Electronic Structure of Novel Two-dimensional Materials and Graphene Heterostructures

Malte Rösner

Universität Bremen

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Malte Rösner
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I can’t see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do.

R. P. Feynman (1960)
Abstract

Today a well-equipped library of two-dimensional materials can be synthesized or exfoliated, ranging from insulating hexagonal boron nitride, to semi-metallic graphene, and metallic as well as superconducting transition metal dichalcogenides and many others. Due to strong intra-layer covalent bondings, but weak inter-layer Van-der-Waals interactions, these layered materials can be stacked in a Lego-like fashion to artificial heterostructures which do not occur in nature. Thereby, these novel systems offer the possibility to combine specific properties of each of its constituents to tailor the heterostructure’s properties on demand which might allow for completely new device classes. In fact, these kind of systems are already constructed and studied in labs around the world.

In order to guide these efforts, we need an in-depth understanding of these complex heterostructures starting with its smallest components, namely the different two-dimensional materials and their mutual interactions. To this end, we study electronic and optical properties of novel two-dimensional materials in this thesis. In more detail, we here aim to investigate functionalized graphene, graphene heterostructures and doped or optically excited molybdenum disulfide (MoS$_2$) monolayers for which we combine \textit{ab initio} based models with many-body or multi-scale approaches.

The first part is devoted to functionalized graphene and is subdivided into the investigation of disorder-induced optical effects of fluorographene and into a detailed study of the Coulomb interaction in graphene heterostructures in form of multilayer graphene, intercalated graphite and few-layer graphene within a dielectric environment. In the case of fluorographene we use a multi-scale approach to study the effects of realistic disorder patterns to the optical conductivity. Thereby, we provide important insights into the role of non-perfect fluorination of graphene. Regarding the graphene heterostructures we present a novel approach to easily and reliably derive Coulomb-interaction matrix elements in these structures. This method is used to study the robustness of bilayer graphene’s ground state to changes in its dielectric surrounding.

In the second part of the thesis we study a variety of many-body effects that arise in doped and optically excited MoS$_2$ monolayers. Once again, by deriving simplified yet accurate models from first-principles we are able to investigate many-body excitations like plasmons or excitons as well as many-body instabilities like superconductivity or charge-density wave phases. Regarding the latter, we are able to extend the electron-doping phase diagram of MoS$_2$ by the formation of a charge-density-wave phase and reveal its potential coexistence with the superconducting state. In the field of many-body excitations we study in detail excitonic line shifts upon optical excitations and
we precisely describe different types of plasmonic excitations under electron or hole doping in MoS₂. Finally, we make use of the fundamental properties of the many-body interactions in layered materials in order to externally induce heterojunctions within homogeneous semiconducting monolayers by non-local manipulations of the Coulomb interaction.
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1. Introduction

Since the isolation of graphene monolayers by K. S. Novoselov and A. K. Geim [1, 2], which earned them the Noble Prize in Physics in 2010 [3, 4], the part of the scientific community which investigates two-dimensional materials has been exponentially growing. Since then, the library of available layered materials kept constantly growing including up to now graphene, graphene derivatives (like fluorographene or graphane), graphene equivalents (like silicene or germanene), hexagonal boron nitride, transition metal dichalcogenides, two-dimensional oxides (like TiO$_2$ or WO$_3$), and many others [5].

Besides having remarkable properties on their own, like extreme electrical conductivities or mechanical flexibilities, layered materials offer the fundamentally new opportunity to tailor material properties on demand either by surface treatments or by guided stacking on top of each other [5, 6, 7, 8]. In comparison to conventional epitaxial growth of heterostructures, the latter comes with the distinct advantage that it does not require any lattice-match conditions due to the weak Van-der-Waals interactions between the layers. This might lead to a paradigm change as already conceived by R. P. Feynman in 1960 in his famous lecture “There’s Plenty of Room at the Bottom” [9] and as it is described in the “Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems” of the European Graphene Flagship [10].

This might yield a novel framework to construct transistors, batteries, opto-electronic compounds, sensors, photo-voltaic cells, and so on.

In fact, it remains to be seen in the (near?) future, whether or not these overwhelming predictions can be fulfilled. Therefore, we need a deep understanding of both, the pristine layers and their mutual interactions in order to recognize how specific properties in these heterostructures can be tuned. This, in turn, is a challenging task since electrons are confined to atomically thin structures in layered materials which results in enhanced sensitivities to atomistic geometrical details. Additionally, sizable electron-phonon and strong electron-electron interactions due to the reduced screening are present in these materials. Hence, many-body effects and structural details play a major role in defining the electronic structure of these novel two-dimensional materials.

The scope of this thesis is to investigate this interplay for novel two-dimensional materials and graphene heterostructures by theoretical means. To this end, we will derive so-called low-energy models based on \textit{ab initio} calculations using solely geometrical details of the specific lattice structures. These models serve afterwards as the basis for sophisticated many-body considerations or multi-scale treatments. This combination of calculations from first principles and model descriptions offers the con-
1. Introduction

considerable advantage that the following many-body or multi-scale treatments have not to be performed on the full system, but only on those energy ranges which are most important for the problem under consideration. Hence, it combines the accuracy of first-principles calculations with the capabilities of the subsequent higher-level theory, which is often unfeasible if it involves the full ab initio basis. In fact, this separation has routinely been applied in recent years, e.g., in the field of strongly correlated electron problems. Here, density functional theory is used as an ab initio starting point to derive material-realistic Hubbard models including information about the electronic dispersion and the Coulomb interaction which are treated afterwards within many-body theories such as the (un)screened Hartree-Fock approximation [11, 12, 13, 14] or the so-called dynamical mean field theory [15, 16, 17].

Here, we will apply this concept to investigate the electronic and optical properties of functionalized graphene in form of fluorographene, graphene multi layers and intercalated graphite as well as molybdenum disulfide monolayers. Based on our first-principle calculations we derive material-realistic models following Einstein’s philosophy “Every-thing should be as simple as possible, but not simpler.”. Applied to the model-building process, this means that our models should include exclusively those parts of the full descriptions which will certainly be needed within the subsequent many-body treatments or multi-scale approaches – neither more nor less. The exact definition of the required parts is thereby given by the material property of interest.

Before we present the corresponding physical results, we introduce in chapter 2 the theoretical framework in which all results from the subsequent chapters are gained. Therefore, we introduce a general definition of our model Hamiltonian and, in order to calculate the model ingredients, the density functional theory, the GW approximation as well as the density functional perturbation theory.

Chapter 3 is devoted to functionalized graphene in form of fluorographene and graphene heterostructures. After briefly discussing the materials under consideration in section 3.1, we turn to the optical properties of fluorographene in section 3.2. Here, the experimental data shows optical band gaps of the order of 3 eV which can not be understood from a theoretical point of view by considering a pristine and perfect layer. Therefore, we will study the influence of structural disorder to the optical conductivity of fluorographene as obtained from the so-call tight-binding propagation method. The latter relies on an ab initio based tight-binding model. Hence, here we need to derive material-realistic tight-binding models (i.e., including single-particle energies only) which are capable of describing multiple disorder configurations of large real-space super cells.

Regarding graphene heterostructures, we aim to understand how the electronic ground state of bilayer graphene is controlled by its environment. As shown by Scherer et al., the bilayer graphene ground state sensitively depends on the Coulomb-interaction strength and its long-range behaviour [18]. Therefore, we introduce in section 3.3 a novel modeling approach to feasibly and accurately derive Coulomb-interaction matrix elements of heterogeneous layered materials derived from ab initi
calculations of the corresponding homogeneous host material. This approach is applied to model the Coulomb interaction in mono- and bilayer graphene, graphite and iridium intercalated graphite. Furthermore, the approach allows us to study the influence of dielectric environments which is used to study the ground-state dependence of bilayer graphene to variations in the dielectric surrounding.

In chapter 4 we aim to describe many-body effects arising in MoS$_2$ monolayers under charge doping or optical excitations. Although the MoS$_2$ ground state has extensively been studied, as briefly outlined in section 4.1, there is a lack of knowledge concerning these doped or excited states. We try to close this gap (at least a bit) by the investigation of arising many-body instabilities in form of superconductivity and charge-density-wave formation as well as many-body excitations in terms of excitonic and plasmonic characteristics.

To this end, we need to derive models from first-principles which describe electronic and phononic properties as well as electron-electron and electron-phonon interactions. We start with the introduction of a generalized Hubbard model in section 4.2 which describes feasibly and accurately the electronic band structure as well as the Coulomb-interaction matrix elements of MoS$_2$ in its ground state in the Wannier basis.

Before we use this model, we additionally calculate phononic properties in form of dispersions and electron-phonon couplings for a variety of electron doping levels in section 4.3 in order to describe the arising superconducting state. Thereby, we gain a detailed understanding of this phase and additionally find a possibly coexistent charge-density-wave state.

In section 4.4 we turn to excitonic properties of MoS$_2$ monolayers under optical excitation which is described utilizing the so-called semiconductor Bloch equations in combination with the generalized Hubbard model as introduced in section 4.2. Here, we find sizable band gap and exciton binding energy shrinkages (under excitation) yielding a net redshift of the most prominent features within the absorption spectra.

 Afterwards we turn to plasmonic excitations under electron or hole doping in section 4.5, which are described using the random phase approximation to derive the dynamical screening based (once again) on the model from section 4.2. Here, we describe the plethora of possible plasmonic excitation channels and the dependence on outer dielectric screening effects.

Finally, in section 4.6, we investigate in more detail how these outer screening effects can affect the ground state of a homogeneous semiconducting monolayer. In more detail, we consider effects arising due to non-local manipulations of the Coulomb interaction due to laterally varying dielectric environments. By utilizing an appropriate real-space model we find that the local changes of the Coulomb interaction can induce a spatial band-gap modulation within the semiconducting layer, leading to a novel kind of heterojunction.

Altogether, we present a variety of ab initio-based modeling schemes in order to study various many-body properties and characteristics of novel two-dimensional materials. Thereby, we will find balanced mixtures of model accuracies and levels of
1. Introduction

many-body theories in order to derive these properties for the corresponding materials as accurately as possible.
2. Ab Initio Description of Single-Particle and Many-Body Properties of Solids

The following chapter introduces the theoretical framework in which all material-realistic models as used in chapter 3 and chapter 4 are obtained. We start with a brief introduction of the solid-state Hamiltonian in different representations in section 2.1. Afterwards we introduce a variety of approximations and methods which are needed to derive each ingredient of these models from first principles. Therefore, we present schemes to describe electronic single-particle energies on a mean-field level within the density functional theory in section 2.2, which is augmented by properly introducing the full Coulomb interaction and its effects using the GW approximation in section 2.3. Finally, we discuss the description and effects of the lattice dynamics with the help of density functional perturbation theory in section 2.4.

Here and in the following we highlight the main references for the subsequent texts in form of small “disclaimers” at the very beginning of the corresponding sections or subsections. The attentive reader will recurrently find Martin’s book [19], the Jülich lecture notes [20] and [21] as well as the reviews by Onida et al. [22] and Marzari et al. [23] among the listed references. Indeed, these have been continuously used as references for all of the subsequent discussions.

2.1. Hamilton Operators

The following brief introductions of the solid-state Hamiltonian and the Born-Oppenheimer approximation are short excerpts from the book by Czycholl [24] and the original paper by Born and Oppenheimer [25]. Similar and more detailed discussions can be found in a variety of text books like in Refs. [26, 27, 28, 29, 30].

In its most general form, the many-body Hamiltonian of interacting electrons and ions is given by

$$H = T + V,$$

where $T$ denotes the kinetic energies of the electrons and ions and $V$ their pairwise
interactions. The kinetic terms can be separated via

\[ T = T_e + T_i = \sum_{i} \frac{p_i^2}{2m_e} + \sum_{I} \frac{P_I^2}{2M_I}, \]  

(2.2)

where \( m_e \) and \( M_I \) describe the masses of the \( i \)-th electron and \( I \)-th ion. Correspondingly, we label the electronic and ionic momenta \( p_i = -i\hbar \nabla_i \) and \( P_I = -i\hbar \nabla_I \) with small and capital letters. The interaction terms are given by

\[ V = V_{ee} + V_{ii} + V_{ei} = \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \sum_{i > j} \frac{Z_i Z_j e^2}{|R_i - R_j|} - \sum_{i \neq j} \frac{Z_I e^2}{|r_i - R_I|}, \]  

(2.3)

where \( V_{ee}, V_{ii} \) and \( V_{ei} \) describe the electron, ion and their mutual interactions, respectively. \( r \) and \( R \) are the spatial coordinates of the electron and ions and \(-e\) and \( Ze\) are their charges. Based on this Hamiltonian we have to find a solution to the Schrödinger equation

\[ H \Psi(r, R) = E \Psi(r, R) \]  

(2.4)

to describe, for instance, the spectrum of the corresponding system. This involves the total wave function \( \Psi(r, R) \) for sets of electronic and ionic coordinates \( r \) and \( R \). Having in mind that this task has to be performed by considering the electronic and ionic dynamics and their pairwise interactions for approximately \( 10^{23} \) particles in a solid-state body, it is obvious that various levels of approximations have to be applied to find a solution to this problem. However, before we introduce these approximations in the following sections, we give and shortly discuss the second-quantization representation of the Hamiltonian defined in Eqs. (2.1)–(2.3) in reciprocal space (thus for translational invariant systems) in the harmonic approximation:

\[ H = \sum_{k_n \sigma} \epsilon_n(k)c_{k_n \sigma}^\dagger c_{k_n \sigma} \\
+ \sum_{q \nu} \omega_\nu(q) \left( b_{q \nu}^\dagger b_{q \nu} + \frac{1}{2} \right) \\
+ \sum_{k_n' \sigma \nu} g_{nn'}^{\nu \sigma}(k, q) \left( b_{q \nu} + b_{q \nu}^\dagger \right) c_{k+n \sigma}^\dagger c_{k \sigma} \\
+ \frac{1}{2} \sum_{k' k q \nu \sigma \sigma'} U_{nn'}^{\nu \sigma}(k, k', q) c_{k+q \nu \sigma}^\dagger c_{k' \nu \sigma'}^\dagger c_{k' \nu \sigma'} c_{k \nu \sigma}. \]  

(2.5)

These four terms describe the electronic and phononic dynamics, the electron-phonon coupling and the electron-electron (Coulomb) interaction within a solid-state body.
2.1. Hamilton Operators

While the fermionic operators $c^+_k n \sigma$ and $c_k n \sigma$ create and annihilate an electron with momentum $k$ in the band $n$ and with spin $\sigma$, the bosonic operators $b^+_q \nu$ and $b_q \nu$ create and annihilate phonons with momentum $q$ and band index $\nu$. Correspondingly, the single-particle operator matrix elements $\varepsilon_n(k)$ and $\omega_\nu(q)$ describe the electronic and phononic band structures and $g_n^\nu(k, q)$ and $U_n^\nu(k, k', q)$ define the electron-phonon and electron-electron coupling strengths.

Besides the involved harmonic approximation, this Hamiltonian corresponds to the most general description of a solid-state body. A full diagonalization would yield a complete interacting spectrum including the effects of many-body instabilities like superconductivity, charge- or spin-density-waves and it would allow for quantitative descriptions of many-body excitations like excitons or plasmons. Thereby the most relevant material properties like transition temperatures or excitation energies are rendered by the exact values of the involved matrix elements. Thus, it is crucial to derive these quantities as accurate as possible in order to precisely describe the properties of a solid-state material. Furthermore, we need sophisticated many-body methods which are able to deal with Hamiltonians of this form. These two steps of calculating matrix elements and “solving” the resulting Hamiltonian form indeed the general recipe used throughout this thesis to obtain all presented results. Therefore, the rest of this chapter is devoted to the first-principles based derivation of material-realistic models. Afterwards we will use and approximately solve these models in chapter 3 and chapter 4 to obtain our final results.

2.1.1. Born-Oppenheimer Approximation

One of the most fundamental approximations is the adiabatic Born-Oppenheimer decoupling of the electronic and ionic dynamics, which will be used in most parts of this thesis and is therefore introduced in this section. It traces back to the vast differences of the electronic and ionic masses which lead to quite different time scales for the motions of the electrons and ions. Therefore, the electronic dynamics can be considered to follow instantaneously the motions of the nuclei. This motivates to consider the ionic movement as a perturbation ($T_i$) to the electronic system ($H_e$) by separating the Hamiltonian from Eqs. (2.1)–(2.3) according to

$$H = H_e + T_i \quad \text{with} \quad H_e = T_e + V_{ee} + V_{ei} + V_{ii}$$

Doing so, the interacting electron system feels just a static potential of the ions at the positions $\mathbf{R}$ which enter $H_e$ solely as parameters. Hence, we are in principle able to find a solution of the electronic Schrödinger equation for fixed ion positions $\mathbf{R}$:

$$H_e \psi_n(\mathbf{r}, \mathbf{R}) = [T_e + V_{ee} + V_{ei}(\mathbf{R}) + V_{ii}(\mathbf{R})] \psi_n(\mathbf{r}, \mathbf{R}) = E_n(\mathbf{R}) \psi_n(\mathbf{r}, \mathbf{R}).$$

The same obviously holds for the Hamiltonian defined in Eqs. (2.1)–(2.3). Indeed, these equations include even anharmonic processes, which are neglected in the Hamiltonian from Eq. (2.5).
Using this solution within the Born-Oppenheimer ansatz [25] we approximate the total wave function as a product of the electronic $\psi_n(\mathbf{r}, \mathbf{R})$ and ionic $\chi_n(\mathbf{R})$ wave functions

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_n \chi_n(\mathbf{R})\psi_n(\mathbf{r}, \mathbf{R}).$$ \hspace{1cm} (2.8)

Using this ansatz to find a solution of the full Hamiltonian yields:

$$H\Psi(\mathbf{r}, \mathbf{R}) = \sum_n \left[ E_n(\mathbf{R}) + T_i \right] \chi_n(\mathbf{R})\psi_n(\mathbf{r}, \mathbf{R})$$

$$= \sum_n E_n(\mathbf{R})\chi_n(\mathbf{R})\psi_n(\mathbf{r}, \mathbf{R})$$

$$- \sum_i \frac{\hbar^2}{2M_i} \left( \nabla_i^2 \chi_n(\mathbf{R})\psi_n(\mathbf{r}, \mathbf{R}) + 2\nabla_i \chi_n(\mathbf{R})\nabla_i \psi_n(\mathbf{r}, \mathbf{R}) + \chi_n(\mathbf{R})\nabla_i^2 \psi_n(\mathbf{r}, \mathbf{R}) \right)$$

$$= \sum_n \psi_n(\mathbf{r}, \mathbf{R})\left[ E_n(\mathbf{R}) + T_i \right] \chi_n(\mathbf{R})$$

$$- \sum_i \frac{\hbar^2}{2M_i} \left( 2\nabla_i \chi_n(\mathbf{R})\nabla_i \psi_n(\mathbf{r}, \mathbf{R}) + \chi_n(\mathbf{R})\nabla_i^2 \psi_n(\mathbf{r}, \mathbf{R}) \right).$$ \hspace{1cm} (2.9)

The last terms include derivatives of the electronic wave functions with respect to the ionic positions. These are non-adiabatic contributions which describe electronic excitations due to the dynamics of the ionic system. A detailed analysis of these contributions reveals that the term $\propto \nabla^2 \chi$ is in general negligible compared to the dominant $\propto \nabla \chi \nabla \psi$ one [24]. However, in many situations it is even justified to neglect both terms. By applying $\int d\mathbf{r} \psi_m^*(\mathbf{r}) \ldots$ to the expression from Eq. (2.9) upon neglecting the non-adiabatic terms we get

$$E \chi_m(\mathbf{R}) = [ E_m(\mathbf{R}) + T_i ] \chi_m(\mathbf{R}),$$ \hspace{1cm} (2.10)

which is the Schrödinger equation for the lattice dynamics. Hence, the adiabatic Born-Oppenheimer approximation separates the electron and ion dynamics. Thereby, the electronic energies $E_m(\mathbf{R})$ define an effective potential of the ionic motion and thus implicitly define optimal lattice structures and bonding properties (as minima of $E_0(\mathbf{R})$ with respect to the ionic positions $\mathbf{R}$). By solving the electronic Schrödinger equation in a first step, we are now able to derive the lattice dynamics in a second step.

### 2.2. Single-Particle Energies

As discussed in the previous section, a solution of the electronic Schrödinger equation from Eq. (2.7) would allow to study the physics of the full Hamilton operator from Eqs. (2.1)–(2.3) or Eq. (2.5). Unfortunately, this is not possible without applying several approximations. To this end, we introduce in section 2.2.1 the density
2.2. Single-Particle Energies

Functional theory (DFT) which was developed by P. C. Hohenberg, L. J. Sham and W. Kohn\(^2\) in the 1960s. It can be seen as a powerful tool to approximatively derive single-particle electron energies which allows for detailed insights into the electronic properties of solid-state materials. Although DFT calculations in the Kohn-Sham formulation remain somehow problematic due to missing analytic expressions for the involved functionals, the available approximations perform remarkably well making DFT to one of the most important \textit{ab initio} theories. This is corroborated by several thousands of scientific articles applying DFT published each year [31] and its extraordinary efficiency to solve the highly complex problem of (weakly) correlated electrons within a solid-state body. Next to plane-wave basis sets, we will utilize Wannier functions in section 2.2.2 to derive “hopping” matrix elements for lattice models in real space which will serve as the basis for a variety of tight-binding models used in many contexts of this thesis.

2.2.1. Density Functional Theory

The following introduction to density functional theory closely follows the book by Martin [19]. Most of the subsequent derivations and discussions can be found there and in references therein.

Density functional theory aims to find approximate solutions to the full electronic many-body problem in the Born-Oppenheimer approximation given by the slightly generalized Hamiltonian

\[
H = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i v_{\text{ext}}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\left| r_i - r_j \right|}, \tag{2.11}
\]

Here, we use the electronic kinetic term from Eq. (2.2), the electron-electron interaction from Eq. (2.3) and a general external potential \(V_{\text{ext}} = \sum_i v_{\text{ext}}(r_i)\). The latter can describe (spin-independent) external fields and might include localized or periodic ionic potentials as well as their interactions. Thus, the Hamiltonian from Eq. (2.11) is capable of describing the electronic many-body problem of single atoms, molecules as well as condensed matter. In order to solve the corresponding eigenvalue problem for the ground state,

\[
H \psi_0(\mathbf{r}) = E_0 \psi_0(\mathbf{r}), \tag{2.12}
\]

DFT utilizes the electronic ground-state density \(n_0(\mathbf{r})\) as the basic variable instead of the many-body wave function \(\psi(\mathbf{r})\). This comes with the clear advantage that the

\(^2\)Although, P. C. Hohenberg and L. J. Sham provided indispensable contributions, W. Kohn plays the essential role in the development of density functional theory and was therefore the only one honored by the Noble Prize in Chemistry in 1998 (next to J. A. Pople).
ground-state density is just a function of the position $\mathbf{r}$, while $\psi(\mathbf{r})$ is a linear combination of Slater determinants and thus a function of all electron positions $\mathbf{r}$. However, it is a priori not obvious that the ground-state density can be used to uniquely define and find the ground-state energy. To this end it needed the genius of Hohenberg and Kohn who presented in their seminal work from 1964 [32] a corresponding proof based on two theorems.

**Hohenberg-Kohn Theorems**

Both of the following theorems apply to interacting particles in an external potential $V_{\text{ext}}$, which can be described by a Hamiltonian such as given in Eq. (2.11).

**Theorem I:** The electronic ground-state density $n_0(\mathbf{r})$ uniquely determines the external potential $V_{\text{ext}}$.

This can be easily shown using the definition of the electron density ($N$ is the number of electrons) operator

$$n(\mathbf{r}) = \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$$  \hspace{1cm} (2.13)

to describe the external potential

$$V_{\text{ext}} = \int d^3 \mathbf{r} \ n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) = \int d^3 \mathbf{r} \ \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_i) v_{\text{ext}}(\mathbf{r}) = \sum_{i}^{N} v_{\text{ext}}(\mathbf{r}_i).$$  \hspace{1cm} (2.14)

If there would exist two different external potentials $V_{\text{ext}}^{(1)} \neq V_{\text{ext}}^{(2)}$ (which differ by more than a constant) for the same density $n_0(\mathbf{r})$, there would be different Hamiltonians $H^{(1)} \neq H^{(2)}$ and correspondingly different ground-state wave functions $\psi_0^{(1)}$ and $\psi_0^{(2)}$ which, however, share the same ground-state density $n_0(\mathbf{r})$ by construction. Using these Hamiltonians and wave functions we find

$$\langle \psi_0^{(1)} | H^{(1)} | \psi_0^{(1)} \rangle = E_0^{(1)} < \psi_0^{(2)} | H^{(1)} | \psi_0^{(2)} \rangle$$  \hspace{1cm} (2.15)

$$\langle \psi_0^{(2)} | H^{(2)} | \psi_0^{(2)} \rangle = E_0^{(2)} < \psi_0^{(1)} | H^{(2)} | \psi_0^{(1)} \rangle$$  \hspace{1cm} (2.16)

while Eqs. (2.11) and (2.14) lead to

$$\langle \psi_0^{(2)} | H^{(1)} | \psi_0^{(2)} \rangle = \langle \psi_0^{(2)} | H^{(2)} | \psi_0^{(2)} \rangle - \langle \psi_0^{(2)} | H^{(2)} - H^{(1)} | \psi_0^{(2)} \rangle$$

$$= E_0^{(2)} - \int d^3 \mathbf{r} \ n_0(\mathbf{r}) \left( v_{\text{ext}}^{(2)}(\mathbf{r}) - v_{\text{ext}}^{(1)}(\mathbf{r}) \right)$$  \hspace{1cm} (2.17)

$$\langle \psi_0^{(1)} | H^{(2)} | \psi_0^{(1)} \rangle = \langle \psi_0^{(1)} | H^{(1)} | \psi_0^{(1)} \rangle - \langle \psi_0^{(1)} | H^{(1)} - H^{(2)} | \psi_0^{(1)} \rangle$$

$$= E_0^{(1)} + \int d^3 \mathbf{r} \ n_0(\mathbf{r}) \left( v_{\text{ext}}^{(2)}(\mathbf{r}) - v_{\text{ext}}^{(1)}(\mathbf{r}) \right).$$  \hspace{1cm} (2.18)
Hence, adding the inequalities from Eqs. (2.15) and (2.16) using the expressions from Eq. (2.17) and (2.18) we find the contradiction

\[ E_{0}^{(1)} + E_{0}^{(2)} < E_{0}^{(1)} + E_{0}^{(2)} \]  

(2.19)

which finally proves that there cannot be different potentials \( V_{\text{ext}}^{(1)} \) and \( V_{\text{ext}}^{(2)} \) to the same ground-state density \( n_{0}(r) \) and \( n_{0}(r) \) thus uniquely defines \( V_{\text{ext}} \). Since \( V_{\text{ext}} \) in turn uniquely defines \( H \) (and thus all material properties), the theorem furthermore tells us that the density is indeed a reasonable basic variable to solve the given eigenvalue problem.

**Theorem 2:** There exists a functional \( E[n(r)] \) of the charge density \( n(r) \) which is minimized by the ground-state density \( n_{0}(r) \).

This functional can be generally defined as

\[ E_{\text{HK}}[n(r)] = \langle \psi | H | \psi \rangle = T[n(r)] + V_{\text{ee}}[n(r)] + \int d^{3}r v_{\text{ext}}(r)n(r), \]  

(2.20)

where \( F_{\text{HK}}[n(r)] \) is a universal functional including the electron kinetic \( T \) and interaction \( V_{\text{ee}} \) terms which solely depend on the electronic density. The third term in Eq. (2.20) describes the electron interactions with the external potential and the mutual ion interactions (which is actually not a functional of the electron density). From the first theorem we already know that the ground-state density \( n_{0}(r) \) is uniquely connected to the wave function \( \psi_{0} \) and the Hamiltonian \( H \), while any other density \( n_{0}(1) \) is connected to \( \psi_{0}(1) \) and \( H(1) \). Based on these simple assumptions we directly see

\[ E_{0} = \langle \psi_{0} | H | \psi_{0} \rangle < \langle \psi_{0}^{(1)} | H | \psi_{0}^{(1)} \rangle \]  

(2.21)

and thus find

\[ E_{\text{HK}}[n_{0}(r)] < E_{\text{HK}}[n_{0}^{(1)}(r)]. \]  

(2.22)

Therefore, \( E_{\text{HK}}[n(r)] \) is indeed minimized by the ground-state density \( n_{0}(r) \). Thus, it is sufficient to know \( E_{\text{HK}}[n(r)] \) in order to gain the ground-state’s energy and density.

Hence, the former ad-hoc assumption that the electron density can be used as a basic variable to find the system’s ground-state energy is now proven. Furthermore, Hohenberg and Kohn additionally provided a minimization scheme to find it. However, to this end an analytic expression for the Hohenberg-Kohn functional \( E_{\text{HK}} \) from Eq. (2.20) is needed, which is unfortunately given only for the last term while the first terms are not known for interacting electrons. Therefore, approximations are needed to describe the functional dependencies of the electron kinetics and interactions to
2. Ab Initio Description of Single-Particle and Many-Body Properties of Solids

the electron density. A very first approximation of this kind was already given by Thomas [33] and Fermi [34] in 1927 (thus about 40 years before Hohenberg and Kohn published their theorems), who independently approximated the kinetic energy as a functional of the local density of a non-interacting electron gas. Both of them included the electrostatic Coulomb interaction (Hartree energy) but neglected exchange effects among the electrons, which was corrected later on by Dirac in 1930 [35]. The resulting Thomas-Fermi-Dirac functional is given by

\[ E_{TFD}[n(r)] = C_1 \int d^3r \ n(r)^{5/3} + C_2 \int d^3r \ n(r)^{4/3} + \frac{1}{2} \int d^3rd^3r' \ \frac{n(r)n(r')}{|r-r'|} + \int d^3r \ v_{ext}(r)n(r). \tag{2.23} \]

The constants \( C_1 = \frac{\alpha}{10}(3\pi^2)^{2/3} \) and \( C_2 = -\frac{\pi}{4}(\frac{3}{2})^{1/3} \) correspond to the local approximations of the kinetic and exchange energies of the electron gas, respectively. By minimizing this functional with respect to the density under the constraint of a fixed number of electrons, the corresponding ground-state density can be derived. Unfortunately, the involved approximations to the functional are too crude, so that, for instance, binding energies in molecules or solids cannot be described accurately and \( E_{TFD}[n(r)] \) cannot be used to reliably deal with solid states.

The breakthrough for DFT came with the introduction of an auxiliary single-particle system by Kohn and Sham together with useful approximations to the involved functionals. By doing so, DFT became a numerically feasible theory which is capable of describing a large variety of systems.

Kohn-Sham Auxiliary System

The ingenious idea of Kohn and Sham was to introduce an auxiliary single-particle system which has the same ground-state density as the full many-body system [36]. Thus, by solving the much simpler independent-particle problem the full many-body problem is automatically solved as well. Although there is no rigorous proof allowing for a general application of this scheme [19] it is assumed for practical calculations that the so-called "non-interacting V-representability" of the charge density is given as long as \( n(r) \) is smooth [39, 40]. However, accepting this assumption is tempting

\footnote{A density \( n(r) \) is called V-representable as long as there exists an external potential \( V_{ext} \) which leads to \( n(r) \) for the resulting ground state. The Hohenberg-Kohn theorems and proofs as given above indeed require V-representability of \( n(r) \) (the first Hohenberg-Kohn theorem solely states that if there is an external potential \( V_{ext} \) it is uniquely defined by the corresponding density, but it does not state that there must exists an external potential \( V_{ext} \)). However, for the full interacting system this requirement could be relaxed by Levy and Lieb [37, 38] who were able to redo the corresponding proof requiring \( n(r) = \langle \Psi|\hat{n}|\Psi \rangle \) with \( \Psi \) being a normalized \( N \)-particle wave function (\( N \)-representability) only. Up to now, it is not clear if this holds for the non-interacting systems as well.}
since a single-particle problem of the form suggested by Kohn and Sham
\[ H_{KS} = -\frac{\hbar^2}{2m} \nabla^2 + v_{KS}(r) \]  
(2.24)
can easily be solved numerically, whereas many-body systems are much harder to handle. Hereby, the problem has been reformulated to construct an appropriate effective local Kohn-Sham potential \( v_{KS}(r) \) resulting in a ground-state density which equals the one of the original many-body problem. To this end Kohn and Sham casted the Hohenberg-Kohn functional from Eq. (2.20) into a non-interacting form
\[ E_{KS}[n(r)] = T_s[n(r)] + E_{\text{Hartree}}[n(r)] + E_{xc}[n(r)] + \int d^3r \, v_{\text{ext}}(r)n(r) \]  
(2.25)
which is minimized with respect to the charge density under the constraint of a constant particle number in order to derive a single-particle Schrödinger equation. Thereby, the latter will include a formal definition of the Kohn-Sham potential \( v_{KS}(r) \).

In contrast to the many-body formulation of the energy functional from Eq. (2.20) we are now dealing with a single-particle system which allows for a simple definition [19] of the independent-particle kinetic energy functional
\[ T_s[n(r)] = \frac{-\hbar^2}{2m_e} \sum_{\varepsilon_n < E_F} \int d^3r \, |\nabla \Phi_n(r)|^2 \]  
(2.26)
and the corresponding classical Hartree energy functional
\[ E_{\text{Hartree}}[n(r)] = \frac{1}{2} \int d^3rd^3r' \, \frac{n(r)n(r')}{|r - r'|} \]  
(2.27)
while the electron density is given by
\[ n(r) = \sum_{\varepsilon_n < E_F} |\Phi_n(r)|^2, \]  
(2.28)
involving the Fermi energy \( E_F \), single-particle wave functions \( \Phi_n(r) \) and corresponding energies \( \varepsilon_n \). \( E_{xc}[n(r)] \) describes the missing many-body interactions of the electrons, namely the quantum mechanical exchange and correlation energies. By comparing \( E_{HK} \) and \( E_{KS} \) we can generally define it via
\[ E_{xc}[n(r)] = \langle T \rangle + \langle V_{ee} \rangle - T_s[n(r)] - E_{\text{Hartree}}[n(r)], \]  
(2.29)
where the expectation values \( \langle T \rangle \) and \( \langle V_{ee} \rangle \) have to be evaluated within the original many-body wave functions of the full problem (\( T \) and \( V_{ee} \) correspondingly describe the full kinetic and interaction energies). If this exchange and correlation functional were known, the exact many-body ground state could be found within the auxiliary system.
However, this is not possible and appropriate approximations have to be applied. But before these approximations are discussed in more detail, the Kohn-Sham potential has to be derived using the method of Lagrange multipliers. Due to the simple relation of the electronic density and the single-particle wave function given in Eq. (2.28), the corresponding minimization with respect to the density can also be performed with respect to the single-particle wave function, but now under the constraint of orthogonal and normalized wave functions [19, 24]. Doing so, we get for \( N \) electrons

\[
\delta \Phi^*_i(r) \left\{ E_{KS}[n(r)] - \sum_{j=1}^N \lambda_j \left( \int d^3r \ |\Phi_j(r)|^2 - 1 \right) \right\} = 0, \tag{2.30}
\]

where \( \delta \Phi^*_i(r) \{ . . . \} = \frac{\delta}{\delta \Phi^*_i(r)} \) is the functional derivative\(^4\) with respect to \( \Phi^*_i(r) \) and \( \lambda_j \) are Lagrangian multipliers enforcing the normalization constraint for each wave function. The involved functional derivatives of the Kohn-Sham functional

\[
\frac{\delta E_{KS}}{\delta \Phi^*_i(r)} = \frac{\delta T_s}{\delta \Phi^*_i(r)} + \frac{\delta E_{\text{ext}}}{\delta n(r)} + \frac{\delta E_{\text{Hartree}}}{\delta n(r)} + \frac{\delta E_{\text{xc}}}{\delta n(r)} \frac{\delta n(r)}{\delta \Phi^*_i(r)} \tag{2.31}
\]

can be readily evaluated (at least in parts) using

\[
\frac{\delta T_s}{\delta \Phi^*_i(r)} = -\frac{\hbar^2}{2m_e} \nabla^2 \Phi_i(r) \quad \text{and} \quad \frac{\delta n(r)}{\delta \Phi^*_i(r)} = \Phi_i(r), \tag{2.32}
\]

while the functional derivative of the constraint yields

\[
\frac{\delta}{\delta \Phi^*_i(r)} \sum_{j=1}^N \lambda_j \left( \int d^3r \ |\Phi_j(r)|^2 - 1 \right) = \lambda_i \Phi_i(r) \tag{2.33}
\]

which finally results in a single-particle Schrödinger equation

\[
\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}(r) - \lambda_i \right] \Phi_i(r) = [H_{KS} - \lambda_i] \Phi_i(r) = 0 \tag{2.34}
\]

with \( \lambda_i = \varepsilon_i \) playing the role of the single-particle energies [42]. In addition we found a definition of the effective Kohn-Sham potential given by the sum of the external and Hartree as well as the unknown exchange-correlation potentials

\[
v_{KS}(r) = \frac{\delta E_{\text{ext}}}{\delta n(r)} + \frac{\delta E_{\text{Hartree}}}{\delta n(r)} + \frac{\delta E_{\text{xc}}}{\delta n(r)} = v_{\text{ext}}(r) + v_{\text{Hartree}}(r) + v_{\text{xc}}(r). \tag{2.35}
\]

\(^4\)Like a normal derivative a functional derivative is given as the linearization of the given functional \( F \) around the function \( f \) in the direction \( h \):

\[
\frac{\delta F[f]}{\delta f} = \lim_{\epsilon \to 0} \frac{1}{\epsilon} (F[f + \epsilon h] - F[f]).
\]

See, for instance, Ref. [41] for more details and properties of the functional derivatives.
2.2. Single-Particle Energies

Figure 2.1.: Kohn-Sham self-consistency cycle. Based on trial wave functions a trial density is constructed and used to define the Kohn-Sham potential. With the latter the Kohn-Sham Hamiltonian is defined and can be diagonalized which yields new wave functions and thus a new density. The whole procedure is iterated until self-consistency is reached.

While $v_{\text{ext}}$ and $v_{\text{Hartree}}$ are known, the remaining problem is to approximate $v_{\text{xc}}$ or correspondingly $E_{\text{xc}}$. This is a distinct advantage in comparison to the ansatz by Thomas, Fermi and Dirac which needed to approximate the relatively large kinetic and Hartree terms as well. Here, we are left with approximations to relatively small quantum mechanical exchange and correlation corrections only. For smooth or slowly varying $n(r)$ the latter can be described as a local (or nearly local) functional of the form

$$E_{\text{xc}}[n(r)] = \int d^3r \, n(r) \varepsilon_{\text{xc}} ([n], r), \quad (2.36)$$

where $\varepsilon_{\text{xc}}([n], r)$ is the corresponding energy per electron which depends only locally on the density $n(r)$ near to the point $r$. Thus, as soon as $\varepsilon_{\text{xc}}([n], r)$ is described as outlined in the following paragraph, the ground-state density can be found self-consistently. Therefore, one starts with a trial density to calculate the Kohn-Sham potential from Eq. (2.35) and uses the resulting wave functions from the solution of the Kohn-Sham equation (2.34) to generate a new density. This procedure is repeated until a self-consistent solution is found, as it is shown in Fig. 2.1.

Approximative Functionals

As mentioned in the previous section, the exact form of the exchange-correlation functional is not known. Nevertheless, it is possible to derive quite simple approximative expressions by assuming that the exchange-correlation potential is purely local like in a homogeneous electron gas. In the so called local density approximation (LDA) it is then given by:

$$E_{\text{xc}}^{\text{LDA}}[n(r)] = \int d^3r \, n(r) \varepsilon_{\text{xc}}^{\text{hom}} (n(r)). \quad (2.37)$$
The exchange-correlation energy density \( \varepsilon_{xc}^{\text{hom}} \) can be divided into two separate parts, namely the exchange \( \varepsilon_{x}^{\text{hom}} \) and the correlation \( \varepsilon_{c}^{\text{hom}} \) terms. While a general analytic expression for the former can be given for the homogeneous electron gas by

\[
\varepsilon_{x}^{\text{hom}}(n) = -\frac{3}{4}e^2 \left(\frac{3n}{\pi}\right)^{1/3},
\]

(2.38)
a corresponding expression for the correlation term is only known in the high or low density limits [27]. Nevertheless, there are several interpolating expressions (e.g. by Perdew and Zunger [43] or Vosko, Wilkes and Nusiar [44]) which involve different parameter sets which can be fitted to most accurate quantum Monte Carlo (QMC) results for the spin-unpolarized electron gas [45]. With these definitions the exchange-correlation functional is known. Hence, the Kohn-Sham potential can be derived and the corresponding single-particle problem can be solved self-consistently. Although the underlying approximation that the charge density varies only slowly in space should be valid just for simple metals, in which the electrons behave more or less like in a homogeneous gas, the local density approximation works surprisingly well, even for materials in which this assumption is not justified. Detailed analysis of the so-called exchange-correlation hole, which is introduced within the method of coupling-constant integration, demonstrates that this unexpected behavior of the LDA traces back (at least partially) to the fulfillment of specific physical sum rules [46]. This is here granted by construction which is based on corresponding derivations from the homogeneous electron gas.

Nonetheless, there are several situations in which the local density approximation fails to accurately reproduce experimental data. For instance in molecules in which the charge density strongly varies in space. To handle these materials the semi-local generalized gradient approximation (GGA) to the exchange-correlation functional has been developed which takes the local density and its gradient into account:

\[
E_{xc}^{\text{GGA}}[n(r)] = \int d^3r \ n(r) \varepsilon_{xc}^{\text{hom}}(n(r), \nabla n(r)).
\]

(2.39)

For this situation a variety of different formulations for the exchange-correlation energy can be derived, which can be found in the literature abbreviated by PW91 [47], PBE [48] and many more [49, 50, 51].

**Incorporation of the Spin**

Up to now, the spin dependencies have been disregarded. Nevertheless, from a formal point of view, it can be straightforwardly introduced by separating both spin channels and defining the total density as

\[
n(r) = n^\uparrow(r) + n^\downarrow(r).
\]

(2.40)
Thereby the exchange correlation functional $E_{\alpha}^{xc}[n^\uparrow(r), n^\downarrow(r)]$ and corresponding energy densities $\varepsilon_{\alpha}^{xc} (n^\uparrow(r), n^\downarrow(r))$ become functionals or functions of the spin-dependent densities and the spin $\alpha \in \{\uparrow, \downarrow\}$. Strictly speaking, this holds just for the case of collinear spin arrangements in which the spin quantization axis is the same for all points in space. As soon as non-collinear spin systems (with a locally varying spin axis) shall be described, a generalized $2 \times 2$ spin density matrix has to be introduced, 

$$n^{\alpha \beta}(r) = \sum_{\varepsilon_n < E_F} \Phi_{n}^{\alpha*}(r) \Phi_{n}^{\beta}(r),$$  

which yields a generalized Kohn-Sham Hamiltonian $H^{\alpha \beta}$ [under the restriction $N = \sum_{\alpha} \int d^3 r \ n^\alpha(r)$] [52]. By using a local coordinate system aligned to the local spin quantization axis similar exchange-correlation functionals can be used and the auxiliary Kohn-Sham system can be solved self-consistently to gain spin-resolved data. More details are given in Refs. [52, 53, 54, 19] and references therein. In the following we will write the spin index solely for systems with broken spin degeneracy and neglect it otherwise.

**Basis Sets and Pseudopotentials**

The introduction of the Kohn-Sham auxiliary system came with the advantage of introducing a single-particle problem which was claimed to be easily solvable. Although it is true that the treatment of a single-particle system is more simple compared to a many-body problem, the numerical effort to solve it can still be quite high. The Kohn-Sham system is solved by expanding the problem in a single-particle basis, leading to a matrix representation of $H_{KS}$. The diagonalization of this matrix leads to the energies $\varepsilon_n$ and the corresponding wave functions $\Phi_n(r)$.

