \lim_{k \to 0} \frac{1}{2} P \int d^{2}\rho M_{aa}(\vec{\rho}) \cos(k u) p_a - \frac{2\pi}{A} p_a
\]  
(3.42)
\[
= E_{\text{appl},a} - \frac{4\pi p_a}{A}.
\]  
(3.43)

Substituting this result in Equation (3.16) and using the fact that $P_a = p_a/A$, we find for $\varepsilon_a$ (and an analogous equation for $\varepsilon_b$):
\[
\varepsilon_a = \frac{1}{1 - \frac{4\pi}{A} \chi_a}.
\]  
(3.44)

All that is left to do is determine the matrix elements of $M_A$ and $M_B$. From the symmetry of Equations (3.35), (3.37) and (3.38), we see that $M_{A,ab} = M_{A,ba} = 0 = M_{B,ab} = M_{B,ba} = 0$ and $M_{A,aa} = -M_{A,bb}$ and $M_{B,aa} = -M_{B,bb}$. This leaves us with only one element of each matrix to be determined. Considering $M_A$ first, we split the summation of Equation (3.37)
into two parts. For \( \rho_i < R \) (with \( R \) large) we perform the summation explicitly (taking \( k = 0 \)), while for \( \rho_i \geq R \) we replace the summation by an integral:

\[
M_{4,aa} = \sum_{\rho_i \in \mathcal{A}, \rho_i \neq 0, \rho_i < R} M_{3a}(\rho_i) + \lim_{k \to 0} \frac{1}{2A} \int_{R}^{\infty} \rho d\rho \int_{0}^{2\pi} d\phi M_{3a}(\rho) \cos(k \rho \cos \phi),
\]

which is exact in the limit \( R \to \infty \). The sum is evaluated numerically; its value is \(-0.009677 a_0^{-2}\) in the limit \( R \to \infty \). The integral becomes \(-\pi/(2A)\) after first taking the limit \( k \to 0 \) and then the limit \( R \to \infty \). We can calculate \( M_{4,aa} \) in a similar way. The sum yields \(0.012035 a_0^{-2}\) and the integral becomes again \(-\pi/(2A)\). Therefore, \( M_4 \) and \( M_8 \) are:

\[
M_4 = \begin{pmatrix}
-0.030068 a_0^{-2} & 0 \\
0 & 0.030068 a_0^{-2}
\end{pmatrix},
\]

(3.46)

\[
M_8 = \begin{pmatrix}
-0.008357 a_0^{-2} & 0 \\
0 & 0.008357 a_0^{-2}
\end{pmatrix}.
\]

(3.47)
Chapter 4

Practical considerations for calculations

ABSTRACT

The scheme to calculate one- and two-particle excitations by using the GW approximation and the Bethe-Salpeter equation as outlined in the previous Chapters may be elegant, but a straightforward implementation would not yield a computationally feasible program. For feasible calculations on realistic systems, we have to exploit a number of techniques, most notably the space-time formulation of the GWA developed by Rojas, Needs and Godby (in its mixed-space formulation), the use of symmetry, Fast-Fourier Transforms, and a novel in-house developed Coulomb-divergence smoothing technique.

A number of observations form the basis of the space-time (more accurately: the real-space/imaginary-time) formalism [38, 39]:

- In real space and imaginary time, the calculation of $\Sigma(r, r', it)$ takes a simple form, $\Sigma(r, r', it) = iG(r, r', it)W(r', r, it)$, rather than a multi-dimensional convolution in an energy-momentum representation.

- In imaginary time an eigenfunction expansion of the Green function has a fast converging decaying energy exponential, rather than a slowly converging oscillating one in real time.

- In imaginary time (energy), the structure of the screened interaction $W$ and the self-energy $\Sigma$ is much smoother as a function of time (energy) than in real time (energy).

- For large $|r - r'|$, $\Sigma(r, r', i\omega)$ goes to zero, limiting the numerical work to a region with a certain radius $R$ around $r$.

In the following, we will assume that the system is periodic in all three space directions; we apply periodic boundary conditions in all three directions. The method can also be applied to systems with periodicity in only two or one directions or non-periodic systems. These situations would be applicable for the study of surfaces, isolated polymer chains, and atoms or clusters, respectively.

### 4.1 Mixed-space and Fourier-space formulation

Suppose we have a two-point function $F(r, r')$ with the symmetry of the crystal. Because of the crystal periodicity, we can restrict one of the arguments to the unit cell, spanned by the lattice vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$. The other runs over a larger cell, which we will call the real-space interaction cell. The size of this interaction cell is determined by the decay length of as a function of $|r - r'|$. The size of the interaction cell is an integer multiple of the unit-cell size in either of the three directions, $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$. This multiple is the number of $\mathbf{k}$-points in the corresponding direction, $n_{k,a}$, $n_{k,b}$ and $n_{k,c}$. The total number of $\mathbf{k}$-points is then given by $n_k = n_{k,a}n_{k,b}n_{k,c}$. A finite number of $\mathbf{r}$-points in the unit cell is chosen. These numbers are $n_{r,a}$, $n_{r,b}$ and $n_{r,c}$ in the $\mathbf{a}$-, $\mathbf{b}$- and $\mathbf{c}$-direction, respectively. The total number of grid points is then $n_r = n_{r,a}n_{r,b}n_{r,c}$. To clarify this, it is instructive to look at Figure 4.1. We have chosen a two-dimensional unit cell with lattice vectors $\mathbf{a}$ and $\mathbf{b}$. The number of $\mathbf{k}$-points are $n_{k,a} = 3$ and $n_{k,b} = 2$ ($n_k = 6$); the number of $\mathbf{r}$-points $n_{r,a} = 3$ and $n_{r,b} = 4$ ($n_r = 12$).

---

1For anisotropic systems, this decay may be direction dependent. For instance, in the case of polymers, the decay along the chain will be slower than the decay perpendicular to the chain. Therefore, the real-space interaction cell in the perpendicular directions can be smaller than in the direction along the chain.
In the mixed-space formalism [100], \( F(\mathbf{r}, \mathbf{r}') \) transforms to \( F_k(\mathbf{r}, \mathbf{r}') \) as follows:

\[
F_k(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{n_k} F(\mathbf{r} + \mathbf{R}_i, \mathbf{r}') e^{-i \mathbf{k} \cdot (\mathbf{r} + \mathbf{R}_i)},
\]

\[
F(\mathbf{r}, \mathbf{r}') = \frac{1}{n_k} \sum_{\mathbf{k}} F_k(\mathbf{r}, \mathbf{r}') e^{i \mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')},
\]

where \( \mathbf{R}_i \) is a real-space lattice vector given by:

\[
\mathbf{R}_i = i_{k,a} \mathbf{a} + i_{k,b} \mathbf{b} + i_{k,c} \mathbf{c},
\]

with \( 1 \leq i_{k,a} \leq n_{k,a} \) and likewise for \( i_{k,b} \) and \( i_{k,c} \). A sample vector \( \mathbf{R}_i \) has been drawn in Figure 4.1. We use periodic boundary conditions:

\[
F(\mathbf{r} + n_{k,a} \mathbf{a}, \mathbf{r}') = F(\mathbf{r}, \mathbf{r}' + n_{k,a} \mathbf{a}) = F(\mathbf{r}, \mathbf{r}'),
\]

and likewise for \( n_{k,b} \mathbf{b} \) and \( n_{k,c} \mathbf{c} \). The operators \( F_k(\mathbf{r}, \mathbf{r}') \) are fully periodic: \( F_k(\mathbf{r} + \mathbf{a}, \mathbf{r}') = F_k(\mathbf{r}, \mathbf{r}' + \mathbf{a}) = F_k(\mathbf{r}, \mathbf{r}') \) and likewise for \( \mathbf{b} \) and \( \mathbf{c} \), so that \( \mathbf{r} \) and \( \mathbf{r}' \) can be chosen in the unit cell. Note that (for non-magnetic systems): \( F_k(\mathbf{r}, \mathbf{r}') = F_{-k}(\mathbf{r}, \mathbf{r}') \).

Associated with each lattice vector is a reciprocal lattice vector, e.g. for \( \mathbf{a} \):

\[
\mathbf{K}_a = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}.
\]

\( \mathbf{K}_b \) and \( \mathbf{K}_c \) are then obtained by cyclic permutation of the lattice vectors. For numerical reason it is sometimes more convenient to switch to a representation in Fourier space only,
i.e., transform $F_k(r, r')$ to $	ilde{F}_k(K, K')$, where $K$ and $K'$ are reciprocal lattice vectors, given by $K = i_{r,a}K_a + i_{r,b}K_b + i_{r,c}K_c$. This transformation is given by:

$$F_k(r, r') = \frac{1}{\Delta V} \sum_{K,K'} \tilde{F}_k(K, K') e^{iKr-iK'r'},$$

(4.6)

$$\tilde{F}_k(K, K') = \frac{\Delta V}{\pi r} \sum_{r,r'} F_k(r, r') e^{-iKr+iK'r'},$$

(4.7)

where $\Delta V$ is the volume element belonging to each $r$-point, $\Delta V = a \cdot (b \times c)/n_r$. The reason to sometimes switch to reciprocal space is that we have to include only those Fourier coefficients $F_k(K, K')$ (note that we are following the common practice to drop the tilde) that fall inside the largest possible sphere that fits into the reciprocal-space interaction cell. In the case of the 2D reciprocal-space interaction cell in Figure 4.1, this eliminates only $1 - \pi/4 \approx 0.21\%$ of the Fourier coefficients, for 3D systems, the reduction is much larger, $1 - \pi/6 \approx 47\%$. Since most operations in the calculation scale as $N^2$ or $N^3$ (with $N$ the size of the system), this results in a huge reduction of the amount of work, since the cost of doing the Fast Fourier Transform (FFT) from $\tilde{F}_k(r, r')$ to $F_k(K, K')$ (or backwards) scales only as $N \log N$.

### 4.2 The use of symmetry

The mixed-space functions $F_k(r, r')$ can be thought of as $n_r \times n_r$ matrices. Since we have to perform matrix inversions, which scale as $n_r^3$, the amount of computational resources required (both in terms of time and memory, both in RAM and on disk) are still prohibitively large. To give an example for the 'Situation I' calculations in Chapter 5, $n_r = n_{r,a}n_{r,b}n_{r,c} = 24^3 = 13824$. Using single precision complex numbers to store $\tilde{F}_k(r, r')$ would then require 8 bytes $\times 13824^2/2 \approx 750$ Mb, for one frequency or time, at one $k$-point only (the factor 1/2 is due to the fact that we only have to store the upper or lower triangular part of the matrix: $F_k(r, r') = F_k(r', r)$. Using 4 $k$-points, and 16 frequencies, we would have to store 48 Gb. While this may just be feasible using present day computers, it most certainly was not when this project started.

#### 4.2.1 Symmetrization - high-symmetry $k$-points

By using the symmetry of the system (assuming we have $n_{op}$ symmetry operations at a certain $k$-point), the original matrix of size $n_r \times n_r$ can be split into $n_{op}$ blocks of size $n'_r \times n'_r \approx (n_r/n_{op}) \times (n_r/n_{op})$. The "$\approx$" sign is replaced by "=" in the limit of large $n_r$ only. For the example given above $n_{op} = 8$ and $n_{op} = 4$ at $k = 0$ and at general $k$-points along the chain, respectively, resulting in matrices with $n'_r$ between 1200 and 2000, and 3300 and 3600, respectively.
The separation of the matrix into blocks can be done by symmetrization of the basis set. The concept of symmetrization is most easily explained when we think of the real-space grid as a basis set consisting of \( n_r \) delta-functions, each of which is located at a real-space point. The basis function located at \( \mathbf{r} \) will be called \( \delta_\mathbf{r} \). If we can find linear combinations of the basis functions \( \{ \delta_\mathbf{r} \} \), say \( \{ \zeta_j \} \) (with \( 1 \leq j \leq n_r \)), such that

\[
F_k^{ij} = F_k^{ij'} \delta_{p(j)p(j')},
\]

where \( p(j) \) is the irreducible representation to which the basis function \( \zeta_j \) belongs, we have split the matrix \( F_k(\mathbf{r}, \mathbf{r}') \) into blocks, albeit in a different basis. Equivalently, it can be said that the basis functions \( \zeta_j \) and \( \zeta_{j'} \) couple only if they transform according to the same irreducible representation, in the case of a one-dimensional representation. In the case of a multi-dimensional representation, \( \zeta_j \) and \( \zeta_{j'} \) couple only if they belong to the same row of that representation. \( F_k^{ij} \) is related to \( F_k(\mathbf{r}, \mathbf{r}') \) by:

\[
F_k^{ij'} = \langle \zeta_j | F_k(\mathbf{r}, \mathbf{r}') | \zeta_{j'} \rangle
\]

(4.9)

\[
= \sum_{rr'} U_{rr'}^j F_k(\mathbf{r}, \mathbf{r}') U_{r'j'}
\]

(4.10)

While it may seem that we have introduced the need to perform two costly \( n_r \times n_r \) matrix multiplications, this is not the case: only specific elements of \( U_{rr} \) are non-zero. The matrices \( U_{rr} \) may be constructed by the so-called projection-operator methods, details of which are given in Reference [101]. We also refer to this book for more details on this symmetrization procedure, which will be used in the Situation-I and -II calculations in Chapter 5.

4.2.2 General \( k \)-points

A disadvantage of taking the symmetry of the system into account, is that more symmetry requires more computer code to be written. Moreover, for non-general \( k \)-points, the amount of symmetry is so low, that the symmetrization (and programming) costs do not outweigh the gain.

The arguments \( \mathbf{r} \) and \( \mathbf{r}' \) of the operator \( F_k(\mathbf{r}, \mathbf{r}') \) run over the whole unit cell. We can use the symmetry of the unit cell to restrict one of the arguments, \( \mathbf{r} \), to the irreducible wedge of the unit cell. This restricted \( \mathbf{r} \) will be called \( \tilde{\mathbf{r}} \). The irreducible wedge is defined/constructed in such a way, that by applying all the symmetry operators to the space-points in it, we again obtain the whole unit cell. Equivalently we can say that to each point \( \tilde{\mathbf{r}} \) in this wedge, we assign a star of points, which can be created from the point in the wedge by applying all of the symmetry operations. This means we only have to calculate all functions \( F_k(\mathbf{r}, \mathbf{r}') \) with \( \mathbf{r} = \tilde{\mathbf{r}} \) only, and obtain \( F_k(\mathbf{r}, \mathbf{r}') \) for general \( \mathbf{r} \) in the unit cell by:

\[
F_k(\mathbf{r}, \mathbf{r}') = F_k(\tilde{\mathbf{r}}, \mathbf{r}') e^{ik \cdot (\mu^{-1}(\tilde{\mathbf{r}}) - \mathbf{r})},
\]

(4.11)
where \( \rho^{-1}(\mathbf{r}) \) indicates the inverse of the point-group element that creates point \( \mathbf{r} \) from \( \mathbf{f} \). Equation (4.11) holds for all points \( \mathbf{r} \) in the star of \( \mathbf{f} \). The use of the irreducible wedge is used in the situation-III calculations in Chapter 5 and all calculations in Chapters 6 and 7.

### 4.3 Treatment of the Coulomb interaction

We have developed a novel procedure to deal with the \( k = 0 \) and \( \mathbf{r} = \mathbf{r}' \) singularities of the Coulomb interaction \( v_k(\mathbf{r}, \mathbf{r}') \). We will first describe the procedure for a 3D system and later explain the specific adaptations of this procedure we used for our quasi-1D system.

#### 4.3.1 Elimination of divergencies

In reciprocal space the Coulomb interaction is given by:

\[
v_k(\mathbf{K}, \mathbf{K}') = \frac{4\pi}{|k + K|^2} \delta_{\mathbf{K}, \mathbf{K}'}.
\]

\( v_0(0, 0) \), which would be infinite in Equation (4.12), has to be replaced by a finite value for numerical evaluation. Our approach is to evaluate the integral of the Coulomb interaction multiplied by a smooth, Gaussian cut-off over all space and compare it with the sum for all \( k \) and \( K \) excluding the singularity at \( k = K = 0 \). The integral can be calculated exactly:

\[
I_\alpha = \int d^3q \frac{4\pi}{q^2} e^{-\alpha q^2} = 8\pi^2 \sqrt{\frac{\pi}{\alpha}},
\]

the sum has to be truncated after a certain number of \( K \)-points, depending on \( \alpha, n^0_k \).

\[
S_\alpha = \Delta V \sum_{k, K} v_k(\mathbf{K}, \mathbf{K}) e^{-\alpha |k + K|^2},
\]

where \( \Delta V \) is the volume per \( (k, K) \)-point and the prime indicates that \( k = K = 0 \) is excluded in this sum. For each \( \alpha, n^0_k \) is chosen such that \( S_\alpha \) does not change substantially. In principle, the integral and the sum (the latter for large \( n^0_k \) should yield the same value value if the singularity had not been excluded. Since it has been, we can put:

\[
v_0^c(0, 0) \equiv I_\alpha - S_\alpha
\]

Of course, \( v_0^c(0, 0) \) should not depend on \( \alpha \), which is a cut-off parameter only. Equivalently: we should perform an integral (sum) over the Coulomb interaction, not over the Coulomb interaction severely modified by a Gaussian. This means that \( \alpha \) has to be taken small.
We obtain \( v(\mathbf{r} - \mathbf{r}') \) by a FFT of the regularized \( v_k(\mathbf{K}, \mathbf{K}') \) to real space. We find a finite value for \( v(\mathbf{r} - \mathbf{r}'| = 0) \), solving at the same time the problem with the Coulomb singularity for \( |\mathbf{r} - \mathbf{r}'| = 0 \). The present approach has two advantages over the solution in the original formulation of the space-time method [38], where the authors used a grid for \( \mathbf{r}' \) offset with respect the \( \mathbf{r} \)-grid in order to avoid this singularity. This latter solution not only decreases the symmetry of the system, but it also introduces a new phase factor. Our methods does not have these problems.