Since $k$ is a good quantum number in translationally invariant systems, we can expand the eigenstates using Bloch’s theorem in terms of plane waves $\chi_k(r)$

$$\Phi_i^k(r) = \sum_{G} c_{i,k+G} \chi_{k+G}(r) = \frac{1}{\sqrt{\Omega}} \sum_{G} c_{i,k+G} e^{i(k+G)r},$$  

where $G$ are reciprocal lattice vectors and $\Omega$ is the crystal volume. Doing so, the Kohn-Sham problem from Eq. (2.34) becomes

$$\sum_{G'} \left[ \frac{1}{2} |k + G'|^2 \delta_{G,G'} + v_{KS}(G - G') \right] c_{i,k+G'} = \varepsilon_{i,k} c_{i,k+G},$$  

where the formally infinite sum over $G$ is truncated by the introduction of an energy cutoff

$$\frac{\hbar^2}{2m} |k + G|^2 < E_{\text{cut}}.$$
Thus, the computational effort rises drastically with the number of involved basis-set elements as defined by the energy cutoff. However, the basis has to be capable of describing both, the wave function around the nuclei and in the interstitial region. Since the potential around the nuclei varies rapidly, whereas it is more or less constant in the rest of the system, the wave function strongly oscillates in the vicinity of the atomic cores and is quite smooth in the interstitial region as sketched out in Fig. 2.2. This means to capture the wave function properties around the nuclei properly within a plane-wave basis set, a high number of Fourier components \((c_i, k)\) would be needed (corresponding to a high energy cutoff). To circumvent this issue, there are basically two methods which introduce either so called augmented plane waves or pseudopotentials.

The augmented plane wave (APW) method [56] divides the whole space into augmentation spheres around the nuclei and the interstitial region (like a muffin-tin). Within a muffin-tin sphere the potential \(V(r)\) is assumed to be spherically symmetric and spherical harmonics \(Y_L^p(r)\) can here be utilized to construct a solution to the radial Schrödinger equation

\[
-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} \right) + V(r) - \varepsilon \right] r u_L(\varepsilon, r) = 0. \tag{2.45}
\]

These localized atomic wave functions are combined with the former plane waves for the interstitial region resulting in

\[
\chi_{k+G}^{\text{APW}}(r) = \left\{ \begin{array}{ll}
\sum_L a_{L,k+G}^\mu Y_L^p(r_\mu) u_L(\varepsilon, r_\mu) & r \in \text{muffin-tin} \quad \mu \\
\exp(i(k + G)r) & r \in \text{interstitial}
\end{array} \right.. \tag{2.46}
\]

Here, \(\mu\) labels the muffin-tin region around the nucleus \(\mu\) and \(L\) describes the angular momentum and magnetic quantum numbers \(L = \{l, m_l\}\). The coefficients \(a_{L,k+G}^\mu\) have to be chosen in a way that both parts of the wave functions match at the boundary of the muffin-tin sphere. This is actually a non-trivial task since the functions \(u_L(\varepsilon, r_\mu)\)
are energy dependent. By setting these energies to a fixed value the variational freedom of the APW ansatz would be lost and the corresponding results would lack accuracy. In fact, it turns out that these functions depend on the band energies which are not known at this stage. Therefore, we end up with a non-linear problem. In order to linearize this problem, the ansatz has to offer enough variational freedom even for fixed energies in Eq. (2.45). This can be achieved by expanding $u_{L}(\varepsilon, r_{\mu})$ in a Taylor series around a reference energy $\varepsilon_{r}$. Thereby the energy derivative $u_{L}(r_{\mu})$ is involved (offering more variational freedom) leading to the extended ansatz

$$
\chi_{L}^{\text{LAPW}} \left( \mathbf{r} \right) = \left\{ \sum_{L} \left[ a_{L,k+G}^{\mu} u_{L}(r_{\mu}) + b_{L,k+G}^{\mu} \dot{u}_{L}(r_{\mu}) \right] Y_{L}(r_{\mu}) \exp \left( i(\mathbf{k} + \mathbf{G})\mathbf{r} \right) \right\} 
\begin{array}{cc}
\mathbf{r} \in \text{muffin-tin} & \mu \\
\mathbf{r} \in \text{interstitial} & \\
\end{array}
$$

Here, $u_{L}(r_{\mu})$ and $\dot{u}_{L}(r_{\mu})$ do not depend on $\varepsilon$ anymore (just on the reference energy $\varepsilon_{r}$) and can be calculated by standard linear algebra diagonalization, which is why these functions are called linearized augmented plane waves (LAPW) [57]. Within both basis function sets (APW and LAPW) an additional cutoff for the angular momentum $l$ (in $L$) has been introduced which has to correspond to the specific atom under consideration.

The LAPW scheme allows for high-accuracy calculations for a wide range of materials and structures and can be further generalized to the so called full potential linearized augmented plane wave (FLAPW) basis [58]. To this end, all approximations concerning the potential shape within the augmentation spheres are withdrawn and the “full potential” is taken into account.

Another approach to deal with the strongly oscillating character of the wave function close to the nuclei within a plane-wave basis is to replace the nuclei’s Coulomb potential $V$ (and the effect of core electrons) with an effective one, $\tilde{V}$, as indicated in Fig. 2.2. This pseudopotential (PP) is introduced to remove the nodal structure of the wave function around the core within some radius, whereas the outer wave function is entirely reproduced. Thus, valence electrons can be treated with a reasonable amount of Fourier components in a plane-wave basis. Furthermore, core electrons can be effectively included to the PP in order to reduce the total number of electrons which shall be treated within the DFT calculations. This procedure is adequate and accurate results can be achieved as long as the material’s properties do only marginally depend on the core electrons and are primarily described by the valence states. For a wide range of solids this requirement is fulfilled.

The PPs are constructed by doing an “all-electron” Kohn-Sham calculation (i.e. solving the original problem by utilizing augmented basis sets like APW, LAPW or FLAPW) for the corresponding isolated atom leading to wave functions $\Phi_{l}(\mathbf{r})$ which solve the radial Schrödinger equation from Eq. (2.45). Subsequently, pseudo wave functions $\tilde{\Phi}_{l}(\mathbf{r})$ are constructed which are nodeless for radii smaller than $r_{s}$ and coincide with $\Phi_{l}(\mathbf{r})$ anywhere else (see Fig. 2.2). Using these $\tilde{\Phi}_{l}(\mathbf{r})$ the radial Schrödinger
equation from Eq. (2.45) can be inverted to describe the effective pseudopotential \( \tilde{V}_l(r) \) which will naturally depend on the angular momentum \( l \) as well and is strictly speaking correct just for the involved reference or fitting energy \( \varepsilon \).

Up to this point the only requirement to the pseudo wave function was to be nodeless within the sphere as defined by \( r_s \) and to match the all-electron solution in the outer space. A conventional additional requirement to \( \tilde{\Phi}_l(r) \) is to be norm-conserving, leading to the same integrated charge within the sphere (to fulfill charge conservation)

\[
Q_l = \int_0^{r_s} d^3r \ \Phi_l^2(r) = \int_0^{r_s} d^3r \ \tilde{\Phi}_l^2(r).
\] (2.48)

Indeed, it can be shown that as soon as \( \tilde{\Phi}_l(r) \) is norm-conserving the corresponding PP is “well-behaved” which implies that the PP (generated for a single atom in vacuum) will recover the changes in the eigenenergies upon changes in the chemical environment (e.g. by using it to treat a crystal) correctly [59, 60, 19]. This property is usually called “transferability”.

Next to being transferable, a “good” PP should lead to very smooth pseudo wave function in order to reduce the number of needed Fourier components as much as possible. Those requirements are actually contradicting, since a high transferability is obtained by decreasing \( r_s \) (changes in the chemical environment can then be optimally taken into account), whereas smoothness requires an increased sphere radius.

In order to solve this dilemma, a variety of norm-conserving PPs has been introduced and studied in detail by Hamann, Schlüter and Chiang [59], Vanderbilt [61], Troullier and Martins [62] and many others, which shall not be discussed here.

Although norm-conserving PPs result in quite accurate results for a variety of solid-state materials, systems involving valence states at the beginning of an atomic shell (1s, 2p, 3d, etc.) are hard to treat with these PPs. In these situations the wave functions are already nodeless within the atomic spheres, but change strongly within and on the outside of the sphere. Therefore, many Fourier components have to be involved or / and the sphere radius has to be increased, which results in pseudo wave functions which do not differ much from the original wave functions. Vanderbilt solved this problem by relaxing the norm-conservation constraint and introduced so called ultrasoft PPs [63]. This leads to a different integrated charge within the sphere which has to be compensated carefully. This is done by introducing a generalized eigenvalue problem which involves an overlap matrix which in turn takes care about the changes in the total charge. Within this generalized eigenvalue problem (which becomes a simple eigenvalue problem in the case of norm-conserving PPs) all properties concerning the energy derivatives of the wave function are the same. Thus, the ultrasoft PPs introduce a slightly more complicated treatment of the whole Kohn-Sham system, but lead to very smooth pseudo wave functions even in “complicated” situations.

Yet another approach to deal with the strongly oscillating wave functions around the nuclei was introduced by Blöchl. He combined the “best of both worlds” in his
projector augmented plane wave (PAW) method by introducing local projectors which transform the all-electron wave function within the augmentation spheres to smooth pseudo ones [64]. As in the pseudopotential methods the variational quantities will be the plane waves in the interstitial region, while the full all-electron wave function or operators can be reconstructed using the before mentioned projectors. Thus, the “simplicity” of the PP methods is combined with the accuracy of all-electron (FL)APW descriptions.

To this end the full all-electron wave function \( \Phi \) is expressed as a linear transformation \( T \) of a pseudo one \( \tilde{\Phi} \) which coincides with \( \Phi \) in the interstitial region and is smooth within the augmentation spheres

\[
|\Phi\rangle = T |\tilde{\Phi}\rangle .
\]

This is achieved by dividing \( T \) into several pieces that act just within the spheres \( \mu \) and a trivial part \( (=1) \) for the remainder

\[
T = 1 + \sum_{\mu} T_{\mu}.
\]

In detail \( T_{\mu} \) is defined as

\[
T_{\mu} = \sum_{i_{\mu}} \left( |\phi_{i_{\mu}}\rangle - |	ilde{\phi}_{i_{\mu}}\rangle \right) \langle \tilde{\phi}_{i_{\mu}} |,
\]

where \( i_{\mu} = \{n,l,m\} \) labels a set of indices and \( \phi_{i_{\mu}} \) (\( \tilde{\phi}_{i_{\mu}} \)) describe the all-electron (pseudo) partial waves within the sphere \( \mu \). These partial waves form a basis for the complete wave function within the sphere,

\[
|\Phi\rangle = |\Phi_{\mu}\rangle = \sum_{i_{\mu}} c_{i_{\mu}} |\phi_{i_{\mu}}\rangle \text{ within } \mu,
\]

\[
|\tilde{\Phi}\rangle = |\tilde{\Phi}_{\mu}\rangle = \sum_{i_{\mu}} \tilde{c}_{i_{\mu}} |\tilde{\phi}_{i_{\mu}}\rangle \text{ within } \mu,
\]

and are solutions to the radial Schrödinger equation, like the \( \phi_{l}(r) \) of the (FL)APW method. The all-electron and the pseudo partial wave function coincide in the interstitial region, but differ within the spheres (the pseudo partial waves are meant to be smooth here). The partial wave functions are connected by the same transformation \( T \) as the complete wave functions \( |\phi_{i_{\mu}}\rangle = T |\tilde{\phi}_{i_{\mu}}\rangle \) which has the consequence that the coefficients \( c_{i_{\mu}} \) and \( \tilde{c}_{i_{\mu}} \) in Eq. (2.52) must be the same. These coefficients are calculated by projections of the total pseudo wave function \( \tilde{\Phi} \) onto localized wave functions within the spheres

\[
c_{i_{\mu}} = \langle \tilde{\phi}_{i_{\mu}} | \tilde{\Phi} \rangle .
\]
2. Ab Initio Description of Single-Particle and Many-Body Properties of Solids

By using this definition in Eq. (2.52),

\[ |\tilde{\Phi}\rangle = \sum_{i_\mu} |\tilde{\phi}_{i_\mu}\rangle \langle \tilde{\phi}_{i_\mu}| \Phi \rangle \text{ within } \mu, \]  

(2.54)

the relation \( \sum_{i_\mu} |\tilde{\phi}_{i_\mu}\rangle \langle \tilde{\phi}_{i_\mu}| = 1 \) is obtained which implies that

\[ \langle \tilde{\phi}_{i_\mu} | \tilde{\phi}_{j_\mu} \rangle = \delta_{ij}. \]  

(2.55)

With these properties the projectors \( \langle \tilde{\phi}_{i_\mu} | \langle \tilde{\phi}_{i_\mu} \rangle \) from Eq. (2.51) are defined and the total wave function from Eq. (2.49) can be written as

\[ |\Phi\rangle = |\tilde{\Phi}\rangle + \sum_{\mu} \sum_{i_\mu} \left( |\phi_{i_\mu}\rangle - |\tilde{\phi}_{i_\mu}\rangle \right) \langle \tilde{\phi}_{i_\mu} | \tilde{\Phi} \rangle. \]  

(2.56)

Employing the definitions from Eq. (2.52) the construction of the total all-electron wave function within the PAW method becomes clear: The pseudo atomic “on-site” part \( \tilde{\Phi}_\mu \) is subtracted from the complete pseudo wave function \( \tilde{\Phi} \) and the corresponding all-electron “on-site” part \( \Phi_\mu \) is added again, as it is illustrated in Fig. 2.3. Since \( \tilde{\Phi} \) and \( \Phi \) coincide anywhere else, it is obvious that the original complete all-electron wave function is regained. This kind of separation holds for observables of (local) operators \( \hat{A} \) as well, as can be seen from the following:

\[ \langle \hat{A} \rangle = \sum_n f_n \langle \Phi_n | \hat{A} | \Phi_n \rangle = \sum_n f_n \langle \Phi_n | \hat{A} | \tilde{\Phi}_n \rangle, \]  

(2.57)

where \( f_n \) is the occupation of \( |\Phi_n\rangle \) and the pseudo operator \( \hat{A} \) is defined by

\[ \hat{A} = T^\dagger \hat{T} = A + \sum_{ij} \langle \tilde{\phi}_{i}\rangle \left( \langle \phi_{i} | \hat{A} | \phi_{j} \rangle - \langle \tilde{\phi}_{i} | \hat{A} | \tilde{\phi}_{j} \rangle \right) \langle \tilde{\phi}_{j} |. \]  

(2.58)

Applying this to derive the corresponding expressions of the density operator \( n = |\mathbf{r}\rangle \langle \mathbf{r}| \) leads to

\[ n(\mathbf{r}) = \sum_n f_n \left[ \langle \tilde{\Phi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Phi}_n \rangle + \sum_{ij} \langle \tilde{\Phi}_n | \tilde{\phi}_i \rangle \left( \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle - \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle \right) \langle \tilde{\phi}_j | \tilde{\Phi}_n \rangle \right] = \sum_n f_n \tilde{\Phi}(\mathbf{r})^2 + \sum_{ij} D_{ij} \phi_i^\dagger(\mathbf{r}) \phi_j(\mathbf{r}) - \sum_{ij} D_{ij} \phi_i^\dagger(\mathbf{r}) \tilde{\phi}_j(\mathbf{r}), \]  

(2.59)

Figure 2.3.: Schematic construction of the full all-electron wave function within the PAW formalism as described in Eq. (2.56).
2.2. Single-Particle Energies

where the one-center density matrix was defined as

\[ D_{ij} = \sum_n f_n \langle \Phi_n | \tilde{p}_i | \tilde{p}_j | \Phi_n \rangle. \]  \hspace{1cm} (2.60)

Thus, the scheme depicted in Fig. 2.3 applies to the wave function, the charge density and any other (local) observable in the PAW method. In conclusion, we therefore need three ingredients to perform a full DFT calculation within the PAW formalism: (1) The all-electron partial waves \( \phi_{i\mu} \) have to be derived in advance as solutions to the all-electron radial Schrödinger equation for the isolated atoms (e.g. from a FLAPW calculation). (2) These all-electron partial waves have to be used afterwards to fit the smooth pseudo partial waves \( \tilde{\phi}_{i\mu} \). This is done by assuming that \( \phi_{i\mu}(r) = \tilde{\phi}_{i\mu}(r) \) on the outside of the corresponding muffin-tin sphere \( (r > r_{i\mu}) \) and by using, e.g., spherical Bessel functions on the inside of the sphere \[65\]. (3) And finally projector functions for each pseudo partial wave have to be obtained, e.g. by Vanderbilt’s \[63\] or Blöchl’s \[64\] algorithms.

2.2.2. Wannier Functions

In the following section we follow the review article on “Maximally localized Wannier functions” by Marzari et al. \[23\] and the underlying articles by Marzari and Vanderbilt \[66\] as well as Souza et al. \[67\].

Due to the translational invariance of solid-state materials density functional theory calculations are typically performed in reciprocal space. Thereby, the Kohn-Sham equation from Eq. (2.43) is solved within a delocalized Bloch basis and eigenenergies are obtained in terms of band energies \( \varepsilon_n(k) \) for a finite set of \( k \)-points. On the other side, lattice models like the Hubbard or the Anderson impurity models, which are regularly used to study many-body physics, are conventionally formulated in real space using a localized basis. Thus, to infer corresponding model parameters from the \textit{ab initio} calculations in order to gain simplified yet material-realistic descriptions, we need a tool which is capable of transforming the delocalized reciprocal data to localized real-space quantities. For this purpose Wannier functions are utilized here. Sophisticated Fourier-like transforms are used to transform the former Bloch states to Wannier functions which are in turn employed to evaluate the needed matrix elements in real space. This change of basis allows in addition to choose a sub-set or “low-energy” space in order to minimize the basis elements in a well controlled manner.

In the context of single-particle properties we will derive tight-binding (TB) lattice models based on \textit{ab initio} calculations. These models will reproduce the original band structures accurately and can additionally be used to interpolate the former coarse \( k \)-grids to arbitrary points in reciprocal space. This “Wannier-Interpolation” scheme will be used in this thesis to derive highly resolved band-structures from DFT and GW calculations and to describe Coulomb matrix elements in the whole Brillouin zone.
Therefore, the most important definitions and derivations concerning the construction of Wannier functions from \textit{ab initio} Bloch states are given in the following.

Maximally Localized Wannier Functions

In Dirac’s bra ket notation the formal definition of Wannier functions in three dimensions is given by the Fourier transform

\[
| R_n \rangle = \frac{V}{(2\pi)^3} \int_{\text{IBZ}} d^3 k \ e^{-ikR} | \Phi_{nk} \rangle, \tag{2.61}
\]

which corresponds to the real-space function as \( w_{nR}(r) = \langle r | R_n \rangle \) [68]. While the real-space representations of the Bloch functions \( \Phi_{nk}(r) = \langle r | \Phi_{nk} \rangle = e^{ikr} u_{nk}(r) \) are delocalized, the Wannier functions \( w_{nR}(r) \) are strongly localized around \( R \). Unfortunately Eq. (2.61) does not \textit{uniquely} define \( | R_n \rangle \) since the Bloch functions are subject to a certain gauge freedom concerning the overall phase. Thus, a transformation of the form

\[
| \tilde{\Phi}_{nk} \rangle = e^{i\phi_n(k)} | \Phi_{nk} \rangle \tag{2.62}
\]

does not change any physical property (as long as \( \phi_n(k) \) is real and periodic in \( k \)) but changes the resulting Bloch and Wannier wave functions. Therefore, further requirements are needed to obtain a “well” defined Wannier basis. To this end, Marzari and Vanderbilt introduced a generalized gauge transformation

\[
| \tilde{\Phi}_{nk} \rangle = \sum_{m=1}^{J} U_{mn}^k | \Phi_{mk} \rangle, \tag{2.63}
\]

which shall be chosen to \textit{minimize the real-space spread} of the resulting Wannier functions by mixing a composite set of \( J \) bands [66, 23]. This can also be seen as a “maximal” degree of localization of the Wannier functions in real space, leading to “maximally localized Wannier functions” (MLFW), which directly translates to “maximal” smoothness of the transformed Bloch states \( | \tilde{\Phi}_{nk} \rangle \) in reciprocal space\(^5\). In their original formulation the number of Wannier and underlying Bloch functions had to be the same (here \( J \)) and the subspace of used Bloch functions had to be well separated (disentangled) from the rest of the band structure. However, these additional constraints can be relaxed by the introduction of an appropriate disentanglement procedure which generates a suitable subspace in advance [67] as it will be discussed in the following.

\(^5\)Since the Wannier and Bloch functions are connected by a Fourier transform strong localization in real space of the former corresponds to smoothly varying Bloch function in reciprocal space.
In order to minimize the real-space spread Marzari and Vanderbilt introduced a spread functional \( \Omega \)

\[
\Omega = \sum_{n=1}^{J} \left[ \langle \mathbf{0n}|r^2|\mathbf{0n}\rangle - \langle \mathbf{0n}|r|\mathbf{0n}\rangle^2 \right] = \sum_{n=1}^{J} \left[ \langle r^2 \rangle_n - \bar{r}_n^2 \right],
\]

(2.64)

which measures the quadratic spreads of each Wannier function in the unit cell around their centers. In the following we thus aim to minimize \( \Omega \) by varying \( U_{mn}^k \). Once the corresponding optimal transformation matrices are found Eq. (2.63) and Eq. (2.61) are used to construct the Wannier functions. In order to do so, \( \Omega = \Omega_I + \bar{\Omega} \) is separated into a gauge-invariant \( \Omega_I \) and gauge-dependent part \( \bar{\Omega} \) via

\[
\Omega = \sum_{n} \left[ \langle \mathbf{0n}|r^2|\mathbf{0n}\rangle - \sum_{\mathbf{Rm}} \langle \mathbf{Rm}|r|\mathbf{0n}\rangle^2 \right] + \sum_{n} \sum_{\mathbf{Rm} \neq \mathbf{0n}} \langle \mathbf{Rm}|r|\mathbf{0n}\rangle^2, \quad \Omega = \Omega_I + \bar{\Omega},
\]

(2.65)

Since the whole procedure should be carried out in momentum space, \( \Omega \) has to be formulated in reciprocal-space coordinates. The corresponding details shall not be discussed here, but can be found in Refs. [66] and [23]. In the end \( \Omega_I \) and \( \bar{\Omega} \) are reformulated to

\[
\Omega_I = \frac{1}{N} \sum_{k,b} w_b \left( J - \sum_{mn} |M_{mn}^{k,b}|^2 \right)
\]

(2.66)

and

\[
\bar{\Omega} = \frac{1}{N_k} \sum_{k,b} w_b \sum_{m \neq n} |M_{mn}^{k,b}|^2 + \frac{1}{N_k} \sum_{k,b} w_b \sum_{n} (- \text{Im} \ln M_{mn}^{k,b} - b \cdot \bar{r}_n)^2,
\]

(2.67)

where \( N_k \) is the number of points in the \( k \)-mesh, \( J \) is the amount of involved Bloch states, \( b \) are connection vectors of neighbouring \( k \)-points, \( w_b \) are corresponding weighting factors (see Ref. [66]) and

\[
\bar{r}_n = -\frac{1}{N_k} \sum_{k,b} w_b b \text{Im} \ln M_{mn}^{k,b}
\]

(2.68)

is the expectation value of \( r \). In addition we used the matrices \( M_{mn}^{k,b} \) which give the overlaps between Bloch states at neighbouring \( k \)-points

\[
M_{mn}^{k,b} = \langle u_{mk}|u_{n,k+b} \rangle.
\]

(2.69)
The Role of $\Omega_I$: Disentangling the Bloch Bands

$\Omega_I$ can be rewritten with the help of the projector $P_k = \sum_n |u_{nk}\rangle\langle u_{nk}|$ and its complement $Q_k = 1 - P_k$ leading to

$$\Omega_I = \frac{1}{N} \sum_{k,b} w_b \text{Tr} [P_k Q_{k+b}].$$

(2.70)

Since $U^k$ are unitary matrices any gauge transformation according to Eq. (2.63) (acting on the Bloch functions $|u_{nk}\rangle$) will not change the projectors $P$ and $Q$ and $\Omega_I$ therefore stays the same as well. Hence, $\Omega_I$ is indeed gauge independent. In addition, by rewriting $\Omega_I$ with the help of the $P$ and $Q$ we obtain a simple interpretation: The product of the projection operators $P_k Q_{k+b}$ will vanish as soon as $P_k = P_{k+b}$ which corresponds to a situation in which the difference between the subspaces at $k$ and $k+b$ vanishes. $\Omega_I$ therefore measures the smoothness of the changes between neighbouring subspaces $S(k)$ and $S(k+b)$ or the “changes of characters” from $S(k)$ to $S(k+b)$. Thus, in a situation in which $N$ Wannier functions shall be constructed out of a group of $J_k \geq N$ entangled (partially degenerated) bands these changes of characters should be as small or as smooth as possible. To this end, $\Omega_I$ has to be minimized to find a set of optimal subspaces $S(k) \subset F(k)$ for each $k$ from the $J_k$-dimensional Hilbert space $F(k)$ of the entangled bands. As shown by Souza et al. in Ref. [67] the corresponding optimal projector $P_k$ is obtained from the stationarity condition $\delta \Omega_I(|u_{nk}\rangle) = 0$ which can be reformulated to an iterative and self-consistent scheme to solve the eigenvalue problem [67]:

$$\left[ \sum_b w_b P^{(i-1)}_{k+b} \right] |u_{nk}^{(i)}\rangle = \lambda^{(i)}_{nk} |u_{nk}^{(i)}\rangle.$$ 

(2.71)

Thereby, the projector $P^{(i)}_k = \sum_{n=1}^N |u_{nk}^{(i)}\rangle\langle u_{nk}^{(i)}|$ is updated in each iteration step using the eigenvectors $|u_{nk}^{(i)}\rangle$ corresponding to $N$ highest eigenvalues $\lambda^{(i)}_{nk}$. As soon as self-consistency is reached, an optimally smooth subspace $S(k)$ and a minimized $\Omega_I$ is obtained.

A particular advantage of this $\Omega_I$ minimization procedure is the fact that certain constraints can be introduced. For instance, one might require that the Wannier functions will exactly reproduce the Bloch states eigenenergies in a certain “inner” energy window. Thereby those parts of the original band structure which are most important for the subsequent considerations can be fixed.

The Role of $\tilde{\Omega}$: Maximal Localization

So far, we have seen that $\Omega_I$ is in the sense of Eq. (2.63) gauge independent but can be used to disentangle sets of Bloch states. This means, remembering the initial intention

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6If $J_k = N S(k)$ and $F(k)$ are the same and there is no need to perform the disentanglement.

7See Ref. [67] for more details.
and definition of the complete spread functional $\Omega$, that $\tilde{\Omega}$ is in fact describing the degree of localization of the Wannier functions. Hence, $\tilde{\Omega}$ must be minimized by finding adequate rotation matrices $U_k$ (acting on the optimal smooth subspace $S(k)$ only) to gain the maximally localized Wannier functions mentioned at the very beginning. Since $\tilde{\Omega}$ is completely defined by the overlap matrices $M$, the minimization can be achieved by updating it according to

$$M_{(i+1)}^{k,b} = U_{(i)}^{k\dagger} M_{(i)}^{k,b} U_{(i)}^{k+b},$$

using

$$U_{(i+1)}^{k} = U_{(i)}^{k} \exp \left( \Delta W_{(i)}^{k} \right),$$

where $\Delta W$ are properly chosen updates to $U$ which only depend on $M$ as discussed in more detail in Ref. [66]. Hence, with the initial $M_{(0)}$ as calculated from the underlying ab initio calculation and an initial $U_{mn(0)} = \delta_{mn}$ the minimization or localization can be performed without any other ingredient. Having reached the maximal degree of localization the very last update of $U_{(i)}^{k}$ can finally be used to calculate the maximally localized Wannier functions using Eq. (2.63) acting on the “smooth” subspace $S(k)$ and Eq. (2.61) afterwards. Thereby, it is important to note that eventually fixed eigenenergies of states within the smooth subset $S(k)$ will not be changed due to the unitary transformation using $U_{(i)}^{k}$.

**Initial Projections**

For the minimization of $\Omega_I$ we need an initial guess for $S(k)$ or, correspondingly, $|u_n^{(0)}\rangle$. To this end we can utilize $N$ localized trial functions $g_{\alpha}(r)$ onto which the initial $J_k$ Bloch states are projected

$$|\Phi_{\alpha k}^{\text{proj}}\rangle = \sum_{m=1}^{J_k} |\Phi_{mk}\rangle \langle \Phi_{mk}|g_{\alpha}\rangle,$$

where $g_{\alpha}(r)$ should be functions which have the same angular momentum and are localized at the sites of the expected Wannier functions. For example, in the program package Wannier90 [69], which will be frequently used throughout the thesis, orbitals of the hydrogen atom are used for this purpose. In practice the matrix

$$A_{ma}^{k} = \langle \Phi_{mk}|g_{\alpha}\rangle$$

is calculated in advance and used afterwards in Eq. (2.74). Additionally it is used to obtain the overlap matrix $S_{\alpha\beta}^{k} = \langle \Phi_{\alpha k}^{\text{proj}}|\Phi_{\beta k}^{\text{proj}}\rangle = (A^{k\dagger}A^{k})_{\alpha\beta}$ in order to orthogonalize the resulting projected Bloch states

$$|\Phi_{\beta k}^{\text{orth}}\rangle = \sum_{\alpha=1}^{N} \left( S_{k}^{-1/2} \right)_{\alpha\beta} |\Phi_{\alpha k}^{\text{proj}}\rangle = \sum_{m=1}^{J_k} \left( AS_{k}^{-1/2} \right)_{m\beta} |\Phi_{mk}\rangle.$$
This orthogonalized subset of Bloch states $|\Phi_{\alpha, k}^{\text{orth}}\rangle$ can be used afterwards as the starting point of a minimization procedure of $\Omega$ to obtain an optimal (smooth) subspace $S(k)$ as discussed before.

**Alternative Approaches**

The combination of projection and orthogonalization as discussed above is already a proper gauge transformation as defined in Eq. (2.63) for the case of entangled bands. The resulting Bloch states can be used in Eq. (2.61) to get localized Wannier functions. Without further refinements of the gauge the resulting functions are called “one shot” or “first guess” Wannier functions (FGWF) which preserve the trial functions’ symmetries [70]. The latter must not be fulfilled anymore after the minimization of $\tilde{\Omega}$.

Following the ideas of Souza, Marzari and Vanderbilt, it seems to be useful to divide the whole process of deriving MLWF into two pieces, namely minimizing $\Omega_I$ and $\tilde{\Omega}$ separately in the case of disentangled bands in a periodic crystal. Nevertheless, there is no good argument against a direct minimization of the complete $\Omega$. And indeed, as shown by Thygesen et al. an adequate procedure to directly minimize $\Omega$ leads to very similar results in the case of periodic crystals and can even be used for molecules without translational symmetries in which some Wannier orbitals are occupied only partially [71, 72].

Furthermore, other approaches to derive Wannier functions from ab initio calculations can be found in the literature, which do not rely on the direct localization of the Wannier functions. For instance, there are variational approaches like given by Kohn [73] in which energy functionals are varied with respect to localized trial functions [74]. Additionally, there are methods which rely on the construction of Slater-Koster-like model Hamiltonians which can be used subsequently to interpolate the ab initio band structure [75].

However, in the following the method by Souza, Marzari and Vanderbilt will be employed, since their approach results in very accurate descriptions of the systems under considerations, can be controlled precisely and the before-mentioned program package Wannier90 is already linked to all of the here employed DFT packages.

**Single-Particle Matrix Elements and Basis Transformations**

From the $\Omega$ minimization procedure the “rotated” Hamiltonian for the subspace $S(k)$

$$H_{S(k)}^{(\text{rot})}(k) = U_k^H S(k) U_k$$

(2.77)

is known on the initial $k$-grid. Via a standard discrete Fourier transform the real-space representation can be readily derived

$$H_{\alpha\beta}^{(\text{rot})}(R) = \langle R\alpha \mid H \mid R\beta \rangle = \frac{1}{N_k} \sum_k e^{-ikR} H_{\alpha\beta}^{(\text{rot})}(k) = t_{\alpha\beta}(R),$$

(2.78)
where $N_k$ is the number of involved $k$-points [76, 23]. As already indicated, the matrix elements of the real-space Hamiltonian are normally called hopping matrix elements and are denoted by $t_{\alpha\beta}$. As soon as these hopping matrix elements are known, $H^{(\text{rot})}(k)$ can be reconstructed at arbitrary $k'$-points via

$$H^{(\text{rot})}_{\alpha\beta}(k') = \sum_R e^{ik' R} t_{\alpha\beta}(R).$$ \hspace{1cm} (2.79)

In order to derive the resulting band structure the eigenvalues $\tilde{\varepsilon}_{nk'}$ of $H^{(\text{rot})}(k')$ have to be calculated via diagonalization

$$H^{(\text{rot})}(k') |k'n\rangle = \tilde{\varepsilon}_{nk'} |k'n\rangle$$ \hspace{1cm} (2.80)

which yields the eigenenergies and the eigencoefficients $c_{\alpha n}(k')$ which can be used to transform arbitrary matrix elements from the orbital basis $|k'\alpha\rangle$ to the eigen- or band-basis $|k'n\rangle$

$$|k'n\rangle = \sum_{\alpha} c_{\alpha n}(k') |k'\alpha\rangle.$$ \hspace{1cm} (2.81)

## 2.3. Coulomb Interactions

The following general introduction to the effects of the Coulomb interaction is based on the review by Onida et al. [22] which was supplemented with the help of the books by Bruus and Flensberg [29] and Altland and Simons [77].

In the previous section we have seen that density functional theory in the Kohn-Sham formalism (KS-DFT) can be applied to a many-electron system in order to obtain the electron density in the system’s ground state. Astonishingly, even crude approximations to the exchange-correlation functional, like the LDA, lead already to quite good results for a variety of ground-state properties, like total energies, geometries, lattice vibrations or magnetic structures. However, the underlying approximations result in severe mispredictions in the case of excitation properties, which can be seen for instance in the overestimated band widths of sodium [78] or nickel [79] (see [80] for a detailed overview of other false predictions). Indeed, LDA has to fail here by definition since it was designed to describe solely ground-state properties. This is a quite crucial problem since most experiments are based on some excitation of the system. For instance, direct or inverse photoemission or absorption experiments involve either electron extractions, excitations from the valence to the conduction bands or electron relaxation from higher to lower states. Thus, a comparison of LDA-DFT results with experimental data is often difficult and in some cases even impossible. One of the most prominent problems of this kind is the consistent underestimation of band gaps in LDA [81, 82]. While germanium is for example an indirect semiconductor, LDA predicts it to have a vanishing band gap [83]. The reason for these problems of KS-DFT is two-sided. On the one
side, there is the approximative treatment of the exchange-correlation functional which might be inappropriate in some situations and lead to a misprediction of ground-state properties. On the other side, there is the misinterpretation of the fictitious Kohn-Sham eigenstates and -energies which lead to incorrectly deduced results in the case of excitation properties. Thus, optically measured band gaps cannot be compared to the band gap derived from Kohn-Sham eigenstates since the introduced auxiliary single-particle system was designed solely to describe the ground-state density.

To overcome these problems several extensions to the original KS-DFT have been proposed which are based on the introduction of optimized effective potentials [84], completely new functionals, which include Coulomb-interaction effects in the Hartree-Fock approximation [85], the inclusion of local Coulomb potentials [86] or self-interaction corrections [43]. But, all of these extensions are still applied in the KS-DFT framework and thus the problems concerning the interpretation of the Kohn-Sham eigenstates still exist. In fact, a systematic improvement is needed to obtain accurate excitation properties which can be achieved by introducing the concept of quasiparticles.

The basic idea of a quasiparticle description can easily be understood within the example of a photoemission spectroscopy experiment. Here, an electron with the kinetic energy $E_{\text{kin}}$ is ejected from the system due to an injected photon with energy $\hbar \omega$. Since both energies are experimentally known, the electron binding energy can directly be given as $\varepsilon = \hbar \omega - E_{\text{kin}}$. In contrast to the interpretation within a simple single-particle picture, the measured energy is in reality not just the single-particle energy, but a renormalized quasiparticle energy. This renormalization arises due to correlations between all electrons which result from the Coulomb interaction among them. Thus, a single electron within a many-body system will never be independent of the other electrons. Regarding the description of this experiment, the excitation energy $\varepsilon$ has to be calculated as the difference between the total energy of the ground state with $N$ electrons $E_N$ and the energy of the resulting $(N - 1)$-electron system $E_{N-1}$, which is not equal to the eigenenergy of a non-interacting single-particle Hamiltonian.

Indeed, we are looking for the excitation energy of an interacting system which can not be calculated in general. However, Landau introduced 1956 the Fermi liquid theory [87] which states that the quantum numbers of a given state of the non-interacting Fermi gas stay the same upon adiabatic inclusion of the interactions as long as there is no electronic phase transition taking place (see also [29, 24, 77, 42]). Thus, we are allowed to describe the excited state of the interacting system in form of an excited state of a nearly non-interacting system of quasiparticles using the same quantum numbers, at least for time scales smaller than the quasiparticle life time. The latter arises due to interaction-induced correlations next to a renormalization of the excitation energy. As we will see in the following, these correlation effects can be described using the so-called self-energy which enters a generalized quasiparticle Schrödinger equation.

Since the Coulomb interaction is responsible for the correlations and thus the renormalization, we will discuss its properties, its ab initio description as well as its effect to the band structure in the following. In more detail, we will review its screening within
the random phase and the constrained random phase approximation in section 2.3.1 and 2.3.2. Afterwards we briefly discuss its matrix elements within the localized Wannier basis in section 2.3.3 before we finally introduce Hedin’s GW approximation in section 2.3.4. Within the latter section we compare several approximative self-energies and discuss in detail modern GW implementations.

2.3.1. Screening in the Random Phase Approximation

In the context of Coulomb-interaction-induced renormalization effects, screening is one of the most important material properties. It is defined by the ability of charges within the system to react to Coulomb-like perturbations. These perturbations might be external electric fields or internal Coulomb potentials arising from injected impurities or simple electrons. In more detail, the screening is described by the so-called dielectric function \( \varepsilon(r, r', t, t') \), which is in general non-local in space and time. In the following, we will define the dielectric function from a macroscopic point of view and will introduce a microscopic theory afterwards to calculate it on an ab initio footing.

Basic Definitions

We will begin with some basic definitions from electrostatics which are needed for the subsequent sections. Since this is by far not complete the interested reader is referred to [88, 89] or [90] for comprehensive overviews and introductions to electrodynamics.

In general, we will use the particle density \( n \), the charge density \( \rho \), the corresponding potential \( \Phi \) and the interaction \( V \) which are given in real space by

\[
\rho(r) = e \cdot n(r) \quad \text{(2.82)}
\]

\[
\Phi(r) = \int d^3 r' \frac{\rho(r')}{|r - r'|} \quad \text{(2.83)}
\]

\[
V(r) = e \cdot \Phi(r), \quad \text{(2.84)}
\]

where \( e \) is the elementary charge. Maxwell’s first equation states that in the absence of temporal changes of the magnetic field (\( \dot{B} = 0 \)) the charge density \( \rho \) is the origin of the electric field \( E \) yielding

\[
\nabla E(r) = \frac{\rho(r)}{\varepsilon_0}, \quad \text{(2.85)}
\]

where \( \varepsilon_0 \) is the so-called vacuum permittivity\(^8\). From that, we can get the Poisson equation by utilizing the definition \( E(r) = -\nabla \Phi(r) \)

\[
\Delta \Phi(r) = -\frac{\rho(r)}{\varepsilon_0} \quad \text{or} \quad \Phi(q) = \frac{1}{\varepsilon_0 q^2} \rho(q), \quad \text{(2.86)}
\]

\(^8\) This constant is known as the electronic constant as well and links electric and mechanical quantities through Coulomb’s law \( F = \frac{1}{4\pi \varepsilon_0} \frac{Q_1 Q_2}{r^2} \) in vacuum.
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in real or Fourier space, respectively. Strictly speaking, these equations hold only for scenarios in which no further material is present (next to the charge distribution \( \rho \)). In situations with additional material we have to use an auxiliary field \( D \) (also called dielectric displacement) defined by the original electric field \( E \) and the polarization \( P \)

\[
D(r) = \varepsilon_0 E(r) + P(r)
\]  
(2.87)

and Maxwell’s first equation becomes

\[
\nabla D(r) = \rho_{\text{ext}}(r),
\]  
(2.88)

now involving an external (or impurity, unbound, free) charge density \( \rho_{\text{ext}}(r) \). The introduced polarization traces back to charges which are influenced by the electric field. In homogeneous and isotropic dielectrics we can define it using a constant susceptibility \( \chi \)

\[
P(r) = \chi \varepsilon_0 E(r).
\]  
(2.89)

However, as soon as the homogeneity and isotropy are lost we have to utilize a non-local susceptibility in order to describe the system’s polarization due to the electric field

\[
P(r) = \varepsilon_0 \int d^3r' \chi(r, r') E(r').
\]  
(2.90)

Combining Eqs. (2.87), (2.88) and (2.90) finally yields Maxwell’s first equation in the presence a polarizable material

\[
\nabla \int d^3r' \left[ \delta(r - r') + \chi(r, r') \right] E(r') = \frac{\rho_{\text{ext}}(r)}{\varepsilon_0}.
\]  
(2.91)

In a homogeneous system this equation can be simplified taking the fact into account that the susceptibility depends on differences of the spatial coordinates \( r - r' \) only. This allows to perform a Fourier transformation in the spatial coordinates yielding

\[
q^2 [1 + \chi(q)] \Phi(q) = \frac{\rho_{\text{ext}}(q)}{\varepsilon_0}.
\]  
(2.92)

Now, we can introduce the dielectric function \( \varepsilon(q) = 1 + \chi(q) \) and define the external potential \( \Phi_{\text{ext}} \) via Eq. (2.86) to derive the simple expression

\[
\Phi(q) = \frac{\Phi_{\text{ext}}(q)}{\varepsilon(q)}.
\]  
(2.93)

Here, we see that the potential \( \Phi \) associated with the electric field \( E \) is defined by the external (or impurity) potential reduced by the screening function \( \varepsilon \). Hence, using Maxwell’s first equation we have derived a first (quite formal) definition of the static screening effects due to the dielectric function which will be discussed in more detail in the following.
2.3. Coulomb Interactions

Macroscopic Definition of the Dielectric Function

To derive a macroscopic definition of the dielectric function we assume that the unperturbed ground-state electron density is given by \( \rho_0(\mathbf{r}) \) which might be gained from DFT. Any additional (dynamical) external charge densities \( \rho_{\text{ext}}(\mathbf{r}, t) \) or potentials \( \Phi_{\text{ext}}(\mathbf{r}, t) \) (due to an additional external or inner charge or due to an applied external field) will induce a reaction of the internal charge carriers in form of a redistribution described by the induced charge density \( \rho_{\text{ind}}(\mathbf{r}, t) \). As for any other charge density, we can define a corresponding induced potential \( \Phi_{\text{ind}}(\mathbf{r}, t) \) which has to be taken into account in the definition of the total perturbing potential

\[
\Phi(\mathbf{r}, t) = \Phi_{\text{ext}}(\mathbf{r}, t) + \Phi_{\text{ind}}(\mathbf{r}, t). \tag{2.94}
\]

Note that the induced charge density and thus the induced potential is a reaction of the internal charges to the external potential and would vanish if the latter vanishes. At the same time the induced charge density screens the overall arising total perturbation. Hence, the internal charge carriers are part of the total perturbation and we are correspondingly dealing with a self-consistent problem, here. In linear response theory we can write the total perturbing potential with the help of the dielectric function \( \varepsilon(\mathbf{r}, \mathbf{r}', t, t') \) which is in general non-local in space and time

\[
\Phi(\mathbf{r}, t) = \int d^3r' \int dt' \frac{\Phi_{\text{ext}}(\mathbf{r}', t')}{\varepsilon(\mathbf{r}, \mathbf{r}', t, t')} \tag{2.95}
\]

Given the fact that \( \Phi_{\text{ext}}(\mathbf{r}, t) \) is independent of the material, all material specific properties corresponding to screening effects are now rendered by the dielectric function. For a translational invariant system (in space and time) the dielectric function becomes a function of space and time differences only \( \varepsilon(\mathbf{r} - \mathbf{r}', t - t') \) and we can use corresponding Fourier transformations to derive analogous expressions of Eq. (2.94) and Eq. (2.95) in reciprocal space and frequency:

\[
\Phi(\mathbf{q}, \omega) = \frac{\Phi_{\text{ext}}(\mathbf{q}, \omega)}{\Phi_{\text{ext}}(\mathbf{q}, \omega) + \Phi_{\text{ind}}(\mathbf{q}, \omega)} = \frac{\Phi_{\text{ext}}(\mathbf{q}, \omega)}{\varepsilon(\mathbf{q}, \omega)} \tag{2.96}
\]

This is in fact fully equivalent to Eq. (2.93). However, here we have clearly defined the external, induced and total (perturbing) potentials which can be used to define the dielectric function in various ways\(^9\)

\[
\varepsilon(\mathbf{q}, \omega) = \frac{\Phi_{\text{ext}}(\mathbf{q}, \omega) + \Phi_{\text{ind}}(\mathbf{q}, \omega)}{\Phi_{\text{ext}}(\mathbf{q}, \omega) + \Phi_{\text{ind}}(\mathbf{q}, \omega)} = 1 - \frac{\Phi_{\text{ind}}(\mathbf{q}, \omega)}{\Phi_{\text{ext}}(\mathbf{q}, \omega) + \Phi_{\text{ind}}(\mathbf{q}, \omega)}
\]

\[
= 1 - \frac{4\pi \rho_{\text{ind}}(\mathbf{q}, \omega)}{q^2 \Phi(\mathbf{q}, \omega)}. \tag{2.97}
\]

\(^9\) In Eq. (2.97) we use atomic units which set \( e = m_e = \hbar = \frac{1}{4\pi\varepsilon_0} = 1 \). Hence, the vacuum permittivity is given by \( \varepsilon_0 = \frac{1}{4\pi} \).
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Since the external potential is assumed to be known, the problem of finding the total perturbing potential is solved as soon as the dielectric function is found.

Although macroscopic considerations can be used to derive a definition of the screening function, we need a microscopic theory in order to calculate it on an ab initio footing. Indeed, it turns out that this is a hard task which has to be solved approximatively, as it will be discussed in the following.

Microscopic Theory for the Dielectric Function

The first model dielectric functions were developed for the interacting electron gas. Important approximations were suggested by Thomas and Fermi [33, 34], Lindhard [91] and by Ehrenreich and Cohen [92]. While the Thomas-Fermi approximation of the dielectric function is only valid in the static ($\omega = 0$) and long-wavelength ($q \rightarrow 0$) limits, the so called random phase approximation (RPA) by Ehrenreich and Cohen is defined for the complete Brillouin zone and all frequencies. Although there are more sophisticated extensions to these approximations taking so-called vertex corrections (as discussed in section 2.3.4) into account [27], the Thomas-Fermi and the RPA descriptions are the most prominent ones due to their simplicity and their accuracy. Since the RPA is a commonly used approximation, we will briefly discuss it here and derive the Thomas-Fermi dielectric function afterwards in the corresponding limits.

In principle, there are two methods to derive the dielectric function within the RPA, namely by utilizing Green functions or by using equation of motion techniques. Here, we will apply the latter and follow Czycholl and Mahan [24, 27] who applied the so called self-consistent-field method by Ehrenreich and Cohen [92] to outline how the dielectric function can be obtained in a multi-band system. In section 4.5 and its appendix A.6 we will additionally use the Green function technique to derive the corresponding terms in the Wannier basis.

Here, we start with the Hamiltonian of the perturbed electron gas in second quantization

$$H = \sum_{kn} \varepsilon_n(k)c_{kn}^\dagger c_{kn} + \sum_{kk'} \langle kn|V(r,t)|k'n'\rangle c_{kn}^\dagger c_{k'n'}, \quad (2.98)$$

where $\varepsilon_n(k)$ are the single-particle energies and $V(r,t) = e\Phi_{ext}(r,t) + e\Phi_{ind}(r,t)$ is the total perturbation due to the external and induced potentials according to Eq. (2.94). We assume that two-particle Coulomb-interaction terms are indirectly taken into account via the dielectric screening included in the definition of full perturbation [see for instance Eq. (2.96)]. Additionally, we assume that the time dependence of $V(r,t)$ is described by a constant oscillation which is switched on adiabatically (described by $e^{\delta t}$) and its momentum dependence can be derived from a Fourier transformation resulting
2.3. Coulomb Interactions

\[ V(r, t) = \frac{1}{V} \sum_q e^{i\mathbf{q} \cdot \mathbf{r}} e^{-i(\omega + i\delta)t} , \]  

(2.99)

where the constant \( V \) is the unit-cell volume. Using this definition the Hamiltonian from Eq. (2.98) becomes

\[ H = \sum_{\mathbf{k} \mathbf{n}} \varepsilon_n(\mathbf{k}) c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k} \mathbf{n}} + \frac{1}{V} \sum_q e^{i\Phi(q, \omega)} n(q) \]  

(2.100)

with \( \Phi(q, \omega) = \Phi(q) e^{-i(\omega + i\delta)t} \) and the operator of particle density

\[ n(q) = \sum_{\mathbf{k} \mathbf{n}'} \langle \mathbf{k} \mathbf{n}' | e^{i\mathbf{q} \cdot \mathbf{r}} | \mathbf{k}' \mathbf{n}'' \rangle c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k}' \mathbf{n}''} . \]  

(2.101)

Thus, we can use the equation of motion technique for \( c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k}' \mathbf{n}'} \) in order to obtain the system’s reaction to the perturbation in form of \( n(q) \). We start with Heisenberg’s equation of motion:

\[ i\hbar \frac{\partial}{\partial t} c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k}' \mathbf{n}'} = [H, c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k}' \mathbf{n}'}] . \]  

(2.102)

The commutator is evaluated piecewise using the \( H^{(0)} \) and \( H^{(1)} \) as defined in Eq. (2.98). The first part results in

\[ \left[ \sum_{\mathbf{k}' \mathbf{n}''} \varepsilon_{n''}(\mathbf{k}'') c_{\mathbf{k}' \mathbf{n}''}^\dagger c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k}' \mathbf{n}''} c_{\mathbf{k} \mathbf{n}} \right] = [\varepsilon_n(\mathbf{k}) - \varepsilon_{n''}(\mathbf{k}'')] c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k}' \mathbf{n}''} , \]  

(2.103)

while the perturbation leads to

\[ \left[ \frac{1}{V} e^{i\Phi(q, \omega)} \sum_{\mathbf{k}' \mathbf{n}''} \langle \mathbf{k}' \mathbf{n}'' | e^{i\mathbf{q} \cdot \mathbf{r}} | \mathbf{k} \mathbf{n} \rangle c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k}' \mathbf{n}''} c_{\mathbf{k} \mathbf{n}} c_{\mathbf{k}' \mathbf{n}''} \right] \]

\[ = \frac{1}{V} e^{i\Phi(q, \omega)} \sum_{\mathbf{k} \mathbf{n}} \left( \langle \mathbf{k} \mathbf{n} | e^{i\mathbf{q} \cdot \mathbf{r}} | \mathbf{k} \mathbf{n} \rangle c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k}' \mathbf{n}''} - \langle \mathbf{k} \mathbf{n}' | e^{i\mathbf{q} \cdot \mathbf{r}} | \mathbf{k} \mathbf{n} \rangle c_{\mathbf{k} \mathbf{n}} c_{\mathbf{k}' \mathbf{n}''} \right) \]

\[ \approx \frac{1}{V} e^{i\Phi(q, \omega)} \langle \mathbf{k} \mathbf{n}' | e^{i\mathbf{q} \cdot \mathbf{r}} | \mathbf{k} \mathbf{n} \rangle \left( c_{\mathbf{k}' \mathbf{n}''}^\dagger c_{\mathbf{k} \mathbf{n}}^\dagger c_{\mathbf{k} \mathbf{n}} - c_{\mathbf{k} \mathbf{n}} c_{\mathbf{k}' \mathbf{n}''} \right) . \]  

(2.104)

In the last step we set \( \{\mathbf{k} \mathbf{n}\} = \{\mathbf{k} \mathbf{n}'\} \) and \( \{\mathbf{k} \mathbf{n}\} = \{\mathbf{k} \mathbf{n}''\} \) for the left and right terms in the brackets, respectively. Thus we neglect non-diagonal terms of the involved operators
c^\dagger_{k_n} c_{k_n} which corresponds to the so-called random phase approximation. Thereby, it is assumed that in the upcoming average all resulting random phases will annihilate each other anyway. Doing so, we get
\[ i\hbar \frac{\partial}{\partial t} \langle c^\dagger_{k_n} c_{k'_{n'}} \rangle = \hbar (\omega + i\delta) \langle c^\dagger_{k_n} c_{k'_{n'}} \rangle \]
\[ = [\varepsilon_n(k) - \varepsilon_{n'}(k')] \langle c^\dagger_{k_n} c_{k'_{n'}} \rangle \]
\[ + \frac{1}{V} e^\Phi(q, \omega) \langle k'_{n'} | e^{i qr} | k_n \rangle \left( \langle c^\dagger_{k'_{n'}} c_{k'_{n'}} \rangle - \langle c^\dagger_{k_n} c_{k_n} \rangle \right) \tag{2.105} \]
or equivalently
\[ \langle c^\dagger_{k_n} c_{k'_{n'}} \rangle = \frac{1}{V} e^\Phi(q, \omega) \langle k'_{n'} | e^{i qr} | k_n \rangle \frac{f_{k'_{n'}} - f_{k_n}}{\varepsilon_{n'}(k') - \varepsilon_n(k) + i\omega + i\delta} \tag{2.106} \]
where we introduced the Fermi functions \( f_{kn} = \langle c^\dagger_{k_n} c_{k_n} \rangle \) and used the oscillating time dependency as assumed in the beginning. In order to describe the expectation value of the full particle density as defined in Eq. (2.101) we need to multiply this expression by the matrix element \( \langle k_n | e^{i qr} | k'_{n'} \rangle \) and sum over all momenta and band indices which results in
\[ \langle n(q) \rangle = \frac{1}{V} \sum_{k'_{n'}} e^\Phi(q, \omega) \langle k'_{n'} | e^{i qr} | k_n \rangle^2 \frac{f_{k'_{n'}} - f_{k_n}}{\varepsilon_{n'}(k') - \varepsilon_n(k) + i\omega + i\delta} \tag{2.107} \]
If we additionally assume \( k' = k - q \) (since the involved matrix elements will annihilate all other summands) we finally get
\[ \langle n(q) \rangle = \frac{1}{V} \sum_{k_{nn'}} e^\Phi(q, \omega) \langle k-q_{n'} | e^{i qr} | k_{nn} \rangle^2 \frac{f_{k-q_{n'}} - f_{k_{nn}}}{\varepsilon_{n'}(k-q) - \varepsilon_n(k) + i\omega + i\delta} \tag{2.108} \]
Taking into account that \( \langle n(q) \rangle \) is proportional to the induced density \( n_{\text{ind}}(q, \omega) \) [27, 24], the corresponding potential \( \phi_{\text{ind}} \) is defined by \( \langle n(q) \rangle \) as well and \( V_{\text{ind}} \) can given by
\[ V_{\text{ind}}(q, \omega) = \frac{4\pi e^2}{q^2} \langle n(q) \rangle. \tag{2.109} \]
This can be written as a product of the bare three-dimensional Coulomb potential \( v_q = \frac{4\pi e^2}{\c_{q^2}} \), the total perturbing potential \( V(q, \omega) = e\Phi(q, \omega) \) and the polarization functions \( \Pi^0(q, \omega) \):
\[ V_{\text{ind}}(q, \omega) = v_q V(q, \omega) \Pi^0(q, \omega). \tag{2.110} \]
The involved RPA polarization function is obtained by comparison with Eq. (2.108) yielding
\[ \Pi^0(q, \omega) = \sum_{k_{nn'}} \langle k-q_{n'} | e^{i qr} | k_{nn} \rangle^2 \frac{f_{k-q_{n'}} - f_{k_{nn}}}{\varepsilon_{n'}(k-q) - \varepsilon_n(k) + i\omega + i\delta}. \tag{2.111} \]
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\[ V = v + \Pi \]

**Figure 2.4.**
Dyson equation for the screened interaction corresponding to Eq. (2.114). Wiggly lines correspond to bare (single line) and screened (double line) interactions. The polarization function \( \Pi \) which renormalizes the interaction is indicated as a circle.

Finally, we make use of Eq. (2.96)

\[
V(q, \omega) = V_{\text{ext}}(q, \omega) + V_{\text{ind}}(q, \omega) = \frac{V_{\text{ext}}(q, \omega)}{1 - v_q \Pi^0(q, \omega)} = \frac{V_{\text{ext}}(q, \omega)}{\varepsilon_{\text{RPA}}(q, \omega)}
\]

and thus define the dielectric function within the random phase approximation

\[
\varepsilon_{\text{RPA}}(q, \omega) = 1 - v_q \Pi^0(q, \omega).
\]

This is a quite remarkable result, since we have shown using the equation of motion technique and the macroscopic definition of the dielectric function that the latter can be obtained microscopically *solely* from the knowledge of the electronic band structure. Thus, the dielectric function is independent of the external potential and is a mere material property.

A very similar result can be obtained using the formalism of Green functions and Feynman diagrams starting from the evaluation of a particle density-density correlation function [27, 29] leading to

\[
V(q, \omega) = \frac{v_q}{1 - v_q \Pi(q, \omega)}.
\]

which becomes equal to Eq. (2.112) when the external potential \( V_{\text{ext}}(q, \omega) \) is the bare Coulomb potential \( v_q \) and the *total polarization* \( \Pi(q, \omega) \) is approximated via \( \Pi^0(q, \omega) \). In fact, we are dealing here with a Dyson equation (as it will be introduced in section 2.3.4) for the screened interaction which is shown in terms of Feynman diagrams in Fig. 2.4. From a diagrammatic point of view, the random phase approximation corresponds to a *subset of diagrams* which are used in the definition of the total polarization which renormalizes the bare Coulomb potential. As we will see in section 2.3.4, within the RPA the full polarization is approximated as a so-called *bubble diagram* which includes an electron and a hole propagator only, while any vertex corrections are neglected which leads to the infinite series shown in Fig. 2.5.

**Thomas-Fermi Limit**

As mentioned in the beginning, one of the very first and successful approximations to the dielectric screening was given by Thomas and Fermi. Although it can be derived
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\[ V \approx v + \ldots \]

\[ \text{Figure 2.5.} \]
Screened Coulomb interaction in the random phase approximation. Single (double) wobbly lines describe the bare (screened) interactions and solid lines correspond to the bare electronic propagators as defined in section 2.3.4.

independently from the random phase approximation by assuming that the total charge density can be described locally as independent densities of a free-electron system [27, 24, 29], it is quite satisfying that it can be deduced from the RPA in the corresponding limits as well. It is straightforward to show that in the static (\( \omega = 0 \)) and long-wavelength (\( q \to 0 \)) limits using a single partially occupied band (\( n = n' \)) the RPA polarization function becomes [29]

\[ \Pi^{0}_{\text{TF}}(q \to 0, \omega = 0) = -N(E_F). \]  

(2.115)

Thus, in cases in which these limits are satisfied (for instance in the case of conventional metals) the screening properties of the system are entirely described by the density of states at the Fermi energy \( N(E_F) \). Accordingly, the dielectric function can be described as

\[ \varepsilon_{\text{TF}}^{3D} = 1 + \frac{(q_{\text{TF}}^{3D})^2}{q^2} \quad \text{or} \quad \varepsilon_{\text{TF}}^{2D} = 1 + \frac{q_{\text{TF}}^{2D} q}{q^2} \]  

(2.116)

depending on the dimensionality and using the corresponding Thomas-Fermi wave vectors

\[ q_{\text{TF}}^{3D} = \sqrt{\frac{4\pi e^2}{V} N(E_F)} \quad \text{and} \quad q_{\text{TF}}^{2D} = \frac{2\pi e^2}{A} N(E_F), \]  

(2.117)

where \( V \) and \( A \) are the volume and area of the primitive unit cell, respectively. For \( q \to 0 \) these dielectric functions obviously diverge, leading to an Yukawa-like potential in real-space which vanishes in the long-range limit. This is a typical behaviour for metals, since the intrinsic screening charges are able to move in a nearly free fashion and can thus effectively screen any impurity charge.

In the context of semiconductors with fully occupied valence and completely empty conduction bands which are separated by a band gap \( \Delta \), the screening behaviour in these limits is different. Here, the polarization function becomes

\[ \Pi^{0}_{\text{SC}}(q \to 0, \omega = 0) \approx -\frac{e^2 n_0 \alpha^2 q^2}{\Delta}, \]  

(2.118)
where the involved matrix element $M = \langle k-q\nu'|e^{iqr}|kn \rangle$ was approximated by $M = \alpha q$ leading to a dielectric function of the form

$$\varepsilon_{3D}^{\text{SC}}(q \to 0, \omega = 0) \approx 1 + \frac{4\pi e^2 \alpha^2 n_0}{\Delta}$$

(2.119)

with $n_0$ being the electron density in three dimensions [24]. As we will discuss in detail in section 3.3 the two-dimensional limit is given by

$$\varepsilon_{2D}^{\text{SC}}(q \to 0, \omega = 0) \to 1$$

(2.120)

due to vanishing screening in the long-wavelength limit.

### 2.3.2. Constrained Random Phase Approximation

The following introduction to the constrained random phase approximation follows the original work by Aryasetiawan et al. [93] complemented by details on its implementation from Miyake et al. [94], Shih et al. [95] and, especially, Kaltak [96].

A major ingredient to the material-specific models we aim at are Coulomb matrix elements. As we have seen in the previous section on the random phase approximations the effects of screening are essential for a realistic description of the Coulomb interaction and correspondingly arising material properties. These screening processes might be described as virtual transitions between all occupied and unoccupied states. Thus, we end up with a conceptional problem as soon as we neglect a wide range of states in order to simplify the material-specific model, since we will loose phase space in which the before-mentioned virtual excitations take place. To setup a well defined down-folding scheme, the resulting screening effects of the neglected part of the system have to be accounted for, while those screening processes which will be described within the subsequent theory (which utilizes the simplified model) have to be excluded from the definition of the involved Coulomb matrix elements. To this end the complete Fock space is divided into a model part $F_m$ and a rest part $F_r$

$$F = F_m \oplus F_r$$

(2.121)

on which the model $\Pi_m$ and the rest $\Pi_r$ polarizations can be evaluated. Their sum reconstructs the complete polarization $\Pi$

$$\Pi = \Pi_m + \Pi_r.$$  

(2.122)

Using this separation within the definition of the completely screened Coulomb inter-
action from Eq. (2.114) results in

\[
V = [1 - v\Pi]^{-1} v \\
= [1 - v\Pi_m - v\Pi_r]^{-1} v \\
= \left[ 1 - \frac{v}{1 - v\Pi_r} \Pi_m \right]^{-1} \frac{v}{1 - v\Pi_r} \\
= [1 - W_r\Pi_m]^{-1} W_r.
\] (2.123)

Here, we see that as long as we are constrained to use the model polarization \(\Pi_m\) (since the information about all other bands is not available), the partially screened Coulomb interaction \(W_r\) defined by

\[
W_r = \frac{v}{1 - v\Pi_r}
\] (2.124)

instead of the bare interaction \(v\) has to be used to calculate \(V\). This is the essence of the so-called constrained random phase approximation (cRPA) which ensures a proper inclusion of all screening processes on the RPA level [93].

In Fig. 2.6 we show the band structure of SrVO\(_3\) from Ref. [97] in which the so-called “correlated” or model part is colored red. As said before, each summand of the RPA polarization defined in Eq. (2.111) might be interpreted as a virtual excitation from an occupied state \(\{k-q\nu\}\) to an unoccupied one \(\{k\nu\}\) which are indicated in Fig. 2.6 by dashed lines. While some of these virtual excitations do strictly take place within the model subspace (red), other virtual excitations occur in, originate from or end in the

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\(^{10}\)In the case of SrVO\(_3\) the set of \(t_{2g}\) bands (arising from \(V\) \(d_{xy}, d_{xz}\) and \(d_{yz}\) orbitals) around the Fermi energy is supposed to be “strongly correlated” due to substantial Coulomb interactions within the localized \(V\) \(d\) orbitals. The modeling process therefore aims to describe these composite bands in order to treat it afterwards within higher-level theories like DMFT.
2.3. Coulomb Interactions

rest of the Fock space (blue). Only the first ones (red) contribute to screening effects within the model subspace and thus to the model polarization $\Pi_m$. The remaining virtual excitations define the rest polarization $\Pi_r$. Although we need to know $\Pi_r$, it is more convenient to calculate the model $\Pi_m$ and the full polarization $\Pi$ in advance and derive $\Pi_r$ afterwards as their difference. Hence, in order to calculate $W_r$ we have to evaluate

$$\Pi_m = \sum_{\{kn\} \in F_m} |\langle k-q'n'|z^{-iqr}|kn\rangle|^2 \frac{f_{n'}(k-q) - f_n(k)}{\hbar \omega + i\delta + \varepsilon_{n'}(k-q) - \varepsilon_n(k)}$$  

as well as the full polarization $\Pi$ from Eq. (2.111) in a first step. Afterwards $\Pi_r = \Pi - \Pi_m$ is used within Eq. (2.124) to get $W_r$ as well as the partially screened Coulomb kernel $W_r(r, r', \omega)$ via appropriate Fourier transformations.

As long as the model subspace is clearly separated from the rest Fock space and the corresponding indices (which fulfill $\{kn\} \in F_m$ and $\{k-qn'\} \in F_m$) are known, the evaluation of Eq. (2.125) can be carried out without any approximations by introducing static energy windows [93, 98] and the treatment would be in principle exact. Unfortunately, this holds for a few systems only. In most cases, the model subspace is entangled with the rest of the system and the required restrictions $\{kn\} \in F_m$ and $\{k-qn'\} \in F_m$ are difficult to fulfill. Here, the specific choice of static energy windows (maybe in combination with some simple “band choosing algorithms”) can have a strong influence to the resulting values for $W_r$ [94].

To overcome this problem, projection schemes (e.g. as introduced in section 2.2.2) can be applied either to introduce new sets of Bloch functions $|\tilde{\phi}_{nk}\rangle$ which replace $|\phi_{nk}\rangle$ in Eq. (2.111) or to define weights which restrict the full summation in Eq. (2.111) correspondingly.

The former method was used by Miyake and coworkers [94]. They introduce projection operators to define the Bloch functions of the model subspace

$$|\tilde{\phi}_{nk}\rangle = \hat{P} |\phi_{nk}\rangle,$$  

while the rest subspace is accordingly given via $|\tilde{\phi}_{nk}'\rangle = (1 - \hat{P}) |\phi_{nk}\rangle$. Doing so Miyake et al. realized that although the sets of wave functions $|\tilde{\phi}\rangle$ and $|\tilde{\phi}'\rangle$ are orthogonal to each other, they do not necessarily form orthogonal basis sets for the corresponding subspaces. Since in this case transitions within the subspaces do not correspond to well defined single particle transitions as discussed before, they orthogonalize $|\tilde{\phi}\rangle$ and $|\tilde{\phi}'\rangle$ independently. Thereby they introduce a disentanglement scheme and gain well defined sets of wave functions, which can be used to calculate $\Pi_m$, $\Pi_r$, and $\Pi$. However, hybridization effects between the subspaces are neglected in this case which changes the original band structure and might distort the results.

Otherwise, the projection scheme might be used to define certain weights $\gamma_{nk}\gamma_{n'k-q}$ which restrict the full $k$, $n$ and $n'$ summations from Eq. (2.125) to accumulate contributions
from the model subspace only

\[
\Pi_m = \sum_{kmn'} |\langle k-qn'|e^{-i\mathbf{q}r}\mathbf{k}\rangle| \frac{f_n'(\mathbf{k} - \mathbf{q}) - f_n(\mathbf{k})}{\hbar\omega + i\delta + \varepsilon_n'(\mathbf{k} - \mathbf{q}) - \varepsilon_n(\mathbf{k})} \gamma_{n'k-q}^{nk}.
\] (2.127)

To this end, Şaşıoğlu et al. [99] as well as Shih et al. [95] proposed to use weights of the following form

\[
\gamma_{n'k-q}^{nk} = \sum_{\alpha} |A_{\alpha n}^k|^2 \sum_{\beta} |A_{\beta n'}^{k-q}|^2,
\] (2.128)

where projection matrix-elements \(A_{\alpha n}^k\) to the model subspace are used [for instance as defined in Eq. (2.75)]. This definition seems to be appropriate, since it accounts for the probabilities that the electron resides in the model subspace before (\(\alpha\)-sum) and after (\(\beta\)-sum) the virtual transition and thus restricts the sum in Eq. (2.127) to fulfill \(\{kn\} \in F_m\) and \(\{k-qn'\} \in F_m\). However, Kaltak shows that the weights according to Eq. (2.128) are just “educated assumptions” and that a detailed evaluation of the underlying Kubo-Nakano formula for the response of the model subspace instead yields [96]

\[
\gamma_{n'k-q}^{nk} = \sum_{ijkl} P_{n'kn}^{kq} P_{n'k}^{k-q} P_{n'k-q}^{k-q} P_{n'k-q}^{k-q},
\] (2.129)

where projectors of the following form are used

\[
P_{n'kn}^{kq} = \sum_{\alpha} A_{\alpha n}^{kq} A_{\alpha m}^{kq}.
\] (2.130)

In contrast to the weights by Şaşıoğlu et al. and Shih et al. from Eq. (2.128) Kaltak’s weights include four projectors (and not just two) of this kind and additionally involve corresponding off-diagonal elements. Thus, Kaltak’s weights lead to additional screening channels within the model subspace which enhances \(\Pi_m\) and thereby reduces the rest screening / polarization \(\Pi_r\). Therefore, the weights from Eq. (2.129) lead in general to less screened and thus enhanced \(W_r\), as shown for the series of 3d transition metals in Ref. [96].

In addition to the specific weighting method, the underlying Wannier construction (e.g. to define \(A_{\alpha n}\)) influences the result as well. Hereby the degree of localization, the initial basis set and the disentanglement algorithm are the most important tuning knobs.

In order to minimize these “dependencies” in the following, we will construct Wannier functions without performing any kind of localization and use the disentanglement approach by Souza et al. [67] (as far as possible). This allows us to describe the original \(ab\ initio\) band structures as close as possible including the corresponding orbital
2.3. Coulomb Interactions

weights. Thereby, we use minimal orbital basis sets which describe composite blocks of bands which can not be additionally isolated for symmetry reasons (see the detailed discussions of the underlying full band structures of graphene and molybdenum disulfide in sections 3.1 and 4.1.2, respectively). Finally, we are restricted to use the weighting method by Şaşıoğlu et al.\textsuperscript{11}.

2.3.3. Coulomb-Interaction Matrix Elements in the Wannier Basis

As soon as the bare, fully or partially screened Coulomb kernel is known, corresponding matrix elements can be evaluated in order to use the resulting values in Eq. (2.5) to define our material-specific Hamiltonian. Here, we will rather focus on some properties of these matrix elements within the Wannier basis than on calculation details. For the latter the interested reader is referred to [76, 100, 101] or [96].

We start with the most general form of the Coulomb matrix elements in reciprocal space

\[ U_{\alpha\beta\gamma\delta}^{kk'q} = \int d^3r \int d^3r' \phi^*_{\alpha k-q}(r) \phi^*_{\beta k'+q}(r') U(r, r', \omega) \phi_{\gamma k'}(r') \phi_{\delta k}(r), \]  

(2.131)

where the momentum conservation of the Coulomb scattering process is already accounted for. Note that in the case of screened Coulomb matrix elements \( U_{\alpha\beta\gamma\delta}^{kk'q} \) is in general frequency dependent due to the dynamic polarization function. The involved Bloch functions are defined by\textsuperscript{12}

\[ \phi_{\alpha k}(r) = \sum_R e^{ikR} w_{\alpha R}(r) \]  

(2.132)

using Wannier functions \( w_{\alpha R}(r) \) of a certain orbital character \( \alpha \) which are localized within a unit cell around \( \mathbf{R} \). Now, we can use this definition in Eq. (2.131) which yields

\[ U_{\alpha\beta\gamma\delta}^{kk'q} = \sum_{R_1 \ldots R_4} \int d^3r \int d^3r' w^*_{\alpha R_4}(r) w_{\beta R_2}(r') U(r, r', \omega) w_{\gamma R_3}(r') w_{\delta R_1}(r) \times e^{i(R_1-R_4)k'} e^{i(R_3-R_2)k} e^{i(R_1-R_2)q}, \]  

(2.133)

\textsuperscript{11}The implementation of the weighting method as defined in Eq. (2.129) within the VASP code is still under development, while the weighting method by Şaşıoğlu et al. and Shih et al. is available within the SPEX code.

\textsuperscript{12}Note that according to Eq. (2.61) we use an asymmetric definition for the Fourier transform

\[ |\phi_{\alpha k}\rangle = \sum_R e^{ikR} |w_{\alpha R}\rangle \quad \Leftrightarrow \quad |w_{\alpha R}\rangle = \frac{1}{N} \sum_R e^{-ikR} |\phi_{\alpha k}\rangle, \]

which corresponds to \( \langle \phi_{\alpha k} | \phi_{\beta k'} \rangle = N \delta_{\alpha\beta} \delta_{kk'} \). See Ref. [23] for more details on normalization conventions.
where quite complicated  \( k \)-, \( k' \)- and \( q \)-dependencies have been introduced. However, rearranging the whole expression,

\[
U_{\alpha\beta\gamma\delta}^{kk'q} = \int d^3r \int d^3r' \ U(r,r',\omega) \sum_{R_1R_4} \sum_{R_2R_3} w_{\alpha R_1}(r)w_{\beta R_3}(r) e^{i(R_4 - R_1)k} e^{iR_1q} \sum_{R} w_{\beta R_2}(r')w_{\gamma R_3}(r') e^{i(R_3 - R_2)k'} e^{-iR_2q},
\]  

(2.134)

shows that the \( k \)- and \( k' \)-dependencies strongly depend on the degree of localization of the Wannier functions. A close look at the \( \{R, R_j\} \) sums reveals that there is no \( k \)- or \( k' \)-dependence in the summand with \( R_i = R_j \). For the other summands the degree of overlap between the Wannier functions \( w_{\alpha R_i}(r) \) in the \( i \)-th unit cell and \( w_{\beta R_j}(r) \) in the \( j \)-th cell defines the \( k \)- or \( k' \)-dependencies. Thus, these dependencies will be weakened with the degree of localization and vanish as soon as all involved Wannier functions are clearly localized to a single unit cell. In order to simplify the notation and to point out some further symmetries and properties we will assume in the following that the Wannier functions are indeed strongly localized leading to

\[
\sum_{R, R_j} w_{\alpha R_i}(r)w_{\beta R_j}(r) e^{i(R_j - R_i)k} e^{iR_iq} = \sum_{R} w_{\alpha R}(r)w_{\beta R}(r) e^{iRq}
\]

(2.135)

and

\[
U_{\alpha\beta\gamma\delta}^{q} = \sum_{R} \int d^3r \int d^3r' \ w_{\alpha 0}(r)w_{\beta R}(r')U(r, r', \omega)w_{\gamma R}(r')w_{\delta 0}(r) e^{iRq},
\]

(2.136)

which can be interpreted as the Fourier transform of the corresponding matrix element in real space

\[
U_{\alpha\beta\gamma\delta}^{q} = \sum_{R} U_{\alpha\beta\gamma\delta}^{R} e^{iRq}
\]

(2.137)

with

\[
U_{\alpha\beta\gamma\delta}^{R} = \int d^3r \int d^3r' \ w_{\alpha 0}(r)w_{\beta R}(r')U(r, r', \omega)w_{\gamma R}(r')w_{\delta 0}(r).
\]

(2.138)

Hence, as long as the \( k \)- and \( k' \)-dependencies are weak or even non-existent, long range or non-local (\( R \neq 0 \)) Coulomb matrix elements can easily be evaluated from their reciprocal representation via the corresponding inverse Fourier transform

\[
U_{\alpha\beta\gamma\delta}^{R} = \frac{1}{N} \sum_{q} U_{\alpha\beta\gamma\delta}^{q} e^{-iRq}.
\]

(2.139)

Since the Coulomb kernel is proportional to \( |r - r'|^{-1} \), we can identify some basic symmetries from Eq. (2.137) and Eq. (2.138) by interchanging \( r \) and \( r' \)

\[
U_{\beta\alpha\delta\gamma}^{q} = U_{\alpha\beta\gamma\delta}^{-q} \quad U_{\beta\alpha\delta\gamma}^{R} = U_{\alpha\beta\gamma\delta}^{-R}
\]

(2.140)

\[
U_{\gamma\delta\alpha\beta}^{q} = (U_{\alpha\beta\gamma\delta}^{-q})^* \quad U_{\gamma\delta\alpha\beta}^{R} = (U_{\alpha\beta\gamma\delta}^{-R})^*.
\]

(2.141)
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These matrix elements strongly depend on the degree of overlap between the Wannier functions. In the end, the largest Coulomb matrix elements will arise for $\alpha = \delta$ and $\beta = \gamma$,

$$
U^q_{\alpha\beta\beta\alpha} = \sum_R \int d^3r \int d^3r' U(r, r', \omega) |w_{\alpha 0}(r)|^2 |w_{\beta R}(r')|^2 e^{iRq} \\
= \sum_R U^R_{\alpha\beta\beta\alpha} e^{iRq},
$$

(2.142)

which are the Fourier components of the so-called density-density Coulomb matrix elements given by

$$
U^R_{\alpha\beta\beta\alpha} = \int d^3r \int d^3r' |w_{\alpha 0}(r)|^2 |w_{\beta R}(r')|^2 U(r, r', \omega)
$$

(2.143)

in real space. While these matrix elements will always be real (for the bare interaction or $\omega = 0$), their Fourier representations might have an imaginary part. In more detail, $U^q_{\alpha\beta\beta\alpha}$ will show an imaginary part as long as $U^R_{\alpha\beta\beta\alpha} \neq U^{-R}_{\alpha\beta\beta\alpha}$, otherwise the Fourier components of the density-density matrix element will be real as well. Whether or not this requirement is fulfilled depends on the chosen Wannier functions and the underlying lattice structure.

2.3.4. GW Approximation

The subsequent brief introduction to the GW approximation closely follows the lecture notes by Friedrich and Schindlmayr [102] which was complemented with the help of the reviews by Aryasetiawan and Gunnarsson [80] and Onida et al. [22].

In this section we will introduce the GW approximation which is systematically derived using many-body perturbation theory. Thereby, Coulomb-interaction-induced dynamically screened exchange correlation effects are taken into account yielding, for instance, strongly improved band gaps in the case of semiconductors. This is the major advantage over the Hartree-Fock approximation. Especially in two-dimensional systems this sophisticated treatment of the Coulomb interaction is of prime importance. On one side these interactions are quite strong in materials with reduced dimensionality (due to a reduced screening) on the other side they are screened in quite a specific way (see section 3.3 for more details). Thus, a mean-field description of the Coulomb interaction (as used in density functional theory) or the neglect of screening effects are crude approximations which are overcome by using the GW approximation.

Since the GW approximation is formulated using a many-body perturbation theory (MBPT) framework we will briefly introduce the most important quantities and discuss Hedin’s famous set of equations and the corresponding GW and associated approximations afterwards.
Green Function

The central quantity of MBPT is the (time ordered) Green function which is given by

\[ G(\mathbf{r}, \mathbf{r}'; t) = -i \left\langle \Psi^N_0 \left| \hat{T} \left[ \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right] \right| \Psi^N_0 \right\rangle, \tag{2.144} \]

where \( |\Psi^N_0\rangle \) is the \( N \)-electron ground state, \( \hat{T} \) is the time-ordering operator and \( \hat{\psi}(\mathbf{r}, t) \) is a field operator in the Heisenberg picture which annihilates an electron at a position \( \mathbf{r} \) and time \( t \). For \( t' < t \) the Green function \( G(\mathbf{r}, \mathbf{r}'; t) \) measures the probability to find an electron at \( \mathbf{r} \) and \( t \) after an electron is added to the system at \( \mathbf{r}' \) and \( t' \). Since this can be seen as an electron propagation through the many-body system, the Green function is called propagator as well. If \( t' > t \) the Green functions describes the propagation of a hole. During the propagation the particle interacts with the many-body system leading to detailed information about correlation effects rendered in \( G(\mathbf{r}, \mathbf{r}'; t) \).

By inserting the closure relation on the \( \mathcal{P} \) particle space

\[ \sum_i |\Psi^N_{i+1}\rangle \langle \Psi^N_{i+1}| = \mathbb{1}_{N+1} \tag{2.145} \]

in Eq. (2.144) followed by a Fourier transformation to frequency space, \( G(\mathbf{r}, \mathbf{r}', \omega) \) can be expressed in the so-called Lehmann representation\(^{13}\) \[22, 102\]

\[ G(\mathbf{r}, \mathbf{r}', \omega) = \sum_i \frac{\psi^N_{i+1}(\mathbf{r}) \psi^{N+1}_{i+1\ast}(\mathbf{r}')}{\omega - \varepsilon^N_{i+1} + i\eta} + \sum_i \frac{\psi^{N-1}_{i}(\mathbf{r}) \psi^{N-1\ast}_{i}(\mathbf{r}')}{\omega - \varepsilon^{N-1}_{i} - i\eta} \tag{2.146} \]

using the Lehmann amplitudes

\[ \psi^N_{i+1}(\mathbf{r}) = \langle \Psi^N_0 | \hat{\psi}(\mathbf{r}) | \Psi^N_{i+1} \rangle \text{ and } \psi^{N-1}_{i}(\mathbf{r}) = \langle \Psi^N_0 | \hat{\psi}^\dagger(\mathbf{r}) | \Psi^N_{i} \rangle \tag{2.147} \]

and excitation energies

\[ \varepsilon^{N+1}_i = E^{N+1}_i - E^N_0 \text{ and } \varepsilon^{N-1}_i = E^N_0 - E^{N-1}_i. \tag{2.148} \]

Here, we make use of the ground-state energy \( E^N_0 \) of the \( N \)-electron system as well as corresponding energies \( E^{N\pm1}_i \) of excited states of the \( (N \pm 1) \)-electron systems. Utilizing this definition, \( \varepsilon^N_0 \) describes exactly the energy measured by a photoemission experiment mentioned in the introduction to this section. As it can be seen in the Lehmann representation, the Green function exhibits poles at these excitation energies emphasizing its extraordinary role in the description of correlation effects in many-body systems.

\(^{13}\) A small imaginary part \( i\eta \) has to be introduced in order to guarantee convergence of the Fourier transform involved in the definition of the frequency-dependent Green function \[22, 102\].
2.3. Coulomb Interactions

Spectral Function

Like the density of states, we can define a density of excited states which is called 
*spectral function* and is given by ($\mu$ is the chemical potential)\textsuperscript{14}

$$A(r, r', \omega) = - \text{sgn}(\omega - \mu) \frac{1}{\pi} \text{Im} G(r, r', \omega). \quad (2.149)$$

The spectral function is indeed quite important, since it can be measured in experiments (in contrast to the Green function) and includes fundamental details of the correlation effects. In a non-interacting system it reduces to the normal density of states described by a series of $\delta$-functions at the single-particle energies. As soon as interactions and thus correlation effects are introduced, the spectral function becomes

$$A(r, r', \omega) = \sum_i \psi_i^N(r) \psi_i^{N^*}(r') \frac{\Gamma_i}{(\omega - \varepsilon_i)^2 + \Gamma_i^2}, \quad (2.150)$$

which shifts the $\delta$-peaks from the single-particle values to the many-body excitation energies $\varepsilon_i$ and broadens the $\delta$-peaks at the same time\textsuperscript{15}. As long as these shifts and broadening effects are not too strong (e.g. the $\delta$-peak structure is still recognizable) we can describe the problem within the Fermi-liquid theory using *quasiparticles* [22].

Self-Energy, Dyson Equation and Quasiparticle Equation

The *interacting* Green function $G$ as given in Eq. (2.144) is meant to include all Coulomb-interaction-induced correlation effects. Additionally, we can define a *non-interacting* Green function $G_0$

$$G_0(k, \omega) = \frac{1}{\omega - H_0(k)}, \quad (2.151)$$

which is derived from a single-particle Hamiltonian $H_0(k)$ which includes the kinetic term from Eq. (2.32) and the external $v_{\text{ext}}$ as well as the Hartree potential $v_{\text{Hartree}}$ from Eq. (2.35) (but *no* exchange-correlation potential). To connect both Green functions the concept of a self-energy is introduced. The basic idea is that even in an interacting system quasiparticles can be defined as *renormalized* real particles which are dressed by a cloud of virtual electron-hole pairs [22, 29]. The corresponding renormalization is described by the self-energy $\Sigma$ which includes all exchange and correlation effects. It is defined by the *Dyson equation* via the differences of the interacting and non-interacting Green functions,

$$\Sigma(k, \omega) = G_0^{-1}(k, \omega) - G^{-1}(k, \omega) \quad (2.152)$$

\textsuperscript{14}See for instance Ref. [102] for a detailed derivation.

\textsuperscript{15}While the energy shifts are proportional to the real part of the self-energy $\Sigma$ from Eq. (2.152) the broadenings are proportional to the imaginary part of $\Sigma$ [27, 29, 42].
2. Ab Initio Description of Single-Particle and Many-Body Properties of Solids

\[ G = G_0 + G_0 \Sigma G \]

**Figure 2.7.**
The Dyson equation connects the non-interacting Green function \( G_0 \) (single lines) with the interacting one \( G \) (double lines) with the help of the self-energy \( \Sigma \).

in momentum space which becomes

\[
G(r, r', \omega) = G_0(r, r', \omega) + \int d^3r'' \int d^3r''' G_0(r, r'', \omega) \Sigma(r'', r''', \omega) G(r''', r', \omega) \tag{2.153}
\]

in real space as shown Fig. 2.7 in terms of Feynman diagrams. Thus, like the non-interacting function the full Green function becomes

\[
G(k, \omega) = \frac{1}{\omega - H_0(k) - \Sigma(k, \omega)} \tag{2.154}
\]

and the problem is solved as soon as the self-energy is known. In fact, the GW approximation is an approximative description of the self-energy. As we will see in the following, we will gain a correction to the results from DFT with the help of the GW description. To this end, we utilize the *quasiparticle equation* which extends the eigenvalue problem from Eq. (2.34) to include correlation effects due to the Coulomb interaction rendered by the self-energy. The quasiparticle equation is obtained from the *equation of motion* for the full Green function \( G \) [102]

\[
i \frac{\partial}{\partial t} G(r, r', t) = \delta(r - r') \delta(t - t') + H_0(r) G(r, r', t)
- i \int d^3r'' v(r, r'') G^{(2)}(r'', r', r, r''). \tag{2.155}
\]

In this form, the equation of motion for \( G \) couples \( G \) to a two-particle Green function \( G^{(2)} \) and thus generates an infinite series which has to be truncated at some point. This truncation can be done following Hedin using variational differentiations with respect to some external potential resulting in the inclusion of the self-energy and exclusion of higher order Green functions [103, 80, 102]. After some algebra, the equation of motion for a stationary system reads

\[
[\omega - H_0(r)] G(r, r', \omega) - \int d^3r'' \Sigma(r, r'', \omega) G(r'', r', \omega) = \delta(r - r'). \tag{2.156}
\]

By using the Lehmann representation of \( G(r, r', \omega) \) from Eq. (2.146) and after taking the limit \( \omega \to \epsilon_j \) (quasiparticle approximation) the equation of motion yields [102]

\[
H_0(r) \psi_j(r) + \int d^3r' \Sigma(r, r', \epsilon_j) \psi_j(r') = \epsilon_j \psi_j(r). \tag{2.157}
\]
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This *quasiparticle equation* extends the conventional eigenvalue problem of the single-particle Schrödinger equation from Eq. (2.34) to include correlation effects as rendered by the self-energy. Since the self-energy is non-local, non-hermitian and energy dependent, we are dealing here with a non-linear problem (note the \( \varepsilon_j \) dependence of \( \Sigma \)) leading to complex energies \( \varepsilon_j \) and quasiparticle states \( \psi_j(\mathbf{r}) \) which are non-orthogonal. Nonetheless, this quasiparticle equation is quite useful, since it is capable of describing quasiparticle energies directly (in contrast to the corresponding Green function).