### 4.3.2 3D versus quasi-1D systems

For 3D systems, with periodicity in all three directions, the Coulomb interaction is now constructed. If we want to study a single, isolated polymer chain, which has periodicity in one direction only, with the present formalism, we have to avoid 'crosstalk' between periodic images of the chain in the perpendicular directions. We do this by dividing space into regions of points that are closer to the atoms of a specific chain than to those of any other. Subsequently, we cut off the Coulomb interaction \( v(\mathbf{r} - \mathbf{r}') \), obtained in the way described above, by setting it zero if \( \mathbf{r} \) and \( \mathbf{r}' \) belong to different regions. Thus we obtain an interaction \( \tilde{v}(\mathbf{r}, \mathbf{r}') \). In the construction of the Coulomb interaction \( v(\mathbf{r} - \mathbf{r}') \), we take a regular grid of \( k \)-points with a spacing in the \( y \)- and \( z \)-direction approximately equal to that in the \( x \)-direction. From the cut-off interaction \( \tilde{v}(\mathbf{r}, \mathbf{r}') \) we obtain \( \tilde{v}_k(\mathbf{r}, \mathbf{r}') \) (and drop the tilde) in mixed space from Equation (4.1) with \( k \) now in the 1D Brillouin zone.

### 4.4 The space-time formalism for the self-energy

In the space-time formalism, we calculate the one-particle Green function for imaginary times

\[
G_k(\mathbf{r}, \mathbf{r}', i\tau) = \begin{cases} 
  i \sum_{\nu} u_{\nu k}(\mathbf{r}) u_{\nu k}^*(\mathbf{r}') e^{-(\epsilon_k - \epsilon_{\nu}) \tau} & \text{for } \tau < 0, \\
  -i \sum_{c} u_{c k}(\mathbf{r}) u_{c k}^*(\mathbf{r}') e^{-(\epsilon_k - \epsilon_{c}) \tau} & \text{for } \tau > 0,
\end{cases}
\]  

(4.16)

where \( u_{\nu k}(\mathbf{r}) = \phi_{\nu k}(\mathbf{r}) e^{-i \mathbf{k} \cdot \mathbf{r}} \) and \( \epsilon_{\nu} \) (with \( \nu = c, v \)) are DFT-LDA wavefunctions and the corresponding energies (with \( v \) and \( c \) referring to valence and conduction states, respectively). \( \epsilon_F \) is the Fermi energy (set in the middle of the DFT-LDA gap). In the following, we will switch freely between time- and energy/frequency representation. The irreducible polarizability function in the Random Phase Approximation (RPA) is given by:

\[
R_k(\mathbf{r}, \mathbf{r}', i\tau) = -2i \sum_{q} G_q(\mathbf{r}, \mathbf{r}', i\tau) G_{q-k}(\mathbf{r}', \mathbf{r}, -i\tau).
\]  

(4.17)
For the 1D (isolated chain) calculations the screened Coulomb interaction is given by:

$$W_k(r, r', i\omega) = \left[ v_k^{-1}(r, r') - P_k(r, r', i\omega) \right]^{-1},$$  \hspace{1cm} (4.18)

where $v_k(r, r')$ is the regularized cut-off Coulomb interaction described in the previous section. Equation (4.18) is to be read as a matrix inversion, not a point-by-point inversion. For the 3D (crystalline polymer) calculations, we first transform $P_k(r, r', i\omega)$ to reciprocal space (as explained in Section 4.1), and hence the screened Coulomb interaction is given by:

$$W_k(K, K', i\omega) = \left[ v_k^{-1}(K, K') - P_k(K, K', i\omega) \right]^{-1}. \hspace{1cm} (4.19)$$

After the inversion we transform $W_k(K, K', i\omega)$ back to real space. The expressions for the electronic self-energy are then again the same for both the 1D and 3D cases (except that the former case has a one-dimensional Brillouin zone):

$$\Sigma_k(r, r', i\tau) = i \sum_q G_q(r, r', i\tau) W_{k-q}(r, r', i\tau). \hspace{1cm} (4.20)$$

We split the self-energy in an exchange part $\Sigma^x$ and a correlation part $\Sigma^c$:

$$\Sigma^x_k(r, r') = \sum_q \imath G_q(r, r', -i\delta)v_{q-k}(r', r), \hspace{1cm} (4.21)$$

$$\Sigma^c_k(r, r', i\tau) = \sum_q \imath G_q(r, r', i\tau) W^c_{k-q}(r, r', i\tau), \hspace{1cm} (4.22)$$

where $\delta$ is an infinitesimally small positive time, and $W^c$ is the screening interaction:

$$W^c_k(r, r', i\omega) \equiv W_k(r, r', i\omega) - v_k(r, r'). \hspace{1cm} (4.23)$$

This latter step is advantageous, since for larger $\omega$, $W_k(r, r', i\omega)$ approaches $v_k(r, r')$ and hence $W^c_k(r, r', i\omega)$ goes to zero. Next, we calculate the matrix elements of $\Sigma^c_k(r, r', i\omega)$ and $\Sigma^c_k(r, r')$:

$$\Sigma^c_{ijk}(i\omega) = \int \int drr' \phi_{jk}^*(r) \Sigma^c_k(r, r', i\omega) \phi_{jk}(r)$$

$$\approx (\Delta V)^2 \sum_{r,r'} \phi_{jk}^*(r) \Sigma^c_k(r, r', i\omega) \phi_{jk}(r), \hspace{1cm} (4.24)$$

where $\Delta V$ is the volume per $r$-point, and a similar expression holds for $\Sigma^c_{ijk}$. To calculate the QP energies, we have to analytically continue $\Sigma^c_{ijk}(i\omega)$ to the real frequency axis. We do this by fitting $\Sigma^c_{ijk}(i\omega)$ to the following formula:

$$\Sigma^c_{ijk}(E) = a_{ijk}^0 + \sum_{l=1}^n \frac{a_{ijk}^l}{E - b_{ijk}^l}, \hspace{1cm} (4.25)$$
with $E$ the complex energy. It turns out that excellent fits can be obtained using $n = 2$. By using the RHS of Equation (4.25), we can obtain $\Sigma_{i \neq k}(E)$ at any point in the complex $E$ plane. For most systems it is sufficient to calculate the diagonal elements of $\Sigma_{i \neq k}$ and $\Sigma_{i \neq k}(E)$ only, i.e., those elements with $i = j$. We can then obtain the QP energies $E_{ik}$ by solving iteratively:

$$E_{ik} = \epsilon_{ik} + \Sigma_{i \neq k}^x(E) + \Sigma_{i \neq k}^x - V_{i \neq k}^{xc}.
\tag{4.26}$$

Typically a few iterations of Equation (4.26), starting from the DFT-LDA eigenvalues, are enough to find a well-converged set of $E_{ik}$. If non-diagonal elements are taken into account as well, Equation (4.26) becomes a matrix equation.

### 4.5 Solution of the Bethe-Salpeter equation

We have obtained the one-particle excitations energies $E_{ik}$ from Equation (4.26) and the static screened interaction $W(\mathbf{r}, \mathbf{r}', \omega = 0)$ from Equation (4.18) (or (4.19), in which case an additional FFT to real space is performed). We have to modify the expansion of the two-particle excitation wave function in Equation (2.82) slightly, taking the crystal periodicity into account:

$$\chi_{i,q}(\mathbf{r}_c, \mathbf{r}_h) = \sum_{k,c,v} A_{k,cv} \phi_{c,k}(\mathbf{r}_c) \phi_{c,k+q}(\mathbf{r}_h),
\tag{4.27}$$

with $k$ in the first Brillouin zone and $Q$ gives the momentum of the excitation. For purely optical excitations we have $Q = 0$. We have already left out the $B$-part of the expansion [see Equation (2.82)]. This means that the equation to be solved becomes:

$$[E_{ik} - E_{ik}] A_{k,cv}^i + \sum_{k',e',v'} [2V_{k,e',v'}^{xx} \delta_{s,0} - W_{k,e',v'}] A_{k',e',v'}^{i} = E_{ik} A_{k,e,v}^{i}.
\tag{4.28}$$

In fact, this equation has to be solved twice, for $s = 0$ (singlet excitons) and $s = 1$ (triplet excitons). The binding energy $E_b^i$ of the $i$-th exciton is then given by: $E_b^i = E_g - E^i$, where $E_g$ is the one-particle gap.

All that is left to do, is to calculate the matrix elements $V_{k,e',v'}^{xx}$ and $W_{k,e',v'}$ given by:

$$V_{k,e',v'}^{xx} = \int d^3 r \int d^3 r' \phi_{e',k}(\mathbf{r})^{\dagger} \phi_{e,k}(\mathbf{r}) v(\mathbf{r}, \mathbf{r}') \phi_{e,k}(\mathbf{r})^{\dagger} \phi_{e,k}(\mathbf{r}),$$

$$W_{k,e',v'} = \int d^3 r \int d^3 r' \phi_{e,k}(\mathbf{r})^{\dagger} \phi_{e,k}(\mathbf{r}) W(\mathbf{r}, \mathbf{r}', \omega = 0) \phi_{e,k}(\mathbf{r})^{\dagger} \phi_{e,k}(\mathbf{r}),$$

with

$$V_{k,e',v'}^{xx} \approx (\Delta V)^2 \sum_{\mathbf{r}, \mathbf{r}', v} u_{e,k}(\mathbf{r}) u_{e,k}(\mathbf{r})^{\dagger} v_{e,k}(\mathbf{r}) v_{e,k}(\mathbf{r}),
\tag{4.29}$$

and

$$W_{k,e',v'} \approx (\Delta V)^2 \sum_{\mathbf{r}, \mathbf{r}', v} u_{e,k}(\mathbf{r}) u_{e,k}(\mathbf{r})^{\dagger} W(\mathbf{r}, \mathbf{r}', \omega = 0) u_{e,k}(\mathbf{r}) u_{e,k}(\mathbf{r}).$$

\tag{4.30}$$
Note that the amount of work to be done to calculate these matrix elements using Equations (4.29) and (4.30) scales as $n_v^2 n_p^2 n_r^2$ and the amount of work to diagonalize the resulting BSE in Equation (4.28) as $n_v^3 n_p^3$, where $n_v$ and $n_p$ are the number of valence bands and conduction bands taken into account in the expansion of the exciton wave functions in Equation (4.27). Due to symmetry, most matrix elements $V_{k_e,k'_{e'}v'}^{x}$ and $W_{k_e,k'_{e'}v'}^{x}$ are zero. Therefore we first perform a calculation taking all valence and many conduction bands (typically, $n_c \approx 1.5 n_v$) into account, at low $n_r$, to find out which bands contribute to the lowest few excitons. A measure for this is given by $\sum_k |A_{k_e,kv}|^2$. As $\sum_{k_{e'}} |A_{k_{e',kv'}}|^2 = 1$, we include those $(c,v)$-combinations such that $\sum_{k_{e'}} |A_{k_{e',kv'}}|^2 = 0.995$, where the prime is used to indicate that only those $(c,v)$-combinations with the largest contributions have been included. This gives a convergence of the excitation energies of typically 0.01 eV or better; it reduces the amount of work for the calculation of the matrix elements by a factor $\sim n_{op}^4$, and the amount of work in the diagonalization by a factor $\sim n_{op}^6$.

### 4.6 Other properties of the exciton

From the exciton wave function Equation (4.27) we can obtain the exciton-hole distance probability distribution in the chain $(x)$ direction $P_t(x_e - x_h)$:

$$ P_t(x_e - x_h) = \int \int d^3 r_e d^3 r_h \delta(x_e - x_h) |\chi_t(r_e, r_h)|^2 $$

and the root-mean-square electron-hole distances $r_{rms}$ along the chain:

$$ r_{rms}^2 = \int \int d^3 r_e d^3 r_h (x_e - x_h)^2 |\chi_t(r_e, r_h)|^2. $$

Alternatively, we can also choose to fix the electron (hole) at a certain point $a_e$ ($a_h$) and calculate the corresponding distribution functions. Mathematically, this corresponds to inserting a delta-function $\delta(r_e - a_e)$ ($\delta(r_h - a_h)$) in Equations (4.31) and (4.32). The corresponding probability and root-mean-square distance will be called $P'$ and $r'_{rms}$. These quantities give an expression of the size and shape of the exciton.

The dipole matrix element $\mu_{i,||q}$ between the ground state and the $i$-th exciton along a certain wave vector $q$ follows from the expansion coefficients $A_{k_{e,v}}^i$:

$$ \mu_{i,||q} = \sqrt{\frac{2}{nk}} \sum_{k_{e,v}} A_{k_{e,v}}^i \mu_{k_{e,v},||q}, $$

with

$$ \mu_{k_{e,v},||q} = \lim_{|\ell| \to 0} \int d\vec{r} \phi_{e,k+\ell,||q}(\vec{r}) \frac{\phi_{e,k}(\vec{r})}{|q|} $$

(4.34)
and the dipole matrix element \( \mu_{ji, \parallel q} \) between the \( i \)-th exciton and the \( j \)-th exciton along a certain wave vector \( q \) is given by:

\[
\mu_{ji, \parallel q} = \lim_{|q| \to 0} \int \int \chi_j^\dagger(r_e, r_h) \frac{e^{i q \cdot (r_e - r_h)}}{|q|} \chi_i(r_e, r_h) \, dr_e \, dr_h.
\]  

(4.35)

This means that the polarizability of the \( i \)-th exciton along the chain, if the chain is along the \( x \)-axis, is given by:

\[
\alpha_{xx,i} = 2 \sum_{j \neq i} \frac{|\mu_{ji, \parallel k_e}|^2}{E_j - E_i} - 2 \frac{|\mu_{ii, \parallel k_e}|^2}{E_i},
\]  

(4.36)

where the latter term represents the dipolar coupling to the ground-state.
Chapter 5

Electronic and optical gaps in conjugated polymers

ABSTRACT

We calculate the electronic and optical excitations of conjugated polymers using the $GW$ approximation for the electronic self-energy, and include excitonic effects by solving the electron-hole Bethe-Salpeter equation. Three different situations are studied: (I) excitations on an isolated chain, (II) excitations on a chain embedded in a medium with the appropriate frequency-dependent dielectric constants, and (III) excitations in a polymer crystal. Only in situation II we find good agreement with the available experimental data. In situation I the disagreement is attributed to the lack of long-range screening of the Coulomb interaction; in situation III to the large degree of wave-function overlap between adjacent chains, which is not expected to be present in realistic (disordered and substituted) systems.

5.1 Introduction

As explained earlier in Chapter 1, semiconducting conjugated organic polymers have received increasing interest in recent years, especially since the discovery of electroluminescence [4] of these materials. The charge carriers and excitations in these materials have been studied extensively both experimentally and theoretically, but many important fundamental issues still remain unresolved. For instance, the magnitude of the exciton binding energy in these materials is still disputed [10]. This is a very important quantity, since e.g. in photovoltaic devices (solar cells) one would like to have a small binding energy, which facilitates the fast separation of charges, while in electroluminescent devices such as LEDs a larger exciton binding energy, to increase the probability of fast (radiative) annihilation of electron-hole pairs, is desirable.

In conventional semiconductors such as Si and GaAs the optical excitations are well described in terms of very weakly bound electron-hole pairs (so-called Wannier excitons) with a binding energy of the order of 0.01 eV. In crystals made of small organic molecules such as anthracene, the exciton is essentially confined to a single molecule (Frenkel exciton), leading to a binding energy of the order of 1 eV. The question is where exactly conjugated polymers fit in between conventional semiconductors on the one hand and molecular crystals on the other.