**Hedin's Equations and Corresponding Approximations**

Up to now, the self-energy is defined on an abstract level only. In order to calculate it we follow Hedin who introduced the following set of equations \[103\]

\[
\Sigma(12) = i \int G(13)W(1^+4)\Gamma(32; 4)d(34) \tag{2.158}
\]

\[
\Gamma(12; 3) = \delta(12)\delta(13) + \int \frac{\delta \Sigma(12)}{\varepsilon G(45)}G(75)\Gamma(67; 3)d(4567) \tag{2.159}
\]

\[
\Pi(12) = -i \int G(23)G(42)\Gamma(34; 1)d(34) \tag{2.160}
\]

\[
\varepsilon(12) = \delta(12) - \int v(13)\Pi(32)d(3) \tag{2.161}
\]

\[
W(12) = \int v(13)\varepsilon^{-1}(32)d(3). \tag{2.162}
\]

Here, \( v(12) \) describes the bare Coulomb interaction and we use the abbreviations \( 1 = (\mathbf{r}_1, \mathbf{t}_1), \ 1^+ = (\mathbf{r}_1, \mathbf{t}_1 + \eta) \) (\( \eta \) being an infinitesimal positive number) and \( \delta(12) = \delta(\mathbf{r}_1 - \mathbf{r}_2)\delta(t_1 - t_2) \).

The self-energy \( \Sigma \), as the central quantity of interest, is defined by the Green function \( G \), the *screened* Coulomb interaction \( W \) and the *vertex function* \( \Gamma \). In contrast to the discussion of the screened Coulomb interaction from above, the screening of \( W \) involves here the *total* polarization \( \Pi \) (and not \( \Pi^0 \)) which is defined by the RPA bubble (see Fig. 2.5) augmented by the vertex function \( \Gamma \). Since in turn the latter is defined by the self-energy, the Green function and itself, Eqs. (2.158) – (2.159) in combination with the Dyson equation (2.152) define a closed set of equations to calculate \( \Sigma \) or \( G \) *self-consistently* as shown in the left panel of Fig. 2.8.

Starting with a non-interacting Green function \( G_0 \), the vertex \( \Gamma \) has to be calculated which is used afterwards to derive the full polarization \( \Pi \). With the help of \( \Pi \) the fully

---

\[16\] See also the more recent reviews on the *GW* approximation by Aryasetiawan and Gunnarsson [80], Hedin [106] or Onida *et al.* [22] as well as the lecture notes by Friedrich and Schindlmayr [102]. The very first implementation and corresponding calculations (beyond the electron gas) by Hybertsen and Louie and Godby *et al.* can be found in [107] and [82].
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Figure 2.8.: 
Left: Hedin’s self-consistency cycle to calculate the full self-energy from Ref. [104]. The dashed arrow indicates the GW approximation which neglects vertex corrections (with $P = \Pi$). Right: Feynman diagrams corresponding to the definition from Eqs. (2.158) – (2.159) from Ref. [105]. Single (double) lines correspond to the bare (renormalized) electron propagator and single (double) wobbly lines describe the bare (fully screened) Coulomb interaction. The first row depicts the Dyson equation (including the Hartree term) and the following rows describe the vertex, polarization, screened Coulomb interaction and the self-energy, respectively, corresponding to Eqs. (2.158) – (2.159).
2.3. Coulomb Interactions

screened Coulomb interaction is evaluated which is used together with $G$ to define the GWT self-energy as depicted in the last row of the right panel of Fig. 2.8. If a solution to this problem could be found without any further approximation the result would in principle be exact. Unfortunately, this is not feasible for realistic situations. The evaluation of the functional derivative together with the overall complex structure of the corresponding integral in the definition of the vertex function makes its calculation extremely challenging (even with the help of modern supercomputers) and adequate approximations are needed [108, 22]. The most obvious approximation of this kind is to neglect vertex corrections by setting

$$\Gamma(12; 3) = \delta(12)\delta(13),$$

which directly leads to

$$\Sigma_{GW}(12) = iG(12)W(1^+2)$$

$$\Pi_{RPA}(12) = -iG(12)G(21).$$

Now, the self-energy is defined by $G$ and $W$ only which is why this treatment is called the GW approximation. In more detail, we see that due to the neglected vertex the polarization function $\Pi$ reduces to its RPA form as discussed in section 2.3.1 and shown in Fig. 2.5. Hence, the GW approximation is directly connected to the random phase approximation. Within the picture of the self-consistency cycle depicted in the left panel of Fig. 2.8 the GW approximation corresponds to the “shortcut” indicated by the dashed arrow. Thereby, we neglect electron-hole interactions (and thus excitonic effects) as well as higher-order corrections to the polarization and screening resulting, for instance, in poor descriptions of plasmonic satellites [80, 22]. However, spectral features like electronic band widths and band gaps are still strongly improved in comparison to KS-DFT results.

Although the GW approximation already yields a set of equations which can in principle be solved by numerical means (see next section for more details), it is still a formidable task and additional simplifications might be desirable. Indeed, there are further approximations which have extensively been studied and which will be shortly discussed in the following.

A prominent simplification of the GW self-energy was introduced by Hedin himself and is called “Coulomb hole and screened exchange” (COHSEX) [103]. The underlying idea is to divide the total self-energy $\Sigma = iGW$ into an exchange $\Sigma_x = iGv$ and a correlation $\Sigma_{cor} = iGW$ part with $W = W - v$. These parts are approximated afterwards [109]. Formally the static COHSEX approximation can be derived by taking the static limit of the real part of the GW self-energy which results in [107, 110, 109, 111]

$$\Sigma_x \approx \sum_{\text{occ}} \psi_i^\dagger(r)\psi_i^*(r')W(r, r', \omega = 0)$$

51
and

$$\Sigma_{\text{cor}} \approx \Sigma_{\text{COH}}(r, r') = \frac{1}{2}\delta(r - r')\tilde{W}(r, r', \omega = 0).$$

(2.168)

Hence, in the COHSEX approximation the exchange term is approximated by the static screened exchange self-energy, while the correlation part is described by a static Coulomb hole. The first part accounts for quantum mechanical exchange contributions and the latter term describes the classically arising charge hole upon electron removal or addition. From a physical point of view, the dynamical response is replaced by a static screening function. Although it is obvious that an external perturbation can lead to a dynamical response of the system (which is neglected here), it is \textit{a priori} not clear whether this is a crude approximation or not. As shown in Ref. [111] it turns out that the static screened-exchange contribution closely follows the full dynamical one, while the static approximation of the Coulomb-hole term deviates strongly from its frequency-dependent counterpart. Nevertheless, the COHSEX approximation can lead to reasonable values for band widths and gaps, although the latter ones are normally slightly overestimated [22, 109, 111]. Furthermore, in comparison to a full GW calculation the COHSEX approximation is much simpler to handle, since it involves only occupied states and the resulting quasiparticle equation becomes linear. Altogether, the COHSEX self-energy might be an adequate approximation as long as numerical simplicity is needed.

Instead of neglecting just the dynamical properties of the screening, the screening could be neglected completely resulting in

$$\Sigma_{\text{HF}}(12) = iG(12)v(1^+2),$$

(2.169)

which is known as the Hartree-Fock approximation [112, 109]. Here, the bare instead of the screened Coulomb interaction is used. The solution to the resulting self-consistent problem can be found by optimizing a single Slater determinant as an ansatz for the many-body wave function. Hence, it is clear that as soon as the many-body wave function can not be approximated in this way the Hartree-Fock treatment breaks down. Nevertheless, there are examples for which this approximation is adequate and yields quite accurate results concerning \textit{differences in total energies}, although in the most cases band gaps are strongly overestimated due to the lack of screening effects [22, 109].

Finally, it is interesting to note that the quasiparticle equation (2.157) which was derived within a MBPT framework reduces to the Kohn-Sham equation (2.34) from DFT if the self-energy is approximated by the \textit{static} and \textit{local} Kohn-Sham exchange-correlation functional $v_{xc}$ from Eq. (2.35):

$$\Sigma_{\text{DFT}}(12) = v_{xc}(1)\delta(12).$$

(2.170)

Thus, the $GW$ approximation can be seen as a generalization of the KS-DFT scheme introducing dynamical screening processes and the non-locality of the exchange correlation.
### Solving the GW Quasiparticle Equation

Although the quasiparticle ground state $|\Psi^{QP}\rangle$ in a correlated system is in general given by a linear combination of Slater determinants $|\Psi_n\rangle$

$$|\Psi^{QP}\rangle = \sum_n a_n |\Psi_n\rangle,$$  \hspace{1cm} (2.171)

it might be appropriate to approximate it by a single determinant as long as the weights $a_n$ of the other determinants are small enough. Indeed, it turns out that this approximation is often accurate if the DFT Kohn-Sham Slater determinant is used

$$|\Psi^{QP}\rangle \approx |\Psi^{KS}\rangle$$  \hspace{1cm} (2.172)

[81, 107, 113]. The quasiparticle Hamiltonian then reads in terms of the Kohn-Sham single-particle wave functions $\Phi^{KS}_n$ and energies $\varepsilon^{KS}_n$

$$H^{QP}_{mn} = \langle \Phi^{KS}_m | H_{KS} + \Sigma(E) - V_{xc} | \Phi^{KS}_n \rangle$$

$$= \varepsilon^{KS}_m \delta_{mn} + \langle \Phi^{KS}_m | \Sigma(E) - V_{xc} | \Phi^{KS}_n \rangle. \hspace{1cm} (2.173)$$

Detailed analysis of the introduced \textit{GW} corrections to the diagonal and off-diagonal elements shows that the second-order corrections to the resulting quasiparticle energies (from the off-diagonal corrections) are negligible in many cases as long as the quasiparticle energies and the initial KS energies are “close” to each other [114, 108, 115]. Hence, we might not need to perform an additional diagonalization of the quasiparticle Hamiltonian given in Eq. (2.173) and get instead a much simpler correction to the KS energies in the form of

$$E^{QP}_m \approx \varepsilon^{KS}_m + \langle \Phi^{KS}_m | \Sigma(E^{QP}) - V_{xc} | \Phi^{KS}_m \rangle. \hspace{1cm} (2.174)$$

Within this first-order perturbation theory correction to the KS energies we have to account for the KS exchange-correlation potential by subtracting it. Otherwise, we would double count these contributions which are already included in the \textit{GW} self-energy.

To solve this simplified but still non-linear equation the full frequency dependence of the self-energy has in principle to be known. To simplify this situation the self-energy is \textit{linearized} around the KS energies [114, 116, 117, 102]

$$\Sigma(E^{QP}_m) \approx \Sigma(\varepsilon^{KS}_m) + \left. \left( E^{QP}_m - \varepsilon^{KS}_m \right) \frac{\partial \Sigma(E)}{\partial E} \right|_{E=\varepsilon^{KS}_m} \hspace{1cm} (2.175)$$

leading to

$$E^{QP}_m \approx \varepsilon^{KS}_m + Z_m \langle \Phi^{KS}_m | \Sigma(\varepsilon^{KS}_m) - V_{xc} | \Phi^{KS}_m \rangle, \hspace{1cm} (2.176)$$
including the *quasiparticle renormalization factor*

\[ Z_m^{-1} = 1 - \left\langle \Phi_m^{KS} \left\| \frac{\partial \Sigma(E)}{\partial E} \right|_{E=\epsilon_m^{KS}} \Phi_m^{KS} \right\rangle, \quad (2.177) \]

which accounts for the reduced quasiparticle weights \( Z_m < 1 \) due to arising satellite structures away from the quasiparticle resonances [118].

Eq. (2.176) allows to calculate the quasiparticle corrections due to the \( GW \) self-energy solely on the basis of DFT results. This scheme, usually called \( G_0 W_0 \), often yields quite good spectral functions with reliable band gaps [107, 80, 22]. In cases in which \( G_0 W_0 \) calculations do not result in satisfying results, for instance compared to experiments, several types of self-consistency might be introduced. The most simple one would be to iterate Eq. (2.176) by using the resulting quasiparticle energies as new starting points. This partial self-consistency is called \( GW_0 \) since the polarization function and thus the screened Coulomb interaction is not updated during the self-consistency steps. By updating the polarization function as well, one would end up in a fully self-consistent \( GW \) calculation. However, it turns out for exactly solvable models that this treatment results in worse spectroscopic properties in terms of quasiparticle lifetimes, satellite structures and band widths, although total energies might be more accurate [22]. This behavior might result from a poor starting point (namely the DFT calculation) in combination with the neglected vertex corrections in the \( GW \) approximation.

In order to derive a more sophisticated starting point for \( G_0 W_0 \) calculations, van Schilfgaarde et al. introduced a so-called quasiparticle self-consistent \( GW \) (QSGW) scheme to generate an optimal \( H_0 \). The authors aim to minimize the deviation between the mean-field exchange-correlation potential \( V_{xc} \) and the resulting many-body self-energy \( \Sigma \) in the \( G_0 W_0 \) approximation. Therefore, their scheme updates \( V_{xc} \) on the basis of the “hermitianized” \( \Sigma_{G_0 W_0} \) in each iteration step. The updated \( V_{xc} \) is used afterwards to generate a new \( G_0 \) and with it a new \( \Sigma_{G_0 W_0} \). Thus, although the \( G_0 W_0 \) approximation is used within each step the whole scheme can be called a self-consistent \( GW \) calculation. Indeed, they find well reproduced band widths and gaps [119, 120]. Next to this QSGW scheme there are methods which utilize hybrid functionals or LDA+U treatments to gain an optimized starting point for the \( G_0 W_0 \) calculation, although the QSGW approach seems to be more general and independent of parameters.

The inclusion of vertex contributions in order to overcome the \( GW \) approximation and introduce a \( GWT \) treatment can be carried out in different ways which shall not be described here. The interested reader is referred to Ref. [22] and references therein.

**Evaluation of the Self-Energy**

For concrete calculations matrix elements of the self-energy have to be evaluated. This is normally done by decomposing it into an exchange \( \Sigma_x \) and a correlation \( \Sigma_{cor} \) part.
2.3. Coulomb Interactions

(as it was already introduced in the discussion of the COHSEX approximation to the self-energy). In the FLAPW basis the resulting terms are of the following form

\[
\langle \Phi_{nq}^{KS}, | \Sigma_{\text{cor}}(\omega) | \Phi_{nq}^{KS} \rangle = \frac{i}{2\pi} \sum_{k} \sum_{n', \mu, \nu} \sum_{n} M^{\mu \nu}_{n'n}(q, k) \times \int_{-\infty}^{+\infty} d\omega' \frac{\bar{W}_{\mu \nu}(k, \omega')}{\omega + \omega' - E_{n'}^{KS}(q + k) + i\eta \text{sgn}[E_{n'}^{KS}(q + k)]},
\]

(2.178)

where we used the product basis \( \chi_{\mu} \), which is defined by the product of basis functions \( \chi_{\mu} = \phi_{\alpha}^{\mu} \phi_{\beta}^{\mu} \) with \( \mu = \{ \alpha, \beta \} \). Within this basis the matrix elements \( M \) and \( \tilde{M} \) as well as the bare \( v \) and correlated (screened) \( W = W - v \) Coulomb interactions can be defined \([80, 121, 122, 102]\). Since the FLAPW basis set consists of spherical harmonics and plane waves in order to describe the electronic wave functions as close as possible \( \chi_{\mu} \) mixes these functions and the resulting basis is called a mixed product basis. Thereby, effects of the core electrons are completely taken into account. Within the PAW formalism some additional effort is needed to describe these effects \([123]\). However, in both basis sets the self-energy terms are of the form as given in Eq. (2.178) and (2.179) which indicate the basic “bottlenecks” of a \( GW \) calculation. As long as an adequate treatment of the \( q \rightarrow 0 \) behavior of the bare Coulomb interaction is introduced \([124, 121]\), the evaluation of \( \Sigma_{x} \) as defined in Eq. (2.179) does not consume much computational time, since it involves only occupied states and is independent of the frequency. This is different for the evaluation of \( \Sigma_{\text{cor}} \). Here, basically three tasks have to be performed:

1. \( \bar{W}(k, \omega) \) has to be calculated within the RPA which involves the evaluation of the polarization function \( \text{[see Eq. (2.111)]} \) on a finite \( \omega \) mesh using both occupied and empty states within the whole Brillouin zone.

2. With the help of \( \bar{W}(k, \omega) \) and the KS energies the integral in Eq. (2.178) has to be evaluated.

3. The summations over the complete Brillouin zone and all bands (once again occupied and empty ones) have to be performed.

Especially the evaluation of the \( \omega \)-integral can be quite difficult, since the involved integrand has a rich structure with poles at the KS energies. It can be carried out either on imaginary frequencies (in which the integrand becomes very smooth) together with an appropriate analytic continuation afterwards \([122]\) or in real frequencies using a proper contour integration \([125]\). Yet another method to perform these tasks was introduced by Shishkin and Kresse who use Kramers-Kronig or Hilbert transformations.
to calculate the polarization and the self-energy efficiently \cite{123}. In addition, so-called plasmon pole models have been frequently applied in the past to simplify the imaginary component of the dielectric function (as needed in the first step) allowing for an analytical evaluation of the frequency integral \cite{126, 127}. Although this is a quite tempting approach, it approximates the dielectric function and thus the screened Coulomb interaction at the cost of additional parameters. Indeed, there are further and more recent attempts to accelerate the evaluation of the screened Coulomb interaction and/or the frequency integral by reducing the number of involved states or the number of involved frequency points. The amount of needed bands can be reduced drastically within the so-called Sternheimer approach, which adopts ideas from the density functional perturbation theory (as discussed in section 2.4.2) \cite{128, 129}. Within this approach only occupied states are needed to evaluate the screened Coulomb interaction without any further approximations. Furthermore, Giustino et al. were able to show that the non-interacting Green function can be evaluated in a similar spirit \cite{130, 131}. Hence, full GW calculations can be carried out by utilizing occupied states only \cite{132}. The number of required frequencies grid points can be reduced by using sophisticated $\omega$ meshes. In combination with elaborated back and forth Fourier transformations, this leads to an efficient algorithm to calculate the RPA correlation energy as shown by Kaltak et al. \cite{133, 134} which can be adopted to evaluate the GW self-energy as well.

**Obtaining the GW Band Structure**

At the end of a GW calculation we derive corrections to the initial (Kohn-Sham) energies for a single $q$-point in reciprocal space. This data might be used to study the Coulomb-interaction-induced corrections to the band gap or to the band width at special points. To derive the corresponding renormalizations for the complete Brillouin zone GW calculations have to be repeated for a whole $q$-point mesh. Depending on the mesh discretization this can take a lot of computational time and might be even unfeasible. To circumvent computational problems of this kind, we will perform GW calculations on relatively small $q$-grids and interpolate the resulting data using Wannier functions afterwards as outlined in section 2.2.2. This procedure corresponds to the construction of GW based tight-binding models which can be diagonalized at arbitrary $q$-points. Although we loose any information about the quasiparticle peak broadenings or lifetimes $\tau$, we get their renormalized eigenenergies over the whole Brillouin zone which can be used, for instance, to obtain the GW band structure. Indeed, the approximation of infinite life times is reasonable for low temperatures and for states in the near of the Fermi energy. In more detail, it can be shown that the quasiparticle lifetime $\tau \propto \mathrm{Im} \Sigma$ is in the GW approximation essentially given by the
imaginary part of the screened interaction \( W \) yielding [29]

\[
\frac{1}{\tau_q} \varepsilon^2(q).
\] (2.180)

Here, the energy \( \varepsilon(q) \) is measured with respect to the Fermi energy. Thus, the inverse lifetime vanishes for small energies around the Fermi energy.

2.4. Lattice Dynamics

The subsequent introduction to the dynamic properties of the lattice closely follows the review by Baroni et al. [135] and is complemented by lecture notes from Heid [136].

Now that we have seen how electronic dispersions from DFT and \( GW \) calculations can be obtained and used to derive the electronic ingredients to our material-realistic model, we turn to the dynamic properties of the lattice. This includes the determination of phononic dispersions and of the coupling between electrons and phonons. To this end, we briefly introduce the classical description of lattice vibrations in section 2.4.1 before we introduce in section 2.4.2 the so-called density functional perturbation theory which is based on a combination of linear-response and density functional theory. Afterwards we discuss in some detail the electron-phonon coupling (section 2.4.3) as well as the phonon self-energy (section 2.4.4) which lays the foundation for the introduction of the Eliashberg theory to describe conventional superconductivity in section 2.4.5.

2.4.1. Classical Description

Applying the Born-Oppenheimer approximation tells us that the electronic ground-state energy \( E_0 \) depends only parametrically on the exact ion positions [see Eq. (2.7)]. Thus, we are able to minimize the total ground-state energy in dependence of these positions in order to find the optimal geometric structure (which is called relaxation). On the other hand, this allows for a detailed study of the ground-state energy response to small perturbations of the ionic positions. Since a phonon is nothing else than a periodic perturbation of this kind, we should be able to gain deep insights into the lattice dynamics properties by investigating the arising effects. To this end, we introduce a small displacement \( u_{sl} \) which modifies the nuclear equilibrium position \( R^0_{sl} = R_l + \tau_s \) of the atom \( s \) at \( \tau_s \) within the unit cell \( l \) at \( R_l \) via

\[
R_I = R^0_{sl} + u_{sl},
\] (2.181)

where we used the shorthand \( I = \{s,l\} \). A corresponding expansion of the electronic ground-state energy \( E_0(R) \) around \( u_I = 0 \) yields

\[
E_0(R) = E_0(R^0) \left[ \sum_{Ia} \frac{\partial^2 E_0(R)}{\partial R_{Ia}} \frac{\partial^2 E_0(R)}{\partial R_{Ja}} \right] R^0 \left[ u_{Ia} u_{Ja} + \frac{1}{2} \sum_{IaJb} \frac{\partial^2 E_0(R)}{\partial R_{Ia} \partial R_{Ja}} \right] R^0 \left[ u_{Ia} u_{Ja} + \ldots \right].
\] (2.182)
Within classical mechanics the first order derivative can be interpreted as the negative force acting on atom $I$ in the Cartesian direction $\alpha$ in the lattice equilibrium

$$F_{I\alpha} = -\frac{\partial E_0(R)}{\partial u_{I\alpha}} = -\Phi^\alpha_{\alpha}(l) = 0,$$  

(2.183)

which has to vanish by definition. The second derivative corresponds to the force acting on an atom $J$ in direction $\beta$ when another atom $I$ is displaced in direction $\alpha$

$$F_{J\beta} = -\sum_{I\alpha} \frac{\varepsilon^2 E_0(R)}{\partial u_{I\alpha} \partial u_{J\beta}} u_{I\alpha} = -\sum_{I\alpha} \Phi^{\alpha\beta}_{\alpha\beta}(l, m) u_{I\alpha}.$$  

(2.184)

Here, we defined the harmonic force constants $\Phi^{\alpha\beta}_{\alpha\beta}(l, m)$ which do not have to vanish in the lattice equilibrium\(^{17}\). These quantities can be seen as the equivalent to mechanic spring constants describing the linear relationship between the displacement and the arising force between two atoms. Within a translational invariant solid state body $\Phi^{\alpha\beta}_{\alpha\beta}(l, m)$ depends on the difference $R = R_l - R_m$ only

$$\Phi^{\alpha\beta}_{\alpha\beta}(l, m) = \Phi^{\alpha\beta}_{\alpha\beta}(R),$$  

(2.185)

allowing for a corresponding Fourier transformation

$$\Phi^{\alpha\beta}_{\alpha\beta}(q) = \frac{1}{N} \sum_R \Phi^{\alpha\beta}_{\alpha\beta}(R) e^{-i q R},$$  

(2.186)

which can be used to define the dynamical matrix $D(q)$ with the matrix elements

$$D^{\alpha\beta}_{\alpha\beta}(q) = \frac{1}{\sqrt{M_s M_t}} \Phi^{\alpha\beta}_{\alpha\beta}(q).$$  

(2.187)

The perturbation $\mathbf{u}_{sl}$ is now of the form $u^\alpha_{sl} = u^\alpha_{sl}(q) e^{i q R_l}$ describing periodic ionic displacements. The diagonalization of the dynamical matrix yields the phononic dispersion $\omega_{\nu}(q)$ and the corresponding eigenvectors (or polarization vectors) $e_{\nu}(q)$ of the phonon modes $\nu$

$$\sum_{I\beta} D^{\alpha\beta}_{\alpha\beta}(q) e_{\nu}^{i\beta}(q) = \omega^2_{\nu}(q) e^{i\alpha\beta}_{\nu}(q).$$  

(2.188)

With $r$ atoms per unit cell and in a three-dimensional space, we end up with $3r$ eigenmodes which can be separated into $3r$ acoustic and $3(r - 1)$ optical branches.

Up to now, we applied nothing else than classical mechanics which allows for a quite simple interpretation of the involved physics: Given the before-mentioned force constants, each ionic nucleus can be seen as a point mass $M_l$ connected by classical springs to its neighbours. Hence, as soon as the harmonic force constants $\Phi^{\alpha\beta}_{\alpha\beta}(q)$ are known, all lattice dynamics properties can be easily derived in the harmonic approximation.

\(^{17}\)In a solid-state material with a purely harmonic potential these elements have to be non-zero, otherwise there would be no lattice structure.
2.4. Lattice Dynamics

2.4.2. Density Functional Perturbation Theory

We have seen in the previous section that the dynamic properties of the lattice can be approximated by the harmonic constants $\Phi_{\alpha\beta}^{st}(q)$ which are defined by derivatives of the electronic ground-state energy. Therefore, we are able to calculate these properties by means of DFT. There are basically three classes of computational strategies which can be applied to obtain phononic properties: Molecular dynamics, frozen-phonon approaches and density functional perturbation theory (DFPT). All of these schemes come with some advantages and disadvantages. For instance, molecular dynamics calculations and frozen-phonon approaches can be used to investigate anharmonic properties like temperature effects in form of thermal expansion or thermal conductivity due to phonon-phonon scattering. However, these approaches rely on super-cell calculations which can include several hundred atoms and are therefore hard to perform by numerical means. On the other side, DFPT involves primitive unit cells only, but can not be utilized to consider temperature or anharmonic\(^{18}\) effects. Since the latter effects are not of special interest for the systems under consideration in this thesis and since we need a method which allows us to systematically tune parameters like the doping level, we will make use of DFPT here. The following paragraphs therefore introduce the most important DFPT basics, while the interested reader is referred to Ref. [138] and Ref. [135] and references therein for more details on the other approaches.

Hellmann-Feynman Theorem, Energy Derivatives and Forces in DFT

In the context of ab initio calculations for materials or molecules the evaluation of forces is of fundamental interest. For instance, its evaluation allows for a prediction of the ground-state geometry which sensitively defines the material’s or molecule’s properties. In fact, every state of the art ab initio package implements an evaluation scheme for so-called Hellmann-Feynman forces based on the Hellmann-Feynman theorem\(^{19}\) which states that the first order derivative of an eigenvalue $E_\lambda$ with respect to an external parameter $\lambda$ is given by the expectation value

$$\frac{\partial E_\lambda}{\partial \lambda} = \left\langle \Psi_\lambda \left| \frac{\partial H_\lambda}{\partial \lambda} \right| \Psi_\lambda \right\rangle,$$

(2.189)

if the eigenvalue is given by $E_\lambda \Psi_\lambda = H_\lambda \Psi_\lambda$. Hence, in order to calculate the force acting on an individual atom the Hellmann-Feynman theorem is applied to the solid-

\(^{18}\) The so-called $(2n+1)$-theorem states that the $(2n+1)$-th order derivative of the ground-state energy can be derived from the first $n$ derivatives of the eigenfunctions [137]. In the following we will see, that DFPT derives the latter up to $n = 1$ order. Hence, DFPT can actually be used to study first-order anharmonic effects which trace back to third order derivatives of the ground-state energy.
2. Ab Initio Description of Single-Particle and Many-Body Properties of Solids

State electronic Hamiltonian $H_e$ from Eq. (2.6) yielding

$$F_I = - \langle \Psi(R) \bigg| \frac{\partial H_e(R)}{\partial R_j} \bigg| \Psi(R) \rangle = - \int d^3r \ n(R, r) \frac{\partial V_{ei}(R, r)}{\partial R_j} - \frac{\partial V_{ii}(R)}{\partial R_i}. \quad (2.190)$$

The second derivative (to obtain harmonic force constants) can be calculated directly

$$\frac{\partial F_I}{\partial R_j} = - \frac{\partial^2 E(R)}{\partial R_j \partial R_j} = - \int d^3r \ \frac{\partial n(R, r)}{\partial R_j} \frac{\partial V_{ei}(R, r)}{\partial R_i} - \int d^3r \ n(R, r) \frac{\partial^2 V_{ei}(R, r)}{\partial R_i \partial R_j} - \frac{\partial^2 V_{ii}(R)}{\partial R_i \partial R_j}. \quad (2.191)$$

While the derivatives of the electron-ion and the ion-ion potential can be performed easily (since the potentials depend only parametrically on $R$), the derivative of the charge density with respect to changes in the ionic positions has to be calculated within linear response theory based on DFT. To this end, there are two approaches, namely the dielectric and the self-consistent method. The former describes the density’s response to the perturbation in terms of the dielectric matrix $\varepsilon$ which involves a lot of empty states (as discussed in section 2.3.1) and Fourier components as well as an inversion of $\varepsilon$ [140, 141, 138]. The latter was independently introduced by Zein et al. [142, 143] and Baroni et al. [144, 145] and leads to the modern formulation of DFPT which does not suffer from the obstacles of the dielectric approach.

Self-Consistent Formulation of Density Functional Perturbation Theory

Within a DFT-based formulation we need to consider the auxiliary effective Kohn-Sham potential $V_{KS}$ from Eq. (2.35), which involves the external potential $V_{ext}$ defined by the ion-ion and electron-ion potential. Hence, we need to evaluate

$$\hat{\partial}_{R_i} E(R) = - F_I = \int d^3r \ n(R, r) \ \hat{\partial}_{R_i} v_{KS}(r) \quad (2.192)$$

and

$$\hat{\partial}_{R_i, R_j} E(R) = - \hat{\partial}_{R_j} F_I = \int d^3r \ n(R, r) \ \hat{\partial}^2_{R_i, R_j} v_{KS}(r) + \int d^3r \ \hat{\partial}_{R_j} n(R, r) \ \hat{\partial}_{R_i} v_{KS}(r), \quad (2.193)$$

where we introduced the abbreviations

$$\hat{\partial}_R f = \frac{\partial f}{\partial R} \quad \text{and} \quad \hat{\partial}^2_R f = \frac{\partial^2 f}{\partial R^2}. \quad (2.194)$$

As already stated above, the main task is to derive the electronic ground-state density response to the periodic perturbation of the ionic positions. To this end, we utilize the definition of the density from Eq. (2.28) which leads to

$$\hat{\partial} n(r) = 2 \ \sum_{\varepsilon_n < E_F} \Phi_n^*(r) \hat{\partial} \Phi_n(r). \quad (2.195)$$
Within first order perturbation theory the perturbed wave function \( \tilde{\Phi}(\mathbf{r}) \) is given by
\[
\tilde{\Phi}_n(\mathbf{r}) = \sum_{m \neq n} \Phi_m(\mathbf{r}) \frac{\langle \Phi_m | \tilde{v}_{\text{KS}} | \Phi_n \rangle}{E_n - E_m},
\]
where \( m \) labels all states (occupied and unoccupied). By applying this term to the definition of the perturbed density
\[
\tilde{n}(\mathbf{r}) = 2 \sum_{\varepsilon_n < E_F \neq m} \Phi^*_n(\mathbf{r}) \Phi_m(\mathbf{r}) \frac{\langle \Phi_m | \tilde{v}_{\text{KS}} | \Phi_n \rangle}{E_n - E_m},
\]
we find that \( m \) becomes restricted to unoccupied states\(^{19}\). By labeling the occupied states as valence (\( v \)) and the unoccupied ones as conduction (\( c \)) states, we end up with
\[
\tilde{n}(\mathbf{r}) = 2 \sum_v \Phi^*_v(\mathbf{r}) \tilde{\Phi}_v(\mathbf{r})
\]
with
\[
|\tilde{\Phi}_v\rangle = \sum_c |\Phi_c\rangle \frac{\langle \Phi_c | \tilde{v}_{\text{KS}} | \Phi_v \rangle}{E_v - E_c}
\]
\[
= P_v \frac{\tilde{v}_{\text{KS}} |\Phi_v\rangle}{E_v - H_{\text{KS}}},
\]
where we used the projector \( P_v = \sum_c |\Phi_c\rangle \langle \Phi_c | \) and the Kohn-Sham Hamiltonian \( H_{\text{KS}} \) from Eq. (2.24). This equation can be rearranged to the Sternheimer equation
\[
(E_v - H_{\text{KS}}) |\tilde{\Phi}_v\rangle = P_v \tilde{v}_{\text{KS}} |\Phi_v\rangle = (1 - P_v) \tilde{v}_{\text{KS}} |\Phi_v\rangle
\]
which acts solely on the subspace of occupied states. Together with the response of the Kohn-Sham potential
\[
\tilde{v}_{\text{KS}}(\mathbf{r}) = \tilde{v}_{\text{ext}}(\mathbf{r}) + e^2 \int d^3r' \frac{\tilde{n}(\mathbf{r}') + \tilde{v}_{\text{xc}}}{|\mathbf{r} - \mathbf{r}'|} \frac{|\tilde{n}|_{n=n(\mathbf{r})}}{n(\mathbf{r})}
\]
the equations (2.198), (2.200) and (2.201) define the self-consistent formulation of the DFPT to calculate the perturbed electronic ground-state density \( \tilde{n} \) which can be used to readily calculate the lattice dynamics.

More details, e.g. concerning the implementation in modern DFT codes or extensions to spin and relativistic effects, can be found in Refs. [138, 135, 136, 146]. Specifically, the details on the implementation of DFPT for periodic lattices reveals that all \( \mathbf{q} \)-dependent perturbations are entirely decoupled [135, 136]. Thus, phonon dispersions and, as we will show in following, electron-phonon coupling matrix elements can be calculated for specific points or along given paths.

\(^{19}\)Due to the fact that Eq. (2.195) restricts \( n \) to occupied states all \( n/m \) combinations from the subset of the valence bands indices would annihilate each other.
2. Ab Initio Description of Single-Particle and Many-Body Properties of Solids

Figure 2.9:
Renormalization of the electron-phonon vertex. Bare vertices are indicated as solid dots, electron and phonon propagators by solid and curly and Coulomb interactions by wobbly lines. (a) shows the diagrams which contribute to the renormalization of the electron-phonon vertex: the bare vertex, electronic screening (here in the random phase approximation) and phononic screening (here just the lowest order). (b) depicts the phononic contributions to the renormalization of the electron-phonon vertex according to Migdal’s theorem [147]. The diagrams are taken from Ref. [29].

2.4.3. Electron-Phonon Coupling
Within the DFPT the electron-phonon coupling matrix elements are given by transitions between unperturbed Kohn-Sham states upon changes in the potential due to an ionic perturbation

\[ d_{knn'}^{\alpha s} = \langle \Phi_{n'k+q} | \hat{c}_{\nu}(q) \hat{v}_{KS} | \Phi_{nk} \rangle. \]  

These matrix elements can readily be evaluated as soon as self-consistency within a DFPT calculation for a given perturbation \( u_{\alpha}^{\alpha}(q) \) has been reached, since the quantities \( \hat{c}_{\nu}(q) \hat{V}_{KS} | \Phi_{nk} \rangle \) are determined as byproducts of the solution to the Sternheimer equation (2.200). With the help of the resulting polarization vectors \( e_{\nu}(q) \) and phonon dispersions \( \omega_{\nu}(q) \) these matrix elements can be transformed to the so-called normal-mode representation yielding

\[ g_{knn'}^{\nu \nu'} = \sum_{\alpha} d_{knn'}^{\nu \alpha} \frac{e_{\nu}(q)}{\sqrt{2M_\nu \omega_{\nu}(q)}}. \]  

The resulting matrix elements can be interpreted as scattering amplitudes between the electronic states \( \Phi_{nk} \) and \( \Phi_{n'k+q} \) by absorbing or emitting a phonon with momentum \( \pm q \) and mode \( \nu \) (hence, momentum conservation has already been applied) as shown in form of Feynman diagrams in Fig. 2.9 (a).

At this point, it is important to note that these electron-phonon vertices are in principle renormalized due to both, the electronic and phononic systems. The electronic contributions to the renormalization arise upon screening effects to the phonon propagator described, for instance, in the random phase approximation as shown in Fig.
2.4. Lattice Dynamics

Figure 2.10.: Dyson equation for the RPA screened phonon propagator taken from Ref. [29]. Single (double) lines correspond to the bare (renormalized) propagators and dots describe the bare electron-phonon vertex.

2.9 (a). Phononic contributions would arise due to processes like indicated in Fig. 2.9 (b). However, Migdal has shown that corresponding renormalization effects are of the order $O(p^a)$ (even for diagrams of higher order) and can thus be neglected [147]. The remaining electronic screening effects are incorporated in DFPT due to the variation of the electronic density $\tilde{\phi}n$ within the definition of $\tilde{\phi}_{\text{KS}}$ which results from virtual excitations of the electrons upon the applied perturbation. In contrast, the bare vertex is derived from

$$d^{(0)q_s}_{knm'} = \langle \Phi_{n'k+q} | \tilde{\phi}_{uv}(q) v_{\text{ext}} | \Phi_{nk} \rangle,$$  

which excludes the response of the Hartree and exchange potentials and thus neglects any electronic screening.

2.4.4. Phonon Self-Energy

We have already discussed the phononic propagator, e.g. in terms of Feynman diagrams in Fig. 2.9, but we still lack a corresponding mathematical definition. Like in the electronic case, the unrenormalized or bare phonon propagator can be given as the time-ordered expectation value

$$D_0(q\nu, t - t') = -i \langle \Psi^N_0 | \hat{T} \left[ \hat{A}_{q\nu}(t) \hat{A}_{-q\nu}(t') \right] | \Psi^N_0 \rangle$$  

using the operator $\hat{A}_{q\nu} = \hat{b}_{q\nu} + \hat{b}_{-q\nu}^\dagger$ in the time domain and by

$$D_0(q\nu, \omega) = \int_{-\infty}^{+\infty} dt D_0(q\nu, t) e^{i\omega t} = \frac{2\Omega_{q\nu}}{\omega^2 - \Omega_{q\nu}^2 + i\delta}$$  

in the frequency domain [27, 29]. Here, we used the bare phononic dispersion $\Omega_{q\nu}$ and a finite broadening $\delta$ ($\omega$ are real frequencies). The interacting phonon propagator can be defined by the Dyson equation

$$D(q\nu, \omega) = \left[ D_0(q\nu, \omega)^{-1} - \Sigma_{ph}(q, \omega) \right]^{-1} = \frac{2\Omega_{q\nu}}{\omega^2 - \Omega_{q\nu}^2 - 2\Omega_{q\nu}\Sigma_{ph}(q, \omega)}$$  

63
using the phonon self-energy $\Sigma_{\text{ph}}$. As depicted in Fig. 2.10, the latter can be described using the random phase approximation after applying Migdal’s theorem (see [29] for more details). As in the case of the electron propagator the self-energy introduces a shift

$$\omega_{q\nu}^2 = \Omega_{q\nu}^2 + 2\Omega_{q\nu} \Re\{\Sigma_{\text{ph}}(q, \omega)\} \quad (2.208)$$

and a broadening

$$\gamma_{q\nu} = \frac{\Omega_{q\nu}}{\omega_{q\nu}} \Im\{\Sigma_{\text{ph}}(q, \omega)\} \quad (2.209)$$

of the quasiparticle peaks in dependence of the real and imaginary part of $\Sigma_{\text{ph}}$ [148]. While the shifts are properly taken into account (on the level of the RPA) within the DFPT, the broadenings are not [136]. Nevertheless, as shown by Allen [148] the broadenings can be approximated for metals in the limit $T \to 0$ by

$$\gamma_{q\nu} = 2\pi\omega_{q\nu} \frac{1}{N_k} \sum_{k_{\text{nn}}'} |g_{k_{\text{nn}}'}|^2 \delta(E_{kn} - E_F) \delta(E_{k+q_{\nu}} - E_F) \quad (2.210)$$

and we get a full description of the renormalized phononic propagators from a self-consistent DFPT calculation.

### 2.4.5. Conventional Superconductivity Within Eliashberg Theory

In the following we will give a very brief introduction to the most important equations of the Migdal-Eliashberg theory closely following Ref. [149]. The interested reader is referred to the review articles by Allen and Mitrović [150] and Marsiglio and Carbotte [151] as well as to the original articles by Eliashberg [152, 153] and Scalapino et al. [154].