*Ab-initio* calculations, on a variety of conjugated polymers, within the local-density approximation to density-functional Theory (DFT-LDA) yield equilibrium structures in very good agreement with experiment [91, 92, 93, 94]. Unfortunately, the one-particle energies resulting from DFT can formally not be interpreted as excitation energies [53], nor are excitonic effects taken into account in these calculations. An *ab-initio* many-body calculation within the *GW* Approximation (GWA) was performed for polyacetylene (PA) [102]. The authors claim that their quasi-particle (QP) gap, not including excitonic effects, is in agreement with the experimental absorption gap. This result seems to be in contrast with a more recent calculation by Rohlfing and Louie [103] of both one- (QP) and two-particle (exciton) excitation energies for PA and poly-phenylene-vinylene (PPV) chains. Their absorption gaps are in good agreement with experiments, but the inclusion of excitonic effects proves to be crucial for this. However, their exciton binding energy of 0.9 eV for PPV is much larger than the experimental values, recently obtained using STM injection spectroscopy: 0.35 ± 0.15 eV for an alkoxy-substituted PPV [8] and 0.48 ± 0.14 eV for unsubstituted PPV [9].

In this Chapter, we study the electronic and optical excitations of conjugated polymers using many-body Green-function techniques. As these techniques are rather time-consuming, we start our studies for an isolated chain of polythiophene (PT) in vacuum, hereafter referred to as situation I. Such a calculation is relatively simple, since we do not need to bother with the exact interchain orientation and distance, and the system has more symmetry, hence reducing the amount of work. Moreover, DFT-LDA calculations for con-
jugated polymers yield one-particle gaps for isolated chains that are not much different from those obtained for crystalline geometries \[93, 94\]. Therefore, a reasonable starting point for more advanced one-particle and two-particle excitation calculations using the GW approximation and Bethe-Salpeter equation (BSE) seems to be the isolated chain.

Unfortunately, all experiments on conjugated polymers are performed on either thin-film or bulk systems\(^1\), where an unknown degree of interchain interactions may alter the optical properties of the single chain. Since DFT-LDA (and most gradient corrections to LDA too) is a local theory, the effect of these interactions may be masked in DFT-LDA. Calculations for a three-dimensional crystal are at least one order of magnitude more involved, so we first choose a different approach to include interchain interactions. In situation II, we place a single chain in a medium with the appropriate frequency-dependent dielectric constants. Finally, in situation III a polymer crystal is studied. In situation II, the only interchain interaction we have is the interchain polarization. In situation III, the interchain wavefunction hybridization is also included. We will perform studies for both PT (situations I, II and III) and PPV (situation III only); PT was chosen as a starting point, since its single chain has eight symmetry operations, while the PPV single chain has only four. This means that the calculations for PT are less involved than the corresponding calculations for PPV.

\[\text{5.2 The quasi-particle and Bethe-Salpeter equations}\]

In all three situations, we follow the computational scheme as outlined in Chapter 2, which we briefly recapture here. We use the Car-Parrinello scheme to obtain the geometries of the polymers. From these calculations we also find the DFT-LDA eigenvalues and -functions which we use as a starting point for our GWA calculation [following Equations (4.16) through (4.26)] to solve the quasi-particle equation:

\[
\left[ -\frac{\nabla^2}{2} + V_{\text{ion}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) \right] \phi_{nk}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', E_{nk}) \phi_{nk}(\mathbf{r}') = E_{nk} \phi_{nk}(\mathbf{r}),
\]

which yields the one-particle energies \(E_{nk}\), i.e., the electron and hole energies and hence also the one-particle bandgap \(E_g\). These one-particle, or quasi-particle (QP) energies, and the screened interaction following from the GWA calculation, form the input of the matrix-formulation of the BSE [Equations (4.27)-(4.30)]:

\[
[E_{nk} - E_{ek}] A_{kek'} + \sum_{k', \delta, \sigma} \left[ 2 V_{kek', k', \delta, \sigma} \delta_{s,0} - W_{kek', k', \delta, \sigma} \right] A_{kek'} A_{kek'} = E_{nk} A_{kek'},
\]

\(^1\)Some experiments are performed in solution; while in dilute solutions the interaction between the individual polymers may be negligible, the solvent may affect the electronic and optical properties as we will see in Chapter 7.
\[ \gamma \text{ (deg)} \]

<table>
<thead>
<tr>
<th></th>
<th>PT</th>
<th>PPV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>( a(a_0) )</td>
<td>14.8022</td>
<td>14.8022</td>
</tr>
<tr>
<td>( b(a_0) )</td>
<td>15.0000</td>
<td>15.0000</td>
</tr>
<tr>
<td>( c(a_0) )</td>
<td>15.0000</td>
<td>15.0000</td>
</tr>
<tr>
<td>( \gamma ) (deg)</td>
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<td>90</td>
</tr>
<tr>
<td>( n_{r,a} )</td>
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<td>( n_{r,b} )</td>
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<td>1</td>
</tr>
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<td>( n_{k,c} )</td>
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<td>1</td>
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<td>( \alpha ) (deg)</td>
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<td>45</td>
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<tr>
<td>( \phi_{nk} )</td>
<td>Single chain</td>
<td>Single Chain</td>
</tr>
<tr>
<td>( v(\mathbf{r}, \mathbf{r}') )</td>
<td>Cut-off</td>
<td>Cut-off</td>
</tr>
<tr>
<td>( W(\mathbf{r}, \mathbf{r}', i\omega) )</td>
<td>Equation (4.18)</td>
<td>Equation (3.7)</td>
</tr>
</tbody>
</table>

**TABLE 5.1:** Differences between situations I, II, and III for PT and the parameters for the situation III calculation for PPV. The crystal structure of polythiophene is given in Figure 3.1; as PT is orthorhombic the monoclinic angle \( \gamma \) is equal to zero. Details on the Coulomb cut-off procedure can be found in Section 4.3; for details of the construction of the screened interaction see Sections 4.4 and 3.1.1.

which yields the two-particle excitation energies \( E^i \) and exciton binding energies \( E^i_b \) (from \( E^i_b = E_g - E^i \)). Here, \( A^i_{kcv} \) are the expansion coefficients in the exciton wavefunction:

\[
\chi^i(\mathbf{r}_e, \mathbf{r}_h) = \sum_{kcv} A^i_{kcv} \phi_{nk}(\mathbf{r}_e) \phi^*_nk(\mathbf{r}_h). \tag{5.3}
\]

In the expansion, we take only the \( \pi \) and \( \pi^* \) bands into account (for situation I and II) and both (hybridized) \( \pi \) bands and \( \pi^* \) bands (for situation III); for PPV we take four valence and four conduction bands into account.

The differences between the three situations studied here are in the wave functions \( \phi_{nk} \), the cut-off of the Coulomb interaction \( v(\mathbf{r}, \mathbf{r}') \), and the screened interaction \( W(\mathbf{r}, \mathbf{r}', i\omega) \). These differences are listed in Table 5.1. The length of the chain was optimized for the single chain only; for the crystal we took the Car-Parrinello single-chain length and the perpendicular parameters from experiment [88, 89]. The lower number of real-space grid points \( n_{r,a}, n_{r,b} \) and \( n_{r,c} \) for situation II applies only to the interchain part of the screening in Equation (3.7); this number can be taken much lower, since this part has much less structure than the isolated-chain part of the screening. On the other hand, more \( \mathbf{k} \)-points are required; the reason for this is that the excitations in situation II are more delocalized than those of situation I. Using these parameters, the QP gap has converged to within 0.05
eV; the exciton binding energies to 0.1 eV. The calculations (not counting the DFT-LDA calculations) typically took two and four weeks for situation I and II respectively (on a Cray C916) and four weeks for the situation III calculations (on a SGI Origin 2000) for PT.

The unit cell of crystalline polyphenylenevinylene [90] is monoclinic. Due to the way the reciprocal lattice vectors are constructed [see Equation (4.5)], the fact that the unit cell is monoclinic means that (i) the k-points in the calculation are no longer strictly along the chain; we no longer have a subset of k-points of the form \((k_x, 0, 0)\), and (ii) the band gap is no longer at the center or at an edge of the first Brillouin zone, but at a general k-point. Fortunately, the k-point with the smallest band gap is in the set. Other details can be found in Table 5.1.

5.3 Results - Polythiophene

5.3.1 One-particle excitation energies: quasi-particles

The calculated GWA QP band structures for all three situations are shown in Figure 5.1; a more detailed schematic of the states around the band gap at relevant k-points is given in Figure 5.2. The direct band gap decreases from 3.59 eV in situation I to 2.48 eV in situation II, and 1.75 eV in situation III. In situation I and II, the band gap is direct, and located at the center of the Brillouin zone \(\Gamma\), in situation III the indirect band gap \(\Gamma \rightarrow Z\) is 0.15 eV smaller than the direct band gap at Z. Since optical transitions are not possible across the indirect gap, the relevant band gap in situation III is the direct gap at Z. Note that for situation I and II, we performed one GW iteration; for situation III two iterations were performed, updating the one-particle energies only, as explained in Section 2.3. This second iteration results in a one-particle gap that is 0.2 eV larger than the gap after the first iteration.

Both the interchain polarization (included in situation II and III) and the interchain wavefunction hybridization (included in situation III) substantially alter the one-particle spectrum. A direct experimental determination of the one-particle gap is not available in PT. In polymers, the one-particle gap is an elusive property. It was only recently determined directly for a variety of polymers (not including PT) using STM techniques [8, 9]. The one-particle gap can, however, be estimated from the experimental optical gap of 1.8-2.0 eV [104] and the exciton binding energy as derived from an electro-absorption experiment of 0.6 eV [105], giving \(E_g = E_{opt} + E_b\), yielding \(E_g = 2.4-2.6\) eV, in good agreement with the results for situation II. Note that the values are extracted from two different experiments performed on different regioregular alkyl-substituted PT. In all three cases, we find a substantial increase of the DFT-LDA band gap, which is 1.22 eV for situation I and II, and 0.76 (1.18) eV at Z (\(\Gamma\)) for situation III. If we assume that a second iteration of the
FIGURE 5.1: The one-particle excitation energies (in eV) as calculated with the GWA for PT for situations I through III. Note that in situation III we have a double number of bands as compared to situation I and II, since there are two chains in the unit cell. In situation I and II the Brillouin zone is one-dimensional and only the bands along the ΓX-direction have been plotted; in situation III, where we have a three-dimensional Brillouin zone, we have plotted the band structure along the path ZΓXUZ.

The GW scheme in situation I and II would also increase the gap by approximately 0.2 eV, we still have good agreement with experiment.

5.3.2 Two-particle excitation energies: excitons

The two-particle excitation spectrum for the lowest few excitons in all three situations is given in Figure 5.3. The exciton binding energy of the lowest singlet exciton decreases from 1.85 eV in situation II to 0.76 eV in situation I and 0.15 eV in situation III. Note that the change of the optical gap, the difference between the QP gap - which also changes by more than 1 eV, as was shown in the previous Subsection - and the exciton binding
energy is hardly affected; it changes from 1.74 eV in situation I to 1.73 eV in situation II and 1.60 in situation III. The values of 1.74 and 1.73 eV are in very good agreement with the experimental luminescence gap of 1.8 eV [104], which is smaller than the often cited absorption gap of PT of 2.0 eV [104, 106].

The inclusion of interchain screening and wave-function hybridization also has a dramatic effect on the splittings of the various exciton levels. The exchange splitting of the lowest exciton seems to be the least affected; it is reduced from 0.51 eV in situation I to 0.39 eV in situation II and 0.25 eV in situation III. Note that the exchange interaction is not screened [see Equation (4.29)]; hence the screening can only reduce the exchange interaction indirectly, e.g., by increasing the average electron-hole distance. The $B_u$-$A_g$ splitting reduces from 0.89 eV in situation I, to 0.53 eV in situation II, and 0.05 eV in situation III. For the $A_g$ exciton, the exchange splitting is negligible, since the probability to find the electron and the hole forming the exciton with zero relative distance is zero. Again, for both the exchange splitting and the $B_u$-$A_g$ splitting we only have agreement with the available experimental data in situation II. In Figure 5.4 we have plotted the electron-hole distance probability distribution $P(r_e)$, as given by Equation (4.31). The corresponding root-mean-square distances are 18 a.u. in situation I, 24 a.u. in situation II and 25 a.u. in situation III.
5.3.3 Dielectric constants

In situation II, we have to calculate the dielectric constant \( \varepsilon_i(i\omega) \) with \( i = a, b, c \) the three crystal axes, using Equations (3.32) and (3.44). In the \( GW \) scheme for situation III, they are a byproduct of the calculation. For \( \omega = 0 \) they correspond to the real zero-frequency dielectric constants, which have been listed in Table 5.2.

<table>
<thead>
<tr>
<th>Crystal Axis</th>
<th>Situation II</th>
<th>Situation III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \varepsilon(\omega = 0) )</td>
<td>( GW1 )</td>
</tr>
<tr>
<td>( a )</td>
<td>10.8</td>
<td>21.4</td>
</tr>
<tr>
<td>( b )</td>
<td>3.3</td>
<td>3.5</td>
</tr>
<tr>
<td>( c )</td>
<td>2.8</td>
<td>4.5</td>
</tr>
</tbody>
</table>

TABLE 5.2: The zero-frequency dielectric constants of the bulk along the crystal axes, in situation II and III, the latter after one and two \( GW \) iterations.

FIGURE 5.3: The two-particle (exciton) excitation energies for the lowest few excitons in situations I, II and experiment (E), from references [104, 105]) on the left, and in situation III on the right.
FIGURE 5.4: The electron-hole distance probability distribution along the chain $P'(x_e)$ for the lowest optically active exciton, for situation I (top), II (middle) and III (bottom). The position of the hole is kept fixed, at $\sim 1$ a.u. above the inversion center.
5.4 Results - Polyphenylenevinylene

The Brillouin zone and the \( \mathbf{k} \)-points at which the QP spectrum is calculated are given in Figure 5.5. The calculated GWA band structure is given in Figure 5.6. A close up of the bands around the QP band gap is given in Figure 5.7. We performed only one iteration in the GW scheme here; we expect the QP gap to be increased in a second iteration by about 0.2 eV, as for PT. The minimum direct band gap is 2.01 eV, at the \( \mathbf{k} \)-point on the right in Figure 5.7. The excitonic spectrum is given in Figure 5.8. The absorption gap is 1.66 eV; significantly smaller than the experimental value of 2.4 eV [107]. However, this absorption gap will also be increased if a second GW iteration is performed. The exciton binding energy, 0.34 eV, is somewhat smaller than the experimental value for unsubstituted PPV of 0.48 ± 0.14 eV [9]. The singlet-triplet splitting for the lowest two excitons, 0.30 and 0.35 eV, is significantly smaller than the experimental value of 0.9 eV [108]. We observe that the lowest exciton has a much smaller dipole matrix element (one order of magnitude smaller) than that of the one but lowest exciton, which would drastically quench the luminescence of the system, as optical excitations would be 'trapped' in this lowest exciton state. Generally, the crystalline calculation for PPV agrees even less with experiment than the crystalline calculation for PT.

![Brillouin zone and k-points](image)

**FIGURE 5.5:** The Brillouin zone of crystalline PPV, indicated by the (almost) hexagonal shape. The bold crosses indicate the \( \mathbf{k} \)-point set generated by the GW program (some of which have been moved from their original position, indicated by plusses, by inversion symmetry. The dotted arrow indicates the chain direction. The labeled arrows indicate lines along which the band structure is plotted in Figure 5.6.
FIGURE 5.6: The GW band structure of crystalline PPV, plotted along the lines indicated in Figure 5.5. All energies in eV.

FIGURE 5.7: The GW band structure of crystalline PPV around the quasi-particle gap along line 4 (see Figure 5.5); the minimum band gap occurs at the last k-point. All energies in eV.

5.5 Discussion

5.5.1 Comparison of the three geometries of polythiophene

For the three different PT geometries we obtain drastically different values for the electronic and optical excitation energies. The band gap and exciton binding energy and splittings
are too large compared to experiment in situation I, whereas they are too small in situation III; only in situation II we have good agreement with experiment. The exciton binding energy in situation III deserves extra attention. The minimum energy to create a fully separated electron-hole pair is equal to the indirect band gap, of 1.6 eV (see Figure 5.2). As the absorption (of the lowest exciton) also starts at 1.6 eV (see Figure 5.3), one might argue that the exciton binding energy is very small in this situation. In fact, in the STM determination of the exciton binding energy for this system, it would be vanishingly small, as this technique samples the indirect band gap [8, 9, 119]. However, in the case of crystalline silicon, the indirect band gap is 1.2 eV and the direct band gap is 3.4 eV; the absorption starts only slightly below this latter value. Hence the exciton binding energy, which is of the order of 0.01 eV, is here also defined relative to the direct band gap. Hence, in the case of PT we should follow this convention and the exciton binding energy is indeed 0.15 eV, not vanishingly small.

Note that the optical gap is hardly affected by, first of all, the introduction of bulk screening, when going from situation I to situation II, and, secondly, by introducing wave-function hybridization between neighboring chains. This optical gap of 1.73 eV (in situation II) compares well to the experimental luminescence gap of 1.8 eV [104], which is slightly smaller than the absorption gap of 2.0 eV [104, 106]. There are two reasons why we should compare our result to the former gap.

The first reason is that absorption occurs everywhere in a sample, both in the ordered and disordered parts, but luminescence occurs predominantly in the most ordered parts with the longest conjugation lengths. This is because, prior to recombination, excitons diffuse to

---

**FIGURE 5.8**: The lowest excitons in crystalline PPV; all energies in eV.
those parts of the sample where they have the lowest energy [80, 109]. The second reason is that after photo-excitation, the rings, which may be twisted around their common C-C bond, tend to co-planarize in the excited state, due to the fact that the excited state is slightly more quinoid than the aromatic ground state [10]. As we are performing our calculations for a perfect, co-planar chain of PT, we should therefore compare our optical gap to the luminescence gap. Note that in principle it is possible that excitons trapped in defects or disordered parts of the sample have a lower energy than in a fully conjugated, defect-free polymer. However, the luminescence spectrum of Reference [104] can be fully understood in terms of the $^1B_u$ exciton decay and its vibronic side bands, which means that such defects are either rare or that excitons trapped by such defects decay non-radiatively.

It would be best to compare our results for situation III with data obtained for high-quality oligomer crystals, but the best resolved data are available for $\alpha$-4T and $\alpha$-6T only [110, 111] and not for longer oligomers, making a reliable extrapolation to $\alpha$-\infty T, the polymer, impossible. The situation-I results could be compared to the extrapolation of gas-phase experiments on oligomers, but unfortunately, most studies for isolated molecules are performed in dilute solutions, and not in the gas phase.

Having established this, we can conclude that it is absolutely necessary to include at least the interchain polarization or screening effects due to neighboring chains, which is what is done in situation II. In situation III, this screening is included, as well as the wave-function hybridization due to neighboring chains. The inclusion of these latter effects leads to an underestimation of both the one-particle gap and the exciton binding energy. Again, the change of these two properties cancels in the absorption gap to a large degree. There are three possible explanations for the discrepancies between situation III and experiment; a geometrical, a physical and a methodological explanation. These will now be discussed.

**Disagreement between assumed and real geometry**

Most experiments are performed on substituted polymers, i.e., some of the hydrogen atoms on the backbone or rings are replaced by large alkyl ($-C_nH_{2n+1}$) or alkoxy ($-OC_nH_{2n+1}$) side-groups to improve the polymers’ processability. These substituents dramatically alter the crystal structure from the crystal structure of the unsubstituted chain.

Moreover, polymers (substituted or unsubstituted) very rarely crystallize in a very ordered fashion. This means that effective hybridization of wave functions between adjacent chains, as assumed in situation III, may well be impossible. In fact, in an experimental study of crystalline, unsubstituted PT, a density $\rho = 1.21$ g/cm$^3$ was found [88]. For the crystal structure of situation III, $\rho = 1.54$ g/cm$^3$. If we assume the disorder in the size of the unit cell in the chain direction to be small (which is plausible since in that direction we have covalent bonds only), this means that the average interchain distances in the sample are $\approx 12\%$ larger than for the crystal structure in situation III. Moreover, even in the ordered regions of the sample, the average displacement of the atoms from the perfect lattice site...
is \( \approx 0.3 \) Å [88]. Since the amount of wave-function overlap between two chains depends exponentially on the interchain distance, effective hybridization is practically impossible, even in more ordered samples. As the interchain polarization between chains decays algebraically, the amount of interchain screening is not as much affected by such a small displacement.

This means that experimental studies effectively look at isolated polymer chains in a dielectric medium, which is exactly what we study in situation II, the situation in which we have good agreement with the experimental data for the exciton binding energies and splittings, and the quasi-particle gap. We can 'switch off' the hybridization effects by averaging the the \( \pi \)-band and the band below it, and the \( \pi^* \) band and the band above it, at \( \Gamma \). This gives a QP gap of 2.5 eV, in good agreement with the experimental value. For comparison with the value of situation II, where only one GW iteration was performed, we should subtract 0.2 eV, the gap correction in the second GW iteration from the value of 2.5 eV.

Note that in the case of oligomers, crystals of very high purity and crystallinity can be obtained. This means that for these systems, assumed and experimental geometry are exactly the same and the wavefunction hybridization and the resulting band widths can be expected to be of the same order as those predicted here for PT, i.e., \( \sim 0.5 \) eV, at least for low temperatures.

**Decoherence of hybridization due to thermal fluctuations**

A well-known effect in the oligomer crystals mentioned in the previous paragraph is the strong temperature dependence of the electron and hole mobilities [112]. Contrary to the situation in disordered systems, where mobility is thermally activated, the mobility in these systems decreases when going from 0 to \( \sim 300 \) K, where a cross-over to thermally activated behavior occurs. The initial decrease is attributed to an electron or hole mass renormalization, induced by thermally activated molecular rotation phonon modes (fluctuation of the angle \( \alpha \) in Figure 3.1), which decrease the interchain coupling and wave-function overlap [113]. As most experiments are performed at 77 K or higher, effective interchain wave function hybridization may be suppressed by these fluctuations, leading to the same picture as sketched in the preceding paragraphs, namely that of an isolated chain in a dielectric medium.

**Overestimation of hybridization effects in DFT-LDA**

In DFT-LDA the long-range decay of the exchange-correlation potential is incorrect [114], viz. exponential rather than the expected \( 1/r \)-decay. Therefore, LDA puts too much charge in the outer regions. The effect is most pronounced in regions with the lowest charge density, in our case the regions between the chains. Surprisingly, gradient corrections to LDA do not correct this [114]. This means that part of the large hybridization (\( \approx 0.5 \)
<table>
<thead>
<tr>
<th>Geometry</th>
<th>$\pi$-stacked, $d=7.56$ a.u.</th>
<th>rotated and shifted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional</td>
<td>Ref</td>
<td>$\Delta_{HOMO}$</td>
</tr>
<tr>
<td>BLYP</td>
<td>[48, 51]</td>
<td>0.343</td>
</tr>
<tr>
<td>BP</td>
<td>[48, 49]</td>
<td>0.342</td>
</tr>
<tr>
<td>LB94</td>
<td>[114]</td>
<td>0.289</td>
</tr>
<tr>
<td>LDA</td>
<td>[115]</td>
<td>0.356</td>
</tr>
<tr>
<td>PW</td>
<td>[50]</td>
<td>0.340</td>
</tr>
</tbody>
</table>

**Table 5.3**: Hybridization of the isolated thiophene molecule C$_4$H$_4$S HOMO and LUMO energies (in eV) in the dimer (C$_4$H$_4$S)$_2$, calculated within DFT using five different potential and energy functionals.

In order to see if the hybridization of the wavefunctions in situation III is artificially large due to an error in the LDA, we performed a number of DFT calculations using various functionals as implemented in the ADF package [59]. In this package, the LB94 functional [114] is implemented. That functional was explicitly constructed to have a $1/r$ decay. Apart from this specific functional, more standard functionals, viz. BLYP [48, 51], BP [48, 49], LDA (in a slightly different parameterization) [115], and PW [50] were also used for comparison. We performed calculations for the thiophene dimer, (C$_4$H$_4$S)$_2$, in two different geometries: $\pi$-stacked on top of each other, and rotated and shifted with respect to each other in such a way to represent the relative ordering of the rings in the crystal of situation III. The geometry of the isolated molecule was obtained within DFT-LDA and kept fixed for both geometries and all functionals. The results for the hybridization of HOMO and LUMO energies are given in Table 5.3.

A number of interesting facts can be learned from Table 5.3. First of all, LDA and most standard gradient corrections (BLYP, BP and PW) give the same hybridization (within the accuracy of the method); secondly the LB94 potential, which has the correct behavior for long range and hence should be more reliable for weak, intermolecular interactions, give a hybridization which is only 15-25% smaller than that of the other functionals. Note that the hybridization of the HOMO and LUMO for the shifted and rotated geometry (corresponding to the relative orientation of the rings of adjacent chains in our crystalline situation III) is smaller by a factor 4 than the DFT-LDA predictions for situation III as
given in Figure 5.2). However, in this dimer configuration, each ring couples with only one other ring, in the crystal there are six rings in the immediate surroundings of each ring (e.g., for the ring at the origin in Figure 3.1: two of its own periodic images above and below it and the ring at the center of the same cell and three of its periodic images), resulting in a larger hybridization than in the dimer studied here.

Even though the long-range behavior of the LDA is incorrect, which is believed to be troublesome for weak, intermolecular interactions, the hybridization of the wave functions in LDA is not dramatically wrong. This is in line with LDA results for graphite, where good results for the interplanar distance were obtained [116], the binding distance and energy in the benzene dimer [117] and the interchain distance for \( \pi \)-stacked polythiophene [118]. This strongly suggests that despite being formally incorrect for long-range interactions, the LDA still gives reasonable results, and can therefore be relied upon to give a good estimate for the hybridization of the wavefunctions.

To conclude this discussion: the large wave function hybridization for situation III is not artefact of the LDA, as we argued in the previous paragraphs. However, temperature effects which activate rotational phonon modes can destroy the coherence of the wavefunction hybridization in experiments. Moreover, in these experiments, the interchain order is low, even for the most ordered, unsubstituted polymers, which also decreases the wave-function hybridization, meaning that most experiments are performed on situation II-type samples.

### Table 5.4

<table>
<thead>
<tr>
<th>( r_{\text{inter}} ) (a.u.)</th>
<th>Situation II</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_g )</td>
<td>23.2</td>
<td>10.0</td>
</tr>
<tr>
<td>( E_{\text{b}}(1B_u) )</td>
<td>0.64</td>
<td>0.76</td>
</tr>
<tr>
<td>( E_{\text{opt}} )</td>
<td>1.68</td>
<td>1.73</td>
</tr>
<tr>
<td>( ^3B_u \rightarrow ^1B_u )</td>
<td>0.34</td>
<td>0.39</td>
</tr>
<tr>
<td>( ^1B_u \rightarrow ^1A_g )</td>
<td>0.45</td>
<td>0.53</td>
</tr>
</tbody>
</table>

**Table 5.4:** Quasi-particle \( (E_g) \) and optical \( (E_{\text{opt}}) \) gaps and binding energies \( (E_{\text{b}}) \), as a function of the cut-off distance \( r_{\text{inter}} \) (see Equation 3.3). Exciton transition energies are also listed. All data in eV.

### 5.5.2 Interchain screening as a function of \( r_{\text{inter}} \)

In situation II, we have used a cut-off parameter \( r_{\text{inter}} \), the distance beyond which the interchain screening is switched on, in Equation (3.3). Above, we have used \( r_{\text{inter}} = 10 \) a.u., corresponding to the interchain distance in the crystal structure of References [88, 89], as displayed in Figure 3.1. We performed similar calculations for \( r_{\text{inter}} = 8 \) a.u. and
\( r_{\text{inter}} = 12 \text{ a.u.} \) These data, for all three values of \( r_{\text{inter}} \) are listed in Table 5.4. The QP band gaps are 2.32 and 2.61 eV, respectively. The \(^1\text{B}_u\) binding energies are 0.64 and 0.86 eV and hence the optical gaps are 1.68 and 1.73 eV, respectively. This means that the optical gap is quite insensitive to the choice of \( r_{\text{inter}} \). This is consistent with the fact that in the limit \( r_{\text{inter}} \to \infty \), which corresponds to no interchain screening, we should find the isolated chain absorption gap of 1.74 eV. The energy differences between the excitons are even less sensitive to \( r_{\text{inter}} \). The good agreement with experiment and the fact that especially the optical gap and the energy separation between the excitons are hardly influenced by varying \( r_{\text{inter}} \) are also a posteriori justifications for our model screening interaction Equation (3.7).

### 5.5.3 Effective masses

As mentioned in the description of the methods in Chapter 2, reasonable agreement for the one-particle excitation spectra can be achieved by shifting the DFT-LDA conduction bands upwards by a certain energy value. A good indication of how good this approximation is, is the change of the electron and hole effective masses between DFT-LDA and GW. The effective-mass tensor is given by:

\[
\frac{1}{m_{ij}(k)} = \frac{\partial^2 E_n(k)}{\partial k_i \partial k_j},
\]

with \( n \) the band index, and \( i \) and \( j \) equal to either \( x, y \) and \( z \). The most relevant effective mass is that in the direction of the largest dispersion, i.e., along the chain \( (i = j = x, \mathbf{k} = \Gamma) \). In situations I and II, the DFT-LDA effective masses are 0.15 \( m_e \) and 0.17 \( m_e \) for the \( \pi \) and \( \pi^* \) bands, respectively. These decrease by approximately 15% in the GW calculation; the band widths increase concomitantly. In situation III the reduction of the effective masses is comparable. This means that the effect of the GW calculation can be described by an almost rigid shift of the conduction bands with respect to the valence bands. In the next chapter, this will be exploited to perform calculations of excitonic properties based on DFT-LDA one-particle energies, rather than GW one-particle energies.

### 5.5.4 Polyphenylenevinylene

The results for PPV support the conclusion, already drawn for PT, that GW and BSE calculations for the optical and electronic properties of conjugated polymers should not be performed for a fully crystalline situation, as this introduces more wave-function hybridization than is present in the experiments. It is interesting to see that while the splitting of the QP levels due to coupling between the two chains within the unit cell is approximately the same for PT and PPV \( (\approx 0.5 \text{ eV}) \), the dispersion in the \( \Gamma Z \)-direction (PT) and along line 4 (PPV; see Figure 5.5), both corresponding to directions in which the polymer chains
are $\pi$-stacked, is very large for PT (0.6 eV for state 50) but relatively small in PPV (< 0.2 eV). This is due to the fact that in PT, the rings are exactly on top of each other, while in PPV they are not, due to the monoclinic cell.

It would be pointless to compare the calculations for crystalline PPV with the calculations performed by Rohlfling and Louie [103] on an isolated chain of PPV, since the situation-I and situation-III calculations for PT also yield vastly different results. We can, however, compare the situation-I and situation-II results for PT and extrapolate from there to the results of a hypothetical situation-II calculation for PPV. Rohlfling and Louie find and exciton binding energy of 0.9 eV, which is in excess of the experimental values of $0.35 \pm 0.15$ eV [8], obtained by a direct STM measurement for an alkoy-substituted PPV, and $0.48 \pm 0.14$ eV for unsubstituted PPV [9]. The inclusion of interchain screening effects by embedding the PPV chain in a dielectric medium will drastically reduce their calculated binding energy and may well lead to agreement with this experiment.

## 5.6 Conclusions

We have calculated the quasi-particle band structure and lowest-lying exciton binding energies of polythiophene in three situations: a single, isolated chain in vacuum (situation I), a single chain in a dielectric medium with dielectric constants appropriate for polythiophene (situation II) and crystalline polythiophene (situation III). In situation I, where there is only intrachain screening, we find a large band gap and large exciton binding energies, due to the absence of long-range screening. After including interchain screening, which is responsible for the long-range screening in situation II, we find that both the band gap and exciton binding energies are drastically reduced, and we find an exciton binding energy and splitting in good agreement with experiment. Remarkably, the optical gap is hardly affected. By including both interchain screening and wave-function hybridization effects in situation III, we find that the band gap and exciton binding energies are reduced once more, and we find a small reduction of the optical gap (0.13 eV).

Since most polymers are not well-ordered, let alone crystalline, situation II should be the preferred geometry for future calculations of the electronic and optical properties of conjugated polymers. Hence, in most experiments an exciton binding energy in the 0.5 eV range should be found. In situations were there is wave-function hybridization (not only in crystalline situations, but also in aggregate- or excimer-forming systems), a smaller exciton binding energy can result. This is consistent with recent experiments performed on ladder-type poly-para-phenylene, where a sample-dependent exciton binding energy was found: 0.45 eV in the disordered regions and 0.1 eV in the aggregate-forming regions [119].

We suggest that these conclusions hold for conjugated polymers in general. This means that the results presented here give a possible resolution of the exciton binding energy debate. The exciton excitation energy (from the ground state) is hardly influenced by the
inclusion of interchain screening or wave function hybridization; the one-particle energies, on the other hand, are influenced and, concomitantly, so is the exciton binding energy. Experiments yielding different values for the exciton binding energies for the same polymers, may thus be explained in terms of a different amount of wave-function hybridization in the various experiments.

We conclude that a correct many-body description of the electronic and optical properties of bulk polymer systems should include the effect of interchain screening. An important consequence of this conclusion is that neither Hartree-Fock nor DFT-LDA calculations should be relied upon in this context, since Hartree-Fock does not contain screening effects at all and since the exchange-correlation potential in DFT-LDA only depends on the local density and cannot describe the non-local effects due to the long-range screening. Moreover, since exciton effects play such a large role in conjugated polymers, it is essential to take these effects into account, which is not done in DFT-LDA or Hartree-Fock either. Since most experiments are performed on substituted, inherently disordered and polymer systems, assuming an ordered crystalline geometry introduces an unrealistic amount of interchain wave-function overlap, which drastically reduces both the band gap and the exciton binding energy.
Chapter 6

Excitonic properties of conjugated polymers from the Bethe-Salpeter equation

ABSTRACT

The excitonic spectra of a number of conjugated polymers, polythiophene (PT), polyphenylenevinylene (PPV), ladder-type poly-paraphenylene (LPPP), trans-polyacetylene (PA) and polydiacetylene (PDA), are calculated by solving the Bethe-Salpeter equation for the two-body Green function of the electron-hole pair. The only input to the calculation is the bulk dielectric constant. We find intermediate binding energies of 0.4-0.6 eV for the lowest optical $1^1B_u$ exciton, obtaining good agreement with recent experiments for each polymer individually. The agreement for the singlet-triplet splittings and the $1^1B_u$ polarizabilities is satisfactory. This also holds for the $1^1B_u - 2^1A_g$ splittings in PT, LPPP and PPV. For PA and PDA we find the $2^1A_g$ exciton above the $1^1B_u$ exciton, in contrast with experiment; a possible explanation for this discrepancy is the absence of lattice relaxation effects and double excitations in our calculations.