Having introduced and discussed electronic and phononic dispersions and electron-phonon as well as electron-electron interactions, it is natural to ask for superconducting properties. As shown in the seminal work by Bardeen, Cooper and Schrieffer (BCS) an effective attractive interaction between electrons with opposite spin and momentum (Cooper pairs) can be provided by the electron-phonon interaction leading to a superconducting ground state characterized by a finite energy gap $\Delta$ in the quasiparticle spectrum for temperatures below a certain critical threshold $T_c$ [155]. This BCS theory provided the basis for many others who extended the weak coupling BCS theory to a general strong coupling formalism utilizing Green-function techniques as introduced by Gor’kov and Nambu [156, 157].
2.4. Lattice Dynamics

We begin with the introduction of the two-component field operator as used by Nambu and Gor’kov [156, 157]

\[ \Psi_k = \left( \begin{array}{c} c_{k_1} \\ c_{-k_1}^\dagger \end{array} \right), \]  

(2.211)

where \( c_{k_1} \) (\( c_{-k_1} \)) annihilates (creates) an electron with momentum \( k (-k) \) and spin up (down). Using this generalized field operator the Green function

\[ \hat{G}(k, i\omega_n) = T \sum_{\omega_n} e^{i\omega_n \tau} \hat{G}(k, \tau) = -T \sum_{\omega_n} e^{i\omega_n \tau} \left< T \tau \Psi_k(\tau) \Psi_k^\dagger(0) \right> \]

(2.212)

becomes a 2 \times 2 matrix

\[ \hat{G}(k, i\omega_n) = \left( \begin{array}{cc} G(k, i\omega_n) & F(k, i\omega_n) \\ F^*(k, i\omega_n) & -G(-k, -i\omega_n) \end{array} \right) \]

(2.213)

with normal Green functions \( G \) on the diagonal and anomalous Green functions \( F \) on the off-diagonal which describe the propagation of Cooper pairs. As usual, \( T \tau \) is the time-ordering operator in imaginary times \( \tau \), \( T \) is the temperature and \( i\omega_n \) are fermionic Matsubara frequencies\(^{20} \). In the normal state \( \hat{G} \) becomes diagonal while the off-diagonal terms arise for \( T < T_c \) only. To obtain \( \hat{G} \) we utilize Dyson’s equation within the two-component basis

\[ \hat{G}^{-1}(k, i\omega_n) = \hat{G}_0^{-1}(k, i\omega_n) - \hat{\Sigma}(k, i\omega_n) \]

(2.214)

and define \( \hat{G}_0 \) with the help of the \( GW \)-renormalized Kohn-Sham energies \( E_k \)

\[ \hat{G}_0^{-1}(k, i\omega_n) = i\omega_n \hat{\tau}_0 - E_k \hat{\tau}_3. \]

(2.215)

To solve this equation we need an approximation for the self-energy. Within the Migdal-Eliashberg theory it is approximated by a sum of electron-electron \( \hat{\Sigma}_{ee} \) and electron-phonon \( \hat{\Sigma}_{ep} \) contributions \( \hat{\Sigma} = \hat{\Sigma}_{ee} + \hat{\Sigma}_{ep} \), which are given by

\[ \hat{\Sigma}_{ee}(k, i\omega_n) = -T \sum_{k,k',\omega_n'} \hat{\tau}_3 \hat{G}^{ee}(k', i\omega_n') \hat{\tau}_3 W(k - k') \]

(2.216)

\[ \hat{\Sigma}_{ep}(k, i\omega_n) = -T \sum_{k,k',\omega_n'} \hat{\tau}_3 \hat{G}(k', i\omega_n') \hat{\tau}_3 \sum_{\nu} |g_{kk'}^\nu|^2 D_\nu(k - k', i\omega_n - i\omega_n'). \]

(2.217)

\(^{20}\) Matsubara frequencies are naturally introduced in finite-temperature theories. They form a discrete and temperature-dependent set of frequencies and are given for electrons by \( \omega_n = (2\pi + 1)/\beta \) with \( \beta = 1/(k_bT) \) being the inverse temperature defined by the Boltzmann constant \( k_b \) and the real temperature \( T \).
Here, we used the *dressed* phonon propagator $D_{\nu}(q, i\omega_n)$ from Eq. (2.207) and the Pauli matrices $\hat{\tau}_i$. The definition of $\Sigma_{ee}$ involves the *static* screened Coulomb interaction $W(q)$ and the *off-diagonal* terms of the renormalized Green function. Indeed, this approximation to $\Sigma_{ee}$ is nothing else than the (static) $GW$ approximation for the *anomalous* Green functions $F$ (the normal Green functions on the diagonal are meant to be renormalized). Next to the $GW$ approximation, Migdal’s approximation to the electron-phonon vertex is applied and the total self-energy is chosen to be band diagonal.

It is convenient to decompose the resulting self-energy as

$$\hat{\Sigma}(k, i\omega_n) = i\omega_n [1 - Z(k, i\omega_n)] \hat{\tau}_0 + \chi(k, i\omega_n) \hat{\tau}_1 + \phi(k, i\omega_n) \hat{\tau}_1 + \tilde{\phi}(k, i\omega_n) \hat{\tau}_2, \quad (2.219)$$

where $Z$ describes the so-called *mass renormalization function*, $\chi$ an *energy shift*, $\phi$ the *order parameter* and $\tilde{\phi}$ is set to zero (choosing a proper gauge, see [149]). The resulting superconducting gap is given by

$$\Delta(k, i\omega_n) = \frac{\phi(k, i\omega_n)}{Z(k, i\omega_n)}. \quad (2.220)$$

Using these definitions within Eq. (2.214) the *Eliashberg equations* defining $Z$ and $\phi$ can be obtained which have to be solved self-consistently [149]:

$$Z(k, i\omega_n) = 1 + \frac{\pi T}{\omega_n} \sum_{k' n'} \frac{\delta(E_k)}{N(E_F) \sqrt{\omega^2_n + \Delta^2(k', i\omega)\delta(k, k', n - n')}} \lambda(k, k', n - n'), \quad (2.221)$$

$$\phi(k, i\omega_n) = \frac{\pi T}{N(E_F)} \delta(E_k) \sum_{k' n'} \frac{\Delta(k', i\omega_{n'})}{\sqrt{\omega^2_{n'} + \Delta^2(k', i\omega_{n'})}} [\lambda(k, k', n - n') - N(E_F)W(k-k')] .$$

This representation of the *anisotropic* Eliashberg equations is derived under the assumption that the superconducting Cooper pairing is taking place solely close to the Fermi energy. Under this assumption the energy shift $\chi$ vanishes and the $\delta$ functions in Eqs. (2.221) arise. $N(E_F)$ describes the density of states at the Fermi energy and $\lambda$ involves the electron-phonon couplings

$$\lambda(k, k', n - n') = \int_0^\infty d\omega \frac{2\omega}{(\omega_n - \omega_{n'})^2 + \omega^2} \alpha^2 F(k, k', \omega) \quad (2.222)$$

by utilizing the anisotropic *Eliashberg spectral function*

$$\alpha^2 F(k, k', \omega) = N(E_F) \sum_{\nu} |g_{kk'}^{\nu}|^2 \delta(\omega - \omega_{k-k'}). \quad (2.223)$$

The Pauli matrices are given by:

$$\hat{\tau}_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \hat{\tau}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\tau}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\tau}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.218)$$
2.4. Lattice Dynamics

Note that due to the band-diagonal approximation of the self-energy and the restriction to small energies around the Fermi level the electronic band indices are neglected.

These equations can in principle be solved self-consistently using electron-phonon matrix elements and phonon dispersions from density functional perturbation theory and electronic dispersions and Coulomb interactions from \(GW\) calculations. Together with appropriate numerical schemes to perform the analytical continuation (like the Padé approximation \([158, 159]\)), the superconducting gap can be calculated in dependence of \(T\) for real frequencies. However, as shown in Refs. \([149, 160]\) the dispersions and couplings need to be known on extremely fine \(k\) and \(q\) grids (20 to 80 points in each \(k_\alpha\) and \(q_\alpha\) direction). Although in principle all ingredients can be interpolated to very fine grids using appropriate back-and-forth Fourier transformations and Wannier interpolations\(^{22}\), we will apply an approximate solution to the Eliashberg equations as given by Allen and Dynes. Like McMillan \([162]\), Allen and Dynes \([163]\) solved the Eliashberg equations numerically\(^{23}\) for a variety of effective electron-phonon couplings \(\lambda\) and so-called *Coulomb pseudo potentials* \(\mu^*\) and fitted the resulting data to analytically deduced formulas for the critical temperature \(T_c\). The main results by Allen and Dynes is

\[
T_c = \frac{\omega_{\log}}{1.2} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda(1 - 0.62\mu^*) - \mu^*} \right],
\]

where

\[
\lambda = 2 \int d\omega \frac{\alpha^2 F(\omega)}{\omega}
\]

is the averaged electron-phonon coupling constant and

\[
\omega_{\log} = \exp \left[ \frac{2}{\lambda} \int d\omega \alpha^2 F(\omega) \frac{\log(\omega)}{\omega} \right]
\]

is the logarithmic averaged typical phonon frequency using the *isotropic* Eliashberg

---

\(^{22}\) The electronic dispersion and the Coulomb-interaction matrix elements can be evaluated for arbitrary momenta using the Wannier interpolation scheme as introduced in section 2.2.2 and the analytic formulas derived in section 4.2, respectively. The same holds for the phononic band structure as soon as the spring constants \(\Phi_{st}(R)\) in real-space are known [see Eqs. (2.185) to (2.188)]. In the case of electron-phonon matrix elements there exist comparable Wannier interpolation schemes which are described in Refs. \([161, 149]\) but not used throughout this thesis.

\(^{23}\) In more detail they solved the *isotropic* Eliashberg equations for phononic properties which are easy to handle.
function

\[ \alpha^2 F(\omega) = \frac{1}{N_k^2} \sum_{kk'} \alpha^2 F(k,k') \delta(E_{kn}) \delta(E_{k+q\nu}) \]

\[ = \frac{1}{N_k^2} \sum_{knn'} \sum_{q\nu} |g_{knn'}^{q\nu}|^2 \delta(\omega - \omega_{q\nu}) \delta(E_{kn}) \delta(E_{k+q\nu}) \]

\[ = \frac{1}{2\pi N(E_F)} \sum_{q\nu} \frac{\delta(\omega - \omega_{q\nu}) \gamma_{q\nu}}{\hbar \omega_{q\nu}}. \]

The pseudo Coulomb potential \( \mu^* \) is given by the Morel-Anderson potential

\[ \mu^* = \frac{\mu}{1 + \mu \ln(E_F/\omega_c)} \]

which is the retarded version of the dimensionless Coulomb potential

\[ \mu = N(E_F) \langle W(k-k') \rangle_{FS} \]

\[ = \frac{1}{N(E_F)} \sum_{kk'} W(k-k') \delta(E_k) \delta(E_{k'}) \]

The latter is regularly introduced within the isotropic Eliashberg equations by averaging over states close to the Fermi surface. The retarded version of \( \mu \) has to be used since the Matsubara frequency sums in Eq. (2.221) have to be truncated at \( \omega_c \) within a numerical scheme. Thus, scattering processes out of this frequency window are neglected which would reduce the Coulomb potential as described in Eq. (2.228) and shown by Morel and Anderson [164] and Scalapino et al. [154]. Here, the frequency cut-off \( \omega_c \) should be of the order of the maximal phonon frequency.

Although \( W(q) \) and thus \( \mu \) can be calculated within modern GW codes \( \mu \) or \( \mu^* \) are regularly used as adjustable parameters to fit the experimental data. Thus, the Allen-Dynes formula for the critical superconducting temperature can be readily evaluated as soon as a full DFPT calculation has been performed on relatively coarse \( q \) grids.
Within the two-dimensional material library, graphene is still playing an outstanding role due to its extraordinary properties: It is the strongest material being simultaneously very elastic, it exhibits extreme electrical and thermal conductivities and its charge carriers behave like massless Dirac fermions. In addition, graphene is the first two-dimensional atomic (large-scale) crystal ever created. One of its most fundamental and most important properties is its semi-metallic ground state. Due to the honeycomb lattice, graphene’s $\pi$ orbitals form the famous Dirac cone arising from two linearly dispersing states intersecting each other at the Brillouin zone’s $K$ points. This dispersion gives graphene’s $\pi$ charge carriers their massless character. In turn, these properties are responsible for a variety of special effects observed in graphene monolayers ranging from the half-integer quantum hall effect [2, 165], to Klein tunneling [166, 167] or a close-to-constant, non-vanishing absorption of light (despite its mono-atomic thickness) [168]. Unfortunately, these outstanding properties come with the drawback of a vanishing band gap yielding, for instance, poor on-off ratios in field-effect transistor devices. This makes pristine graphene to an unfavorable basis for device construction but is at the same time the source of significant progress in the field of graphene functionalization. These functionalization schemes can be separated into two classes, namely chemi- and physisorption. While it is obvious that the former directly influences the system, e.g. in a chemical sense, and can thus lead to a band-gap opening, the effects of the latter are more subtle due to its indirect nature. To name just a few effects of this kind, we might think of Moiré-like external potentials which break specific symmetries or screening effects of substrates which can change internal interactions. Whether or not these modifications can open a band gap in graphene and thus help to functionalize it has to be analyzed in detail for each situation.

To this end, we will address two specific problems arising from each of these functionalization schemes. In section 3.2 we will deal with chemically functionalized graphene in the form of fluorographene (fluorinated graphene) which might be seen as the two-dimensional counterpart of Teflon and has a large band gap of several eV. We will investigate its electronic structure and optical properties upon partial and full fluorination. Therefore, we establish an \textit{ab initio} based multi-orbital tight-binding model which is capable of describing different types of structural disorder and fluorination patterns. Based on large-scale simulations we find that in the case of partially fluorinated graphene the appearance of paired fluorine atoms is more favorable than an
unpaired scenario. Regarding different types of structural disorder, we find distinct fingerprints in the form of mid-gap states within the electronic density of states which can lead to additional excitations within the optical gap. In addition, we propose that upon fluorination locally forming $sp^3$ bonds can be experimentally distinguished from the original graphene $sp^2$ hybrid orbitals by measuring the polarization rotation of passing polarized light. Thus, we provide a comprehensive overview of the electronic and optical properties of fluorinated graphene on a single-particle level.

In section 3.3 we turn to the second class of functionalization approaches. Here, we investigate how the environment is capable of changing Coulomb interactions in layered materials. This effect might be able to modify band gaps or to suppress or enhance specific ground-state phases and is thus of fundamental interest in the field of functionalization. Therefore, we develop an approach to derive realistic Coulomb-interaction terms for free standing and dielectrically embedded layered materials and vertical heterostructures. These interactions are derived from *ab initio* modeling of the corresponding bulk materials utilizing a Wannier function representation of the Coulomb matrix elements in combination with a (constrained) random phase approximation treatment of the screening effects within some low-energy Hilbert space. By properly applying continuum-medium electrostatics to the Coulomb-interaction matrix elements within the Wannier basis, we are able to accurately account for macroscopic screening effects of the dielectric environment of a layered material. First, we use this “Wannier Function Continuum Electrostatics” (WFCE) called approach to deduce the Coulomb interaction of mono- and bilayer graphene from graphite. Thereby, we are able to reproduce direct and full *ab initio* calculations of the corresponding matrix elements within an accuracy of 0.3 eV or better. Afterwards, we use the WFCE approach to investigate to what extent the realistic Coulomb interaction in bilayer graphene can be manipulated by a dielectric environment and find modifications on the eV scale. Finally, we can use these Coulomb interactions to pinpoint the ground state of bilayer graphene with the help of recently derived electronic phase diagrams from Ref. [18]. We find that bilayer graphene is likely to be in an antiferromagnetic ground state which can be clearly stabilized already by small changes in the dielectric environment.

### 3.1. Materials Under Consideration

Before we treat the outlined problems in detail we briefly introduce the materials which will be considered within the corresponding sections. Therefore we focus on the lattice structures and resulting electronic band structures in order to provide the reader with the basic properties of each material which are needed to understand the subsequent considerations and conclusions. This overview is by far not complete and does not cover most of the corresponding material physics. The interested reader is therefore referred to Refs. [169, 170] for comprehensive reviews of graphene’s physics, to Refs. [171, 172, 173, 174, 175] for more details on fluorographene and to Ref. [176] for a
3.1. Materials Under Consideration

Figure 3.1:
Real-space and reciprocal lattice of graphene and the resulting DFT band structure. Carbon atoms are colored yellow. The orbital character of each band is indicated by its width and a specific color. Carbon $\pi$ orbitals are marked in red and $\sigma$ orbitals in yellow.

general overview of graphite intercalation compounds.

3.1.1. Graphene

Graphene is a two-dimensional allotrope of carbon. As shown in Fig. 3.1 (a) it consists of carbon atoms arranged in a flat honeycomb lattice. The carbon $s$, $p_x$ and $p_y$ orbitals hybridize to $\sigma$ bonds ($sp^2$), while the remaining $p_z$ orbitals form the $\pi$-electron system which is entirely delocalized and decoupled from the rest. The $\sigma$ bonds are mostly located within the carbon plane, whereas the $p_z$ orbitals are oriented orthogonal to the layer. The underlying hexagonal Bravais lattice is described by the translation vectors

$$a_1 = \frac{a}{2} \left( \frac{3}{\sqrt{3}} \right) \quad \text{and} \quad a_2 = \frac{a}{2} \left( \frac{3}{-\sqrt{3}} \right), \quad (3.1)$$

where $a \approx 1.42 \text{Å}$ is the nearest-neighbour carbon distance. The corresponding basis consists of two atoms (on the sub-lattices $A$ and $B$) which are, for instance, located at

$$\delta_A = \frac{1}{3} \left( \begin{array}{c} 1 \\ 1 \end{array} \right)_a \quad \text{and} \quad \delta_B = \frac{-1}{3} \left( \begin{array}{c} 1 \\ 1 \end{array} \right)_a \quad (3.2)$$

in the basis of $a_1$ and $a_2$ (indicated by the $a$ subscript) within each unit cell. The resulting reciprocal lattice is spanned by

$$b_1 = \frac{2\pi}{3a} \left( \frac{1}{\sqrt{3}} \right) \quad \text{and} \quad b_2 = \frac{2\pi}{3a} \left( \frac{1}{-\sqrt{3}} \right) \quad (3.3)$$
and the high-symmetry points are given by

\[ K = \frac{1}{3} \begin{pmatrix} 1 \\ 2 \end{pmatrix}, \quad M = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad K' = \frac{1}{3} \begin{pmatrix} 2 \\ 1 \end{pmatrix}. \]  

(3.4)

In Fig. 3.1 (b) we show the band structure as obtained from DFT calculations. The \( \sigma \) bands are colored yellow while the \( \pi \) bands are colored red. There is no hybridization between the \( \sigma \) and \( \pi \) bands which gives rise to the very simple yet accurate tight-binding description of the \( \pi \) states:

\[
H = -t \sum_{\langle ij \rangle_{nn}} \left( a_i^\dagger b_j + h.c. \right) - t' \sum_{\langle ij \rangle_{nnn}} \left( a_i^\dagger a_j + b_i^\dagger b_j + h.c. \right). \tag{3.5}
\]

Here, \( t \) describes nearest-neighbour (nn) and \( t' \) next-nearest-neighbour (nnn) hoppings and \( a_i \) (\( b_i \)) annihilates electrons on sub-lattice \( A \) (\( B \)) in the \( i \)-th unit cell. The most important properties of the \( \pi \)-band dispersion emerge at the \( M \) and the \( K \) \( K' \) points. At \( M \), saddle-points can be found in the band structure which manifest as van-Hove singularities in the density of states. These singularities are located at \( E_{\pi M} = \pm t + t' \) (hence symmetric around the Fermi energy if \( t' \) vanishes). At \( K / K' \) graphene’s famous linear dispersion or Dirac cone arises which can be approximated around these points by

\[
E(k) = \pm v_F |k| + O(q^2) \tag{3.6}
\]

using the Fermi velocity \( v_F = 3t a / 2 \approx 10^6 \text{ m/s} \). This behaviour is unaffected by a non-vanishing \( t' \) in contrast to the electron-hole symmetry which is broken in this case. In deed, one finds based on DFT calculations \( t \approx 3 \text{ eV} \) and \( t' \approx 0.1 \text{ eV} \) [169].

Next to the \( \pi \) and \( \sigma \) bands some additional states around 3 eV at \( \Gamma \) can be seen. These bands belong to quasi-free electron states which have no specific orbital weight and show a quadratic dispersion. They artificially arise within so-called repeated slab calculations (as described in section 3.3) of layered materials and are located somewhere between the adjacent layers within the “vacuum”.

### 3.1.2. Bilayer Graphene

Bilayer graphene consists of two graphene monolayers which are separated by an interlayer distance \( c \approx 3.35 \text{ Å} \) [177]. In its AB or Bernal-stacking configuration the two layers are twisted by 60° and the \( A \) sub-lattices of both layers are aligned as shown in Fig. 3.2 (a). While we can still use graphene’s lattice vectors \( a_1 \) and \( a_2 \), we have to
3.1. Materials Under Consideration

(a) lattice

(b) band structure

Figure 3.2.: Real-space lattice and DFT band structure of AB stacked bilayer graphene. The coloring is the same as used in Fig. 3.1 (b).

utilize a three-dimensional basis consisting of four atoms at

\[ \delta_A = \frac{1}{3} \begin{pmatrix} 1 \\ \frac{1}{3c} \\ 0 \end{pmatrix} a \]

and \[ \delta_{B1} = \frac{1}{3} \begin{pmatrix} -1 \\ \frac{1}{3c} \\ 0 \end{pmatrix} a \]

\[ \delta_A = \frac{1}{3} \begin{pmatrix} 1 \\ \frac{1}{3c} \\ 0 \end{pmatrix} a \]

and \[ \delta_{B2} = \frac{1}{3} \begin{pmatrix} 0 \\ \frac{1}{3c} \\ 0 \end{pmatrix} a \]

using a third lattice vector \( a_3 = (0, 0, h) \) which introduces the “vacuum” distance \( h \) (distance between the repeated slabs). The resulting electronic band structure is shown in Fig. 3.1 (b). If the two layers were entirely decoupled, we would find the monolayers’s band structure but two-fold degenerated. Due a finite coupling like \( t_{\perp} \), which describes electron hoping between the sub-lattices \( A_1 \) and \( A_2 \), this degeneracy is lifted. Most importantly, the linear dispersion at \( K/K' \) is changed to four quadratic bands. Two of these bands touch each other at the Fermi energy, while the other bands are separated by \( \pm t_{\perp} \) (in the most simple tight-binding description) [169]. Hence, bilayer graphene can be described as a conventional semiconductor with a vanishing band gap.

3.1.3. Fluorographene

Fluorographene is a stable graphene derivative obtained from full fluorination of graphene, that is each carbon atom bonds to a single fluorine atom. In the so-called chair configuration, which has been proven to be the most stable structure [178, 175], the fluorine atoms are bond on top of graphene’s \( A \) and below its \( B \) sub-lattice as depicted in Fig.

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Figure 3.3.
Real-space lattice and DFT band structure of fluorographene in its armchair configuration. The carbon atoms and electronic bands are colored as in 3.1 (a), while fluorine atoms and fluorine $s$ and $p$ weights in the band structure are colored grey.

3.3 (a). Upon fluorination the carbon atoms will move out of the graphene plane and the former $sp^2$ hybrid orbitals will change to $sp^3$ hybrids (including the $p_z$ orbital). Using the lattice vectors from the previous section the basis of fluorographene is given by

$$
\delta C_A = \frac{1}{3} \begin{pmatrix} 1 \\ 1 \\ z_C \end{pmatrix}_a \quad \text{and} \quad \delta C_B = -\frac{1}{3} \begin{pmatrix} 1 \\ 1 \\ z_C \end{pmatrix}_a,
$$

$$
\delta F_A = \frac{1}{3} \begin{pmatrix} 1 \\ 1 \\ z_F \end{pmatrix}_a \quad \text{and} \quad \delta F_B = -\frac{1}{3} \begin{pmatrix} 1 \\ 1 \\ z_F \end{pmatrix}_a,
$$

where $z_C = \frac{3}{2}c_C$ and $z_F = \frac{3}{7}c_F$ with $c_C \approx 0.42$ Å and $c_F \approx 1.38$ Å being the carbon-carbon and carbon-fluorine $z$-distances, respectively [see Fig. 3.3 (a)]. In comparison to pristine graphene the lattice constant is slightly increased from $a_0 \approx 1.42\sqrt{3} \approx 2.46$ Å to $a_0 \approx 1.51\sqrt{3} \approx 2.62$ Å.

The $sp^3$ hybridization strongly affects the electronic band structure as shown in Fig. 3.3 (b). Although the former $p_z$ bands are still recognizable, they are shifted in energy and are strongly hybridized with the $sp^2$ states. Most importantly, a band gap of about 3 eV (at $\Gamma$) arises between the fluorine states (which predominately form the upmost valence bands) and the lower $p_z$ band (forming the lowest conduction band). Since the tendency of DFT calculations to underestimate band gaps is well known, many-body calculations in the $GW$ approximation have been used to obtain more realistic gaps. These yield quasiparticle band gaps on the order of 7 eV which is significantly larger than the electronic band gaps from DFT results [179, 178, 175, 180].
3.1. Materials Under Consideration

(a) lattice

(b) band structure

Figure 3.4.: Real-space lattice and DFT band structure of iridium intercalated graphite. The carbon atoms and electronic bands are colored as in 3.1 (a). Iridium atoms and iridium $s$, $p$ and $d$ weights in the band structure are colored purple.

3.1.4. Iridium Intercalated Graphite

In section 3.3.3 we discuss the influence of a metallic substrate (or environment) to the Coulomb matrix elements of monolayer graphene. In order to compare the modeled interaction elements derived from our WFCE approach with full \textit{ab initio} calculations, we introduce the system at hand: iridium intercalated graphite (Gr/Ir). The term “graphite” is a little bit misleading here, since the graphene layers (which form the graphite-like host system) are perfectly aligned, while naturally occurring graphite exhibits a Bernal stacking. Alternatively, this system can be seen as a monolayer of graphene encapsulated in an iridium (metallic) environment. Since this situation is comparable to a graphene monolayer lying on top of an iridium substrate (like studied in Ref. [181]), we adopt the corresponding averaged\(^1\) graphene-iridium distance ($c \approx 3.4 \text{ Å}$). Thus, the minimal unit cell is defined by the three positions

$$
\delta_{CA} = \frac{1}{3} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}_a, \quad \delta_{CB} = \frac{-1}{3} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}_a \quad \text{and} \quad \delta_{Ir} = \begin{pmatrix} 0 \\ 0 \\ \frac{1}{2} \end{pmatrix}_a
$$

(3.9)

with $\mathbf{a}_3 = (0, 0, 2c)$. The resulting electronic band structure is shown in Fig. 3.4 (b). Although there is some hybridization between the $\pi$ bands and iridium states between $\Gamma$ and $M$, the overall band structure of graphene “survives”. The $\pi$ bands including the Dirac cone as well as the $\sigma$ bands can still be clearly seen. The Dirac cone is shifted to

\(^1\) In Ref. [181] graphene on Ir(111) is studied which exhibits a complicated Moiré pattern since the Ir(111) surface unit cell has a slightly smaller lattice constant than graphene. Thus locally different graphene/Ir stackings arise which modulate the carbon-iridium distance. This distance ranges from $c \approx 3.2 \text{ Å}$ to $c \approx 3.6 \text{ Å}$.
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slightly higher energies indicating a charge transfer from the π orbitals to the iridium atoms (hole doping). This behaviour was also encountered in Ref. [181]. The iridium states are mostly located within the π band width and show some flat bands around the Fermi energy. Since some of these bands cross the Fermi level, metallic screening properties will arise due to the iridium sub-system.
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The following results have been gained in collaboration with S. Yuan and M. I. Katsnelson and have been published in Phys. Rev. Lett. **114**, 047403 (2015). I was responsible for all model preparation steps (including ab initio calculations and interpretations) and the supervision of A. Schulz who fitted the model parameters to ab initio results. The resulting multi-scale and multi-orbital tight-binding model served as the basis for the simulations of optical conductivities performed by S. Yuan. The final manuscript was written by S. Yuan and myself and was complemented by M. I. Katsnelson and T. O. Wehling. The reader will find a significant overlap between the original article and the text presented below as well as in the appendix in section A.1.

3.2.1. Absorption Spectra of Pristine Graphene and Fluorographene

As we have seen in the previous section, the dispersions of graphene and fluorographene strongly differ and so do their absorption spectra. In the case of pristine graphene light can be absorbed for arbitrary small energies which translates to a non-vanishing absorption coefficient in the experimental data shown in Fig. 3.5 (a). For increasing energies the absorption spectra is governed by a pronounced peak which arises due to the non-linear electronic dispersion around the van-Hove singularities at the Brillouin zone’s $M$ points. Without considering many-body effects this maximum is located at about 5.2 eV ($\approx 2t$ from the nearest-neighbour TB model) [182] as shown by the blue curve in Fig. 3.5 (a). However, the experimental data reveals a peak position around $E \approx 4.6$ eV [171, 168] [see Fig. 3.5 (a) and (b)] which can be reproduced by theory only upon inclusion of excitonic effects, for instance, by utilizing the Bethe-Salpeter equation\(^2\) (BSE) as shown in Fig. 3.5 (a) [182].

Unfortunately, in the case of fluorographene the theoretical data differs from the experimental findings. As shown by Nair *et al.*, the absorption spectrum of partially fluorinated graphene does not reveal the prominent peak and is decreased over the whole energy range [171] [see Fig. 3.5 (b)]. Upon full fluorination, Nair *et al.* find an optical band gap of approx. 3 eV which is roughly of the same order as found by Jeon *et al.* ($\approx 3.8$ eV) [174]. In comparison to quasiparticle-band-structure calculations within the Bethe-Salpeter approach vertex corrections to the polarization function from Eq. (2.160) are taken into account (in contrast to the description within $GW$ approximation as discussed in section 2.3.4) and thus electron-hole interactions and excitonic effects can be described. We shall not discussed it in more detail here and the interested reader is referred to Refs. [22, 42] for general descriptions as well as to the first calculations by Sham, Rice and Hanke [183, 184] and to more recent works by Onida *et al.* [185], Benedict *et al.* [186], Albrect *et al.* [187] as well as Rohlfing and Louie [188].

\(^2\) Within the Bethe-Salpeter approach vertex corrections to the polarization function from Eq. (2.160) are taken into account (in contrast to the description within $GW$ approximation as discussed in section 2.3.4) and thus electron-hole interactions and excitonic effects can be described. We shall not discussed it in more detail here and the interested reader is referred to Refs. [22, 42] for general descriptions as well as to the first calculations by Sham, Rice and Hanke [183, 184] and to more recent works by Onida *et al.* [185], Benedict *et al.* [186], Albrect *et al.* [187] as well as Rohlfing and Louie [188].
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Figure 3.5: (a) Absorption spectra of pristine graphene from Ref. [168]. Green and black curves show experimental data. The red and blue curves correspond to theoretical calculations with and without excitonic effects from Ref. [182]. (b) Experimental absorption spectra of pristine (blue), partially (green) and fully (magenta) fluorinated graphene from Ref. [171].

within the \( GW \) approximation (which exhibit a band gap of about 7 eV), the experimental optical band gaps are thus much smaller. A natural candidate to explain this discrepancy are excitonic effects which were recently considered in BSE calculations for optical spectra. These yield an optical band gap of 5.1 eV [180], which implies sizable excitonic effects but is still larger than the experimental values. It is argued but not verified that the remaining gap between the theoretical calculations and the experimental observations might be the result of disorder introduced during the fluorination process. To clarify this issue, we perform a systematic study of different types of structural disorder by a combination of \textit{ab initio} calculations and large-scale tight-binding (TB) simulations.

### 3.2.2. Tight-Binding Model for Fully and Partially Fluorinated Graphene

To describe the \( sp^2 \rightarrow sp^3 \) transition upon fluorination, an extended tight-binding (TB) model is required which is capable of handling (i) pristine graphene, (ii) partially fluorinated graphene and (iii) pristine fluorographene. To this end, we use a real-space representation of the electronic single-particle part of the Hamiltonian from Eq. (2.5) which results in a multi-orbital tight-binding Hamiltonian of the form

\[
H = \sum_{\alpha i} \varepsilon_{\alpha i} n_{i,\alpha} + \sum_{\alpha \beta (ij)} t_{\alpha \beta}^{ij} c_{i,\alpha}^\dagger c_{j,\beta},
\]  

(3.10)
3.2. Optical Properties of Partially and Fully Fluorinated Graphene

Figure 3.6.: $G_0W_0$ (red) and TB-model (green) band structures and corresponding density of states of graphene.

Here, $i, j$ are site indices, $\alpha$ and $\beta$ label the orbital basis (carbon: $s, p_x, p_y, p_z$ and fluorine: $p_x, p_y, p_z$), $\langle ij \rangle$ indicates summation over nearest neighbours and $t_{ij}^{\alpha\beta}$ are hopping matrix elements\(^3\). Since it is known that the band gap of fluorographene is underestimated in DFT calculations, we use the $G_0W_0$ method for both, fluorographene and pristine graphene, and interpolate the renormalized quasiparticle energies using Wannier functions. The resulting $G_0W_0$ quasiparticle band structures are used to fit the nearest-neighbour TB models for pristine graphene and fluorographene separately. The corresponding parameters are given in Tab. A.3 and the band structures and density of states (DOS) are shown in Fig. 3.6 and Fig. 3.7.

Although the simplified nearest-neighbour TB models are not able to describe every single detail of the original band structures, the most important features like the linear dispersion around the Dirac point in graphene or the states in the near of the conduction- and valence-band edges in fluorographene are sufficiently reproduced.

In the case of fluorographene we end up with a band gap of 6.3 eV which is about 0.7 eV smaller than recently published $G_0W_0$ results by Karlicky et al. [180]. Next to some differences in the calculation details (like the number of $k$-points, energy cut-offs, etc.), the most important discrepancy between our calculations and those reported in Ref. [180] is the separation distance between adjacent layers (vacuum distance). This vacuum distance is introduced due to the three-dimensional unit cell which has to be used in the VASP code to model two-dimensional systems (see discussion on the “repeated slab method” in section 3.3). Here, the vacuum distance is chosen to be about 10 Å which is one third of the distance used by Karlicky et al. Therefore, screening effects from neighbouring slabs are present resulting in an effective dielectric environment which decreases the Coulomb interaction and lowers the resulting band gap. Here, this effect might be interpreted as mimicking the influence of a dielectric substrate with a static dielectric constant of 1.8 in the long wavelength limit which does not change the qualitative conclusions.

\(^3\)The exact definition of $t_{ij}^{\alpha\beta}$ and the involved direction cosines can be found in Tab. A.1 and Tab. A.2 in the appendix A.1.
To model partially fluorinated graphene, we use a super cell in which fluorine atoms are introduced randomly (or ordered). Thereby, three different carbon-carbon hopping combinations arise: (i) nearest-neighbour hopping between pristine carbon atoms (graphene-like hopping), (ii) hopping between two fluorinated carbon atoms (fluorographene-like hopping) and (iii) hopping between a pristine and a fluorinated carbon atom. Thus, the local environment has to be considered to choose the correct hoppings and on-site energies for partially fluorinated graphene.

An additional problem arises due to a missing common reference energy of pristine and fully fluorinated graphene in the \textit{ab initio} calculations. Therefore, special care must be taken in using the TB on-site energies in the case of partially fluorinated graphene. Here, we determine this common reference energy by matching the \textit{ab initio} local DOS (LDOS) of a single fluorine impurity (and its surrounding) with the corresponding LDOS of the TB model. To this end, we use a relaxed graphene super cell including 16 carbon atoms with a single fluorine impurity and perform a $G_0W_0$ calculation on top of it. These \textit{ab initio} calculations predict a prominent mid-gap state around the Fermi energy in the total density of states [see Fig. 3.8 (a)], which arises mainly due to $p_z$ orbitals of the fluorine impurity as well as due to the fluorinated carbon atom and its neighbouring carbon atom, as shown in the LDOS in Fig. 3.8 (b). In more detail, we find that the maxima of the orbitally resolved mid-gap states from Fig. 3.8 (b) are aligned. Therefore, we adjust the on-site energies of the TB description until this characteristic alignment is reproduced by the TB model as well. The resulting total and local DOS of the TB model are shown in Fig. 3.8 (a) and Fig. 3.8 (c). Due to the nearest-neighbour approximation within the underlying graphene TB model, we still see the particle-hole approximation within the $p_z$ states [see neighbouring carbon $p_z$ LDOS in Fig. 3.8 (c)]. Nevertheless, the impurity state around the Fermi level is well reproduced and the overall DOS shows a satisfying qualitative agreement with the original \textit{ab initio} data for energies $\pm5\,\text{eV}$ around the Fermi energy. The corresponding parameters and further details are given in section A.1.
3.2. Optical Properties of Partially and Fully Fluorinated Graphene

![Graph showing DOS and LDOS](image)

(a) $G_0W_0$ and TB model DOS  
(b) $G_0W_0$ LDOS  
(c) TB model LDOS

**Figure 3.8.:**
Total and local density of states for the graphene super cell (16 carbon atoms, 1 fluorine impurity). (a) Total density of states from the original $G_0W_0$ data (red) and the TB model (green). (b) and (c): Local density of states of the $p_z$ orbital of the fluorine atom (red), the fluorinated carbon atom (green) and a neighbouring carbon atom (blue) from (b) the original $G_0W_0$ calculation and (c) as resulting from the fitted TB model.

### 3.2.3. Simulation Details

In order to model realistic samples in the TB calculations, we perform simulations of systems on the scale of micrometer consisting of $2400 \times 2400$ carbon atoms. Thereby we exclusively consider the chair configuration for neighbouring F atoms. The density of states and optical conductivity are calculated using the TB propagation method [189, 190] which is based on the numerical simulation of random wave propagation according to the time-dependent Schrödinger equation as discussed in section A.1.

### 3.2.4. Electronic and Optical Properties

**Paired vs. Unpaired Fluorination**

We start with considering paired and unpaired fluorine patterns. While in the unpaired scenario the fluorine atoms are distributed without any correlations, the paired pattern is defined by fluorine atoms which are always adsorbed in pairs at neighbouring carbon atoms. The resulting optical conductivities for a variety of fluorine concentrations are shown in Fig. 3.9. The insets present the arising total density of states for pristine graphene and CF$_{0.1}$.

The optical conductivity of pristine graphene found here is very similar to the theoretical absorption spectra *without* excitonic effects as shown in Fig. 3.5 (a). Correspondingly, the optical conductivity of pristine fluorographene exhibits a gap which is of the same magnitude as the band gap of the underlying quasiparticle band structure.

While the pristine cases obviously show identical absorption properties for the paired and unpaired scenario, the corresponding optical conductivities for fractional fluorine concentrations differ. In comparison to the paired fluorine pattern we find in the ab-
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In-plane optical conductivity of partially and fully fluorinated graphene with different concentration of randomly distributed (a) unpaired or (b) paired fluorine adatoms. The density of states of graphene and CF$_{0.1}$ are plotted as insets of panels (a,b) and reveal mid-gap states in the unpaired case (see the sharp peak close to the neutrality point).

Figure 3.9:

In-plane optical conductivity of partially and fully fluorinated graphene with different concentration of randomly distributed (a) unpaired or (b) paired fluorine adatoms. The density of states of graphene and CF$_{0.1}$ are plotted as insets of panels (a,b) and reveal mid-gap states in the unpaired case (see the sharp peak close to the neutrality point).

As can be seen in Fig. 3.9 (a) and (b), the general trend of $\sigma$ at energies below 10 eV is to decrease with fluorination. Interestingly, there is a sharp resonance around 5 eV which can not be found for concentrations below 30%, but intensifies for fluorine...
concentrations up to 70% and vanishes afterwards. We will see in the following that this peak results from fluorine vacancies which are not well defined for small fluorine concentrations and which will nearly vanish for high concentrations. Thus, this peak arises not before a certain threshold and vanishes towards fully fluorination.

In general, for fluorine concentrations larger than $F/C > 50\%$, the atomic structures in the paired and unpaired cases become comparable, leading to similar optical in-plane spectra. Thereby individual peaks below 8 eV are the most prominent properties of the optical conductivity for these fluorine concentrations. As mentioned above, these peaks are fingerprints of certain atomic structures.

**Fingerprints of Disordered Structures**

To investigate these fingerprints in more detail, Fig. 3.10 displays the results of fully and highly fluorinated graphene with structural disorder, including carbon vacancies, fluorine vacancies and fluorine vacancy-clusters\(^4\).

The common effects due to the presence of structural disorder are defect states (partially) within the electronic band gap. The exact positions of these intra-gap states are defined by the type of disorder. For example, the defect resonances in the DOS around $E = 0.78$ eV are due to single carbon vacancies (top row of Fig. 3.10) while the resonances around $E = -0.17/2.45$ eV are due to single/paired fluorine vacancies (second row of Fig. 3.10). The excitations between these intra-gap states and the states above or below the band gap lead to narrow or broad peaks in the optical spectrum below 6.3 eV. For fluorine vacancies we find a pronounced peak at about 5 eV (second row of Fig. 3.10) which has already been discussed above. For fluorine vacancy-clusters, there are many different intra-gap states due to different structures forming a continuous background noise within the optical gap as it can be seen in the last row of Fig. 3.10.

Altogether, our simulations of partially fluorinated graphene show optical excitations below 6.3 eV, but we do not find a clearly reduced optical gap of $\sim 3$ eV as it has been observed in the experiment in any of the considered disorder types. Thus, we conclude that the reduction of the optical gap is not due to structural disorder alone.

**Out-of-plane Optical Conductivity**

Optical experiments can work at normal as well as grazing incidence and measure polarization-dependent spectra. We therefore investigate the out-of-plane optical conductivity along the $z$-direction ($\sigma_{zz}$) and compare it to the in-plane optical conductivity. The dipole operator associated with $\sigma_{zz}$ contains two parts: one is the electron

\(^4\)The latter can additionally be separated into clusters formed by broad areas and armchair or zigzag lines of missing fluorine atoms. Here, we solely show fluorine vacancy-clusters since the main conclusion is not altered by the results from the other structures. The interested reader is referred to the original article [189].
Figure 3.10.:
Left column: Atomic structure with different types of structural disorder. The red dots indicate fluorine adatoms. Middle and right columns: density of states and optical conductivity of fully or highly fluorinated graphene with different types of structural disorder. From top to bottom: Fully or highly fluorinated graphene with randomly distributed carbon vacancies, fluorine vacancies, and fluorine vacancy-clusters.
3.2. Optical Properties of Partially and Fully Fluorinated Graphene

Out-of-plane optical conductivity of partially and fully fluorinated graphene with different concentration of randomly distributed (a) unpaired or (b) paired fluorine adatoms.

Hopping between the carbon atoms which have different $z$-coordinates and the other is the hopping between carbon atoms and absorbed fluorine directly above or below. This results in a zero optical conductivity along the $z$-direction in pristine graphene over the whole spectrum, since there are no differences in the $z$-positions of the carbon atoms. More generally, there are no inter-atomic contributions to $\sigma_{zz}$ from any $sp^2$-like carbon part of the sample. The evolution of $\sigma_{zz}$ upon random and pair fluorination is shown in Fig. 3.11 (a) and (b), respectively. Unlike the in-plane optical conductivity, the out-of-plane conductivities $\sigma_{zz}$ are similar for both unpaired and paired cases in the energy range shown in Fig. 3.11, independently of the fluorine concentration. There are in particular no features in $\sigma_{zz}$ due to the chiral mid-gap states associated with local sub-lattice symmetry breaking in the randomly fluorinated graphene. Thus, polarization analysis of optical spectra yields clear fingerprints for spectral features associated with chiral mid-gap states.

Generally, the nonzero optical conductivity perpendicular to the sheets raises the possibility to rotate the polarization of passing polarized light. As nonzero $\sigma_{zz}$ requires the formation of $sp^3$ orbitals, one is able to distinguish between impurity states originating from adatoms and other in-plane disorder configurations (for example, carbon vacancies, in-plane carbon reconstructions like pentagon-heptagon rings, and coulomb impurities) by measuring the polarization angle.

Intra-Atomic Dipole Contributions

To study the influence of intra-atomic dipole contributions [arising from $R_2$ from Eq. (A.6)] we added them to the calculation of the optical conductivity and found that they are negligible. Fig. 3.12 shows the results for graphene and fluorographene with
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Figure 3.12.: Comparison of optical conductivity with and without intra-atomic dipole contribution in graphene (left) and fluorographene (right).

and without intra-atomic dipole contributions. The values of the overlap functions $\langle s|x|p_x \rangle = \langle s|x|p_y \rangle = 0.04699\text{ nm}$ are calculated from the overlap of carbon’s $s$ and $p_x$ ($p_y$) wave functions using expressions given in Ref. [192]. In general, this intra-atomic dipole contribution slightly increases the value of the optical conductivity. However, a noticeable enhancement of the optical spectra of graphene or fluorographene appears not below energies of 17 eV or 6.3 eV, respectively. This dipole contribution does not change the optical spectrum qualitatively and has no effect on the value of the optical band gap in fluorographene. The same holds for the dipole terms in the case of the out-of-plane optical conductivity (data not shown).

3.2.5. Conclusions

In conclusion, by using a multi-orbital tight-binding model fitted to ab initio calculations we performed a detailed study of the electronic structure and optical properties of partially and fully fluorinated graphene. For partially fluorinated graphene the appearance of paired fluorine atoms is found to be more likely than unpaired atoms by matching the simulated optical spectrum to experimental observations. The presence of structural disorder such as carbon vacancies, fluorine vacancies, or fluorine vacancy-clusters will introduce defect states within the band gap leading to characteristic sharp excitations in the optical band gap of perfect fluorographene. Both, disorder and excitonic shifts, affect the optical spectra on an eV scale and reduce the size of the optical gap. It is thus plausible that their combined effect can reconcile theory and the experimentally observed optical gap. Nevertheless, both mechanisms lead by themselves to sharp resonances below the quasiparticle band gap, which have not been observed experimentally. One would thus have to assume additional broadening of the resonances,
3.2. Optical Properties of Partially and Fully Fluorinated Graphene

e.g. by phonons or further potential fluctuations. Such broadening is ubiquitous in two-dimensional materials [193, 194]. Considering the structural change from purely in-plane carbon positions to a buckled structure, we argue that the measurement of polarization rotation of passing polarized light through functionalized graphene could be an efficient tool to distinguish between optical effects caused in mainly $sp^3$- as compared to $sp^2$-hybridized regions of the sample.
3.3. Coulomb Interactions in Layered Heterostructures

The results presented in this section have been gained in collaboration with E. Şaşıoğlu, C. Friedrich and S. Blügel and have been published in Phys. Rev. B 92, 085102 (2015). The method development was performed by T. O. Wehling and myself with minor support from C. Friedrich. All ab initio calculations have been carried out by myself with some help of E. Şaşıoğlu. The final manuscript was written by myself and was complemented with comments by C. Friedrich and the help of T. O. Wehling. Most parts of the following paragraphs and the corresponding appendix A.2 originate from the published article.

In order to understand how the environment might be capable of functionalizing a layered material by changing its physical properties, we need to know which fundamental properties are changed and how these changes translate to modifications of observables. Here, we will focus on changes of the Coulomb interactions which are a natural candidate to consider environmental effects for two reasons: First of all, the Coulomb interaction is clearly long-ranged due to its $1/r$ dependence. This long-range characteristic leads to a pronounced sensitivity to the environment as can be seen in the sketches of the electric field lines between two charges within a layered system in Fig. 3.13. Secondly, we have already seen in the discussion of the GW approximation that the Coulomb interaction ($W$) is inseparably connected to the definition of the self-energy and thus directly influences a variety of material properties. Hence, we will study in the following how Coulomb-interaction matrix elements for the low-energy models defined in Eq. (2.5) can be derived and modified by a dielectric surrounding.

Realistic Coulomb-interaction matrix elements entering these models should be appropriately screened, i.e., they should account for screening due to those states which are not explicitly treated in the low-energy models, which can be achieved using the constrained random phase approximation as introduced in section 2.3.2. The computational demand of these calculations is comparable to GW calculations which makes the treatment of complex heterostructures, for instance in plane-wave-based approaches, very challenging.

Essentially, two different strategies have been developed to circumvent computational problems in obtaining appropriately screened interactions for thin films or layered materials. First, in long-wavelength approaches to layered materials model dielectric functions based on a description of the two-dimensional screening in terms of macroscopic electrodynamics can be straightforwardly employed (see e.g. Refs. [195, 196]). Second, modified Coulomb interactions involving, e.g., a truncation in the vertical direction [197] or unscreening in terms of model dielectric functions [198] can be employed directly on the fully microscopic GW level to reach faster convergence of
the screened interactions in repeated-slab approaches\(^5\).

While the first set of approaches comes at the advantage of almost no computation cost in obtaining screened Coulomb interactions, it generally relies on \textit{a priori} unknown adjustable parameters. The second set of approaches contains all microscopic material informations but requires a new fully microscopic calculation when the dielectric environment of some layered material (e.g. the substrate) is changed and remains still computationally demanding.

Here, we introduce a bridge between these two complementary classes of approaches and develop an approximate very simple yet accurate approach to derive realistic Coulomb-interaction matrix elements for electrons in free standing layered materials and vertical heterostructures from cRPA modeling of the corresponding bulk materials [left to right in Fig. 3.13 (b)]. To this end, we combine Wannier function representations of the Coulomb matrix elements within some low energy Hilbert space of interest with continuum medium electrostatics, as we explain in section 3.3.2. This allows us to avoid repeated-slab calculations on the cRPA level. In section 3.3.3, we illustrate our Wannier function based approach with the example of graphene, bilayer graphene as well as related heterostructures like Ir intercalated graphite. A particular advantage of the approach introduced here is that one can very easily assess how different envi-

\(^5\) Due to the three-dimensional unit cells which have to be used in conventional \textit{ab initio} packages it is unavoidable to have repeated “images” of the layered system under consideration. As sketched out in Fig. 3.13 (a), these images are separated from the original layer by the super-cell height \(h_{\text{vac}}\) and, most importantly, provide additional screening. Thus, the Coulomb interaction in these kind of repeated-slab calculations will always be smaller compared to the interaction in a completely free standing layer. To avoid these problems the afore mentioned truncation or unscreening schemes have been developed.
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Environments affect Coulomb interactions in realistic layered materials, as we show with the example of bilayer graphene in section 3.3.4.

3.3.1. Model Hamiltonian and Calculation Details

The cRPA approach has to be applied here, since we aim to derive a model Hamiltonian describing solely the carbon $p_z$ orbitals (i.e. the $\pi$ bands). Thus, these states form the model space, while the $\sigma$ bands as well as states at higher energies describe the “rest” space. We can describe such a system with a generalized Hubbard model for the $p_z$ orbitals with the electronic part of the many-body Hamiltonian from Eq. (2.5) in real space

$$H = -t \sum_{\langle ij \rangle, \sigma} c^\dagger_{i \sigma} c_{j \sigma} + U_{00} \sum_i \hat{n}_{i \uparrow} \hat{n}_{i \downarrow} + \frac{1}{2} \sum_{i \neq j \sigma \sigma'} U_{ij} \hat{n}_{i \sigma} \hat{n}_{j \sigma'}$$

(3.11)

where $c_{i \sigma}$ ($c^\dagger_{i \sigma}$) annihilates (creates) an electron with spin $\sigma \in \{\uparrow, \downarrow\}$ at site $i$ and $\hat{n}_{i \sigma} = c^\dagger_{i \sigma} c_{i \sigma}$. The index $i = (i, A \text{ or } B)$ labels the sub lattice (A, B) and the unit cell centered at position $R_i$.

$U_{ij}$ are the effective partially screened Coulomb-interaction terms in real space which are calculated, as stated above, within the constrained random phase approximation to exclude screening effects arising from the $\pi$ orbitals. The corresponding bare ($v$) and partially screened ($U$) Coulomb kernels are evaluated in an all-electron mixed product basis based within the full-potential linearized augmented-plane-wave (FLAPW) method as introduced in section 2.2.1. We note that all of these Coulomb kernels $v(r, r')$ depend explicitly on $r$ and $r'$ and are thus non-local in space. These kernels are afterwards used to calculate the corresponding Coulomb-interaction matrix elements within the Wannier basis spanned by the carbon $p_z$ orbitals whereby Eq. (2.124) becomes a matrix equation with 1 being the unit matrix. A detailed description of all computational details can be found in section A.2.

Furthermore, we would like to note at this early stage of consideration that the neglect of screening effects due to the $\pi$ orbitals will lead to a semiconductor-like screening behaviour of the rest polarization in most of the systems introduced in section 3.1. As we can clearly see in the band structures of mono- and bilayer graphene, the only bands in the vicinity of the Fermi energy are of $p_z$ character. Hence, neglecting them leads to a fully gaped band structure. This is different in iridium intercalated graphite since here partially filled bands originating from iridium are present and yield a metallic screening even within the described cRPA procedure.
3.3. Coulomb Interactions in Layered Heterostructures

3.3.2. Combination of Wannier Functions and Continuum Electrostatics: The WFCE Approach

In this section we explain our approach to derive appropriately screened Coulomb-interaction matrix elements for electrons in two-dimensional materials (e.g. graphene) and their heterostructures on the basis of Coulomb-interaction matrix elements from parent three-dimensional bulk systems (e.g. graphite). To this end, we first recall the continuum electrodynamic description of layered materials, free standing monolayers as well as heterostructures. Afterwards, the continuum formulation is embedded into a quantum lattice description in terms of localized Wannier functions.

Continuum Electrostatic Description

The problem of screening in terms of continuum electrostatics in a layered material is illustrated in Fig. 3.14 and has been considered in Refs. [199, 200, 201]. We aim to generalize these works to include non-local screening effects within the dielectric layer. Therefore, we will replace the dielectric constant $\varepsilon_1$ by an appropriate dielectric function $\varepsilon_1(q_z)$.

To this end we have to relate the bulk dielectric function $\varepsilon_B(r, r')$ to $\varepsilon_1(q_z)$. We assume that the former has been determined from first principles. As we will explicate later, we only modify the leading eigenvalue of the microscopic dielectric matrix derived from the dielectric kernel $\varepsilon_B(r, r')$ so that we may assume $\varepsilon_B(q)$ to be a scalar function. The embedding is not as easily done as in Refs. [201, 200, 199], because we face the problem of non-localities, in particular the $q_z$-dependence which describes the periodicity of the bulk material in $z$-direction. Clearly, an assumption on how non-localities translate from bulk to monolayers or heterostructures has to be made. Here, we continue with the simplest possible approximation and neglect all non-localities in $z$-direction, i.e. we replace $\varepsilon_B(q)$ by

$$\varepsilon_1(q_z) = \frac{h}{2\pi} \int_{-\pi/h}^{\pi/h} dq_z \varepsilon_B(q_z, q_z),$$  \hspace{1cm} (3.12)

where $h$ plays the role of an effective layer thickness. This definition is plausible as the two-dimensional embedding breaks the periodicity in $z$-direction and only the $z$-local
Dielectric problems, which can be solved with the help of image charges. (a) A single dielectric interface. (b) Two dielectric interfaces separated by \( h \) and (c) the arising effective dielectric function within the \( \varepsilon_1 \) area for a constant and finite \( \varepsilon_1 \).

Term of \( \varepsilon_B \) should remain relevant. In this sense, Eq. (3.12) gives this local term as the Fourier transformation to the center of the monolayer, i.e., \( z = 0 \). A similar formula was used in Ref. [197] to define a “two-dimensional macroscopic dielectric function”.

We now assume that \( \varepsilon_1(q||z) \) is constant on the whole width (or height) of the monolayer, i.e., for \( |z| \leq h/2 \), and consider two dielectric materials on both sides with dielectric constants \( \varepsilon_2 \) and \( \varepsilon_3 \) according to Fig. 3.14, which gives

\[
\varepsilon(q||z) = \begin{cases} 
\varepsilon_2 & z > \frac{h}{2} \\
\varepsilon_1(q||z) & |z| \leq \frac{h}{4} \\
\varepsilon_3 & z < -\frac{h}{4} 
\end{cases}
\]  

To find the appropriately screened interaction \( U^{2D}(q||z) \) between two electrons in the central layer, we consider the electrostatic problem of an oscillating two-dimensional charge density \( \rho(q||z) = \rho^{2D}(q||z)\delta(z) \) in the center of the monolayer, which is at \( z = 0 \). The resulting electrostatic potential \( \Phi(q||z) \) is not the same as in the bulk due to modified screening and the fact that we are now considering a two-dimensional charge density confined to \( z = 0 \).

In the dielectric continuum model, the modification of the screening is caused by the formation of image charges at the interfaces between the dielectrics. Let us first consider a single interface like it is illustrated in Fig. 3.15 (a), where the dielectric constant changes from \( \varepsilon_1 \) to \( \varepsilon_2 \), and a test charge \( q_1 \) is positioned in region 1. For an observer in region 1, the induced polarization has the form of an image charge of magnitude \( q_2 = q_1(\varepsilon_1 - \varepsilon_2)/(\varepsilon_1 + \varepsilon_2) \) that is located in region 2 at an equal distance from the interface as the test charge [89]. If one has more than one interface, as in the case of our dielectric model and like depicted in Fig. 3.15 (b), the charge is reflected infinitely many times (as light between two parallel optical mirrors), giving rise to an infinite number of image charges located at

\[
z(l) = l \cdot h \quad \text{with} \quad l = \pm 0, \pm 1, \pm 2, \ldots
\]
perpendicular to the interfaces with ever decreasing magnitudes
\[
q_j(l) = q_1 \left( \frac{\varepsilon_1 - \varepsilon_j}{\varepsilon_1 + \varepsilon_j} \right)^{|l|} \tag{3.15}
\]
with \( j = 2 \) and \( j = 3 \) for the upper (right) and lower (left) interface, respectively.

Several works have treated this situation, a dielectric monolayer sandwiched between two semi-infinite dielectric materials [199, 200, 201]. We use here a special case of a formula derived in Ref. [201], giving the effective two-dimensional dielectric function in momentum space
\[
\varepsilon_{2D}^{\text{eff}}(q_{||}) = \frac{\varepsilon_1(q_{||}) \left[ 1 - \tilde{\varepsilon}_2(q_{||})\tilde{\varepsilon}_3(q_{||})e^{-2q_{||}h} \right]}{1 + \left[ \tilde{\varepsilon}_2(q_{||}) + \tilde{\varepsilon}_3(q_{||}) \right] e^{-q_{||}h} + \tilde{\varepsilon}_2(q_{||})\tilde{\varepsilon}_3(q_{||})e^{-2q_{||}h}}, \tag{3.16}
\]
where the ratio
\[
\tilde{\varepsilon}_j(q_{||}) = \frac{\varepsilon_1(q_{||}) - \varepsilon_j}{\varepsilon_1(q_{||}) + \varepsilon_j} \tag{3.17}
\]
has been introduced. With this equation, the two-dimensional screened interaction (in the long-wavelength limit, see below) can be written as
\[
U^{2D}(q_{||}) = \frac{v^{2D}(q_{||})}{\varepsilon_{2D}^{\text{eff}}(q_{||})}, \tag{3.18}
\]
where \( v^{2D}(q_{||}) = v^{3D}(q_{||}, z = 0) \) is the bare interaction in the 2D system.

By evaluating Eq. (3.16) with the help of Eq. (3.12) we are now able to calculate the screened interaction between electrons in the free standing or embedded two-dimensional monolayer directly from the three-dimensional layered bulk properties with the main approximation being the neglect of all non-localities of dielectric response in the vertical direction. We will assess the quality of this approximation in section 3.3.3.

**Wannier Function Based Formulation**

The generalized Hubbard model from Eq. (3.11) involves matrix elements in terms of Wannier functions which has to be linked to the continuum electrostatic description developed in the previous section. For real materials like graphene or transition metal dichalcogenides these models involve multiple Wannier orbitals per unit cell and the corresponding Coulomb matrix elements must in general not be restricted to density-density interaction terms. Then we have to deal with full tensorial representations of the interactions \( U_{\alpha\beta\gamma\delta}^{kk'}q \) which depend in general on two initial momenta \( k, k' \) and the momentum transfer \( q \) and four orbitals as defined in Eq. (2.133). In this case
further approximations are helpful to derive from the bulk Coulomb interaction the corresponding monolayer terms. First, we will neglect the non-vanishing overlap between Wannier functions in different unit cells, which means tracing out the $k$ and $k'$ dependencies. Then, the Coulomb interaction depends on momentum transfer $q$ but not on the initial momenta $k$ and $k'$.

To combine the macroscopic electrostatic description of the previous section with the representation in a Wannier basis, we represent the bare and screened Coulomb interaction as well as the dielectric function as quadratic matrices using generalized indices $	ilde{\alpha} = \{\alpha, \delta\}$ and $	ilde{\beta} = \{\beta, \gamma\}$: $U_{\tilde{\alpha}\tilde{\beta}}(q) \equiv U_{\tilde{\alpha}\tilde{\beta}}(q)$. The resulting matrix elements are used within

$$H_{ex} = \sum_{\tilde{\alpha}\tilde{\beta}} U_{\tilde{\alpha}\tilde{\beta}}(q) \sum_{k\sigma} c_{\alpha\sigma}^\dagger (k - q)c_{\delta\sigma}(k) \sum_{k'\sigma'} c_{\beta\sigma'}^\dagger (k' + q)c_{\gamma\sigma'}(k') \quad (3.19)$$

$$= \sum_{\tilde{\alpha}\tilde{\beta}} U_{\tilde{\alpha}\tilde{\beta}}(q) \hat{n}_{\tilde{\alpha}}(q)\hat{n}_{\tilde{\beta}}(-q). \quad (3.20)$$

and might be interpreted as interaction energies between generalized charge-density waves

$$n_{\tilde{\alpha}}(q) = \sum_{k\sigma} \langle c_{\alpha\sigma}^\dagger (k - q)c_{\delta\sigma}(k) \rangle \quad \text{and} \quad n_{\tilde{\beta}}(-q) = \sum_{k'\sigma'} \langle c_{\beta\sigma'}^\dagger (k' + q)c_{\gamma\sigma'}(k') \rangle. \quad (3.21)$$

In Fourier space the leading eigenvalue and eigenvector of $U_{\tilde{\alpha}\tilde{\beta}}(q)$ correspond to the charge-density modulations with the longest wavelength, i.e. those charge-density waves where screening effects due to the environment are supposed to be strongest. This statement can most easily be understood in real space. To this end we utilize the real-space representation of the Coulomb matrix

$$U_{\tilde{\alpha}\tilde{\beta}}(R) = \frac{1}{N_q} \sum_q U_{\tilde{\alpha}\tilde{\beta}}(q)e^{-iqR} \quad (3.22)$$

for a simplified situation in which solely density-density interactions are taken into account in a basis consisting of two Wannier functions ($\alpha \in \{A, B\}$) only. In such a situation the Coulomb-interaction tensor is reduced to a matrix

$$U_{ij} = \begin{pmatrix} U_{AA}(R_{ij}) & U_{AB}(R_{ij}) \\ U_{BA}(R_{ij}) & U_{BB}(R_{ij}) \end{pmatrix}, \quad (3.23)$$

which might describe graphene’s $p_z$ orbitals on the sub-lattices $A$ and $B$. Taking into account that $U_{ij}$ has to be symmetric ($U_{BA} = U_{AB}$) and setting $U_{AA} = U_{BB}$ (which is a reasonable assumption in the case of graphene) the Coulomb matrix can readily be diagonalized

$$U_{ij} = \begin{pmatrix} U_{AA}(R_{ij}) & U_{AB}(R_{ij}) \\ U_{AB}(R_{ij}) & U_{AA}(R_{ij}) \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} U_1(R_{ij}) & 0 \\ 0 & U_2(R_{ij}) \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad (3.24)$$
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using the leading \((U_1)\) and the second eigenvalue \((U_2)\)

\[
U_1(R_{ij}) = U_{AA}(R_{ij}) + U_{AB}(R_{ij})
\]

(3.25)

\[
U_2(R_{ij}) = U_{AA}(R_{ij}) - U_{AB}(R_{ij}).
\]

(3.26)

By plugging Eq. (3.24) into the non-local interaction terms \((i \neq j)\) of the Hamiltonian from Eq. (3.11) we find

\[
H_{e\neq j}^{1\neq j} = \frac{1}{4} \sum_{i \neq j, \sigma, \sigma'} [U_1(R_{ij}) (\hat{n}_{iA\sigma} + \hat{n}_{iB\sigma}) (\hat{n}_{jA\sigma'} + \hat{n}_{jB\sigma'})
\]

\[
+ U_2(R_{ij}) (\hat{n}_{iA\sigma} - \hat{n}_{iB\sigma}) (\hat{n}_{jA\sigma'} - \hat{n}_{jB\sigma'})]
\]

\[
= \frac{1}{4} \sum_{i \neq j} [U_1(R_{ij}) \delta \hat{n}_i \delta \hat{n}_j + U_2(R_{ij}) \delta \hat{n}_i \delta \hat{n}_j]
\]

(3.27)

with

\[
\hat{n}_i = \sum_{\sigma} \hat{n}_{i\alpha\sigma} \quad \text{and} \quad \delta \hat{n}_i = \sum_{\sigma} (\hat{n}_{iA\sigma} - \hat{n}_{iB\sigma}).
\]

(3.28)

Here, \(\hat{n}_i\) measures the total charge of the \(i\)-th unit cell, while \(\delta \hat{n}_i\) accounts for its internal charge variations. The former can be linked to electric monopoles and the latter to electric dipoles. Hence, the leading eigenvalue \(U_1\) describes unavoidable Coulomb penalties of monopole-like interactions between different unit cells. In contrast, \(U_2\) corresponds to Coulomb penalties due to charge variations within the unit cells. Therefore, the Coulomb eigenvalues are connected to different length scales: \(U_1\) renders effects on macroscopic (inter-cell) distances, while \(U_2\) is linked to microscopic (intra-cell) details. Correspondingly, the leading eigenvalue is indeed inseparably connected to charge fluctuations with the longest wavelength, which holds for arbitrary situations due to the symmetric and purely real form of the Coulomb matrix\(^6\). By definition, continuum medium electrostatics describes the macroscopic response of a medium to long-wavelength electric field / potential variations. We thus correct the leading eigenvalue of \(U_{\delta \beta}(q)\) according to the algorithm from the previous section, while we assume for all other eigenvalues the same screening as in the bulk.

The full algorithm which we refer to as “Wannier Function Continuum Electrostatic” (WFCE) approach can be divided into several steps, which are illustrated in the flowchart of Fig. 3.16, to obtain the partially screened Coulomb interaction of a two-dimensional sub-system directly from its three-dimensional host. We start with the bare, \(v^{3D}(q)\), and partially screened Coulomb-interaction matrices \(U^{3D}(q)\) obtained

\(^6\) Being symmetric and real leads to the fact that the leading eigenvector will consist of positive entries only. Thus, the leading eigenvalue will always be connected to the sum of orbital and spin resolved occupations \(\hat{n}_{i\alpha\sigma}\) and not to their (partial) differences.
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\[ v^{3D}(\mathbf{q}), U^{3D}(\mathbf{q}) \]

\[ \Rightarrow \varepsilon^{3D}(\mathbf{q}) = \left[ v^{3D}(\mathbf{q}) \right]^{1/2} \left[ U^{3D}(\mathbf{q}) \right]^{-1} \left[ v^{3D}(\mathbf{q}) \right]^{1/2} \]

**q_z Fourier transform:**

\[ v^{3D}(\mathbf{q}, z = 0) = N_{q_z}^{-1} \sum_{q_z} v^{3D}(\mathbf{q}) e^{i q_z z} \]

\[ \varepsilon^{3D}(\mathbf{q}, z = 0) = N_{q_z}^{-1} \sum_{q_z} \varepsilon^{3D}(\mathbf{q}) e^{i q_z z} \]

\[ v^{2D}(\mathbf{q}_\parallel) = v^{3D}(\mathbf{q}_\parallel, z = 0), \quad \varepsilon^{3D}(\mathbf{q}_\parallel, z = 0) \]

**Decomposition:**

\[ v^{2D}(\mathbf{q}_\parallel) = v^{2D}_1(\mathbf{q}_\parallel) \left| v^{2D}_1(\mathbf{q}_\parallel) \right\rangle \left\langle v^{2D}_1(\mathbf{q}_\parallel) \right| + v^{2D}_{\text{Rest}}(\mathbf{q}_\parallel) \]

\[ \varepsilon^{2D}_1(\mathbf{q}_\parallel, z = 0) = \langle v^{2D}_1(\mathbf{q}_\parallel) \left| \varepsilon^{3D}(\mathbf{q}_\parallel, z = 0) \right| v^{2D}_1(\mathbf{q}_\parallel) \rangle \]

\[ \varepsilon^{3D}(\mathbf{q}_\parallel, z = 0) = \varepsilon^{3D}_1(\mathbf{q}_\parallel, z = 0) \left| v^{2D}_1(\mathbf{q}_\parallel) \right\rangle \left\langle v^{2D}_1(\mathbf{q}_\parallel) \right| + \varepsilon^{3D}_{\text{Rest}}(\mathbf{q}_\parallel, z = 0) \]

**2D model dielectric matrix:**

\[ \varepsilon^{2D}_1(\mathbf{q}_\parallel) = \varepsilon^{2D}_{\text{eff}} \left[ \varepsilon^{3D}(\mathbf{q}_\parallel, z = 0), \hat{h} \right] \]

\[ \varepsilon^{2D}_{\text{Rest}}(\mathbf{q}_\parallel) = \varepsilon^{3D}_{\text{Rest}}(\mathbf{q}_\parallel, z = 0) \]

\[ \varepsilon^{2D}(\mathbf{q}_\parallel) = \varepsilon^{2D}_1(\mathbf{q}_\parallel) \left| v^{2D}_1(\mathbf{q}_\parallel) \right\rangle \left\langle v^{2D}_1(\mathbf{q}_\parallel) \right| + \varepsilon^{2D}_{\text{Rest}}(\mathbf{q}_\parallel) \]

\[ \Rightarrow U^{2D}(\mathbf{q}_\parallel) = \left[ v^{2D}(\mathbf{q}_\parallel) \right]^{1/2} \left[ \varepsilon^{2D}(\mathbf{q}_\parallel) \right]^{-1} \left[ v^{2D}(\mathbf{q}_\parallel) \right]^{1/2} \]

**q_\parallel Fourier transform:**

\[ U^{2D}(\mathbf{r}_\parallel) = \frac{1}{N_{\mathbf{q}_\parallel}} \sum_{\mathbf{q}_\parallel} U^{2D}(\mathbf{q}_\parallel) e^{i \mathbf{q}_\parallel \cdot \mathbf{r}_\parallel} \]

\[ U^{2D}(\mathbf{r}_\parallel) \]

**Figure 3.16.:**

Flowchart of the Wannier function continuum electrostatics (WFCE) algorithm to obtain the screened Coulomb matrix elements of a freestanding monolayer directly from the Coulomb interaction of the corresponding layered bulk material.
3.3. Coulomb Interactions in Layered Heterostructures

from the \textit{ab initio} calculations for the three-dimensional bulk of the layered material. With these quantities we define the symmetric 3D dielectric function

\[
\varepsilon^{3D}(\mathbf{q}) = \left[ v^{3D}(\mathbf{q}) \right]^{1/2} \left[ U^{3D}(\mathbf{q}) \right]^{-1} \left[ v^{3D}(\mathbf{q}) \right]^{1/2}, \tag{3.30}
\]

We now aim to link this dielectric matrix to the interactions taking place between electrons within one monolayer and connect it to model dielectric functions derived in the context of continuum electrostatics. To this end, we consider the bare \textit{intra-layer} electronic interaction

\[
v^{3D}(\mathbf{q}), z = 0 = \frac{1}{N_q} \sum_{q_z} v^{3D}(\mathbf{q}, q_z) e^{i q_z z}, \tag{3.31}
\]

which is the same in the bulk layered material and in the monolayer, bilayer, etc. [i.e. \(v^{3D}(\mathbf{q}, z = 0) = v^{2D}(\mathbf{q})\)]. \(N_q\) is the number of points used in the \(q_z\)-summation. \(v^{2D}(\mathbf{q})\) can be decomposed exactly

\[
v^{2D}(\mathbf{q}) = \langle \mathbf{q} \rangle | v^{2D}(\mathbf{q}) \rangle \langle v^{2D}(\mathbf{q}) | + v^{2D}_{\text{rest}}(\mathbf{q}), \tag{3.32}
\]

where \(v^{2D}_{\text{eff}}(\mathbf{q})\) is the leading eigenvalue of \(v^{2D}(\mathbf{q})\), \(| v^{2D}(\mathbf{q}) \rangle \) is the corresponding eigenvector and \(v^{2D}_{\text{rest}}(\mathbf{q})\) contains the rest. Using the leading eigenvector of the bare Coulomb interaction, we are able to perform an analogous exact decomposition of the intra-layer 3D dielectric matrix

\[
\varepsilon^{3D}(\mathbf{q}), z = 0 = \varepsilon^{3D}_{\text{eff}}(\mathbf{q}) | v^{2D}(\mathbf{q}) \rangle \langle v^{2D}(\mathbf{q}) | + \varepsilon^{3D}_{\text{rest}}(\mathbf{q}), z = 0, \tag{3.33}
\]

where the “head element” \(\varepsilon^{3D}_{\text{eff}}(\mathbf{q}), z = 0\) of the dielectric matrix is defined as

\[
\varepsilon^{3D}_{\text{eff}}(\mathbf{q}), z = 0 = \langle v^{2D}(\mathbf{q}) | \varepsilon^{3D}(\mathbf{q}), z = 0 | v^{2D}(\mathbf{q}) \rangle . \tag{3.34}
\]

To obtain the dielectric matrix of the 2D system \(\varepsilon^{2D}(\mathbf{q})\) we replace \(\varepsilon^{3D}_{\text{eff}}(\mathbf{q})\) in Eq. (3.33) by the model dielectric function \(\varepsilon^{2D}(\mathbf{q})\) from Eq. (3.16):

\[
\varepsilon^{2D}(\mathbf{q}) = \varepsilon^{2D}_{\text{eff}}(\mathbf{q}) | v^{2D}(\mathbf{q}) \rangle \langle v^{2D}(\mathbf{q}) | + \varepsilon^{2D}_{\text{rest}}(\mathbf{q}) \tag{3.35}
\]

with \(\varepsilon^{2D}_{\text{eff}}(\mathbf{q})\) from Eq. (3.16) being set to \(\varepsilon^{3D}(\mathbf{q}), z = 0\) from Eq. (3.33), while the rest matrix remains unchanged. Here, we use the fact that the microscopic (short-range) screening properties of the monolayer should be very similar to that of the bulk \((\varepsilon^{2D}_{\text{rest}} = \varepsilon_{\text{rest}}^{3D})\). We will later see that this is a good approximation.

Together with the bare intra-layer interaction the screened intra-layer interaction is given by

\[
U^{2D}(\mathbf{q}) = \left[ v^{2D}(\mathbf{q}) \right]^{1/2} \left[ \varepsilon^{2D}(\mathbf{q}) \right]^{-1} \left[ v^{2D}(\mathbf{q}) \right]^{1/2}. \tag{3.36}
\]
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### 3.3.3. From Graphite to Graphene Heterostructures

We derive effective Coulomb interactions of monolayer graphene (MLG), bilayer graphene (BLG) and Ir intercalated graphite (Gr/Ir) from the interactions calculated for bulk graphite in the WFCE approach and benchmark our results against direct \textit{ab initio} calculations for these systems as well as analytical expressions which are valid in the long wavelength limit. In all cases, we consider Coulomb matrix elements in terms of Wannier functions for the carbon $p_z$ orbitals.

**Bulk Graphite**

The left panel of Fig. 3.17 shows the leading eigenvalue of the bare and screened Coulomb interaction in AB stacked graphite which plays the role of the initial bulk interaction of graphite. The right panel shows the momentum-dependent leading eigenvalue of the dielectric function for different values of $q_z$. The red markers for $q = 0$ indicate the parallel (circle) and perpendicular (square) limits of the screening.

From $U^{2D}(q_{||})$ a Fourier transformation with respect to $q_{||}$ finally leads to screened Coulomb matrices in real space

$$U^{2D}(r_{||}) = \frac{1}{N_{q_{||}}} \sum_{q_{||}} U^{2D}(q_{||}) e^{i q_{||} r_{||}},$$

which can be used in extended Hubbard models like given in Eq. (3.11). Here, $N_{q_{||}}$ is the number of points used in the $q_{||}$-summation.

### Figure 3.17.:

**Left:** Leading eigenvalues of the bare and screened Coulomb matrix elements of graphite for $q_z = 0$ obtained from \textit{ab initio} calculations together with the analytical description of the unscreened interaction (dashed blue line). The (light) gray area indicates the interval of all other eigenvalues of the (bare) screened Coulomb matrix. **Right:** Momentum-dependent leading eigenvalue of dielectric function of graphite obtained from cRPA calculations for different values of $q_z$. The red markers for $q = 0$ indicate the parallel (circle) and perpendicular (square) limits of the screening.
material, here. The former is perfectly interpolated by the analytic expression

\[ v_1(q) = \frac{4\pi e^2}{V q^2} \]  

which is illustrated in Fig. 3.17 for the \( q_z = 0 \) direction. Here, \( e \) is the elementary charge and \( V \) is the unit-cell volume per atom\(^7\). The fact that the leading eigenvalue of the bare Coulomb interaction in terms of Wannier orbitals matches the long wavelength continuum description from Eq. (3.38) within large parts of the Brillouin zone very closely motivates us to consider exactly this part of the Coulomb interaction in the WFCE approach.

The leading bare interaction eigenvalue is basically independent of any microscopic properties. This is different in the case of the screened interaction. Here, microscopic and macroscopic properties are involved through the dielectric screening of the real material background, as can be seen from the right panel of Fig. 3.17. In the limit of small \( q = |q| \to 0 \) the tensorial character of the dielectric function becomes obvious. Here, we find \( \varepsilon_\parallel \approx 3.2 \) for the in-plane fields and \( \varepsilon_\perp \approx 2.2 \) for the out-of-plane direction. At larger momentum transfer \( q \), the direction dependence of the dielectric function is less pronounced. Besides the leading eigenvalues of the Coulomb matrices the energetic interval of the other eigenvalues is marked by the (light) gray shaded areas in the left panel of Fig. 3.17 for the (bare) screened interaction. These matrix elements correspond to electronic density variations within the unit cell and correspondingly short wavelengths.

**Freestanding Mono- and Bilayer Graphene**

We derive the screened Coulomb interactions in freestanding mono- and bilayer graphene using the bulk graphite data in the WFCE approach. The leading eigenvalues of the Coulomb interaction and the corresponding effective dielectric functions are shown in dependence of momentum transfer in Fig. 3.18. While the comparison of results from direct \textit{ab initio} calculations and from the WFCE approach reveals generally very good agreement, there are some systematic deviations between both approaches in the limit of \( q \to 0 \). To understand the origin of these deviations it is instructive to compare the bare Coulomb-interaction matrix elements obtained from WFCE and \textit{ab initio} results to the analytical expression for the bare Coulomb interaction between electrons confined to a two-dimensional film in the long-wavelength limit:

\[ v_1^{2D}(q_\parallel) = \frac{\hbar}{2\pi} \int_{-\pi/\hbar}^{+\pi/\hbar} \frac{4\pi e^2}{V q^2} dq_z = \frac{4e^2 \arctan \left( \frac{\pi}{q_\parallel \hbar} \right)}{A q_\parallel} \]  

\(^7\)The treatment within the eigenbasis introduces a factor equal to the number of atoms in the unit cell. Therefore \( V \) instead of the conventional unit-cell volume \( V \) is used in Eq. (3.38).
where $\tilde{A}$ is the unit cell area per atom and the effective height $h$ can be chosen to be the interlayer distance $h = d \approx 3.35\,\text{Å}$ for the monolayer and $h = 2d$ for the bilayer. At small momentum transfer ($q \parallel h \approx 1$), this bare interaction approaches the well known limit $v_1^{2D}(q_{\parallel}) \to \frac{2\pi e^2}{\tilde{A}q_{\parallel}}$. The term $\arctan\left(\frac{\pi}{q_{\parallel}h}\right)$ in Eq. (3.39) plays the role of a “form factor” which accounts for the effective height $h$ of the two-dimensional layer. For both, the monolayer and the bilayer, the WFCE results match the analytic expression (which becomes exact for $q_{\parallel} \approx 0$) almost perfectly in contrast to the ab initio data. The ab initio calculations performed here are in fact super-cell calculations with periodic boundary conditions (or periodic-slab calculations as discussed in the introduction). In order to obtain the freestanding limit, we employ an extrapolation to infinite super-cell height (as described in section A.2), which becomes somewhat inaccurate for small $q$. Thus, the deviation of ab initio and WFCE Coulomb matrix elements as well as dielectric functions at small $q$ is likely due to this extrapolation problem in the ab initio data.

At intermediate $q$ the WFCE and the ab initio dielectric function are in very good agreement. For both, mono- and bilayer graphene, the screening rises from 1 to a maximum at intermediate $q$ and slightly decreases afterwards towards the edges of the first Brillouin zone [197]. Here, the non-locality ($q$-dependence) of the screening becomes clearly visible. In the long wavelength limit the screening vanishes, since we are dealing with a free standing two-dimensional layer, which is embedded in an infinite three-dimensional vacuum. By decreasing the wavelength, or increasing $q_{\parallel}$, the Coulomb interaction starts to be screened like in a three-dimensional bulk system, which manifests as an increased value of the dielectric function. The main differences

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{monolayer_graphene.png} \hspace{1cm} \includegraphics[width=\textwidth]{bilayer_graphene.png}
\caption{Leading eigenvalue of the dielectric function (outer frame), bare and screened Coulomb matrices (inner frame) of monolayer (left) and bilayer graphene (right). Red markers indicate ab initio calculations and gray markers the WFCE values.}
\end{figure}
3.3. Coulomb Interactions in Layered Heterostructures

between the effective dielectric functions in mono- and bilayer graphene are the gradients towards the intermediate maxima and the absolute values of the maxima, which are steeper and higher in the bilayer. I. e. the long range Coulomb interaction is less screened in the monolayer than in the bilayer, while the short range screening is more or less the same. The screened Coulomb interaction obtained from WFCE interpolates the corresponding cRPA data very well, as can be seen from Fig. 3.18. Thus, we have proven that the WFCE approach to calculate the two-dimensional Coulomb repulsion directly from the three-dimensional bulk data without introducing additional parameters works very well.

Graphene in a Metallic Surrounding

Regarding the change in electronic interactions, the opposite extreme case to going from bulk graphite to free standing monolayers is the case of graphene embedded in some metallic environment. Perfect metallic screening by the environment corresponds to $\varepsilon_2, \varepsilon_3 \to \infty$, in contrast to the case of $\varepsilon_2 = \varepsilon_3 = 1$ for monolayers surrounded by vacuum. In experiments, graphene is frequently grown on metals like Ir [202] or Cu [203] or can be surrounded by metals, e.g. in graphite intercalation compounds [176]. Here, we consider Coulomb interactions in graphene surrounded by Ir.

To this end, we calculate Coulomb interactions for a periodically repeated slab composed of a graphene monolayer and a “monolayer” of iridium (see section 3.1.4) by means of cRPA. This system can also be interpreted as Ir intercalated graphite. To model this system with the WFCE approach we assume perfect metallic screening by Ir, $\varepsilon_2, \varepsilon_3 \to \infty$, and use the effective height $h = 3.35 \text{ Å}$ of graphene, as before. The resulting leading eigenvalues of the Coulomb interaction within the carbon $p_z$ Wannier orbitals as well as the corresponding effective dielectric function are shown in Figure 3.19. The metallic surrounding leads to diverging $\varepsilon_2^{2D}(q)$ at long wavelengths $q \to 0$ in the cRPA and in the WFCE approach, as it must be. In contrast to free standing mono- and bilayer graphene the screened interactions in Gr/Ir do not diverge at small $q$, where the Coulomb interaction is now efficiently screened by the metallic
environment.

The overall characteristics of interactions and screening as obtained fromWFCE agree with the cRPA calculations. Nevertheless there is a systematic underestimation of the screening $\varepsilon^{2D}(q)$ on the order of $\approx 17\%$ by the WFCE approach as compared to the cRPA. Hence, the screened Coulomb interactions are correspondingly overestimated by WFCE, here. On physical grounds it is clear that the WFCE approach can become inaccurate when there is hybridization between e.g. a monolayer of graphene and some metallic surrounding. In this case the assignment of an effective height $h$ to the graphene layer and a separation into a subsystem of graphene and “the environment” is ambiguous. The underestimation of the screening in the WFCE approach can indeed be cured by decreasing the effective height to $h \approx 2.8 \text{Å}$ of the modeled monolayer. Treating $h$ as an adjustable parameter, that is derived from e.g. cRPA calculations is one possibility if, for instance, very complex heterostructures shall be considered and the intercalated system is used as the bulk starting point in WFCE. Here, we are taking graphite as the bulk starting point to treat Ir intercalated graphite and keep $h = 3.35 \text{Å}$ to stay with a parameter free model.

**Coulomb Interactions in Real Space**

In order to use the Coulomb terms obtained within the WFCE approach in a generalized Hubbard model, in which interaction matrix elements enter in real-space representation, we perform a Fourier transformation:

$$ U^{2D}_{\alpha\beta}(\mathbf{r}) = \frac{1}{N_{q||}} \sum_{q_{||}} U^{2D}_{\alpha\beta}(\mathbf{q}_{||}) e^{i\mathbf{q}_{||} \cdot \mathbf{r}}. \quad (3.40) $$

In the case of graphite an additional sum over the $q_z$ component is performed. The resulting values for density-density like $U_{\alpha\beta}(r)$ as obtained from cRPA and WFCE are given in Table 3.1 and depicted in Fig. 3.20 for mono- and bilayer graphene as well as graphite and the Gr/Ir system.
3.3. Coulomb Interactions in Layered Heterostructures

### Table 3.1:

<table>
<thead>
<tr>
<th>System</th>
<th>(U_0)</th>
<th>(U_1)</th>
<th>(U_2)</th>
<th>(U_3)</th>
<th>(U_4)</th>
<th>(U_5)</th>
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<td>8.1/8.2</td>
<td>3.6</td>
<td>2.2/2.2</td>
<td>1.9</td>
<td>1.5/1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>monolayer graphene (MLG)</td>
<td>9.7</td>
<td>5.3</td>
<td>3.8</td>
<td>3.5</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>(c)RPA</td>
<td>9.8/10.0</td>
<td>5.3</td>
<td>3.8/3.8</td>
<td>3.4</td>
<td>2.9/2.9</td>
<td>2.6</td>
</tr>
<tr>
<td>bilayer graphene (BLG)</td>
<td>9.1/9.2</td>
<td>4.7</td>
<td>3.2/3.2</td>
<td>2.9</td>
<td>2.5/2.5</td>
<td>2.3</td>
</tr>
<tr>
<td>(c)RPA</td>
<td>9.2/9.3</td>
<td>4.7</td>
<td>3.3/3.2</td>
<td>3.0</td>
<td>2.5/2.5</td>
<td>2.3</td>
</tr>
<tr>
<td>iridium intercalated graphite (Gr/Ir)</td>
<td>5.1</td>
<td>1.5</td>
<td>0.5</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>(c)RPA</td>
<td>6.1/6.2</td>
<td>1.8</td>
<td>0.6/0.6</td>
<td>0.4</td>
<td>0.2/0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Note:**

\(\text{WFCE}^\dagger\) due to the fact that AB stacked graphite is used to construct the monolayer and Gr/Ir data in the WFCE approach, some interactions are given for both sub lattices separately since the sub-lattice symmetry is artificially broken.

The screened Coulomb interaction in monolayer graphene is over the whole \(r_\parallel\) range bigger than the corresponding values of bilayer graphene, graphite, and Ir intercalated graphene. Since the bare Coulomb interactions (not shown here) are nearly the same in all cases, variations of the background screened interactions are almost entirely due to the successively stronger screening when going from monolayer graphene via bilayer graphene and graphite to graphene encapsulated in a metal.

In agreement with Ref. [204], we find sizable non-local effective Coulomb interactions for graphene, bilayer graphene and graphite, which can be however strongly reduced due to screening by the environment. This can be seen from comparison to the Gr/Ir case. Here, the Coulomb interaction is strongly reduced at all \(r_\parallel\) under consideration, i.e. by about a factor of 2 for the local terms and more than a factor of 10 for interaction terms beyond fourth nearest neighbours.

The comparison of effective Coulomb interaction obtained from direct \(c\)RPA and WFCE calculations shows generally very good quantitative agreement with deviations of less than 10%. The only exception is in the Gr/Ir data. Here, the local Coulomb interactions are overestimated by the WFCE approach by about 1 eV, which is likely a result of the approximated effective monolayer height, as discussed above. Nevertheless, even in this “worst-case” the WFCE approach accounts for \(\sim 80\%\) of the increased screening provided by the metallic environment.
3. Functionalized Graphene: Adsorbates and Heterostructures

Figure 3.21.:  
Left: WFCE density-density matrix elements of the background screened Coulomb interactions for bilayer graphene in real space for different dielectric surroundings ($\varepsilon_2 / \varepsilon_3$). Right: Corresponding dielectric functions in momentum space.