6.1 Introduction

Conjugated polymers [11, 120] and oligomers [121] are attracting interest as candidates for the active material in electronic and optical devices, such as transistors, light-emitting diodes and photovoltaic devices. Crucial for the optimization of these devices is knowledge of the electron and hole transport and electron-hole recombination mechanisms, and the excitation spectra. One of the important aspects of the excitation spectra is the exciton binding energy. A small exciton binding energy means that the electronic and optical properties of conjugated polymers can be described starting from a solid-state band picture; a large binding energy means that a molecular exciton picture has to be invoked. Despite years of intense research, no consensus about the magnitude of the binding energy of an important material like polyphenylenevinylene (PPV) has been reached. The discussions at recent conferences [12] about the interpretation of the available experimental data reflect the prolonged discussion [10] between the advocates of small [14] (∼ 0.1 eV or less), intermediate [9] (∼ 0.5 eV) and large [15] (∼ 1.0 eV) exciton binding energies.

On the theoretical side, a similarly large spread of values for the exciton binding energy has been found [122]. Since most theoretical models are semi-empirical, it is usually hard to separate the real physical effects in these models from effects arising from different or inconsistent parametrizations. Fully first-principles calculations, containing no adjustable parameters, of excitonic properties of extended systems have only recently become computationally feasible [24, 25]. A recent study [103] yielded a binding energy of 0.9 eV for PPV. However, this value was calculated for a chain in vacuum, and therefore no interactions between the chain and neighboring chains were taken into account. In the preceding Chapter, we showed that by including interchain contributions into the screened Coulomb interaction in polythiophene (PT), the exciton binding energy is drastically reduced, from 1.86 eV for a chain in vacuum to 0.76 eV for a chain in the bulk. We argued that a similar reduction would take place in PPV upon the inclusion of interchain screening, possible bringing the value of 0.9 eV closer to the experimental values. By also including the interchain wave-function hybridization we found a worse agreement with experiment than by only including the interchain polarization and screening effects. This is because inclusion of this hybridization reduces the one-particle gap, while leaving the energy of the lowest optical excitation more or less unaffected.

Here, we perform many-body calculations for the excitonic spectrum of a number of polymers, including the important interchain screening of the Coulomb interaction by using the bulk dielectric constant in the screened interaction, but not including the interchain wave-function hybridization effects. The latter approximation is well justified since most experiments are performed on substituted polymers, with little interchain order, which would prevent hybridization of wave functions between neighboring chains in most cases. This Chapter is outlined as follows: in the next Section we give a brief summary of the theoretical and computational methods, in Section 6.3 we present the results for a variety of conjugated polymers: polythiophene (PT), polyphenylenevinylene (PPV), ladder-type
FIGURE 6.1: The repeat units of the conjugated polymers studied in this Chapter, starting in the upper left corner, going clockwise: ladder-type poly-
para-phenylene, polyphenylenevinylen, polydiacetylene, polyacetylene and polythiophene

poly-
para-phenylene (LPPP), trans-polyacetylene (PA) and polydiacetylene (PDA). The molecular structures are given in Figure 6.1. Section 6.4 is devoted to an extensive discussion of the results and Section 6.5 contains our conclusions.

6.2 Methodology

Our computational method can be sketched as follows: first, the geometry of the isolated polymer chain is obtained, either from a density-functional calculation in the local-density approximation (DFT-LDA) calculation (PT, PPV, and LPPP) or from diffraction experiments (PA and PDA). Rather than calculating one-(quasi-)particle excitation energies, we calculate DFT-LDA eigenvalues only, which we use as an input to the final step, in which the interactions between two one-particle excitations (electron and hole) are taken into account to compute the exciton binding energies, by solving the Bethe-Salpeter Equation [36, 37] (BSE).
6.2.1 Geometry

DFT calculations (in this case within the Local Density Approximation, referred to as DFT-LDA) generally yield reliable results for covalent bonds (errors in length and angle < 1%). Such calculations have been shown to fail for PA [123], yielding a too small dimerization of the $sp^2$ carbon-carbon bonds in the backbone. While inclusion of many-body correlations in the calculation of the geometry can resolve this error [124, 125], we take the geometry of PA and PDA (for which we found the same problem to occur) from experiment. Since the physics relevant to excitonic properties occurs on the backbone, and the side-chains and substituents used in experiments serve mainly to increase the polymer’s processability, we replace them by hydrogen atoms, and assume a planar geometry. In substituted PDAs the exciton binding energy, which is known very accurately experimentally, varies somewhat (from 0.45 to 0.55 eV) with the different substituents [17]. Changes of the exciton binding energy as a function of substituents of a somewhat larger magnitude have been observed in PPV [9].

We perform the calculations on isolated chains in a periodically repeated supercell, for which we take the size perpendicular to the chain direction large enough to prevent interaction between the periodically repeated images of the chain. A typical unit cell can be seen in the upper left corner of Figure 3.1, for PT. Hence, we ignore wavefunction overlap between adjacent chains; we made plausible in the previous Chapter that these play a small role in most experiments. The interchain screening effects on the Coulomb interaction are introduced in a later stage of the calculation; the geometries of isolated chains and chains in the bulk are not much different.

6.2.2 One-particle excitations: quasi-particles

The one-particle excitation energies $E_{nk}$ can be evaluated by solving the quasi-particle equation for the quasi-particle wave functions $\phi_{nk}$ [cf. Equation (2.55)]:

$$\left[-\frac{\nabla^2}{2} + V_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r})\right] \phi_{nk}(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}',E_{nk})\phi_{nk}(\mathbf{r}') = E_{nk}\phi_{nk}(\mathbf{r})$$

where $V_H$ is the Hartree potential, $V_{\text{ion}}$ the potential of the atoms (which we replace by a pseudo-potential [65]), and $\Sigma$ the electronic self-energy. The periodicity in the chain direction leads to a one-dimensional wave-vector ($k$) dependence of the quasi-particle energies and wave functions. Within the GW approximation [35] for the self-energy, as outlined in Chapter 2, very reliable quasi-particle energies have been obtained. In the previous Chapter, we showed that the one-particle gap in PT can be reliably predicted using the GW approximation for the self-energy. In DFT-LDA, $\Sigma$ is approximated by $\Sigma(\mathbf{r},\mathbf{r}',\omega) = V_x(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$, where $V_x$ is the exchange-correlation potential. The locality and energy-independence of this approach makes it computationally much faster in comparison with the GW approximation. Since DFT is a ground-state theory only, the
Excitation energies calculated with it have strictly speaking no meaning. Comparison of DFT and GW calculations for a wide variety of semiconductors, has proven that while the gap (also called one-particle or quasi-particle gap) separating the occupied and unoccupied states is too small in DFT compared to the GW values, the shape of the energy bands is more or less correct in DFT. More specifically, we showed this to be the case in the preceding Chapter for PT. Since in the BSE the energy of the exciton is defined relative to the quasi-particle gap $E_g$, the DFT quasi-particle values give us a reliable exciton spectrum relative to the quasi-particle gap. See also Figure 6.2.

### 6.2.3 Two-particle excitations: excitons

The exciton wave function $\chi(\mathbf{r}_e, \mathbf{r}_h)$ is expanded in terms of electron (conduction) and hole (valence) wave functions [cf. Equations (2.82) and 4.27]:

$$
\chi_i(\mathbf{r}_e, \mathbf{r}_h) = \sum_{k,c,v} A_{k,c,v}^i \phi_{ck}(\mathbf{r}_e) \phi_{ek}^i(\mathbf{r}_h)
$$

(6.2)
The exciton binding energies \( E_b \) then follow from [cf. Equations (2.83) and (4.28)]:

\[
[E_{ck} - E_{hok} - E_g + E_0^2] A_{kk'} + \sum_{\tilde{k},\tilde{e},\tilde{\nu}} [2W_{kk',\tilde{k},\tilde{e},\tilde{\nu}} \delta_{s,0} - W_{kk',\tilde{k},\tilde{e}'}] A_{kk'} = 0
\]  

(6.3)

where \( E_g \) is the quasi-particle gap, \( E_b \) the exciton binding energy (for which we use a different convention than in the rest of this thesis; it is negative throughout this Chapter; if we say 'larger binding energy' we mean 'larger in absolute value') and \( W_{kk',\tilde{k},\tilde{e},\tilde{\nu}} \) and \( V_{kk',\tilde{k},\tilde{e}'} \) are the matrix elements of the static \((\omega = 0)\) screened Coulomb interaction and the exchange matrix elements (present for singlet, \( s = 0 \), excitons only) of the bare Coulomb interaction, respectively. For more details, we refer to Chapter 4.

### 6.2.4 Screened interaction

If we base our exciton description on one-particle energies calculated with the GW approximation, we have access to the full details of the static screened Coulomb interaction, \( W(\mathbf{r}, \mathbf{r'}, \omega = 0) \). Here we will base the BSE calculations directly on DFT calculations. We approximate \( W \) by:

\[
W(\mathbf{r}, \mathbf{r'}, \omega = 0) = W_s(|\mathbf{r} - \mathbf{r'}|) = \frac{1}{\varepsilon |\mathbf{r} - \mathbf{r'}|},
\]  

(6.4)

where \( \varepsilon \) is the dielectric constant of the bulk polymer. This immediately takes care of screening effects due to the surroundings of the chain, which we showed to be crucial for a correct description of the exciton properties. In an ordered situation, where the polymer chains are aligned, the dielectric constant will be anisotropic, and the question arises whether the dielectric constant perpendicular to the chains or the dielectric constant parallel to the chains should be used. While it may appear that the latter should be used this is \textit{not} the case, as we showed in Section 3.1.1. We take \( \varepsilon = \varepsilon_\perp = 3.0 \), a typical value for the polymers at hand, and also supported by our calculations for ordered PT given in the preceding Chapter.

### 6.2.5 Off-chain excitons

In equations (6.2)-(6.4) we have assumed that the electron and the hole forming an exciton are located on the same chain, i.e., we look at on-chain, or direct, excitons only. Experimental evidence [126] suggests that in some processes in LPPP excitons are formed that have the hole and the electron on separate chains, i.e., off-chain, or indirect, excitons [127]. Moreover, an unknown fraction of these off-chain excitons should be stable with respect to on-chain excitons, i.e., have a higher binding energy. The mean off-chain binding energy should of course be lower than the mean on-chain binding energy, otherwise the off-chain
excitons, with no direct radiative pathway to the ground state, would quench the luminescence, which is not observed. Since two counteracting effects are at work (the decreasing exchange interaction due to reduced wave-function overlap for the off-chain exciton will increase the binding energy while the increased distance between the electron and the hole will decrease the binding energy) it is not a priori clear what the resulting energy for the off-chain exciton will be.

The off-chain excitons can be described within the method outlined above if we assume that no hybridization between the wave functions on adjacent chains takes place. If we look at the form of the matrix elements of the \( W \) [see also Equation (4.30)]:

\[
W_{k_{0}v,k_{0}'v'} = \int \int d^3r d^3r' \phi_{kv}(r') \phi_{kv}(r) \frac{1}{\varepsilon |r - r'|} \phi_{k_{0}v'}^{*}(r') \phi_{k_{0}v'}(r),
\]

we can easily write down \( W_{k_{0}v,k_{0}'v'}(d) \), where \( d \) is the vector along which the second chain containing the hole is shifted with respect to the first:

\[
W_{k_{0}v,k_{0}'v'}(d) = \int \int d^3r d^3r' \phi_{kv}(r + d) \phi_{kv}(r) \frac{1}{\varepsilon |r - r' - d|} \phi_{k_{0}v'}^{*}(r' + d) \phi_{k_{0}v'}(r).
\]

Under the assumption that the wave functions on both chains are the same, we have \( \phi_{kv}(r + d) = \phi_{kv}(r) \). By a similar argument the matrix elements \( V_{k_{0}v,k_{0}'v'}(d) \) take the form:

\[
V_{k_{0}v,k_{0}'v'}(d) = \int \int d^3r d^3r' \phi_{k_{0}v'}^{*}(r') \phi_{k_{0}v'}^{*}(r' + d) \frac{1}{|r - r' - d|} \phi_{kv}(r' + d) \phi_{kv}(r),
\]

6.2.6 Additional considerations

The major advantage of using the DFT-LDA quasi-particle energies and a screened interaction of the form of Equation (6.4) instead of the DFT/GW/BSE procedure as outlined in Chapter 4, is that the most time-consuming computational step in the latter procedure, the calculation of the screened interaction \( W(r, r', \omega) \), is skipped. We will show in Section 6.3 that there is good agreement between the results of calculations using the present scheme, and those of DFT/GW/BSE calculations performed in the previous Chapter. In the next Chapter, we will show that calculations using Equation (6.4) for the screened interaction yield good results for the radiative lifetimes and polarizabilities of excitons on polymer chains dissolved in benzene, with the benzene dielectric constant, \( \varepsilon = 2.28 \).

All integrals for the matrix elements, Equations (6.5-6.7), appearing in the BSE, Equation (6.3), are performed on a three-dimensional real-space grid with \( \Delta r \sim 1.0 \text{ a.u.} \) (small differences occur for different polymers due to differences in the size of the unit cells). For all polymers 16 \( k \)-points in the one-dimensional Brillouin zone were used, with the exception of PA and PDA, for which 48 and 32 \( k \)-points were used, respectively. With these parameters, the resulting spectra are converged to within 0.05 eV. The accuracy for the polarizabilities is \( \sim 10\% \). Once again, no lattice relaxation is included.
TABLE 6.1: Properties of the lowest optically active $^{1}B_u$ exciton: binding energy $E_b$, reduced mass $\mu$, polarizability $\alpha$ and the root-mean-square electron-hole distance $r_{\text{rms}} = \sqrt{\langle (x_e - x_h)^2\rangle}$ for different polymers. Ab-initio refers to DFT/GW/BSE-type calculations.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Source</th>
<th>$E_b$ (eV)</th>
<th>$\mu$ (m_e)</th>
<th>$\alpha$($10^3 A^3$)</th>
<th>$r_{\text{rms}}$(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT</td>
<td>This work</td>
<td>-0.61</td>
<td>0.076</td>
<td>1.6</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>Experiment$^a$</td>
<td>-0.6</td>
<td>0.065</td>
<td>1-11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ab-initio$^b$</td>
<td>-0.76</td>
<td>0.065</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPV</td>
<td>This work</td>
<td>-0.54</td>
<td>0.048</td>
<td>2.9</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td>Experiment$^c$</td>
<td>-0.48</td>
<td>0.044</td>
<td>3-11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ab-initio$^d$</td>
<td>-0.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPPP</td>
<td>This work</td>
<td>-0.64</td>
<td>0.058</td>
<td>1.6</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>Experiment$^e$</td>
<td>-0.45</td>
<td></td>
<td>2.0</td>
<td>7.0</td>
</tr>
<tr>
<td>PA</td>
<td>This work</td>
<td>-0.43</td>
<td>0.029</td>
<td>6.4</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>Experiment$^f$</td>
<td>-0.5</td>
<td></td>
<td>0.1-1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ab-initio$^e$</td>
<td>-0.4</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDA</td>
<td>This work</td>
<td>-0.47</td>
<td>0.035</td>
<td>5.6</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>Experiment$^g$</td>
<td>-0.53</td>
<td>0.04-0.06</td>
<td>6.6</td>
<td>11.0</td>
</tr>
</tbody>
</table>

$^a$ Reference [105].

$^b$ Chapter 5, situation II.

$^c$ $E_b$ from Reference [9], $\alpha$ from Reference [105].

$^d$ Reference [103], calculation for an isolated chain.

$^e$ $E_b$ from Reference [119], $\alpha$ from Reference [128].

$^f$ Reference [105].

$^g$ Reference [17].