3.3.4. Electronic Ground State of Bilayer Graphene Heterostructures

<table>
<thead>
<tr>
<th>$\varepsilon_2$</th>
<th>$\varepsilon_3$</th>
<th>$U_0$</th>
<th>$U_1$</th>
<th>$U_2$</th>
<th>$U_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>9.2/9.3</td>
<td>4.7</td>
<td>3.3/3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>8.2/8.3</td>
<td>3.7</td>
<td>2.3/2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>1</td>
<td>$\infty$</td>
<td>7.6/7.7</td>
<td>3.1</td>
<td>1.7/1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>$\infty$</td>
<td>$\infty$</td>
<td>7.3/7.4</td>
<td>2.9</td>
<td>1.5/1.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 3.2.:  
Screened Coulomb interaction for bilayer graphene modified through different dielectric environments $\varepsilon_{2,3}$. All values are given in units of eV. Since the AB stacking breaks the sub-lattice symmetry for every second neighbour, some interactions are given separately for the A and B sub lattice (in one of the two layers).

Bilayer graphene is known to host competing symmetry-broken electronic ground states. Theoretical studies have predicted that charge- and spin-density waves (CDW or SDW), quantum-spin-hall states (QSH), nematic, superconducting and excitonic insulator states could emerge in the bilayer [205, 18, 206, 207, 208, 209, 210]. Different experiments have addressed the issue of symmetry-broken ground states in bilayer graphene [211, 212, 213, 214, 215, 216] but the issue remains controversial also from the experimental point of view and it is e.g. unclear whether or not the ground state exhibits a finite electronic excitation gap. In the end, it appears very likely that microscopic material specific details of the effective interactions determine which electronic
3.3. Coulomb Interactions in Layered Heterostructures

Figure 3.22:
Bilayer graphene phase diagrams in dependence on the on-site ($U = U_0$), nearest-neighbour ($V_1 = U_1$), and next-nearest-neighbour ($V_2 = U_2$) Coulomb interactions from Ref. [18]. The colored circles show the approximate positions within the phase diagrams for the values given in Tab. 3.2 (blue (1/1), green (1/5), red (1/$\infty$), yellow ($\infty$/1), red dashed (1/1) from Ref. [204]). The colored horizontal lines indicate the approximate phase boundaries between the QSH and AF-SDW phases for the varying on-site Coulomb-interaction matrix elements, which are otherwise fixed to $U = 2t$ and $U = 3.5t$ (with $t = 2.8$ eV) in the left and right panel, respectively (black horizontal lines).

phases are realized. As a dielectric substrate or also some metallic environment can provide additional screening of the effective Coulomb interactions in bilayer, we investigate how different types of environments affect the electronic ground state of bilayer graphene. To this end we use the WFCE approach to study the influence of a dielectric substrate ($\varepsilon_3 = 5$; $\varepsilon_2 = 1$) and a metallic substrate ($\varepsilon_3 \rightarrow \infty$; $\varepsilon_2 = 1$) as well as a metallic encapsulation ($\varepsilon_2 = \varepsilon_3 \rightarrow \infty$). The results can be seen in Fig. 3.21 as well as in Tab. 3.2.

The effective dielectric function diverges for $q \rightarrow 0$ in the case of the metallic substrate/environment, whereas a finite $\varepsilon_2^{2D}(q = 0) > 1$ can be found for the dielectric substrate, as it must be. The resulting effective Coulomb interactions can be clearly reduced due to environmental screening as comparison with the free standing bilayer data demonstrates. To understand the resulting effects on the electronic ground states, we make use of electronic phase diagrams that are based on recent functional renormalization group studies by Scherer et al. [18] and that give the ground states in form of maps of the nearest- and next-nearest neighbour screened Coulomb interaction for fixed on-site interactions $U_0 = 5.6$ eV ($U_0 = 2t$) and $U_0 = 9.8$ eV ($U_0 = 3.5t$). These diagrams show a general trend which pushes the bilayer ground state from being an antiferromagnetic (AF)-SDW to a QSH state with increasing next-nearest neighbour interaction ($V_2 = U_2$) while the nearest neighbour interaction ($V_1 = U_1$) has a negligible effect (for intermediate $U_2$), as shown in Fig. 3.22. Thereby, the boundary between the AF-SDW and the QSH states moves to higher ($U_2$) energies with increasing on-site
repulsion $U_0$ (see black and colored horizontal lines in Fig. 3.22). The interaction strengths obtained here put the ground state of bilayer graphene to the boundary of the AF-SDW/QSH transition in the free-standing scenario while any environmental screening stabilizes the AF-SDW phase like it is indicated by the colored circles in Fig. 3.22. This finding traces back to the fact that the on-site interactions $U_0$ are less decreased by the outer screening than the next-nearest neighbour interactions $U_2$. Since the influence of the latter to the exact position in the phase diagrams is stronger than that of the former, the electronic ground state gets more and more separated from the AF-SDW/QSH boundary by an increasing environmental screening.

3.3.5. Conclusions

We have established a scheme that combines cRPA calculations of layered materials in the bulk and continuum medium electrostatics to derive effective Coulomb-interaction matrix elements in terms of Wannier functions for free standing 2D materials as well as 2D materials embedded in complex dielectric environments. We call the scheme “Wannier function continuum electrostatics” (WFCE) approach. It allows us to avoid super-cell calculations involving complex environments or large vacuum volumes on the \textit{ab initio} side, which are numerically very costly in implementations using periodic boundary conditions. Already the simplest version presented here predicts effective Coulomb matrix elements for monolayer and bilayer graphene very accurately, i.e. for instance the local Hubbard interaction agrees with the full cRPA calculation within 0.3 eV. The comparisons of full first-principles and WFCE calculations suggest that the WFCE approach is accurate when hybridization between layers in the vertical direction is not too strong, as is the case for Van-der-Waals bonded systems. Currently, the WFCE approach is formulated partly in reciprocal space and is directly applicable to vertical heterostructures as long as the material providing the active orbitals to be considered later in the extended Hubbard model has some lattice translation symmetry. I.e. models for electrons in graphene on even amorphous or incommensurate substrates like SiO$_2$ or hBN could be derived using the WFCE approach in its current formulation. Of course, the WFCE approach might be further generalized in the future to a pure real-space formulation, which would allow to treat systems without or with strongly reduced lattice translation symmetry within the active orbitals and to address systems like twisted bilayer graphene.

Most importantly, our modelling shows that Coulomb interactions can be strongly manipulated in 2D materials like graphene by means of screening provided by the environments which can be substrates, adsorbates or other 2D materials. Given the numerical simplicity of the WFCE approach, we anticipate that it could be very useful in the context of materials design, as effects of different kinds of dielectric environments on Coulomb interactions in layered materials can be modelled quickly and quantitatively, now.
4. Molybdenum Disulfide Monolayers

Next to graphene, in particular the class of transition metal dichalcogenides (TMDCs) regained interest since the exfoliation of graphene monolayers. Back in 1923 one of its most prominent members, molybdenum disulfide (MoS$_2$), has been studied by Dickinson and Pauling for the first time [217], followed by intense studies from the 1960s to 1980s by Frindt et al. [218, 219, 220] and many others [221, 222, 223]. Nowadays, TMDC monolayers can be exfoliated from the bulk and synthesized in form of high-quality large-area mono-crystals [224] which allows for a broad spectrum of experimental studies. Like graphene, all TMDCs have strong intra-layer covalent bonds resulting in robust mechanical properties, while inter-layer coupling arises solely due to Van-der-Waals interactions. Depending on the transition metal and the unit cell geometries, we find metallic and semiconducting layers within the class of TMDCs. Regarding the semiconducting TMDCs, transitions from direct band gaps in the monolayers to indirect band gaps in multilayer systems can be found [225] making these materials to interesting candidates for optical device production. Furthermore, significant spin-orbit couplings and multiple-valley Fermi surfaces might form the basis for spin-or valleytronic devices (in which the electron spin or momentum is used to encode information). Next to these hypothetical applications, first field-effect transistors have already been produced on the basis of MoS$_2$ yielding high on/off ratios on the order of $10^8$ and sizable carrier mobilities [226].

While ground-state properties of TMDCs have been described and discussed in most detail, a general understanding of resulting effects upon doping or optical excitations is still missing. Therefore, we will study specific electronic and optical properties of the most prominent TMDC, namely MoS$_2$, in its monolayer form in the following chapter. Thereby, we will turn our focus to those properties which trace back to many-body effects. In more detail, we study many-body instabilities in form of superconductivity and charge-density-wave phases as well as many-body excitations such as excitonic and plasmonic modes. Additionally, we make use of the fundamental many-body interactions and their effects to the electronic band structure to propose a novel kind of heterojunction.

To this end, we give a general introduction to the most important ground-state properties of pristine MoS$_2$ monolayers in section 4.1. This includes detailed discussions of the electronic and phononic band structures as well as a brief introduction to the most important optical properties.
4. Molybdenum Disulfide Monolayers

Based on the presented electronic properties, we derive in the following section 4.2 a minimal material-specific low-energy multi-orbital generalized Hubbard model which includes a simplified yet extremely accurate description of the low-energy electronic band structure and, most importantly, an exceptional feasible description of the Coulomb interaction in a pristine MoS$_2$ monolayer. The latter is of prime importance due to the outstanding role of the Coulomb interaction in systems with reduced dimensionality making the model to the basis of material-realistic studies of many-body properties.

To study many-body instabilities we use first-principle calculations to examine the sequence of phases in electron doped MoS$_2$ in section 4.3. We observe a succession of semiconducting, metallic, superconducting (SC), and charge-density-wave (CDW) regimes upon increasing the doping level. Both instabilities (SC and CDW) trace back to a softening of phonons which couple the electron populated conduction band minima. Using the Eliashberg theory, we find a superconducting “dome” which reproduces the experimentally observed phase diagram reasonably well. The CDW phase at higher electron doping concentrations, as predicted from instabilities in the phonon modes, is further corroborated by detecting the accompanying lattice deformation in density functional based super-cell relaxations. Interestingly, we find that upon CDW formation, doped MoS$_2$ remains metallic but undergoes a Lifshitz transition, where the number of Fermi pockets is reduced allowing for a coexistence of the SC and CDW phases.

To explore the field of many-body excitations, we start with considering the optical response of MoS$_2$ by solving the semiconductor Bloch equations (SBE, not to be confused with BSE) in section 4.4 using the introduced material-realistic generalized Hubbard model. The treatment within the SBE allows us to study both, ground-state and finite-density spectra. Within the ground state we find optical responses and comparatively large exciton-binding energies on the order of several hundred meV in agreement with recent experiments and theoretical predictions. Upon increasing the carrier densities up to $10^{13}$ cm$^{-2}$ we find a redshift of the prominent excitonic ground-state absorption, whereas higher excitonic lines are found to disappear successively due to non-uniform reductions of the band gaps and binding energies. In addition, we find that strain-induced band variations lead to a redshift of the lowest exciton line by $\approx 110$ meV/\% and change the direct transition to indirect while maintaining the magnitude of the optical response.

Afterwards we analyze the rich phenomenology of plasmonic excitations in MoS$_2$ in various doping scenarios in section 4.5. To this end, we calculate the many-body polarization, the dielectric response function and electron-energy-loss spectra utilizing once again the low-energy Hubbard model. A plethora of plasmon bands are observed, originating from scattering processes within and between the conduction or valence band valleys. We discuss the resulting square-root and linear collective modes, arising from long-range and short-range screening of the Coulomb potential. In more detail, we show that the multi-orbital nature of the electronic bands and the spin-orbit coupling
strongly affects inter-valley scattering processes by gapping certain two-particle modes at large momentum transfers.

Finally, we propose to create lateral heterojunctions in two-dimensional materials based on non-local manipulations of the Coulomb interaction using structured dielectric environments. By means of \textit{ab initio} calculations for MoS$_2$ as well as generic semiconductor models, we show in section 4.6 that the Coulomb-interaction-induced self-energy corrections in real space are sufficiently non-local to be manipulated externally, but still local enough to induce spatially sharp interfaces within a single homogeneous monolayer to form heterojunctions. Thereby, we find a type-II heterojunction band scheme promoted by a laterally structured dielectric environment, which exhibits a sharp band-gap crossover within less than 5 unit cells.

4.1. Ground-State Properties

In the following we will shortly discuss the most important properties of molybdenum disulfide which are needed to understand the results in the subsequent sections. We will focus on the lattice structure and the resulting electronic, phononic and optical properties of a MoS$_2$ monolayer in its ground state, i.e., in its neutral (without any electron or hole doping) and unstrained state. For further details see Refs. [221, 225, 223].

4.1.1. Lattice Structure

As a member of the transition metal dichalcogenides (TMDCs) the formal unit cell of MoS$_2$ consists of a transition metal (M) and two chalcogen (X) atoms. Next to MoS$_2$ there are additional TMDCs based on transition metals from group IV, V and VI in combination with the chalcogen atoms S, Se or Te. All of these TMDCs form monolayers which consist of three sublayer with a transition metal layer in the middle and two outer chalcogen planes. In the hexagonal phase (see right panel of Fig. 4.1) the monolayer forms a honeycomb lattice (top view) with the M atom on sub-lattice A and the X atoms on the sub-lattice B (but separated in z-direction, see left panels of Fig. 4.1). In the tetragonal phase the three atoms occupy different sub-lattices resulting in structures like shown in the right panel of Fig. 4.1. In the following we will focus on the hexagonal phase in which the monolayer is described by the hexagonal Bravais lattice using the translation vectors

\[ \mathbf{a}_1 = a_0 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{a}_2 = \frac{a_0}{2} \begin{pmatrix} -1 \\ \sqrt{3} \\ 0 \end{pmatrix} \quad \text{and} \quad \mathbf{a}_3 = c \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \]  

(4.1)

where $a_0$ is the lattice constant which corresponds to the distance between neighbouring M atoms and $c$ is the super-cell height. This is a slightly different definition in
4. Molybdenum Disulfide Monolayers

Figure 4.1.: Schematic side views of different stackings (2H, 3R and 1T) of MX$_2$ layer in the corresponding bulk phases from Ref. [221] and top views of the hexagonal and tetragonal monolayer from Ref. [227]. Blue and green spheres mark transition metal atoms (M) while chalcogen atoms (X) are colored yellow.

Figure 4.2.: Real-space side and top views of a TMDC monolayer in the 2H phase (left panel) and the corresponding first Brillouin zone (right panel) with all points of high symmetry.
comparison to the one introduced in section 3.1.1. Here, the angle between the in-plane real-space lattice vectors is $120^\circ$, while it was $60^\circ$ in section 3.1.1. Correspondingly, the basis vectors are slightly different and are given here by

$$\delta_M = \left( \begin{array}{c} 0 \\ 0 \\ 0 \end{array} \right)_a \quad \text{and} \quad \delta_X = \frac{1}{3} \left( \begin{array}{c} 1 \\ 2 \\ \pm X_z \end{array} \right)_a,$$

(4.2)

where $X_z = \frac{3}{2} z_0$ with $z_0$ being the $z$-displacements between the X atoms. The resulting reciprocal lattice vectors are given by

$$b_1 = \frac{2\pi}{a_0\sqrt{3}} \left( \begin{array}{c} \sqrt{3} \\ 1 \\ 0 \end{array} \right)_b, \quad b_2 = \frac{2\pi}{a_0\sqrt{3}} \left( \begin{array}{c} 0 \\ 2 \\ 0 \end{array} \right)_b \quad \text{and} \quad b_3 = \frac{2\pi}{a_0c} \left( \begin{array}{c} 0 \\ 0 \\ 1 \end{array} \right)_b. \quad (4.3)$$

Within this basis, the high-symmetry points are given by

$$K = \frac{1}{3} \left( \begin{array}{c} 1 \\ 1 \\ 0 \end{array} \right)_b, \quad M = \frac{1}{2} \left( \begin{array}{c} 1 \\ 0 \\ 0 \end{array} \right)_b \quad \text{and} \quad K' = \frac{1}{3} \left( \begin{array}{c} 2 \\ -1 \end{array} \right)_b. \quad (4.4)$$

Additionally, we will focus on points which lie within the first Brillouin zone, namely

$$\Sigma = \frac{1}{6} \left( \begin{array}{c} 1 \\ 1 \end{array} \right)_b \quad \text{and} \quad \Sigma' = \frac{1}{6} \left( \begin{array}{c} 2 \\ -1 \end{array} \right)_b. \quad (4.5)$$

This hexagonal monolayer belongs to the space group P6m2 and point group D$_{3h}$ and lacks inversion symmetry. The exact values for the lattice constant $a_0$ and the $z$-displacement of the X atoms depend on the material under consideration. However, these numbers are mainly determined by the type of chalcogen atoms. For instance, the lattice constants of the molybdenum based materials MoS$_2$ ($a_0 \approx 3.16$ Å) and MoSe$_2$ ($a_0 \approx 3.30$ Å) do not differ much from the tungsten based counter parts WS$_2$ ($a_0 \approx 3.16$ Å) and WSe$_2$ ($a_0 \approx 3.29$ Å) as long as the same chalcogen atoms are considered [228]. In contrast to the experimental data, DFT based relaxations result in slightly larger (GGA-PBE) or smaller (LDA) values depending on the type of functional. In the case of MoS$_2$ DFT relaxations find $a_0 \approx 3.18$ Å and $z_0 \approx 3.13$ Å using the PBE approximation and $a_0 \approx 3.12$ Å and $z_0 \approx 3.11$ Å using the LDA [229]. Therefore, we will use different lattice constants in the following theoretical considerations depending on the available functional. The $z$-displacements of the chalcogen atoms will be optimized by corresponding energy minimizations.

As in the case of graphene, these monolayers can be stacked to Van-der-Waals bonded bulk crystals in various ways, for instance with a single tetragonal layer (1T) or two (2H) to three (3R) hexagonal layers per bulk unit cell, as shown in Fig. 4.1.
4. Molybdenum Disulfide Monolayers

4.1.2. Electronic Band Structure

In dependence of the transition metal atom type and the lattice structure TMDCs show a metallic or semiconducting ground states. In the case of monolayer MoS$_2$ in its hexagonal form the resulting band structure has a direct band gap of about 2 eV (in DFT) at the $K$ point, as it can be seen in Fig. 4.3. In more detail, we find several electron and hole valleys in the highest valence band and the lowest conduction band at $\Gamma$, $K$ and $\Sigma$. A detailed analysis of the predominant orbital contributions to these “low energy” states reveals major contributions due to molybdenum $d$ orbitals with magnetic quantum numbers $m_l = 0$ ($d_{z^2}$) and $m_l = \pm 2$ ($d_{xy}/d_{x^2-y^2}$). In contrast to these states, molybdenum $m_l = \pm 1$ ($d_{yz}/d_{xz}$) orbitals are not symmetric with respect to the basal plane and are thus completely decoupled and clearly separated from the former. Next to molybdenum $d$ orbitals, there is some sulfur $p$ weight mostly within the lowest conduction bands around $\Gamma$ reaching slightly into the $\Sigma$ valley, as shown in the right panel of Fig. 4.3. These contributions arise essentially from the sulfur $p_x$ and $p_y$ orbitals, while the $p_z$ states have a vanishing role around the band gap separating the valence and conduction bands. Indeed, a close look at the low energy states reveals strong hybridization within the molybdenum $m_l = \{0, \pm 2\}$ block which is responsible for the band-gap opening in MoS$_2$ monolayers [230, 231]. Furthermore, this hybridization leads to strong character variations within the low energy bands yielding a predominant $d_{z^2}$ weight at $\Gamma$ in the highest valence band and at $K$ and $K'$ in the lowest conduction band.

Next to orbital degrees of freedom the spin plays an important role in TMDCs as well due to significant spin-orbit interactions within the involved transition metals.
Although this interaction has a strong effect to the band structure, the $z$-component of the spin approximately remains a good quantum number due to the horizontal mirror symmetry. Therefore, $\{|\uparrow\rangle, |\downarrow\rangle\}$ might be seen as an adequate extension to the basis in order to consider the spin degree of freedom. These properties in combination with the absence of inversion symmetry lead to strong spin-orbit splittings in monolayer TMDCs around the $K/K'$ points [232, 233]. In the case of MoS$_2$ the highest valence band is split up by approx. 150 meV at the $K/K'$ point, while the corresponding splitting in the lowest conduction band is only on the order of 5 meV [232, 234]. As long as there are no magnetic fields, time-reversal symmetry is preserved leading to the fundamental symmetry

$$\varepsilon^\uparrow(\mathbf{k}) = \varepsilon^\downarrow(-\mathbf{k}),$$

which ensures, that the spin components of each band at $K$ and $K'$ as well as at $\Sigma$ and $\Sigma'$ are exactly exchanged.

Finally, we shortly address the absolute value of the direct band gap at the $K/K'$ point. As discussed in section 2.3 the fundamental band gap is regularly underestimated in DFT calculations, which results from the local density approximation (or GGA) used to define the Kohn-Sham single-particle system and the neglect of Coulomb-interaction-induced correlation effects. Since the screening is in two dimensions strongly decreased, the Coulomb interaction is here in general enhanced and long ranged, which 	extit{a posteriori} explains its outstanding role in systems with reduced dimensionality. Hence, the neglect of these interaction effects is a crucial approximation which has to be overcome in order to reliably predict excitation properties such as the band gap. To this end, the $GW$ approximation, as introduced in section 2.3.4, is frequently used in its $G_0W_0$ form. In MoS$_2$ the long range character of the Coulomb interaction as introduced within the $G_0W_0$ treatment enhances the hybridization within the $m_l = \{0, \pm 2\}$ block which results in an enhancement of the band gap, as described and explained in more detail in section 4.6.1. However, it is by far not a simple task to properly converge these calculations. On the one side, there are various calculation parameters (like the $k$-point sampling or energy cut-offs) which have to be carefully converged, as shown in more detail in section A.3.1. On the other side, there is a physical problem: Within the $GW$ calculations the MoS$_2$ sheet is embedded in a three-dimensional unit cell with an effective vacuum distance $h_{\text{vac}}$ separating adjacent sheets. Due to this repeated slab setup artificial screening effects of the Coulomb interactions arise from adjacent slabs which decreases the band gap, as already addressed in section 3.3. To overcome this problem there are basically three options: (i) We can make use of the WFCE approach as introduced in section 3.3 in order to correct the long-range screening properties of the involved Coulomb interaction according to the macroscopic screening properties of the layered material. (ii) Appropriate truncation schemes can be applied to the Coulomb interaction in $z$-direction to suppress the artificial inter-slab interaction [235, 236, 197]. (iii) We can extrapolate the band gap as it
4. Molybdenum Disulfide Monolayers

would be obtained for infinitely separated slabs from several calculations using different vacuum distances [237, 197]. The second and third approaches have already been applied to MoS$_2$ monolayers and yielded direct band gaps of about 2.8 eV [197, 194] to 3.0 eV [237]. Thus, the proper treatment of the Coulomb interaction increases the fundamental band gap in MoS$_2$ monolayers by about 1 eV, which is a huge effect.

Moreover, this strong dependence of the band gap to the Coulomb interaction explains its dependence on its dielectric surrounding: In atomically thin layers, the Coulomb interaction can be drastically manipulated by external screening as shown in section 3.3.4 or in Refs. [199, 238, 239, 240, 241, 242, 243, 244, 245], allowing to control the band gap by the dielectric environment, which will be discussed in section 4.6.

Next to screening effects there might be mechanical strain or stress [246, 247, 248], applied electric or magnetic fields [249, 250], stacking [251] or electron or hole doping [252, 253, 250] as outer tuning knobs which are able to control the value of the direct band gap at $K/K'$ and which can even lead to an indirect band gap due to the lowering of the $\Sigma$ valley.

4.1.3. Phononic Band Structure

In Fig. 4.4 the phononic band structure and density of states, the corresponding Eliashberg function as well as representations of the optical modes in their long-wavelength
limits are shown. Due to the three-atomic basis MoS$_2$ monolayers have nine distinct phonon modes: three acoustic and six optical branches which are, in the case of MoS$_2$, separated by a clear gap of about 10 meV. The acoustic branches can be divided into in- and out-of-plane modes. The former correspond to transversal (TA) and longitudinal (LA) modes which have a linear dispersion in the vicinity of the $\Gamma$ point while the LA mode is higher in energy. The out-of-plane (ZA) mode shows a quadratic dispersion in the near of $\Gamma$ at decreased energies. These flexural modes arise solely in layered materials and result from the bending rigidity of the two-dimensional membrane [255, 256, 170]. At the Brillouin-zone boundary (i.e. between $K$ and $M$) all acoustic modes become rather flat with phonon energies in the range of 20 to 30 meV.

While the acoustic modes are defined by in-phase oscillations of all atoms within the unit cell, the optical modes arise due to counter-phase oscillations. These can be separated into counter-phase motions solely between the sulfur atoms while the molybdenum atoms are in rest (non-polar and homopolar) and counter-phase oscillations between the sulfur and the molybdenum atoms (polar), as shown for the long-wavelength limits in the very right panel of Fig. 4.4. These modes have different symmetries labeled by $E''$, $E'$, $A'_1$ and $A''_2$ (ordered from low to high energies) with $E'$ and $E''$ being degenerated twice at $\Gamma$. In more detail, the $E$ modes can be separated into longitudinal (LO$_i$) and transversal (TO$_i$) branches which are normally split up in polar materials (LO-TO splitting [257, 135]). This splitting arises due to coupling of the lattice with the phonon-mode induced macroscopic electric fields, which effects the LO modes and thus breaks the degeneracy. However, for bulk MoS$_2$ this effect is known to be very small (on the order of 0.5 meV) and it will be even smaller in the monolayer [258, 259, 254] and is therefore neglected here.

In order to study phononic properties from an experimental point of view it is important to know which optical modes are infrared and/or Raman active. Here, we see that all polar modes ($E''$ and $A''_2$) induce dipole moments due to relative motions of the sulfur and molybdenum atoms which results in a non-vanishing infrared sensitivity. Raman activity arises as soon as dipole moments due to deformations of the electron shells are introduced by the incident light. This is the case for the $E''$, $E'$ and $A'_1$ modes.

The corresponding phononic density of states shows maxima in all regions in which the phononic bands flatten, resulting in rather large contributions due to the clearly separated optical modes. As described in section 2.4.5, the Eliashberg function $\alpha^2F(\omega)$ incorporates the electron-phonon coupling and thus renders those parts of the phononic spectra which strongly interact with the electronic system. It is interesting to see that the non-polar modes ($E''$) do not contribute at all to the Eliashberg function [260]. Regarding the acoustic modes, we find significant contributions to $\alpha^2F(\omega)$ due to the rather flat areas of the LA and TA modes. For the flexural modes (ZA) it is known that these couple much less to the electrons [261] which will become more definite in section 4.3.2, where we study the influence of electron doping to the phononic band structure and the electron-phonon coupling.
4. Molybdenum Disulfide Monolayers

4.1.4. Optical Properties

In Fig. 4.5 theoretical [194, 262] and experimental [193] absorption spectra for MoS$_2$ monolayers are shown. Within the experimental data two distinct sharp peaks around 2 eV and a broad peak around 2.7 eV arise. The theoretical data is given for RPA (red) and BSE\(^1\) (green) calculations. The RPA data is gained from the evaluation of the dielectric function on the basis of GW-renormalized electronic bands and does not include any many-body effects beyond the GW approximation. Therefore, the absorption edge around 2.7 eV in the RPA data originates from continuous inter-band absorption processes between the highest valence and the lowest conduction band and thus measures the quasiparticle band gap. The absence of the peaks around 2 eV in the RPA data is a clear hint that they arise due to excitonic absorption processes. And indeed, by considering two-particle processes via solutions of the Bethe-Salpeter equation based on GW input these absorption peaks are derived, as it can be seen in Fig. 4.5 (a) and as it is discussed in Refs. [263, 194, 197]. As discussed in more detail in section 4.4.1, these peaks (labeled as A and B) originate from bound electron-hole pairs from the $K'/K$-valleys. The separation of these peaks results from the spin-orbit splitting of the upmost valence bands (see section 4.2 and section 4.4 for more details). Next to the A and B peaks, additional resonances labeled by A$'$, B$'$ and A$''$ can be found in the calculated absorption spectra corresponding to excited states of the $K'$ and $K'$-valley excitons. Around 2.7 eV another bound excitonic state (C) is indicated which will also be discussed in more detail in section 4.4.1. Like in the RPA data, a more or less continuous absorption is found in the BSE data above the quasiparticle band gap.

By subtracting the excitation energy of a given exciton from the quasiparticle band gap the exciton binding energy $E_b$ can be derived, as indicated for the A exciton in

\(^1\)See footnote 2 on page 77.
Fig. 4.5 (a) resulting in the binding energy $E_b^A$. Here, these binding energies are on the order of several hundred meV which is an order of magnitude larger than what is known for conventional bulk materials [264]. This strong enhancement is, once again, explained by the reduced screening in two-dimensional materials [193, 194, 197, 265, 243]: The electron-hole binding (which defines the exciton) arises due to the Coulomb interaction. A decreased screening yields an increased Coulomb interaction and thus strongly increased exciton binding energies. Hence, the Coulomb interaction plays an essential role to describe optical properties of these low-dimensional materials.
4. Molybdenum Disulfide Monolayers

4.2. Minimal Generalized Hubbard Model

The minimal many-body model presented in the following section has been derived by myself and has been published in Nano Lett. 14, 3743 (2014), where it was used to study optical properties of MoS$_2$ monolayers. Furthermore, the model serves as the basis for the investigation of plasmonic intra- and inter-valley excitations in this material as discussed in section 4.5 and was used in a corresponding work which has been published in Phys. Rev. B 93, 205145 (2016). The reader will find a considerable overlap between the following text including its appendix in section A.3 and the corresponding paragraphs of the article Nano Lett. 14, 3743 (2014).

In the following section we aim to derive simplified yet accurate descriptions of the renormalized band structure and the screened Coulomb matrix elements of MoS$_2$ monolayers in order to gain the possibility to evaluate these elements on-demand without the need of redoing any kind of ab initio calculations. These descriptions will serve as the basis for further many-body treatments of MoS$_2$ under the influence of charge doping or optical excitations. Hence, we separate the renormalizations into those which arise due to the intrinsic correlations in the ground state of MoS$_2$ and those which arise due to additional doping or other excitations schemes. In principle, this must not be done and full many-body ab initio calculation for the excited systems might be performed. However, the corresponding computational demand would not allow for systematic studies or fully converged results. Furthermore, in many situations full calculations are unnecessary since certain renormalization effects affect solely states in a small energy range. Hence, our goal here is in fact to derive easy-to-handle descriptions of the low energy band structure and corresponding Coulomb matrix elements. This low energy part involves in the case of MoS$_2$ the upmost valence band and the two lowest conduction bands of $m_l = \{0, \pm 2\}$ character. Thereby, we will be able to consider hole and/or electron doping effects within sophisticated many-body treatments in the following.

Within the minimal basis we will derive an easy-to-handle tight-binding Hamiltonian $H_{\alpha\beta}(k)$ to describe the GW renormalized band structure at arbitrary $k$-points in the Brillouin zone. Additionally, we will set up simple fit formulas to describe the bare $v_{\alpha\beta}(q)$ as well as the RPA screened $W_{\alpha\beta}(q)$ density-density Coulomb-interaction matrix elements. Altogether, these elements might be seen as a generalized multi-orbital Hubbard model. However, this formulation is slightly misleading, since the “true” Hubbard model would include unrenormalized ingredients only.

4.2.1. Three-Band Tight-Binding Model

A central element of our approach is the tight-binding (TB) Hamiltonian $H_{\alpha\beta}(k)$, which is obtained on the foundation of $G_0W_0$ calculations (see section A.3.1 for all computational details). As explained in section 3.3, GW calculations based on the
repeated-slab method suffer from artificially introduced screening which results here in reduced band gaps. Thus, in order to model a free standing MoS$_2$ layer within the GW approach we have to apply a corresponding correction. To this end, we extrapolate the $G_0W_0$ band gaps $\Delta_K(h_{\text{vac}})$ (at the $K$ point), which are obtained for several vacuum distances $h_{\text{vac}}$ (here varying between 25 and 55 Å), according to

$$\Delta_K(h_{\text{vac}}) = \Delta_K(\infty) + \frac{b}{h_{\text{vac}}}, \quad (4.7)$$

where $b$ is the slope of the linear extrapolation and $\Delta_K(\infty)$ is free-standing limit. From $\Delta_K(\infty)$ and the band gap from the actual TB model we can derive the corresponding correction (sometimes called \textit{“scissor operator”}) which is applied to all conduction bands to gain the extrapolated dispersion. The result of such a correction is shown in Fig. 4.6 (a) in form of a Wannier-interpolated $G_0W_0$ band structure for a free-standing unstrained ($a_0 = 3.18$ Å) MoS$_2$ monolayer. Here, we show the full dispersion in black which includes all molybdenum and sulfur contributions. Using the extrapolation we find a direct band gap of 2.72 eV at the $K$-point in agreement with data from Ref. [197]. The three highlighted (red) bands correspond to a Wannier construction based on projections of the three low-energy bands of interest (the highest valence and the two lowest conduction bands) onto the Mo-$d_{z^2}$, $-d_{xy}$ and $-d_{x^2-y^2}$ orbitals. As mentioned before, these states have predominately molybdenum $d$ ($m_l = \{0, \pm2\}$) orbital character and obviously serve as an excellent basis, as it can be seen in the resulting Wannier interpolated band structure (red) in Fig. 4.6 (a). In more detail, we use the Wannier90 code [69] and apply an inner window which fixes the energies of the complete highest valence band and the energies of the $K/K'$ and $\Sigma$ valleys of the conduction band. Instead of performing a maximal localization, we stay with first guess (but disentangled) projections. Thereby the formally neglected states (most importantly sulfur $p$ orbitals) are indirectly accounted for and dominant orbital features (e.g. $d_{z^2}$ weights at $K/K'$ and $\Gamma$) are maintained. This is important for a proper \textit{a posteriori} inclusion of the spin-orbit coupling as described in the following paragraph.

**Spin-Orbit Coupling**

We treat the spin-orbit coupling (SOC) by considering a Russell-Saunders interaction with a $k$-dependent coupling parameter that is chosen to match the SOC induced splittings at valence- and conduction-band symmetry points to that of a GGA calculation. The TB Hamiltonian then becomes $H_{\alpha\beta}(k) = H_{\alpha\beta}(k) \otimes I + H_{\text{SOC}}(k)$ [234], where $I$ is the $2 \times 2$ unity matrix and

$$H_{\text{SOC}}(k) = \lambda(k) \cdot \mathbf{L} \cdot \mathbf{S} = \frac{\lambda(k)}{2} \begin{pmatrix} L_z & 0 \\ 0 & -L_z \end{pmatrix}, \quad (4.8)$$
4. Molybdenum Disulfide Monolayers

Figure 4.6:
Band structures as obtained from (a) vacuum extrapolated $G_0W_0$ calculations without spin-orbit coupling and (b) DFT (GGA) calculations with spin-orbit coupling. The highlighted bands enter the minimal three-band TB model. While the DFT calculations in (b) takes the spin-orbit coupling on an \textit{ab initio} level into account the tight-binding description utilizes the effective spin-orbit coupling as described in the text.

with

$$L_z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 2i \\ 0 & -2i & 0 \end{pmatrix}. \quad (4.9)$$

$\lambda(k)$ is taken to be a function of $k$ to account for the variation in sulfur $p$ orbital admixture to the effective three-band model throughout the Brillouin zone reducing the spin-orbit coupling strength. We find that

$$\lambda(k) = \lambda_0 \cdot e \cdot \left(1 - \frac{|k|}{|K|}\right)^2 \cdot e^{-(1 - \frac{|k|}{|K|})^2} \quad (4.10)$$

with $\lambda_0 = 73 \text{ meV}$ reproduces the spin-orbit splittings of the DFT (GGA) band structure reasonably well, as can be seen in Fig. 4.6 (b). Here we show the \textit{ab initio} (GGA) band structure (black) in comparison to the modeled band structure (red) as obtained from diagonalization of a three-band (Wannier based) tight-binding model which is augmented by the Russell-Saunders spin-orbit coupling as described above.

4.2.2. Coulomb-Interaction Model

The second important ingredient to our material-realistic model are Coulomb matrix elements. We suggest a simple yet accurate method to obtain \textit{density-density} matrix elements that can be used in various TB-based calculations. For each orbital combination, we provide a fit formula for the bare Coulomb matrix element,

$$v_{\alpha\beta\alpha}(q) = v_{\alpha\beta}(q) = \frac{e^2}{2\varepsilon_0 A} \frac{1}{q(1 + \gamma_{\alpha\beta} q)}, \quad (4.11)$$
4.2. Minimal Generalized Hubbard Model

Figure 4.7:
Orbitally resolved bare \((v)\) and screened \((W)\) Coulomb matrix elements for freestanding, unstrained MoS\(_2\) and various orbital combinations (from left to right and top to bottom: \(d_{z^2}, d_{xy}, d_{x^2-y^2}\)). The insets show the corresponding dielectric functions. Dots represent the original \textit{ab initio} values while solid lines correspond to the fits according to Eqs. (4.11–4.13).

where \(e\) is the elementary charge, \(A\) is the area of the two-dimensional unit cell, and \(\gamma\) is a parameter that appears in a form factor to capture the effective height of the MoS\(_2\) layer affecting short wave lengths. The RPA screened Coulomb matrix elements

\[
W_{\alpha\beta}(q) = \frac{v_{\alpha\beta}(q)}{\varepsilon_{\alpha\beta}(q)}
\]  

(4.12)

require knowledge of the \textit{effective} two-dimensional dielectric function \(\varepsilon_{\alpha\beta}(q)\). Although we could in principle apply the WFCE algorithm described in section 3.3 (using a full RPA screening) to derive the dielectric function of the MoS\(_2\) monolayer from its three-dimensional bulk host system, we avoid it here. Instead we aim to derive simplified \textit{analytic} model descriptions of \textit{all} matrix elements on their own, that is the bare as well as the corresponding screened interaction matrix elements. Therefore, Eq. (4.12) is not to be understood as a matrix product but rather as an \textit{element-wise fit} of the complete density-density screened Coulomb-interaction \textit{matrix}. For each of the
4. Molybdenum Disulfide Monolayers

Table 4.1:
Parametrization of the orbitally-resolved screened Coulomb matrix elements for freestanding, unstrained MoS\(_2\).

<table>
<thead>
<tr>
<th>orbitals</th>
<th>(d) (Å)</th>
<th>(\epsilon^\infty)</th>
<th>(\gamma) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{z^2}) (d_{z^2})</td>
<td>11.70</td>
<td>7.16</td>
<td>1.99</td>
</tr>
<tr>
<td>(d_{z^2}) (d_{xy})</td>
<td>4.56</td>
<td>14.03</td>
<td>2.42</td>
</tr>
<tr>
<td>(d_{z^2}) (d_{x^2-y^2})</td>
<td>4.60</td>
<td>13.97</td>
<td>2.40</td>
</tr>
<tr>
<td>(d_{xy}) (d_{xy})</td>
<td>12.88</td>
<td>6.88</td>
<td>2.32</td>
</tr>
<tr>
<td>(d_{xy}) (d_{x^2-y^2})</td>
<td>7.13</td>
<td>9.90</td>
<td>2.46</td>
</tr>
<tr>
<td>(d_{x^2-y^2}) (d_{x^2-y^2})</td>
<td>12.73</td>
<td>6.92</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Influence of a Dielectric Environment

A particular advantage of the Coulomb-interaction model presented in the previous section is that it is comparatively easy to include screening effects due to homogeneous dielectric environments. This is, for instance, necessary to describe the Coulomb interaction in MoS\(_2\) monolayers in realistic situations in which the layer is placed on top of a substrate or encapsulated by a sub- and a superstrate. In an approximate fashion this can be modeled by using the full dielectric function from Eq. (3.16) instead of the description in Eq. (4.13). Thereby, the dielectric constants \(\epsilon_2\) and \(\epsilon_3\) are re-introduced and describe the dielectric constants of the material above and below the layer. However, thereby one assumes that the macroscopic external screening effects act in the same way on each element of the screened Coulomb-interaction matrix. Since this is not justified in general, one should use the WFCE method from section 3.3. To this end, we need to define a proper screening matrix (note, values defined in Eq. (4.13) do

\[
\epsilon_{\alpha\beta}^{-1}(q) = \frac{1}{\epsilon_{\alpha\beta}^{\infty}} + \frac{1 + (\epsilon_{\alpha\beta}^{\infty} - 1)e^{-qd_{\alpha\beta}}}{\epsilon_{\alpha\beta}^{\infty} + 1 - (\epsilon_{\alpha\beta}^{\infty} - 1)e^{-qd_{\alpha\beta}}}. \tag{4.13}
\]
not correspond to matrix elements of this matrix). Therefore we apply the symmetric
definition [equivalent to the one used in Eq. (3.30)]
\[
\varepsilon(q) = v^{1/2}(q) W^{-1}(q) v^{1/2}(q)
\] (4.14)
using the matrices defined in Eq. (4.11) and Eq. (4.12). Now, the leading or macroscopic eigenvalue \( \varepsilon_m(q) \) can be defined by
\[
\varepsilon_m(q) = \langle v_1(q) | \varepsilon(q) | v_1(q) \rangle.
\] (4.15)
Here, we have to use the eigenfunction \( |v_1(q)\rangle \) which corresponds to the leading eigenvalue \( v_1(q) \) of the bare interaction matrix \( v(q) \). Following the WFCE concept, we know that all macroscopic screening properties are rendered by this function. Correspondingly, additional macroscopic screening effects due to the environment have to be included to this part of the screening matrix which can be achieved by substituting \( \varepsilon_m(q) \) by \( \varepsilon^{\varepsilon_1/\varepsilon_2}(q) \) defined by Eq. (3.16). The full dielectric screening matrix thus becomes
\[
\varepsilon^{\varepsilon_1/\varepsilon_2}(q) = \varepsilon(q) + \left[ \varepsilon^{\varepsilon_1/\varepsilon_2}(q) - \varepsilon_m(q) \right] |v_1(q)\rangle \langle v_1(q)|
\] (4.16)
and the screened Coulomb matrix which includes environmental screening effects is given by
\[
W^{\varepsilon_1/\varepsilon_2}(q) = v^{1/2}(q) \left[ \varepsilon^{\varepsilon_1/\varepsilon_2}(q) \right]^{-1} v^{1/2}(q).
\] (4.17)
4.3. Many-Body Instabilities Under Electron Doping

The results presented in this section have been gained in collaboration with S. Haas and have been published in Phys. Rev. B 90, 245105 (2014). I was responsible for all calculations and for the manuscript preparation. Most of the following text and its appendix in section A.4 originate from the original article.

The lack of screening in two-dimensional materials in combination with van-Hove singularities can lead to strong enhancements of scales in transition metal dichalcogenide monolayers and result in competing instabilities, such as superconductivity (SC) and charge-density-wave (CDW) phases [266, 221]. For example, based on Eliashberg theory it has been argued that by doping the structurally related graphene up to its van-Hove singularity, the effective electron-phonon coupling can be greatly enhanced, leading to superconducting transition temperatures potentially as high as 30 K [267, 160]. Thereby, the quasi-two-dimensional structure of these compounds allows for a high degree of control via tuning knobs such as pressure, strain, doping and adsorbates, but it also makes these materials more vulnerable to the effects of impurity disorder.

The generic phase diagram of the metallic transition metal dichalcogenides features a CDW regime at and close to half-filling, which is suppressed by a competing SC instability upon hole doping or exerting external pressure [268, 269]. For example, pristine 1T-TiSe₂ undergoes a CDW phase transition at approximately 200 K [270]. Upon hole doping via Cu intercalation [271] or application of pressure [272] this phase is suppressed and replaced by competing SC order with transition temperatures \( \sim 2 \ldots 5 \text{ K} \), leading to a phase diagram topology akin to the high-\( T_c \) cuprates, with CDW taking the place of the antiferromagnetic insulator regime in the cuprates, as depicted in Fig. 4.8. This succession of phases can be modeled by combining first-principle calculations with Eliashberg theory, based on a phonon-mediated pairing mechanism [273]. Furthermore, since these materials are quasi-two-dimensional, it can be expected that other low-energy modes, such as plasmons, are present and may contribute to the formation of the SC condensate [269, 274].