6.3 Results

We have listed the exciton binding energies, reduced effective masses (defined as $1/\mu = 1/m_{\pi} + 1/m_{e}$, with $m_{\pi}$ and the $m_{e}$, the effective masses of the hole and electron, respectively), exciton polarizabilities [calculated from perturbation theory using Equation (4.36)], and root-mean-square electron-hole distances $r_{\text{rms}}$ [calculated using Equation (4.32)] of the optically active $^{1}B_u$ excitons in Table 6.1. The energies of the $^{1}B_u$ and $^{2}A_g$ excitons relative to the $^{1}B_u$ exciton are given in Table 6.2, as well as the singlet-triplet ($^{1}B_u-^{1}B_u$) splitting. The $^{2}A_g$ and the $^{2}A_g$ are almost degenerate; due to symmetry the probability of finding an electron and hole with zero relative distance, is zero, and hence the exchange interaction is small. In Figure 6.2, the relevant levels are shown schematically. For PT, we can compare the present results with our previous ab-initio calculations for situation II, as presented in Chapter 5. The results obtained with Equations (6.2)-(6.4) are in good agree-
TABLE 6.2: Energies of the $1^3B_u$ and $2^1A_g$ excitons relative to the $1^1B_u$ exciton. 
*Ab-initio* refers to DFT/GW/BSE-type calculations.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Source</th>
<th>$E_b(1^3B_u) - E_b(1^1B_u)$</th>
<th>$E_b(2^1A_g) - E_b(1^1B_u)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT</td>
<td>This work</td>
<td>-0.43</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>Experiment$^a$</td>
<td>-0.45</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>*Ab-initio$^b$</td>
<td>-0.39</td>
<td>0.53</td>
</tr>
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<td>PPV</td>
<td>This work</td>
<td>-0.57</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>Experiment$^c$</td>
<td>-1.0</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>*Ab-initio$^d$</td>
<td>-0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>LPPP</td>
<td>This work</td>
<td>-0.41</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>Experiment$^e$</td>
<td>-0.62</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>Experiment$^f$</td>
<td>-0.50</td>
<td></td>
</tr>
<tr>
<td>PA</td>
<td>This work</td>
<td>-0.61</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Experiment$^g$</td>
<td>-0.8</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>*Ab-initio$^h$</td>
<td>-0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>PDA</td>
<td>This work</td>
<td>-0.59</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>Experiment$^i$</td>
<td>-0.9</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

$^a$ Reference [104].

$^b$ Chapter 5, situation II.

$^c$ $E_b(1^3B_u) - E_b(1^1B_u)$ from Reference [108], $E_b(2^1A_g) - E_b(1^1B_u)$ from Reference [129].

$^d$ Reference [103], calculation for an isolated chain.

$^e$ Reference [128, 130].

$^f$ Reference [131].

$^g$ Reference [84].

$^h$ $E_b(1^3B_u) - E_b(1^1B_u)$ from Reference [132], $E_b(2^1A_g) - E_b(1^1B_u)$ from Reference [133].

The agreement with these earlier results, although the exciton binding energy is reduced somewhat. This gives us confidence that the results for other polymers will also be reliable. Note that the agreement between the present calculations for PPV and PA and earlier calculations [103] is not so good; this is because these calculations were performed for isolated chains without taking interchain screening into account. To show the dependence of the $1^1B_u$ binding energy on the dielectric constant, we have plotted in Figure 6.3 the binding energy in PPV as a function of the dielectric constant. In Figure 6.3 we have also plotted the exciton binding energy in the different polymers as a function of their reduced mass.

We also have good agreement between our calculated and the experimental exciton polarizabilities. The trend of increasing polarizability is accompanied by a decreasing binding energy and an increasing mean electron-hole distance, as can be seen from the values of $\bar{r}_{rms}$ in Table 6.1 and the electron-hole-distance probability distributions in Figure 6.4.
FIGURE 6.3: Left: the exciton binding energy of the $1^1B_u$ exciton in PPV as a function of the dielectric constant $\varepsilon$, as calculated from Bethe-Salpeter Equation (+), and from a $A/\varepsilon^2$ fit (dashed curve) to these results. Right: the exciton binding energy of the $1^1B_u$ excitons (+) as a function of the reduced mass $\mu$; $\varepsilon = 3.0$ for all polymers. The linear fit (B$\mu$; dashed line) does not include the result for PT. See Section 6.4.1 for details.

FIGURE 6.4: The probability distribution for the electron-hole distance $P(x_e - x_h)$ of the lowest optically active $1^1B_u$ excitons.
FIGURE 6.5: The binding energy of the $1^1B_u$ singlet exciton ($+$) and the $1^3B_u$ triplet exciton ($\times$) as a function of the interchain distance $d$. The lines are a guide to the eye. The second chain is shifted with respect to the first chain perpendicular to the plane of the polymer. $d = 0.0$ a.u. corresponds to an on-chain exciton. Note that the result for $d = 3.5$ a.u. is not physically realistic in the sense that the chains cannot be that close together in a real system. It is given only to show the behavior of the binding energies as a function of $d$.

In Figure 6.5 we have plotted the binding energies of off-chain excitons in LPPP as a function of the distance $d$ between the two chains, using Equations (6.6) and (6.7) for the matrix elements of the screened Coulomb interaction and the exchange interaction, respectively. Because the integral in Equation 6.6 is performed on a grid, only shifts commensurate with this grid have been considered. We shift the second chain in the direction perpendicular to the polymer plane. The binding energy of the relevant $1^1B_u$ off-chain exciton is 0.1 to 0.2 eV lower than its on-chain counterpart. Note that the singlet-triplet splitting is close to zero for off-chain excitons, due to the fact that there is no longer overlap between the electron and hole wavefunctions.

6.4 Discussion

6.4.1 The binding energies and splittings

We find good agreement between our calculations and specific experiments for the exciton binding energy of the lowest optically active exciton in PT, PPV, LPPP, PA, and PDA. Earlier, the onset of photoconductivity in LPPP at 1.1 eV above the $1^1B_u$ absorption was interpreted as being the result of a 1.1 eV binding energy of this exciton [134]. Nowadays, the binding energy in LPPP is generally agreed to be approximately equal to the $1^1B_u$-
$2^1$A$_g$ splitting, i.e., 0.6 to 0.7 eV [128, 135]. The STM measurements on LPPP [119] have lowered this to 0.45 ± 0.15 eV. The same technique has been used to measure the binding energy in PPV [9]. In PDA, $E_b$ was determined directly from a Franz-Keldysh electric field effect[17]; the $E_b$ data for PA and PT were derived from an in principle less reliable electro-absorption measurement [105]. Note that our value for PPV deviates considerably from an earlier DFT/GW/BSE result [103]. However, this calculation was performed for an isolated chain and therefore did not include the important interchain contributions in the screened interaction, which results in an exciton binding energy which is a factor of two too large compared to the experimental value and the present result.

The exciton binding energy in inorganic semiconductors is well described by $E_b = \mu/\varepsilon^2 E_H$, where $E_H$ is the binding energy of the electron in the hydrogen atom. In our case the general trend is indeed that $E_b$ increases with increasing reduced mass $\mu$, but the relation does not follow the relation $E_b \propto \mu$, as can be clearly seen in Figure 6.3. If we exclude PT, we can obtain a reasonable fit to this relation. As can be seen from Figure 6.3, where we have plotted the exciton binding energy in PPV as a function of the dielectric constant, the relation $E_b \propto 1/\varepsilon^2$ is well obeyed. However, the proportionality constant (not taking PT into account) is not $E_H = -13.6$ eV, but larger, viz. -106 eV. This is due to the confinement of the exciton to the chain, a quasi-one-dimensional system. The exceptionally large $\mu$ in PT is not caused by the presence of sulfur (the only thing that set PT apart from the other polymers in terms of its composition; $m_{\pi^*}$ is 20% larger than $m_\pi$, but only the former contains a substantial sulfur contribution. This larger $m_{\pi^*}$ alone can not explain why the reduced mass of excitons in PT is approximately 50% larger than expected from the hydrogen model. Obviously, this simple model for the exciton has a limited validity for the prediction of properties of such complex systems.

A tendency to underestimate (by 0.1 to 0.3 eV) the singlet-triplet splitting can be seen in PPV, LPPP, and PDA. A cause may be the fact that no excitonic lattice relaxation is included in our calculations. While the Huang-Rhys factor, and hence the amount of lattice relaxation energy, for the $1^1$B$_g$ singlets is well known, data for the corresponding triplets is available for LPPP [130] only where it is almost the same as for the singlet. This is not necessarily the case for all conjugated polymers: since states lower in energy are in general more localized, the relaxation energy for this state may be larger. Therefore, in a calculation with lattice relaxation included, the singlet-triplet splitting may well increase by a few tenths of an eV. In fact, in a Density Matrix Renormalization Group (DMRG) calculation of the Pariser-Parr-Pople-Peierls Hamiltonian for PA, the lattice relaxation of the triplet was found to be 0.2 eV larger than that of the singlet [86].

For all polymers we find a binding energy in the intermediate range, 0.4-0.6 eV, with an average deviation of the experimental values of approximately 10%. As mentioned before, there is a wealth of experimental evidence for both large, intermediate, and small binding energies, and there are continuing discussions about the validity of the methods used to obtain these values [9, 11, 12, 14, 105, 119]. Only for PDAs there seems to be no discussion at all; the consensus is that the binding energy is 0.45-0.55 eV [11, 17]. The fact
that we recover this binding energy and, with the same method and without changing the dielectric constant, find binding energies in the same range for other polymers is strong evidence for an intermediate binding energy in conjugated polymers in general. While it is possible to obtain smaller binding energies with this method, as was shown explicitly for PPV, these smaller binding energies are obtained with unrealistically large values of the dielectric constant $\varepsilon$, i.e., $\varepsilon \sim 8.0$ to obtain $E_h \sim 0.1$ eV, as can be seen in Figure 6.3.

6.4.2 Off-chain excitons in ladder-type poly(paraphenylene)

Thermally-stimulated-photoluminescence experiments recently performed on LPPP [126], suggest that at least a fraction of the off-chain excitons is stable with respect to on-chain excitons, i.e., they are expected to be lower in energy - or have a higher binding energy - than their on-chain counterparts. In these experiments a LPPP sample is irradiated by a mercury lamp for 30 s at 4.2 K. After the lamp is switched off and after the afterglow has disappeared, the temperature is increased with a constant heating rate and the luminescence as a function of time/temperature is observed. A peak in the luminescence is observed at 40 K. If all off-chain excitons had a higher binding energy than their on-chain counterparts, they would spectrally diffuse to on-chain exciton levels and decay radiatively immediately after the mercury lamp is switched off.

As mentioned earlier, the mean binding energy of off-chain excitons should be lower than that of on-chain excitons, since no luminescence quenching is observed. Moreover, these off-chain excitons have a charge-transfer character only and are therefore not excimers, which are superpositions of charge-transfer and on-chain excitons. The latter component gives the excimers a radiative pathway to the ground-state resulting in a radiative life-time which is only one order of magnitude larger than that of on-chain excitons. The pure off-chain excitons in LPPP are stable (with respect to on-chain excitons and the following radiative decay) for several minutes or longer.

Indeed we find the off-chain excitons to have a lower binding energy than the on-chain excitons in LPPP. Since in realistic materials, the on- and off-chain-exciton energies have a certain distribution, which for LPPP has a typical width of 0.035 to 0.05 eV, overlap in the low-binding-energy tail of the on-chain excitons and the high-binding-energy tail of the off-chain excitons will result in configurations where the off-chain exciton indeed has a higher binding energy. The experimental data are inconclusive with respect to the question which fraction of the off-chain excitons has a higher binding energy.

6.4.3 The $A_g/B_u$-exciton order in poly(di)acetylene

If no luminescence, which according to Kasha's rule [136] should come from the lowest excited singlet state, is observed in a material, this means that there is a singlet exciton
below the lowest optically active exciton. Optical excitations in such materials become trapped in this 'dark' singlet state, which does not couple to the ground state radiatively. This is the case in PA and PDA, where the $2^1A_g$ state is known to be below the optically active $1^1B_u$ state, in PA by $\sim 0.5$ eV, in PDA by $\sim 0.4$ eV, depending somewhat on the nature of the substituents. While we do find a correct value for the exciton binding energy in PDA, we find in both PA and PDA the $2^1A_g$ above the $1^1B_u$ state, which is qualitatively wrong. This is not a result of our approximations for the screened interaction and the one-particle excitation energies (see Section 6.2); a DFT/GW/BSE calculation for a single chain of PA [103] also finds the $2^1A_g$ state above the $1^1B_u$ state, albeit by a smaller value.

It has been suggested that the $A_g$ state is actually a bound state of two $B_u$ triplets with opposite spin [85], i.e., a four-particle excitation, or at least a superposition of two- and four-particle excitations. This would explain why this state is not described correctly within the two-particle-excitation formalism used here. The fact that this kind of complication does not occur in PT, LPPP or PPV, where the lowest $A_g$ state is above the lowest $B_u$ state, with the correct energy difference, is then a result of the fact that in these polymers much less mixing between two- and four-particle excitations occurs, due to smaller electron-electron correlation.

Another explanation, as yet for PA only, was given by Bursill and Barford [86], who found the $A_g$ exciton above the $B_u$ exciton in the DMRG study mentioned before if no lattice relaxation was included, but below it when lattice relaxation was included. Lattice relaxation resulted in a weak downward shift of the $B_u$ state ($\leq 0.2$ eV for the infinite chain), but in a strong downward shift of the $A_g$ state ($\approx 1.0$ eV). A similar calculation for PDA, without lattice relaxation as yet, results in an $A_g$ state above the $B_u$ state. It is expected that including lattice relaxation in this calculation will also bring the $A_g$ state below the $B_u$ state [137]. The latter is not the case for PT, PPV and LPPP; since with our approach (i.e., without lattice relaxation) we do have good agreement for the $A_g$ state for these polymers relaxation effects for these polymers are probably not markedly different for the $B_u$ and $A_g$ singlet states in these polymers.

The exceptional character of PA and PDA with respect to both the large differences in relaxation energy for the $B_u$ and $A_g$ excitons and the role of four-particle excitations seems to be in line with the fact that the description of their ground-state geometries is also extremely complicated [123, 124, 125], which is also an exception, as discussed earlier in Section 6.2.1. In fact, to reproduce the correct order of the $B_u$ and $A_g$ excitons in PA and PDA, it might be necessary to include both four-particle excitations and lattice relaxation effects in our formalism.

Note that the incorrect description, related to its four-particle character and/or large lattice relaxation, of the $A_g$ state in PDA and PA does not influence the reliability of the prediction of the $1^1B_u$ polarizabilities in these materials. While the perturbation expression for the $1^1B_u$ polarizability couples the $1^1B_u$ exciton to the $2^1A_g$ exciton, the $1^1B_u$ exciton is correctly described with a two-particle formalism, and hence also its polarizability,
irrespective of the nature of the other excitations.

6.5 Conclusions

We have shown that *ab-initio* methods (in this case containing one parameter, the dielectric constant) can be used to give reliable predictions for a number of excitonic properties of conjugated polymers, most notably for the heavily disputed value of the exciton binding energy, for which we find 0.4-0.6 eV for all five polymers studied here, obtaining very good agreement with several experiments for each polymer individually. The important gain in computational speed compared to earlier fully *ab-initio* work for conjugated polymers (Reference [103] and Chapter 5 of this work) is in the approximation of the screened interaction $W(r,r',\omega)$ between the electron and hole forming the exciton, which is computationally very hard to calculate, by a Coulomb interaction screened by the dielectric constant. This approximation gives results which are in agreement with the earlier situation II-type calculations for bulk systems in Chapter 5.
Chapter 7

Polarizabilities and lifetimes of excitons on conjugated polymer chains in solution

ABSTRACT

We investigate the properties of excitons on three different conjugated polymers in solution, both experimentally and theoretically. The theoretical description of the excitons is obtained by solving the electron-hole Bethe-Salpeter equation for the polymers, starting from a calculation within density-functional theory. We compare the calculated radiative lifetimes and polarizabilities of the excitons with experimental results from time-resolved fluorescence decay and flash-photolysis microwave conductivity measurements. The quantitative agreement demonstrates the predictive power of the theoretical approach.

7.1 Introduction

The interest in the electronic and optical properties of semiconducting conjugated polymers has increased enormously since the discovery of electroluminescence [4] of these materials. The microscopic modeling of charge carriers and excitations in these materials is a subject of intensive research at present. Many studies have focused on the magnitude of the binding energy of the lowest singlet exciton ($S_1$). However, this quantity turns out to be very hard to determine experimentally, and no final consensus has yet been reached. In this Chapter we will focus on two other properties of the exciton; its radiative lifetime and polarizability. Both properties are related to the spatial structure of the exciton; the lifetime of an exciton is, in an effective-mass approximation, inversely proportional to the absolute square of the electron-hole envelope function at zero relative distance [138], whereas the polarizability is mainly determined by the tail of this function. We solve the many-body Bethe-Salpeter equation (BSE) to describe the excitons, starting from a calculation within density-functional theory. We will focus on three important conjugated polymers: polyphenylenevinylene (PPV), polythiophene (PT), and poly-$p$-phenylene (PPP).

7.2 Experimental

We compare our computational results with flash-photolysis time-resolved microwave conductivity (FP-TRMC) and fluorescence decay measurements, performed at the Interfaculty Reactor Institute of the Technische Universiteit Delft, The Netherlands. Since unsubstituted polymers are not soluble in non-polar solvents such as benzene, the experiments were performed on dialkoxy-substituted PPVs, alkyl-substituted PTs, and a dialkoxy-substituted PPP. The experimentally determined parameters given for PPV and PT are averages for three polymers differing only in the length of the substituents. Since dialkoxy-substitution can substantially influence the optoelectronic properties of the conjugated backbone, as evidenced by a bathochromic shift of the absorption and emission bands in substituted PPV, the results for the PPV polymer are also compared with those obtained by extrapolation (to $1/n = 0$) for a series of dialkyl-phenyl end-capped phenylene-vinylene oligomers (OPV $n$'s) with the number $n$ of PV units varying from 2 to 5 (see References [139] and [140]). This bathochromic shift does not occur for the dialkoxy-substituted PPP and a direct comparison with the polymer is possible. All measurements were carried out on low-concentration solutions in benzene under conditions for which no intermolecular solute aggregation occurred, $\sim 10$ ppm or $10^{-4}$ molar monomer units.

The fluorescence quantum yields $\phi_{FL}$ were determined to be $\phi_{FL}$ 0.2 (0.5), 0.2, and 0.6 for PPV (OPV $n$'s), PT and PPP, respectively. This fluorescence quantum yield is given by:

$$\phi_{FL} = \frac{k_{rad}}{k_{rad} + k_{nonrad}}$$ (7.1)
where $k_{\text{rad}}$ ($k_{\text{nonrad}}$) is the rate constant for radiative (non-radiative) decay. Since the fluorescence decay time, also measured in the experiments, is given by:

$$\tau_{\text{FL}}^{-1} = k_{\text{rad}} + k_{\text{nonrad}},$$

(7.2)

we have for the radiative lifetime:

$$\tau_{\text{rad}} = \frac{\tau_{\text{FL}}}{\phi_{\text{FL}}},$$

(7.3)

The change in polarizability of the isolated polymer chains on photoexcitation, $\Delta \alpha$, was monitored as the transient change in the dielectric constant, $\Delta \varepsilon$, of the polymer solution on flash-photolysis. Details of the TRMC technique, which can monitor changes in $\varepsilon$ as small as 1 ppm, and the method of deriving $\Delta \alpha$ from the $\Delta \varepsilon$ transient can be found in other publications [139, 141, 142]. Since the molecules are orientated randomly in solution, $\Delta \alpha$ is the isotropic value of the excess polarizability, i.e.:

$$\Delta \alpha = (\Delta \alpha_{xx} + \Delta \alpha_{yy} + \Delta \alpha_{zz})/3,$$

(7.4)

where $\Delta \alpha_{yy}$ and $\Delta \alpha_{zz}$ are orders of magnitude smaller than $\Delta \alpha_{xx}$.

### 7.3 Theoretical

We first calculate the ground-state structure of the polymers. The side-groups of the polymers are replaced by hydrogen atoms to keep the calculations tractable. We use Density Functional Theory in the Local Density Approximation (DFT-LDA) within the Car-Parrinello scheme [34], with a tetragonal supercell. The lattice constants in the perpendicular directions are 15.0 a.u. for PPV and PT, and 14.0 a.u. for PPP, large enough to prevent crosstalk between neighboring chains. Unless specified otherwise, we use atomic units. The length of the unit cell in the chain ($x$-) direction is found to be 12.50 a.u. for PPV, 14.80 a.u. for PT, and 16.24 a.u. for PPP, which agrees with experimental values available in the literature to within 1% [87, 88, 89, 90]. PPV and PT are found to be planar, the angle $\theta$ between two adjacent phenylene rings in PPP is found to be 26°, due to steric interactions between the hydrogen atoms on adjacent rings. We neglect the influence of the solvent on the conformation of the polymers. This influence on the properties investigated in the present study is expected to be small.

In our description of excitons on polymer chains, the exciton binding energies and wave functions are obtained from the Bethe-Salpeter equation, which maps the full many-body Schrödinger equation onto a two-body Schrödinger-like equation for an electron and a hole forming an exciton. The wave functions $\chi_i(\mathbf{r}_e, \mathbf{r}_h)$ of the optically relevant zero-momentum singlet excitons are expanded in products of valence (hole) $\phi_{ek}$ and conduction (electron) $\phi_{ck}$ wave functions [cf. Equation (2.82) and (4.27)]:

$$\chi_i(\mathbf{r}_e, \mathbf{r}_h) = \sum_{kvc} A_{kvc}^i \phi_{ek}(\mathbf{r}_e) \phi_{ck}^*(\mathbf{r}_h),$$

(7.5)
with $\sum_{k} |A_{k}^i|^2 = 1$ and $k$ the wavevector in the one-dimensional Brillouin zone in the chain direction. We limit the discussion to singlet states and suppress the spin part of the wave functions. The expansion coefficients $A_{k}^i$ and the exciton binding energies $E_b^i$ obey [cf. Equation (2.83) and (4.28)]:

$$\left[ E_{ck} - E_{ek} - E_g - E_b^i \right] A_{k}^i + \sum_{k',d'} \left[ 2V_{k,k',d'}^{\xi} - W_{k',d'} \right] A_{k',d'}^i = 0,$$

(7.6)

where $E_g$ is the band gap, and $W_{k,k',d'}^{\xi}$ and $V_{k,k',d'}^{\xi}$ are the matrix elements of the static screened interaction $W(r,r')$ [Equation (4.30)] and the exchange matrix elements of the bare Coulomb interaction $v(r) = 1/|r|$ [Equation (4.29)], respectively. $\phi_{nk}$ and $E_{nk}$ are the quasi-particle wave functions and energies. In our calculation, we replace them by the DFT-LDA wave functions (which are almost identical to the quasi-particle wave functions) and energies and add an amount $\Delta E$ to the energies of the unoccupied states, the so-called ‘scissors operator’, mimicking self-energy effects; the quasi-particle calculations within the GW scheme for PT in Chapter 5 show that this a reasonably good approximation. For instance, the electron and hole effective masses of the $\pi$ and $\pi^*$ band decrease by only 15% when the DFT-LDA eigenvalues are replaced by GW eigenvalues, indicating that the shape of the bands hardly changes in a more advanced quasi-particle calculation. Note that this shift does not influence the exciton binding energy, which is defined relative to the quasi-particle (or one-particle) gap.

Since there is no long-range screening in a quasi-one-dimensional system (see Chapter 5 and References [59, 95, 96]), the screening at long distances is governed by the benzene solvent. At short distances, we expect the difference in dielectric response between the polymer and the benzene (both dominated by a conjugated $\pi$-system) to be low. Therefore, we use for the screened interaction $W(r,r') = v(r-r')/\varepsilon$, with $\varepsilon = 2.28$, the dielectric constant of the benzene solvent. In this manner, we hope to take into account the most important features of the screening in a computationally feasible way. This approximation is also justified a posteriori by the good results obtained with it below. We will again neglect the differences in geometry between the excited states and the ground state.

The radiative lifetime $\tau_{\text{rad}}$ of the lowest singlet exciton $S_1$ is given by the Einstein formula for spontaneous emission [143]:

$$\tau_{\text{rad}}^{-1} = \sqrt{\frac{\varepsilon A_0 \hbar^3}{3e^2}} |\mu_{1,||k_x}|^2,$$

(7.7)

with the dipole matrix element $\mu_{1,||k_x}$ given by Equation (4.33), $\alpha$ the fine structure constant, $c$ the speed of light, and $\omega$ the frequency of the emitted light. The dipole matrix elements perpendicular to the chain direction, $\mu_{1,||k_y}$ and $\mu_{1,||k_z}$, are vanishingly small and hence do not contribute to the radiative lifetime. Equation (7.7) does not contain vibronic effects, which shift some of the intensity to lower energies. Assuming again coupling to one vibronic mode with frequency $\omega_{\text{ph}}$, these effects could be taken into account by replacing $\omega^3$ by $\sum_n (\omega - n \omega_{\text{ph}})^3 F_n$, where $F_n$ are the Franck-Condon factors, with $\sum_n F_n = 1$ and
\( n \) the number of excited optical phonons \([82]\). By analyzing the experimental luminescence spectra \([139]\) we estimate that including vibronic effects would only lead to a \( \sim 10\% \) increase of the calculated lifetimes.

The exciton polarizability is easily calculated using Equation (4.36). What is actually measured in the TRMC experiments, however, is not the exciton polarizability itself, but the excess polarizability, i.e., the difference in polarizability between the excited state and the ground state. In order to compare with experiment, we therefore have to take into account the loss of polarizability due to the fact that the dipolar coupling between the configuration with one exciton (in state \( i \)) and that with two excitons (in states \( i \) and \( j \)) on a polymer chain is reduced compared to the coupling between the configuration with no exciton and that with one exciton (in state \( j \)), because of the Pauli principle. A tedious, but straightforward derivation shows that this loss \( \alpha_{xx,i}^{\text{loss}} \) is given by:

\[
\alpha_{xx,i}^{\text{loss}} = 2 \sqrt{\frac{n_k}{2}} \sum_j \times \frac{\sum_{k'c} A_{k'c}^A \mu_{k'c,||k||c} \left[ \sum_{c',d'} |A_{k'c',c'}|^2 (\delta_{c,c'} + \delta_{c,c'} - \delta_{c',c'} \delta_{c,c'}) \right] \mu_{k||c}^* + c.c.}{E_g - E_{g}^j},
\]

(7.8)

where \( n_k \) is the number of \( k \)-points in the 1D Brillouin zone. The excess polarizabilities perpendicular to the chain direction are zero as the corresponding dipole-matrix elements are small. Hence the excess polarizability to be compared with experiment is given by:

\[
\Delta \alpha_i = (\alpha_{xx,i} - \alpha_{xx,i}^{\text{loss}})/3.
\]

(7.9)

We determined the various cut-off parameters such that an accuracy of 0.05 ns (0.1 ns for PT) for the lifetimes, 10% for the excess polarizabilities and 0.05 eV for the exciton binding energies was obtained. For this we needed to take into account 16 \( k \)-points in the Brillouin zone, typically a few (3-5) valence and conduction (5-8) bands, and a \( 16 \times 16 \times 16 \) real-space grid in the unit cell \((12 \times 16 \times 16 \) for PPV) to evaluate the matrix elements of the screened Coulomb and exchange interactions that appear in the BSE, Equation (7.6). The energy shifts \( \Delta E \) in the ‘scissors operator’ are chosen such that for PPVs (extrapolated OPVn’s), PTs and PPP, we obtain the correct position of the zero-phonon \( S_1 \) fluorescence peak, at 2.2 (2.5), 2.2 and 3.1 eV, respectively. The shifts are 1.8 (2.1), 2.0 and 2.0 eV, respectively.

### 7.4 Results and discussion

The calculated and experimental results for the radiative lifetime \( \tau_{\text{rad}} \) of the \( S_1 \) exciton and its excess polarizability \( \Delta \alpha \) are listed in Table 7.1 for all three polymers. For PT and PPP
we find very good agreement between the measured lifetimes and the ones calculated with Equation (7.7). For PPV the interpretation is less straightforward; as mentioned before, alkoxy-substitution substantially alters the fluorescence spectrum of PPVs. For the PPVs in the experiment we have the zero-phonon fluorescence maximum at 2.2 eV, while the extrapolation of the maxima for the OPV$n$'s is 2.5 eV. As the inverse of the radiative lifetime depends on the frequency of the emitted light to the third power [see Equation (7.7)], this shift can substantially alter the calculated value of the radiative lifetime. As we replace the alkoxy side-groups by hydrogen atoms in the calculation, a comparison with the extrapolation of the unsubstituted OPV$n$ data is more relevant. Taking this into account, the agreement for PPV is also considered to be good.

The calculated excess polarizability for PT is in good agreement with experiment; that of PPV is slightly, but hardly significantly, smaller than the experimental value. For PPP there appears to be an overestimation of the excess polarizability. In all three systems, some rings are, by thermal effects, rotated over more than the equilibrium dihedral angle, leading to a reduction of the conjugation length and hence to more confined excitons with lower polarizabilities. Since the overlap of wave functions between adjacent rings (with a dihedral angle $\theta$) scales as $\cos \theta$, the thermal fluctuations have a much larger effect in PPP, which has a non-zero equilibrium angle, than in PPV or PT.

It turns out that 99% or more of the first term in Equation (4.36), i.e., the coupling between the $S_1$ exciton and the other excitons $S_i$, in the calculation of $\alpha_{ex,S_1}$ results from the coupling to the $S_2$ state. The second term, i.e., the reduction of the polarizability due to coupling with the ground state, in Equation (4.36) results in a small (<< 5%) correction

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\tau_{rad}$ (ns)</th>
<th>$1/3 \alpha_{ex,S_1}$</th>
<th>$1/3 \alpha_{ex,S_1}^{corr}$</th>
<th>$\Delta \alpha_{S_1}$</th>
<th>$\tau_{rms}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPV$^a$</td>
<td>1.96</td>
<td>1.3 ± 0.2</td>
<td>1.24</td>
<td>0.24</td>
<td>1.00</td>
</tr>
<tr>
<td>PPV$^b$</td>
<td>1.34</td>
<td>1.3 ± 0.1</td>
<td>1.24</td>
<td>0.20</td>
<td>1.04</td>
</tr>
<tr>
<td>PT$^c$</td>
<td>2.2</td>
<td>2.5 ± 0.3</td>
<td>0.70</td>
<td>0.12</td>
<td>0.58</td>
</tr>
<tr>
<td>PPP$^d$</td>
<td>1.05</td>
<td>1.2 ± 0.1</td>
<td>0.53</td>
<td>0.05</td>
<td>0.48</td>
</tr>
</tbody>
</table>

$^a$ experimental values averaged for 3 different dialkoxy-substituted PPVs

$^b$ experimental values obtained by extrapolation to $1/n = 0$ of results for a series of OPV$n$'s with $n=2$-5

$^c$ experimental values averaged for 3 different alkyl-substituted PTs

$^d$ experimental values for a dialkoxy-substituted PPP

**TABLE 7.1:** Exciton radiative lifetimes $\tau_{rad}$ (in ns), polarizabilities $1/3 \alpha_{ex,S_1}$, polarizability corrections $1/3 \alpha_{ex,S_1}^{corr}$, excess polarizability $\Delta \alpha_{S_1}$ (all in $10^3 \text{Å}^3$), and root-mean-square electron-hole distances $\tau_{rms}$ (in Å) [from Equation (4.32)] for PPV, PT, and PPP, in a dilute benzene solution.
<table>
<thead>
<tr>
<th></th>
<th>$E_b$ (eV)</th>
<th>$f_{ij}$</th>
<th>$f_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>$S_2$</td>
<td>$f_{01}$</td>
<td>$f_{12}$</td>
</tr>
<tr>
<td>PPV$^a$</td>
<td>0.87</td>
<td>0.29</td>
<td>0.90</td>
</tr>
<tr>
<td>PPV$^b$</td>
<td>0.87</td>
<td>0.29</td>
<td>0.80</td>
</tr>
<tr>
<td>PT$^c$</td>
<td>1.00</td>
<td>0.33</td>
<td>0.72</td>
</tr>
<tr>
<td>PPP$^d$</td>
<td>1.06</td>
<td>0.30</td>
<td>0.75</td>
</tr>
</tbody>
</table>

**TABLE 7.2:** Exciton binding energies $E_b^i$ and oscillator strengths $f_{ij}$ for PPV, PT, and PPP, in a dilute benzene solution. See Table 7.1 for the explanation of the footnotes.

only. The correction $a_{xx,S_1}^{\text{loss}}$ of Equation (7.8) is 10-15% of $a_{xx,S_1}$, as can be seen in Table 7.1. The fact that the polarizability results almost exclusively from coupling of the $S_1$ to the $S_2$ exciton justifies the use of three-level models (the ground state $S_0$ and the exciton states $S_1$ and $S_2$) for the explanation of excitonic properties [144]. Here, it enables us to understand the difference in polarizability between PPV and PT/PPP, which results partly from the difference in energy between the $S_1$ and $S_2$ excitons, but mostly from the larger oscillator strength $f_{ij} = 2|\mu_{ij}|^2(E_{ij}^b - E_{ij}^d)/3$ in PPV. This oscillator strength as well as that between the ground state $S_0$ and the $S_1$ exciton is given in Table 7.2.

To get an impression of the shape of the exciton wave functions, we have plotted in Figure 7.4 the probabilities $P(x_e - x_h)$ to find the electron and hole of the $S_1$ exciton at a separation $x_e - x_h$ along the chain as defined in Equation (4.31). It is observed that the root-mean-square electron-hole distance $\sqrt{\langle (x_e - x_h)^2 \rangle}$, listed in Table 7.1, increases with increasing polarizability, as expected.

As we showed in the preceding Chapter, the exciton binding energy is rather sensitive to the choice of the dielectric constant $\varepsilon$. Therefore, the fact that the binding energies in a benzene solution ($\varepsilon = 2.28$) are larger than those for a bulk polymer ($\varepsilon = 3.0$) is not surprising. This means that the exciton binding energy of 0.87 eV given here for PPV in solution is not in contradiction with recently determined experimental values of 0.35 ± 0.15 eV for bulk alkox substituted PPV [8] and 0.48 ± 0.14 eV for bulk unsubstituted PPV [9].

### 7.5 Conclusions

In conclusion, we have demonstrated that two important properties of excitons on conjugated polymer chains, their polarizability and lifetime, can reliably be obtained from the solution of the many-body Bethe-Salpeter equation. This also strengthens the reliability of this approach for the prediction of other properties which are experimentally less accessible, like the exciton binding energy. More generally, this approach can open the way to a deeper understanding of the optical behaviour of conjugated polymers in terms of their
FIGURE 7.1: The probability $P(x_e - x_h)$ as defined in Equation (4.31) to find the electron and hole at a distance $x_e - x_h$ along the polymer chain (offsets applied). Especially in the tails (no offsets), which dominate the polarizability, the difference between the three polymers is clearly seen.

molecular structure and will be of help in the development of electro-optical devices based on these materials.
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Summary

The discovery, in the middle of the 1970s, of the fact that conjugated polymers (polymers with alternating single and double carbon-carbon bonds in their backbones) can be made electrically conductive by doping initiated a large number of studies, both experimental and theoretical, into the electronic and optical properties of these materials. The subsequent discovery of electroluminescence of a polyphenylenevinylene derivative has enabled the fabrication of polymer light-emitting diodes (pLEDs); in the meantime the first commercially viable matrix displays of conjugated polymers have been demonstrated. Application of conjugated polymers in logic gates and integrated circuits ('chips'), mostly made of polythiophene derivatives, has also been achieved. While in these applications the conjugated polymers merely replace more traditional semiconductors, they have the advantage that they are much easier to process, offer a flexible choice of materials, and, once mass-produced, are much cheaper.

In spite of the rapid development of applications, much of the fundamental physics of conjugated polymers and the devices based upon them is still ill-understood. To a large extent, this lack of knowledge can be attributed to the fact that conjugated polymer systems are ill-defined. Chemical defects are present, large sidegroups or substituents, added to make the polymer soluble and processable, cause the chain to be buckled rather than planar, and the ordering of chains relative to each other is often poor. Each of these effects varies from sample to sample, depending on the precise parameters of the sample preparation.

A property that is heavily disputed in conjugated polymers is the exciton binding energy, the binding energy of an electron-hole pair, for which values ranging from 0.1 to 1.0 eV have been coined. In the low-binding-energy case, a solid-state band picture suffices to describe the electronic and optical excitations in conjugated polymers; for larger binding energies, a molecular exciton picture is more appropriate.

Up to now the modeling of the electronic and optical properties of conjugated polymers has mostly been performed with (often semi-empirical) quantum-chemistry methods, which can not treat extended systems, or with solid-state-based density-functional methods, which do not give reliable one-particle excitation energies and do not include excitonic effects. Only recently first-principles calculations predicting the electronic and optical
excitations of extended systems have become possible, obtaining good agreement with experiments for a wide range of properties and materials. The calculational method is in fact a combination of three methods: density-functional theory to predict the ground-state geometric structure of a material, the so-called GW method to calculate the one-particle spectrum (the energies required to add or remove electrons from the system), and the Bethe-Salpeter equation for the two-particle spectrum (which also includes the interaction between electrons and holes). Combined, these methods, applied to any system, represent the state-of-the-art of first-principles calculations. This is especially true for conjugated polymers as the systems are very large and the calculations computationally very expensive. At the start of this work, not a single calculation with these combined methods had yet been done for conjugated polymers; it was our aim to endeavor this, and to investigate to what extent qualitatively correct predictions could be made. If successful, this might open the way to, e.g., theoretical band gap engineering.

The system that is studied most extensively in this thesis is polythiophene; it was chosen as a starting point because of larger symmetry (and hence smaller computational work load) compared to, e.g., polyphenylenevinylene. We study polythiophene in three geometries: an isolated chain in vacuum, an isolated chain in a bulk polythiophene environment (where the environment is modeled by an ab-initio direction- and frequency-dependent dielectric tensor), and a polythiophene crystal. It turns out that the electronic and optical properties depend critically on the surroundings of the chain. The exciton binding energy in the three cases mentioned above is 1.86, 0.76, and 0.15 eV (with an accuracy of about 0.1 eV), respectively; the one-particle band gap decreases concomitantly. Surprisingly, the optical gap is more or less unaffected.

In the case of the isolated chain in vacuum the Coulomb interaction (calculated in the GW formalism) between two charges is not screened at long distances, leading to large binding energies and band gaps. By including this long-range screening through embedding of the chain in a dielectric medium, both the exciton binding energy and the band gap are decreased, and we obtain good agreement with experimentally determined exciton splittings and with the absorption gap. In the crystalline situation, we also include wave-function overlap between neighboring chains, which lowers the band gap by the splitting of the one-particle states, thus decreasing the exciton binding energy. As most samples are rather disordered and the polymers are substituted, effective wave-function coupling between neighboring chains is most likely impossible in practice, which means that the isolated chain in a dielectric medium is in general the best geometry to perform calculations for conjugated polymer systems.

Our results suggest a possible resolution of the exciton binding-energy debate. The exciton binding energy decreases as the amount of interchain wave-function coupling increases (by an increased interchain order); different values of the exciton binding energy might result from samples with a different amount of order. This effect can be observed experimentally in a ladder-type polyphenylene, where crystalline aggregates have been shown to exist and the exciton binding energy is reduced compared to the disordered situation.
To prove that the methods can also be applied to other polymers, we next perform a number of calculations for a wide variety of polymers, including polyphenylenevinylene. For practical reasons we replace the screening calculated in the GW formalism by the Coulomb interaction divided by a dielectric constant, and use the density-functional quasi-particle energies (instead of the GW quasi-particle energies). We find that the exciton binding energy is in the 0.4–0.6 eV range, obtaining good agreement with specific experiments for each polymer individually. Especially interesting is that we also find good agreement for the only polymer for which there is no discussion about the exciton binding energy: polydiacetylene. Not for all properties the agreement is this good; this can probably be attributed to the fact that no lattice relaxation in the excited states and no four-particle excitations are included.

By using the same techniques we are also able to predict the spatial shapes and the radiative lifetimes of the excitons. For these properties good experimental data are available—in this case for polymers in solution—from microwave-conductivity and fluorescence-decay measurements. Taking the dielectric constant of the solvent to screen the Coulomb interaction, we again find very good agreement between our first-principles predictions and the experimental data.

Concluding, we show in this work that state-of-the-art first-principles solid-state methods can successfully be applied to conjugated polymer systems. An important finding thereby is that it is not possible to make a comparison with experiments performed on bulk polymers or polymers in solution by studying just one chain. The surroundings of the chain have to be taking into account correctly. The best way to do this for bulk polymers is by including the average surroundings, i.e., by embedding the chain in a dielectric medium, rather than by assuming a crystalline structure for the surroundings, since this latter assumption includes more order and hence wave-function overlap than is present in most samples.
Samenvatting

De ontdekking, halverwege de jaren '70, dat geconjuugeerde polymeren (polymeren met afwisselend enkele en dubbele koolstof-koolstof bindingen in de keten) elektrisch geleidend gemaakt kunnen worden door dotering, vormde het startschot voor een groot aantal onderzoeken, zowel experimenteel als theoretisch, naar de elektronische en optische eigenschappen van deze materialen. Dankzij de ontdekking dat een polyfensyleenvinyleen derivaat electroluminescent is, zijn inmiddels de eerste polymere lichtgevende diodes (pLEDs) en matrix displays van pLEDs geproduceerd. Geconjuugeerde polymeren, voornamelijk polythiofeen derivaten, vinden inmiddels ook hun toepassing in logische schakelingen en geïntegreerde circuits, of 'chips'. Hoewel de polymeren in deze toepassingen eigenlijk alleen de meer traditionele half-geleiders vervangen, hebben ze het voordeel dat ze veel gemakkelijker te verwerken zijn, een breed scala aan materiaalkeuzes bieden, en - zodra toepassingen massaal geproduceerd kunnen worden - veel goedkoper zijn.

Ondanks de snelle ontwikkeling van deze toepassingen, is veel van de fysica van geconjuugeerde polymeren en de daarop gebaseerde devices nog slecht begrepen. Dit is voor een groot deel terug te voeren op het feit dat de polymere systemen slecht gedefinieerd zijn. Samples bevatten chemische defecten, en aan de keten worden grote zinseenen toegevoegd om de polymeren beter te kunnen verwerken, die er echter resulteren in een geknikte in plaats van een vlakke keten, en de ordening van de ketens ten opzichte van elkaar slecht of totaal afwezig is. Elk van deze effecten varieert van sample tot sample, afhankelijk van de precieze omstandigheden tijdens het maken van het sample.

Een eigenschap waar nog steeds heftig over gediscussieerd wordt is de excitonbindingsenergie, de bindingsenergie van een elektron-gat paar. Waarden tussen de 0.1 en 1.0 eV zijn hiervoor voorgesteld. Als de excitonbindingsenergie laag is, dan kunnen de elektronische en optische excitaties in geconjuugeerde polymeren worden beschreven met band modellen; voor een grotere bindingsenergie is een molecular exciton beeld meer van toepassing.

Tot nu toe heeft de theoretische modellering van de elektronische en optische eigenschappen voornamelijk plaatsgevonden met (vaak semi-empirische) quantum-chemische methoden, die geen oneindige systemen aankunnen, of dichtheidsfunctionaal methoden, die geen goede waarde voor de één-deeltje excitaties geven, en geen excitonische effecten meenemen. Pas sinds zeer kort is het mogelijk om \textit{ab-initio} berekeningen voor de elektronische en optische
eigenschappen van oneindige systemen te doen waarbij goede overeenstemmingen met een groot aantal experimenten voor een groot aantal materialen wordt verkregen. De rekenmethode is eigenlijk een combinatie van drie methoden: dichtheidsfunctieal theorie om de atomaire structuur van het materiaal te berekenen, de GW benadering om het één-deeltje spectrum te berekenen, en de Bethe-Salpeter vergelijking om het twee-deeltjes spectrum te berekenen (waarbij ook de interactie tussen elektron en gaat wordt meegenomen). Gecombineerd liggen deze methoden, op welk systeem ze ook worden toepast, op de grenzen van het haalbare qua benodigde rekentijd; dit is zeker waar voor geconjugeerde polymeren, die een relatief grote eenheidscel hebben. Bij het begin van dit werk was er nog geen enkele berekening met deze gecombineerde methoden aan geconjugeerde polymeren gedaan; ons doel was ons hier aan te wagen en om te ontdekkingen tot op welke hoogte kwantitatief betrouwbare voorspellingen gedaan konden worden. Indien succesvol, maakt dit - onder andere - ’band gap engineering’ mogelijk.

Het systeem dat het nauwkeurigst bestudeerd wordt in dit werk is polythiofeen, dat als startpunt is gekozen omdat het meer symmetrie heeft (en dus minder rekentijd vereist) dan bijvoorbeeld polyefylenevinyleen. We bekijken polythiofeen in drie situaties: een enkele keten in vacuüm, een enkele keten in een bulk polythiofeen omgeving (waarbij de omgeving gemodelleerd wordt door een \textit{ab-initio} richtings- en frequentie-afhankelijke dielektrische tensor), en een polythiofeen kristal. Het blijkt dat de elektronische en optische eigenschappen zeer sterk afhangen van de omgeving van de keten. De excitonbindingsenergie is voor de genoemde drie gevallen 1.86, 0.76 en 0.15 eV (met een nauwkeurigheid van ongeveer 0.1 eV), respectievelijk; de één-deeltje band gap wordt navenant kleiner, zodat de optische gap, nogal onverwacht, min of meer hetzelfde blijft.

In het geval van de enkele keten in vacuüm is de Coulomb wisselwerking tussen twee ladingen voor grote afstanden niet afgeschermd, wat leidt tot grote bindingsenergieën en een grote band gap. Door de lange-drachts afscherming wel mee te nemen (door de keten in een medium te brengen) worden zowel de excitonbindingsenergie als de band gap verlaagd, wat leidt tot overeenstemming met experimenteel bepaalde excitonopspeltingen en de optische gap. In de kristallijne situatie wordt naast afscherming ook nog de golffunctieverloop tussen nabur-ketens meegenomen, wat de één-deeltje gap verlaagt door de één-deeltje niveaus op te splitsen. Aangezien de experimentele samples nogal wanordelijk zijn en de ketens substituenten hebben, is in deze gevallen effectieve golffunctiekoppeling tussen nabur-ketens onmogelijk, wat betekent dat de enkele keten in een diëlektrisch medium in het algemeen de beste geometrie is om berekeningen aan te doen voor geconjugeerde polymeren.

Deze resultaten suggereren een mogelijke oplossing voor het excitonbindingsenergie debat. De excitonbindingsenergie wordt kleiner naarmate de interketen golffunctiekoppeling groter wordt (wat weer veroorzaakt wordt door een hogere mate van orde); verschillende waarden voor de excitonbindingsenergie kunnen dan verklaard worden door een verschillende mate van orde. Dit effect is duidelijk zichtbaar in een ladder-polyphenyleen, waar experimenteel kristallijne aggregaten zijn aangetoond waarin de excitonbindingsenergie kleiner is dan in
de wanordelijke delen van het sample.

Om te laten zien dat de methoden ook kunnen worden toegepast op andere polymeren, worden vervolgens berekeningen gedaan voor een aantal polymeren, onder andere polyfenoyleen-vinylen. Om praktische redenen vervangen we de afgeschermd wisselwerking zoals die in de GW methode wordt berekend door de Coulomb wisselwerking gedeeld door een dielektrische constante, en gebruiken we dichtheidsfunctionaal één-deeltje energiën in plaats van de GW één-deeltje energiën. We vinden een excitonbindingsenergie tussen 0.4 en 0.6 eV; voor ieder polymer op zich vinden we goede overeenstemming met de experimentele waarden. Interessant is dat de overeenstemming ook goed is voor het enige polymer waarbij er geen discussie over de grootte van de excitonbindingsenergie is: polydiacetylen. Voor sommige eigenschappen komen de voorspellingen minder goed uit; dit is waarschijnlijk te wijten aan het verwaarlozen van ketenrelaxatie effecten in de geëxciteerde toestanden en het niet meenemen van vier-deeltjes excitaties.

Door dezelfde methoden te gebruiken kunnen ook de ruimtelijke vormen en de levensduren voor stralend verval van excitonen op polymeerketens voorspellen. Voor deze eigenschappen zijn experimentele data verkregen uit microgolfgeleiding- en fluorescentievervalmetingen beschikbaar, in dit geval voor polymer ketens in een benzoon oplossing. Door de dielektrische constante van de oplossing te gebruiken om de Coulomb wisselwerking af te schermen, vinden we opnieuw goede overeenstemming tussen onze ab-initio waarden en deze experimentele data.

Concluderend hebben we aangetoond dat ab-initio vaste-stof methoden met success kunnen worden toegepast op geconjugeerde polymeren. Een belangrijke conclusie is dat het niet mogelijk is berekeningen aan een enkele keten te vergelijken met experimenten die verricht zijn aan bulk samples of polymeren in oplossing. De omgeving van de keten moet correct worden meegenomen. De beste manier om dit te doen voor bulk polymeren is door de gemiddelde omgeving mee te nemen, dat wil zeggen door de keten in een dielektrisch medium te leggen, en niet door een kristallijnse structuur aan te nemen voor de omgeving, aangezien dit te veel orde en dus te veel golffunctieoverlap introduceert dan er is in de meeste samples.
List of publications

*Ab-initio calculation of the elastic and electron properties of a novel rigid-rod polymer: PIPD*
J.C.L. Hageman, J.-W. van der Horst, and R.A. de Groot
Polymer *40*, 1313 (1999)

*Ab-initio calculation of excited-state properties of conjugated polymers*
J.-W. van der Horst, P.A. Bobbert, M.A.J. Michels, G. Brocks, and P.J. Kelly

*Ab-initio calculation of the electronic and optical excitations in polythiophene: effects of intra- and interchain screening*
J.-W. van der Horst, P.A. Bobbert, M.A.J. Michels, G. Brocks, and P.J. Kelly

*Ab-initio prediction of the electronic and optical excitations in polythiophene: isolated chains versus bulk polymer*
J.-W. van der Horst, P.A. Bobbert, P.H.L. de Jong, M.A.J. Michels, G. Brocks, and P.J. Kelly

*Predicting polarizabilities and lifetimes of excitons on conjugated polymer chains.*

*Many-body solid-state methods applied to the optical and electronic properties of conjugated polymers*
accepted by Synthetic Metals
Calculation of excitonic properties of conjugated polymers using the Bethe-Salpeter equation
J.-W. van der Horst, P.A. Bobbert, M.A.J. Michels, and H. Bässler

Charge-injection spectroscopy of the LPPP/Au(111)-interface
in preparation
Dankwoord

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