Here, we focus on the phase diagram of electron-doped transition metal dichalcogenides. Since these materials do not show an electron/hole symmetry it is a priori not known which phases will arise and how they compete with each other. Indeed, we find a different topology in the electron-doped regime, thus leading to an interesting set of predictions that can be experimentally tested. Without loss of generality, we focus on the much studied compound MoS₂ because there already is a wealth of data available which allows to scrutinize our approach.

Electron doping of thin-flake MoS₂ has recently been achieved by means of combined liquid/solid high-capacitance gates, leading to effective 2D carrier densities of up to \( n_{2D} \approx 1.5 \times 10^{14} \text{ cm}^{-2} \). Such doping by field-effect gates allows to access larger carrier concentrations compared to chemical substitution, without substantially deforming the
4.3. Many-Body Instabilities Under Electron Doping

Figure 4.8.: Phase diagrams of (a) doped cuprates and (b) TiSe$_2$ under pressure or hole doping due to Cu intercalation from Refs. [277] and [272], respectively. While the cuprates undergo a phase transition from an insulating antiferromagnetic state to superconductivity under doping, TiSe$_2$ starts in a charge-density-wave phase before entering the superconducting state under both, pressure or doping.

lattice [252]. A field-doping-induced superconducting dome was found with onset at $n_{2D} = 6.8 \times 10^{13}$ cm$^{-2}$ and peak with maximum $T_c = 10.8$ K at $n_{2D} = 1.2 \times 10^{14}$ cm$^{-2}$ [252, 275]. Using density functional theory calculations, it has been shown that this superconducting dome is consistent with electron-phonon coupling that is doping dependent due to the change of Fermi surface topology when negative charge carriers are introduced [253].

Here, we push this analysis further and deliver a quantitative description of the superconducting dome and identify a competing CDW phase which occurs at higher doping concentrations. Although this kind of competition is known in the hole-doped regime, it is interesting that the CDW phase exists in the electron-doped regime as well. In this case the Fermi surface topology is totally different and thus the behaviour of the newly found CDW phase is different from the corresponding phase in the hole-doped case: Electron-doped MoS$_2$ remains metallic after CDW formation. While it may turn out to be difficult to achieve such high doping concentrations in MoS$_2$ experimentally by back gating [252], this prediction is a generic feature, and thus should hold for other electron-doped dichalcogenides as well. Example systems for observing the CDW phase predicted here include chemically doped MoS$_2$, as e.g. realized by alkali deposition or intercalation [276].

4.3.1. Methods

We apply density functional theory and density functional perturbation theory to calculate electronic and phononic band structures as well as electron-phonon coupling matrix elements (see section A.4 for computational details). To simulate electron doping an additional (fractional) amount of electrons along with a compensating jellium
background is introduced. The electron doping will be given either in electrons per primitive MoS$_2$ unit cell $x$ or in electrons per cm$^2$ $n_{2D} = x/A$, where $A$ is the area of the unit cell. Due to the periodic slab arrangement within our three-dimensional unit cell artificial inter-layer states will arise which energetic positions are sensitive to the vacuum distance and the additional positive background charges. Therefore care is taken that no inter-layer states are introduced in the low energy band structure close to the Fermi level.

The superconducting transition temperatures are obtained using the Allen-Dynes approximation as introduced in section 2.4.5. To this end we evaluate next to the electronic and phononic band structures the phononic density of states [PDOS or $F(\omega)$], the effective electron-phonon coupling ($\lambda$) and the Eliashberg function [$\alpha^2 F(\omega)$] in dependence of the electronic doping concentration.

The newly found emerging CDW at higher electron concentrations is identified by (i) the occurrence of an unstable phonon mode, (ii) by spontaneous deformation of the honeycomb lattice, as well as (iii) by comparison of energies of the deformed lattice with the unperturbed lattice. For these calculations two different unit cells are used. To calculate the phonon dispersion as well as the corresponding electron-phonon coupling matrix elements we use a primitive $1 \times 1$ unit cell of MoS$_2$. Since these calculations will predict an unstable phonon mode at Brillouin zone $M$ points [see Fig. 4.9 (b)], we perform relaxations of a $2 \times 1$ super-cell, which is commensurate with the resulting CDW and which can host the corresponding lattice deformations. The CDW formation energy discussed below is defined by

$$\Delta E_{\text{CDW}} = \frac{E_{2\times1} - E_{2\times1}^{\text{CDW}}}{2},$$

where $E_{2\times1}$ is the total energy of the relaxed $2 \times 1$ unit cell preserving the $1 \times 1$ symmetries (i.e. just doubling of a $1 \times 1$ primitive cell with relaxed S atoms) and $E_{2\times1}^{\text{CDW}}$ is the corresponding energy of the fully relaxed $2 \times 1$ unit cell which is able to incorporate the CDW.

### 4.3.2. Superconductivity and Charge-Density Waves

We start with a short discussion on the effects of electron doping to the electronic band structure as shown in Fig. 4.9 (a). Here, the doping levels correspond to the metallic regime (blue, only the $K$ valleys are occupied), the SC phase (green, $K$ and $\Sigma$ are occupied), and the CDW phase (red, $K$ and $\Sigma$ are occupied). As demonstrated in section 4.1.2, the low energy states of the conduction band in MoS$_2$ are dominated by two prominent valleys at $K$ and $\Sigma$ which are successively occupied upon electron doping. With increasing charge concentration the $\Sigma$ valley moves towards lower energies, whereas the $K$ valley is less affected [see inset of Fig. 4.9 (a)] [253] which results in an decreasing energetic offset between the minima of these valleys within DFT. Due to the arbitrary alignment at the valence band maximum in Fig. 4.9 (a) no relative
4.3. Many-Body Instabilities Under Electron Doping

Figure 4.9.: (a) Electronic and (b) acoustic part of the phononic band structures of MoS$_2$ monolayers for different doping levels (blue: $x = 0.025$, green: $x = 0.100$, red: $x = 0.150$). The electronic band structures are aligned at the valence band maxima at $K$ and the corresponding Fermi energies are indicated by dashed lines. The inset shows a the $K$ and $\Sigma$ valleys in more detail (aligned at the Fermi energies) to highlight their relative shifts upon doping. The phononic band structure is complemented by several doping levels in between the range of $x = 0$ to $x = 0.15$ (grey).

shifts can be seen here. Nevertheless, at $\Gamma$ in the valence band we see comparable renormalizations as at $\Sigma$ in the conduction band. Within the doping range shown in Fig. 4.9 (a) the band gap at $K$ stays direct and is only slightly increased (less than 30 meV) upon doping. The resulting instabilities are discussed in more detail in the following sections.

Metallic and Superconducting Phase

Here we focus on the acoustic parts of the phonon dispersions of MoS$_2$ since we will see in the following that the optical branches do not considerably contribute to the SC and CDW formation. Accordingly, we show in Fig. 4.9 (b) the acoustic branches for the same electron concentrations as before. We find that upon doping the acoustic in-plane (LA and TA) branches at $M$, $K$ and somewhere between $K$ and $\Sigma$ soften [253]. These softening effects are well known in metallic systems and trace back to Kohn anomalies [278, 27] which arise due to efficient electron-phonon coupling between electronic states on the Fermi surface as we will discuss in more detail below. The parabolic out-of-plane phonons are odd under mirror transformation with respect to the Mo plane and do not couple the conduction band minima at $K$ and $\Sigma$ [261]. There is thus no Kohn anomaly (or related phenomena) leading to softening of these phonons upon electron doping.
As we will see below, the softened regions of the acoustic branches dominate the formation of the SC condensate, with \( \omega_{\text{typ}} \approx 2\pi k_B T_c \approx 5 \text{ meV} \). At a critical electron concentration \( x_c \sim 0.14 \) one of the acoustic modes develops an instability at the \( M \) point indicated by imaginary frequencies [see red curve in Fig. 4.9 (b)]. This instability arises due to the onset of a CDW regime as it is for instance known for TiSe\(_2\) [273]. However, while the CDW regime in TiSe\(_2\) already occurs in its pristine state and is suppressed by pressure or hole-doping giving way to SC [272], the sequence of phases we observe in MoS\(_2\) is reversed.

Let us now turn our focus towards the SC regime at intermediate doping levels. To this end we examine the lattice dynamics encoded in the phonon density of states and the Eliashberg functions for different electron concentrations as shown in Fig. 4.10 (a) and (b). Overall, we find no pronounced changes in the phonon density of states apart from a small reduction of all phonon energies upon electron doping. The Eliashberg functions, as shown in Fig. 4.10 (b), weight the phonon DOS with the electron-phonon coupling matrix elements. Thus, we are able to track those parts of the phonon spectrum which contribute most to the SC condensate. Here, we find that although the high-energy optical modes (\( \sim 35 - 50 \text{ meV} \)) lead to the strongest peaks in the phonon density of states, they do not contribute significantly to the SC phase, as it can be seen in the relative weights of the optical and acoustic branches in the Eliashberg functions. The SC response is rather dominated by the acoustic phonon branches around the \( M \) and \( K \) points. As these modes soften upon electron doping leading to increasing electron-phonon matrix elements (see discussion below), the evolution of the Eliashberg function displays raising peaks within the acoustic branches. The strongest integrated weight is found for a doping concentration of \( x = 0.125 \). However, this concentration does not correspond to the maximum of \( T_c(x) \)
4.3. Many-Body Instabilities Under Electron Doping

\[ \text{electron doping } n_{2D} \left( 10^{14} \text{ cm}^{-2} \right) \]

\[ \text{critical temperature, } T_c(x) \text{ (K)} \]

\[ \text{lattice distortion, } \alpha(x) \text{ (°)} \]

\[ \text{energy gain upon CDW formation } \Delta E_{\text{CDW}} \text{ in K} \]

Figure 4.11:
Temperature-doping phase diagram of MoS\(_2\). Circles belong to the left axis (K) and squares to the right (°). Green lines are obtained from first-principles calculations combined with Eliashberg theory and show the SC critical temperature for different Coulomb pseudopotentials (using a Gaussian smearing of \( \delta = 0.005 \text{ Ry} \)). Black circles are experimental data from Ref. [252]. Also shown is the lattice distortion angle \( \alpha \) (red squares) and the energy gain upon CDW formation \( \Delta E_{\text{CDW}} \) in K (blue circles).

since the interplay of the effective coupling \( \lambda(x) \) and \( \omega_{\text{log}}(x) \) [as defined in Eqs. (2.225) and (2.226), respectively] has to be considered. As it can be seen in the inset of Fig. 4.10 (b) \( \omega_{\text{log}}(x) \) decreases, while \( \lambda(x) \) increases with increasing doping. An optimal proportion is reached at \( x \approx 0.11 \) leading to a maximum of \( T_c \).

Thus, the combined evolution of \( \lambda(x) \) and \( \omega_{\text{log}}(x) \) is one reason for the dome-shaped dependence of the SC transition temperature on the electron-doping concentration, which can be seen in Fig. 4.11. Here, we show experimental data of Ref. [252] along with results of our numerical simulation for different Coulomb pseudopotentials \( \mu^* \).

Besides the coincidence in the position of the maximum in \( T_c(x) \) at \( x \approx 0.11 \) (\( n_{2D} = 1.2 \times 10^{14} \text{ cm}^{-2} \)), we also note that the computed and experimental SC transition temperatures are of the same order of magnitude. This is remarkable, since the Allen-Dynes formula is a rather crude approximation to the Eliashberg theory, which does not account for pair-breaking effects, such as impurities, incorporates Coulomb interactions only statically as \( \mu^* \) and neglects enhanced phase fluctuations in 2D. It is therefore expected to overestimate \( T_c(x) \).

Another important reason for the dome-shaped dependency of the SC transition temperature is due to the outstanding role of the occupation of the \( \Sigma \) valley in combination with specific efficient electron-phonon coupling channels. In Fig. 4.12 we show some exemplary electron-phonon coupling maps \( g^q_k \) defined by

\[
g^q_k = \sum_{\nu \in \{\text{LA,TA,ZA}\}} \left| g_{qn=c_1n=c_1}^{q\nu} \right|, \tag{4.19}\]

which is the summed contribution of all couplings \( g_{qn=c_1n=c_1}^{q\nu} \), as defined in Eq. (2.203) arising from the acoustic branches and the first (and most important) conduction band \( (c_1) \).

These maps are shown for \( k = K \) and \( k = \Sigma \) for the whole Brillouin zone of \( q \) and for different doping levels. Thus, they illustrate the doping dependence of the coupling’s
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efficiencies “starting” from the $K$ (left column) or $\Sigma$ (right column) valley to all other parts of the (electronic) $k$-Brillouin zone.

In both columns we see no changes in the shape of the electron-phonon coupling upon doping but a substantial increasing of the intensities (especially for $q = M$ at $k = K$ and for $q = K$ at $k = \Sigma$). Since the normal-mode representation of the coupling depends on the phonon dispersion $\omega$ and on the perturbation potential $d$ [see Eq. (2.202)] according to $g \propto d/\sqrt{\omega}$, we can analyze the origin of the increased coupling strength in more detail. Indeed, it turns out that there is a negligible effect to the potentials $d$ upon doping and the increase of $g$ is (nearly entirely) due to the decrease of the phonon energies $\omega$. The latter is due to renormalizations of the bare phonon frequencies $\Omega$ as generally defined in Eq. (2.208) and which can be approximated in metals [27] via

$$
\omega_{qv}^2 = \Omega_{qv}^2 + 2\Omega_{qv}\Re\left\{\frac{|g_{qv}^{(0)}|\Pi(q, \omega = 0)}{\varepsilon(q, \omega = 0)}\right\}, \quad (4.20)
$$

where $g_{qv}^{(0)}$ is the bare electron-phonon vertex while $\Pi(q, \omega = 0)$ and $\varepsilon(q, \omega = 0)$ are, respectively, the static electronic polarization and dielectric functions (e.g. in RPA). Thus, the strongest renormalizations arise for momenta at which the (bare) electron-phonon coupling $g^{(0)}$ is efficient and the quotient of the electronic polarization and the dielectric function is large\(^2\). Indeed, we find that the absolute value of the latter is increased upon doping (see section A.4.2) resulting in an overall reduction of the phonon dispersion ($\Pi/\varepsilon \leq 0$), as shown in Fig. 4.9 (b). Since specific bare couplings $g_{qv}^{(0)}$ around the Brillouin zone edges (e.g. in the vicinity of $M$ and $K$) are stronger than those within the Brillouin zone and increase slightly with the doping level, the phonon softening is additionally enhanced at those points resulting in the observed Kohn- Anomalies. Thus, the overall reduction of the phonon energies and the efficient bare coupling at the high-symmetry points are responsible for the increase of the screened electron-phonon coupling strengths upon doping.

Next to the intensities of the electron-phonon coupling maps shown in Fig. 4.12 it is important to study the specific shapes. Regarding the different electronic valleys, we find in the left column ($k = K$) that there is almost no coupling from the $K$ to other $K$ valleys but significant coupling to $\Sigma$ valleys with $q = M$. In the right column ($k = \Sigma$) we see strong electron-phonon couplings from the initial $\Sigma$ valley to other $\Sigma$ valleys with $q = K$ and $q = \Sigma$ as well as from $\Sigma$ to $K$ with $q = M$ (at least for the highest doping). Finally, it is worth to notice that there is nearly no coupling from $\Sigma$ to $\Sigma$ with $q = M$.

---

\(^2\) Please note that the quotient of electronic polarization and the dielectric function is usually called susceptibility. Thus, the term in the brackets from Eq. (4.20) can either be understood as the product of the bare coupling with the electronic susceptibility or as a product of the screened coupling (defined by the bare coupling divided by the electronic screening) and the electronic polarization.
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Figure 4.12.: Electron-phonon coupling matrix elements $g^q_k$ with $k = K$ (left column) and $k = \Sigma$ (right column) for the lowest conduction bands ($n = n^e = c_1$). The maps represent the $q$-dependencies of the sum of all acoustic branches. Green lines indicate the $k$-Brillouin zones while the red lines define the $q$-Brillouin zones. From the top to the bottom row the electron doping is increased from $x = 0.0$, $x = 0.05$ ($K$ occ.) to $x = 0.1$ ($K$ and $\Sigma$ occ.).
Altogether, we find negligible contributions from $K \leftrightarrow K$ coupling but significant contributions form $K \leftrightarrow \Sigma$ interactions for $q = M$ and $\Sigma \leftrightarrow \Sigma$ coupling with $q = K$ and $q = \Sigma$ in agreement with Ref. [253]. Thus, as long as only the $K$ valleys are occupied there is no significant electron-phonon coupling stemming from the acoustic phonon branches which leads to small critical temperatures. As soon as the $\Sigma$ valleys get occupied, several efficient electron-phonon coupling channels are available yielding a strong increase in $T_c$, as it can be seen for $0.04 < x < 0.1$ in Fig. 4.11 which defines the onset of the $T_c$ dome\(^3\).

Beside $\lambda$ and $\omega_{\log}$, the effective Coulomb potential $\mu^*$ is doping dependent as well, since the Fermi surface will change in size and shape upon electron doping. To estimate how such a doping-dependent $\mu^*(x)$ would affect the superconducting dome, we calculated $T_c$ for three different Coulomb pseudopotentials $\mu^* = 0.05, 0.15, \text{and } 0.25$. This range is approximately centered around $\mu^* = 0.13$, which has been suggested in Refs. [253, 162]. The overall trend of an increasing $\mu^*$ is obviously a decreasing $T_c$ since the Coulomb repulsion suppresses the electron pairing. In more detail, we find a stronger dependence of $T_c$ to $\mu^*$ in the intermediate doping regime $0.05 < x < 0.75$ than for high doping levels. First quantitative calculations [279] of $\mu^*(x)$ (based on the Coulomb-interaction model from section 4.2 and the RPA code used in section 4.5) result in a substantial change from $\mu^* \approx 0.3 \text{ to } 0.15$. This change is intimately connected to the occupation of the different valleys, i.e. as long as the $K$ valley is getting occupied upon increasing doping, the Coulomb repulsion is continuously lowered. As soon as the $\Sigma$ valleys become occupied as well the electron repulsion is more or less constant, but significantly decreased which stops the Coulomb-induced $T_c$ reduction. Hence, next to the electron-phonon coupling the electron-electron repulsion plays a major role as well in order to understand the superconducting dome in this material.

**Charge-Density-Wave Phase**

The occurrence of SC and CDW phases in TMDCs is well known. There are several examples in which a phase transition between these two states appears or where CDW and SC phases coexist [276, 280, 281, 282]. A prominent (and controversially debated [283, 284]) example in this sense is the CDW/SC phase transition under pressure in 1T-TiSe\(_2\) [273]. 1T-TiSe\(_2\) and electron-doped MoS\(_2\) have in common, that their Fermi surface consists of multiple pockets with different orbital characters. Additionally, both systems share a strong electron-phonon coupling, which leads to the CDW phase and manifests as an unstable acoustic phonon mode in both systems for $q \approx M$. Nevertheless, there are crucial differences between these two systems: The Fermi surface topologies differ in the number of electron/hole pockets [c.f. Fig. 4.13 (b)]. In bulk 1T-TiSe\(_2\) the Fermi surface consists of electron and hole pockets, while in electron-doped monolayer MoS\(_2\) there are electron pockets only. Additionally, orbital characters near

\(^3\)These findings are not altered due to the contributions of the electron-phonon couplings of the optical phonon branches. See section A.4.3 for more details.
4.3. Many-Body Instabilities Under Electron Doping

Figure 4.13:
Manifestation of the CDW in lattice distortion and band structure. (a) Lattice distortion in MoS$_2$, observed in ab initio calculations via relaxation of 2×1 super cells. (b) Comparison of band topologies involved in the CDW formation in TiSe$_2$ and MoS$_2$. Only in the TiSe$_2$ case, CDW formation can fully gap the Fermi surface. (c) Influence of lattice relaxation effects on the band structures of the 2×1 super cells obtained for a doping level $x = 0.2$. The $d_{xy}/d_{x^2-y^2}$ weight of the bands is illustrated by the (red) width of the bands. The middle panel shows the effect of homogeneous outward relaxation of the S atoms on the conduction band minima as observable from comparison of the MoS$_2$ structure with S positions according to undoped (pristine) and homogeneously relaxed $x = 0.2$ system. The right panel shows the comparison of super-cell band structures for homogeneously relaxed MoS$_2$ and MoS$_2$ featuring the CDW (fully relaxed) at $x = 0.2$.

the Fermi level alter between the two materials. Finally, in monolayer MoS$_2$ there are also phonon modes at around $q \approx K$ and in the vicinity of $q \approx \Sigma$ which soften upon charge doping, in contrast to 1T-TiSe$_2$.

In order to better understand the nature of the SC-CDW phase transition in MoS$_2$, we examine the doping dependence of the $M$-point CDW-induced lattice distortion $\alpha$ in a 2×1 super cell, shown as a red line in Fig. 4.11. Here, $\alpha$ is defined as the angle between three neighbouring Mo atoms subtracted by 60° [$\alpha = \beta - 60^\circ$, see Fig. 4.13 (a)]. For an undistorted honeycomb lattice one finds $\alpha = 0$. By relaxing the atomic structure of the super cell, we observe $\alpha \neq 0$ beyond a critical electron concentration of $x_c \approx 0.14$, as forces arise due to the unstable $M$-point phonon mode. These distortion effects, depicted in Fig. 4.13 (a), become more pronounced with increasing electron doping. We note that in addition to the CDW formation, there is a further homogeneous outward relaxation of the S atoms upon electron doping.

The effects of homogeneous S relaxation and CDW formation on the electronic structure are illustrated in Fig. 4.13 (c) for electron doping $x = 0.2$. In the super-cell
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Brillouin zone, the former band minima at $K$ and $\Sigma$ are folded almost on top of each other at the super-cell $K$ point. In the absence of a CDW, low-energy states originating from $K$ and $\Sigma$ can be distinguished by their orbital band character. The latter states carry a significant $d_{xy}/d_{x^2-y^2}$-weight, whereas the conduction band minimum at $K$ has no such admixture (see Fig. 4.13 (c) left panel). The outward relaxation of the S atoms lowers $d_{xy}/d_{x^2-y^2}$-derived states from $\Sigma$ in energy (Fig. 4.13 (c) middle panel). With increasing CDW amplitude (increasing $\alpha$) the two bands originating from $K$ and $\Sigma$ mix, and this hybridization adds to the splitting of the two bands, c.f. Fig. 4.13 (c) (right panel). This splitting leads to lowering of the electronic energy if the Fermi level lies sufficiently high in the conduction band. The total energy gain upon CDW formation as function of doping level ($\Delta E_{\text{CDW}}$) is shown in Fig. 4.11 (blue line). It illustrates that the CDW formation energies for $x < 0.25$ are comparable to typical Cooper pair condensation energies $\sim 10$ K ($\sim 1$ meV) encountered here, and an interesting competition of the two should emerge.

While the Eliashberg theory of SC order is only applicable as long as the lattice remains stable, it is clear that the competition of CDW and SC order will in any case depend on changes of the Fermi surface due to CDW formation. For the perfect crystal (relaxed structure at zero doping) and a doping level of $x = 0.2$, two bands would intersect the Fermi level near the super-cell $K$ point, and there would be thus two Fermi lines around $K$. Upon outward relaxation of the S atoms (preserving all lattice symmetries) and formation of the CDW, we observe a Lifschitz transition where one of the Fermi pockets disappears, Fig. 4.13 (c) (middle and right panel). The system thus remains metallic in the CDW phase, but the SC transition temperatures should be reduced due to the vanishing phase space for inter-pocket scattering. Persisting metallicity in the CDW phase of MoS$_2$ is indeed ensured by the “topology” of the inter-mixing bands at $K$ and $\Sigma$, Fig. 4.13 (c). In TiSe$_2$, CDW bands with opposite slope are folded on top of each other, and a gap can open upon hybridization. However, in MoS$_2$, the slopes of the back-folded bands have the same sign, and avoided crossings do not lead to a full gap, but only reduce the number of Fermi sheets by one as depicted in Fig. 4.13 (b) and (c).

Since it is known, that the energies of the minima in the conduction band of MoS$_2$ are very sensitive to external strain the before mentioned change in the Fermi surface

![Figure 4.14.](image_url)

**Figure 4.14.**
Lattice distortion angle $\alpha$ upon CDW formation in dependence of the electron doping for different lattice constants.
topology due to the CDW transition might be sensitive to strain as well. To analyze this behaviour we performed super-cell relaxation calculations for different lattice constants and show corresponding lattice distortions upon CDW formation in dependence of the electron doping in Fig. 4.14. The red curve ($a = 3.122 \text{ Å}$) is the same as in Fig. 4.11. Here, we provide the corresponding data for a smaller ($a = 3.110 \text{ Å}$) as well as for two bigger ($a = 3.134 \text{ Å}$ and $a = 3.146 \text{ Å}$) lattice constants. The differences between these values are less than 1%. However, as it can be seen in Fig. 4.14 the critical concentration for the onset of the CDW changes from $x_c \approx 0.14$ to $x_c \approx 0.17$ upon increasing the lattice constant. This is a change of more than 17%. The behaviour at high doping changes as well and tends to bigger distortion angles with an increasing lattice constant. The competition between the CDW and the SC phases is therefore sensitive to both, the electron doping level and external strain.

4.3.3. Conclusions

Electron-doped transition metal dichalcogenides feature CDW and SC instabilities, driven by the softening of an acoustic phonon mode upon charge doping. Due to the band topology, the M-point CDW cannot fully gap the Fermi surface of electron-doped MoS$_2$. Therefore, CDW and SC phases may coexist, albeit with reduced SC transition temperatures. In any case, the SC and CDW instabilities rely on the energy differences between the conduction band minima at $K$ and $\Sigma$. These are highly sensitive to lattice relaxation.

Since MoS$_2$ is optically active, it remains to be seen whether intense photodoping could be a means to trigger the CDW or SC instabilities. This would be a rather unusual effect, since excitations normally suppress order and have been widely used to melt CDWs [285, 286].

The competition of CDW and SC phases is common in metallic transition metal dichalcogenides, such as TiSe$_2$, NbSe$_2$ and TaS$_2$. All these materials differ, however, from MoS$_2$ in that the transition metal atoms lack one (Nb, Ta) or two (Ti) valence electrons in comparison to Mo. Nevertheless, electron-doped MoS$_2$ develops CDW/SC instabilities as well, although entirely different bands are involved. The most prominent resulting difference compared to materials like TiSe$_2$ is the reversed order in the phase diagram of MoS$_2$. 

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4.4. Optical Properties Under Electron-Hole Excitations

The following results have been gained in close collaboration with A. Steinhoff, F. Jahnke and C. Gies and have been published in Nano Lett. 14, 3743 (2014). All of the involved method development has been performed by A. Steinhoff and myself. A. Steinhoff was responsible for the implementation of the semiconductor Bloch equation solver which relies on the material-realistic input of the minimal generalized Hubbard model. The latter was derived from ab initio calculation by myself, as explained in detail in section 4.2. The article was written by A. Steinhoff, C. Gies and myself with additional help from F. Jahnke and T. O. Wehling. The reader will find most parts of the following section and its appendix (section A.5) in the original article.

By today, the most accurate theoretical approach to ground-state optical properties in MoS$_2$ is based on combined first-principle GW and Bethe-Salpeter (BSE) calculations, as briefly discussed in section 4.1.4. Although this combination of methods is well settled, discrepancies in the literature demonstrate the computational challenge in obtaining well converged results [263, 194, 197]. Here, we present an alternative theoretical approach to the conventional Bethe-Salpeter calculations that offers the distinct advantage to go beyond the ground-state level and study the optical response of MoS$_2$ in the presence of excited carriers. On the basis of the material-realistic generalized Hubbard model from section 4.2 we solve the semiconductor Bloch equations [287, 288, 24] for the microscopic electron-hole inter-band polarizations in the complete Brillouin zone in order to obtain the optical response. The semiconductor Bloch equations describe the excitonic states and excitation-induced energy shifts and include inter- and intra-band Coulomb-interaction effects of excited carriers. We show that in MoS$_2$ the large exciton binding energy is reduced accompanied by band-edge shifts of more than 500 meV with increasing carrier density, causing a redshift of the transitions around the K-points. Additional transitions involving further conduction bands (next to the lowest one) remain more stable up to carrier densities of $10^{13}$ cm$^{-2}$.

These results are supported by first measurements of carrier-density-dependent optical spectra of MoS$_2$ [289]. For a bi-axially strained freestanding layer, we find a red-shift of the exciton absorption energy of 110 meV/\%. For the unexcited system, the solution of the semiconductor Bloch equations is equivalent to that of the Bethe-Salpeter equation [290, 22]. In this case and in combination with an effective-mass approximation, the semiconductor Bloch equations lead to the Elliot formula for absorption that has been used for MoS$_2$ before [291, 292]. We demonstrate, however, that at elevated carrier densities the whole Brillouin zone must be considered to describe the spectral properties of MoS$_2$.

\footnote{See footnote 2 on page 77.}
4.4. Optical Properties Under Electron-Hole Excitations

4.4.1. Absorption Spectra

The linear absorption spectrum of MoS$_2$ is calculated by solving the semiconductor Bloch equation (SBE)

$$\frac{d}{dt} \psi_{he}(k, t) = -i [\tilde{\varepsilon}_h(k) + \tilde{\varepsilon}_e(k) - i\gamma] \psi_{he}(k, t)$$

$$+ i\Omega_{he}(k, t) [1 - f_h(k, t) - f_e(k, t)]$$

(4.21)

in time for the microscopic inter-band polarizations

$$\psi_{he}(k, t) = \langle a_h(k)a_e(k) \rangle$$

(4.22)

and the conventional population functions

$$f_h(k, t) = \langle a_h^\dagger(k)a_h(k) \rangle \quad \text{and} \quad f_e(k, t) = \langle a_e^\dagger(k)a_e(k) \rangle,$$

(4.23)

where we set $\hbar = 1$. Here, $a_{e/h}(k)$ ($a_{e/h}^\dagger$) annihilates (creates) an electron or hole with momentum $k$ in the conduction or valence band, respectively. Since non-linear optical properties will not be considered, we neglect the equations of motion for the population functions and assume Fermi distributions of the electrons and holes. $\tilde{\varepsilon}_{e/h}(k)$ describe electron or hole energies which might be renormalized due to additional charge carriers in the valence or conduction bands resulting from electron or hole doping or electron-hole excitations (called plasma in the following). $\Omega_{he}(k, t)$ is the generalized Rabi energy given by

$$\Omega_{he}(k, t) = d_{he}(k) \cdot E(t) + \frac{1}{A} \sum_{kk'kk''} V_{kk'kk''}^e \tilde{\nabla}_{h'e'} \psi_{h'e'}(k, t)$$

(4.24)

containing the plasma-screened Coulomb potential $V$, dipole transition matrix elements $d_{he}(k)$ and the electric field $E(t)$. Furthermore, we assumed an artificial dephasing of $\gamma = 10$ meV. The macroscopic polarization of the system as a response to the electric field is calculated as

$$P(t) = \sum_{kk'he} \langle \psi_{khe}^\dagger d_{khe} + \text{c.c.} \rangle.$$  

(4.25)

From this, the linear absorption spectrum is obtained using classical electrodynamics by considering an electric field propagation vertical to the single-layer plane of $\delta$-extension which yields reflection ($R$) and transmission ($T$) coefficients and thus the absorption by $\alpha = 1 - R - T$. More details on each ingredient and the numerics can be found section A.5.1.
Ground-State Spectral Properties

For the zero-density case (i.e. no additional electrons or holes), the ground-state absorption spectrum, which corresponds to $f_k(k) = 0$, $V = W$ and $\tilde{\epsilon} = \epsilon$ (hence no additional renormalizations, neither to $\tilde{\epsilon}$ nor to $V$), is shown in Fig. 4.15 for the unstrained case (middle) and ±0.6% biaxial strain of the monolayer5 (top and bottom). We find in all three cases a series of peaks comparable to the spectra discussed in section 4.1.4. In more detail, our calculations for the unstrained case yield two peaks around 2.1 eV and 2.2 eV corresponding to the excitonic A and B transitions separated by the valence-band splitting of 130 meV. While the splitting is in very good agreement with experimental findings (see section 4.1.4), the absolute positions of these peaks are slightly blue-shifted. This is most likely an artifact arising due to not fully converged GW calculations. As discussed in section 4.1.2, it is a tough task to gain highly reliable band gaps within a $G_0W_0$ calculation concerning the $k$-mesh convergence. On the basis of the data presented in Ref. [197] we estimate that a fully converged calculation would yield a band-gap reduction of ~ 100 meV. Since the binding energies of 570 and 580 meV for A and B, respectively, are not changed we expect a red-shift of all spectra by a comparable amount. Thereby the A peak would be in the range of 1.9 eV as observed in experiments.

Regarding strain, we find a redshift of the spectrum with increasing lattice constant (trend in Fig. 4.15 from top to bottom). No present work is known to us where bi-
4.4. Optical Properties Under Electron-Hole Excitations

Figure 4.16:
Normalized excitonic wave functions for the ground-state $A$ peak, the first excited-state $A'$ peak and the $C$ peak (from left to right) for the unstrained lattice constant of $a_0 = 3.18 \, \text{Å}$. Shown is the extent over the first Brillouin zone with the $K$ (lowermost corner) and $K'$ (topmost corner) valleys in the six corners and the $\Gamma$ point in the middle. While the ground-state wave function is positive over the whole Brillouin zone, the excited-state wave function crosses the zero plane along one closed line (see white/red circles around the maxima at $K$ in the middle panel).

Axial tensile strain is systematically studied in freestanding monolayer MoS$_2$. However, in comparison to mono-axial strain of MoS$_2$ on a substrate our results of 110 meV/% exceeds the literature values by about a factor of two [248, 293].

To gain more insight into the nature of the MoS$_2$ bound states, we use the Fourier transform of the microscopic polarizations $\psi_{he}(\mathbf{k}, t)$ for each transition between valence and conduction bands $\{he\}$,

$$\psi(\mathbf{k}, \omega) = \sum_{\{he\}} \int_{-\infty}^{+\infty} dt \, \psi_{he}(\mathbf{k}, t)e^{i\omega t},$$

(4.26)

to obtain what we refer to as the excitonic wave function,

$$\chi(\mathbf{k}, \omega) = \frac{\psi(\mathbf{k}, \omega)}{E(\omega)}.$$  

(4.27)

For excitation with circularly polarized light, the $A$-peak wave function, corresponding to an energy of 2.07 eV, is shown in the left panel of Fig. 4.16 for the unstrained lattice. We find strong contributions at the $K$ valley due to direct dipole transitions, whereas the contributions from the $K'$ valley are mainly caused by weak dipole matrix elements, augmented by Coulomb mixing with the $K$ valley. The Bohr radius of the real-space wave function is 1 nm, in agreement with Ref. [194]. Higher excited states of the $A$ exciton are found for example at 2.35 ($A'$) and 2.45 eV ($A''$) and can be identified by nodes of the wave functions ($A'$ wave function is shown in the middle panel of Fig. 4.16). The series of bound $K$-valley states ends at the onset of the continuum of
unbound states which corresponds to the quasiparticle band gap (line endings in Fig. 4.15 on the high-energy side). We identify the prominent peak at about 2.5 eV with the C transition discussed in Ref. [194]. In the ground-state spectra, it is superimposed with an excited state from the K valley. The corresponding wave function is shown in the right panel of Fig. 4.16 and exhibits a strong component around the Γ point.

Finite-density Spectral Properties

The SBE offer the distinct advantage that the influence of excited carriers can be explicitly included, giving access to the density-dependent optical response. We assume the system to be in a thermal quasi-equilibrium state described by Fermi functions $f_\lambda(k)$ with given temperature, carrier density, but different chemical potentials for electrons and holes. Experimentally, this situation might be realized by exciting the system optically, such that equal electron and hole densities are generated, and letting relaxation processes bring the system into a quasi-equilibrium state.

The presence of carriers in the system leads to Pauli blocking of occupied states, plasma screening of the Coulomb interaction, as well as band-structure and Rabi-frequency renormalizations. The Coulomb interaction is screened due to the optically excited plasma via

$$V^{\lambda\lambda'\lambda'}_{kk'kk'} = \frac{1}{\varepsilon_{\text{plasma}}(|k - k'|)}W^{\lambda\lambda'\lambda'}_{kk'kk'}$$

in addition to the dielectric screening of the background charges as discussed in section 4.2.2. The Fermi functions and band-structure renormalizations are calculated self-consistently in advance before we solve the SBE. Thus, the Fermi functions do not experience dynamical changes in time. The Pauli blocking is naturally included due to the occurrence of population factors in the SBE as well as in formula describing the plasma screening [see Eq. (A.14)]. The renormalizations are treated in the Coulomb-Hole Screened-Exchange (COHSEX) approximation as described in section A.5.1.

In Fig. 4.17 room-temperature spectra for carrier densities from 0 to $10^{13}$ cm$^{-2}$ are shown. We find a sizable band-gap shrinkage of more than 500 meV (right panel of Fig. 4.17), causing the higher peaks from the K valley to be successively absorbed into the band edge. The relative exciton absorption strength decreases (which is called bleaching) at moderate carrier densities. The positions of A (and B) transitions exhibit a redshift from 2.07 to 2.00 eV (2.21 to 2.15 eV) with increasing carrier density, which is a consequence of the competition between the shrinking band gap and the reduction of the binding energy due to plasma screening and Pauli blocking. The real-space Bohr radius increases from 1.0 nm in the unexcited system to 1.9 nm at a density of $3 \cdot 10^{12}$/cm$^2$, where the exciton is almost fully absorbed by the band edge. Unlike the K-valley exciton, the C-peak exciton is stable against increasing carrier densities up to $10^{13}$ cm$^2$. Since the C-peak’s wave function exhibits significant weight all over the Brillouin zone, it can not be described within a simplified effective-mass picture at the
4.4. Optical Properties Under Electron-Hole Excitations

Figure 4.17.: Left: Monolayer MoS$_2$ optical absorption spectra for carrier densities from 0 to $10^{13}$/cm$^2$ and 300 K. Calculations are shown for the unstrained structure. Right: Gap shifts and binding energies belonging to the $A$ (solid line) and $B$ (dashed line) exciton transitions for increasing carrier densities.

$K$ and $K'$ valleys alone. The overall finite density results are strongly supported by recent experimental findings [289].

Finite-density results under strain are provided in section A.5.2 and exhibit the same qualitative behaviour. A difference shows up in the amount of redshift of the $K$-valley exciton, which is due to the different population of conduction band minima and corresponding Hartree-Fock renormalizations as well as plasma screening contributions at elevated carrier densities. This in turn is a consequence of the changing energetic position of the $\Sigma$ point under strain. The results again demonstrate that a description of spectral properties in the excited system requires sampling of the whole first Brillouin zone and not just the $K$ and $K'$ valleys.

4.4.2. Conclusions

The accuracy of the generalized Hubbard model from section 4.2 is underlined by calculations of absorption spectra which yield excitonic structures as observed in experiments. Using these reliable models we are able to show that it is necessary to go
beyond effective-mass approximations since significant carrier population can build up at the \( \Sigma \) point and modify the carrier-density-dependent behaviour. Moreover, the \( C \)-exciton peak dominating the spectra at elevated carrier densities is beyond the physics of \( K \) and \( K' \) valleys.

Furthermore, we find strong band-gap shrinkage in the presence of moderate carrier densities that is of the same order as the large exciton binding energy, making this a prominent effect for optical properties. The peak position of the ground-state transition shifts to lower energies with increasing excited-carrier density, a finding that is supported by a recent experiment [289]. The \( A \) and \( B \) absorption shows only mild bleaching before disappearing into the band edge at high carrier densities, and it appears to be challenging to obtain optical gain in this material system.

From here, correlation effects can systematically be included to access optical nonlinearities, as well as trionic and biexcitonic signatures recently discussed in MoS\(_2\) [294, 295, 289].
4.5. Intra- and Inter-Valley Plasmonic Excitations

The results presented in this section have been obtained in collaboration with R. Groenewald and S. Haas and have been published in Phys. Rev. B 93, 205145 (2016). The method development and the corresponding implementation based on the generalized Hubbard model from section 4.2 have been performed in most parts by myself with assistance from R. Groenewald and support from T. O. Wehling. The corresponding manuscript was written in large parts by myself with contributions from R. Groenewald, S. Haas and T. O. Wehling. The reader will find a considerable overlap between the published article and the text of the following section.

Plasmons are the quantized collective oscillations of the electrons of the Fermi sea. Following Bruus and Flensberg we can show their existence by making use of Eq. (2.93) or Eq. (2.96) in a slightly rearranged form: \( \Phi(p, q) \epsilon(q, \omega) = \Phi_{\text{imp}}(p, q) \). Here, we see that the total potential is indeed allowed to perform oscillations in space and time without being driven by any external potential as long as \( \epsilon(q, \omega) = 0 \) is fulfilled [29]. Thus, these excitations are intimately connected to the dielectric screening and optical properties of a material. In two dimensions the plasmonic dispersion exhibits a characteristic low-energy acoustic mode \( \omega \propto \sqrt{q} \) originating from low-momentum electron scattering [296, 297], which has been observed experimentally [298, 299] and studied extensively from a theoretical point of view in graphene [300, 301, 302, 303, 304]. Furthermore, it has been predicted that additional linear plasmons with \( \omega \propto q \) arise due to high-momentum scattering processes between degenerated valleys such as \( K \) and \( K' \) in graphene [305].

Thereby, these low-energy modes might form the basis to build optical devices, wave guides or so called plasmonic circuits [306, 307, 303, 308] or, similar to the effect of phonons, might couple electrons leading to instabilities, such as charge-density wave- and superconducting phases [309, 274, 310, 311].

Compared to graphene an analogous but even richer phenomenology can be expected in the structurally related monolayer TMDCs. These materials host rich plasmonic physics including an interplay of plasmons with charge-density waves [312, 313, 314] and first plasmon based applications have already been proposed [315, 316, 317]. Here, we focus on the representative example of doped MoS\(_2\) whose low-energy band structure can be described by three bands originating predominantly from Mo \( d \) orbitals, as discussed in detail in section 4.1.2. These low-energy states give rise to prominent valleys at wave vectors \( K/K' \) and \( \Sigma \) in the lowest conduction band as well as at \( K/K' \) in the highest valence band, leading to Fermi surfaces as depicted in Fig. 4.18. Next to strongly varying orbital characteristics within the Fermi surface, substantial spin-orbit coupling (SOC) in these materials [232] gives rise to additional changes of the valleys at \( K/K' \) in the highest valence band and at \( \Sigma \) in the lowest conduction band. Although all of these characteristics can be experimentally sampled by means of field-effect electron or hole doping [318], the resulting impact to the plasmonic dispersions
4. Molybdenum Disulfide Monolayers

(a) band structure

$K$ $\Sigma$

(b) Fermi surfaces

Figure 4.18.: 
(a) Sketch of the considered doping scenarios. Solid lines represent the highest valence and the lowest conduction bands around $K$ and $\Sigma$ without SOC. Upon inclusion of SOC the band structure is modified as indicated by the dashed lines. In this case a significant SOC-induced splitting is found at $K$ in the valence band and at $\Sigma$ in conduction band. The grey (dotted) lines represent the different Fermi levels corresponding (from top to bottom) to the “high electron”, “low electron” and “hole doping” concentrations. (b) Sketch of the Fermi surfaces in hole and (high) electron doped monolayer MoS$_2$ without spin-orbit coupling. The different orbital characters are indicated by red ($d_{z^2}$) and blue ($d_{xy}$ and $d_{x^2-y^2}$) filled surfaces. Points of high symmetry are indicated by different markers.

is not known, yet.

To close this gap, we present an extensive study of the plasmon dispersion at arbitrary momenta along paths throughout the whole Brillouin zone for different doping levels. Specifically, we are interested in inter-valley plasmons which have not been studied in TMDCs so far. In order to highlight the multi-orbital character of the Fermi surface and the presence of spin-orbit coupling we consider hole and electron doped cases, as depicted in Fig. 4.18. In the hole doped example we show how spin-orbit coupling affects the inter-valley plasmons while the electron-doped case is used to study the influence of the multi-pocket structure of the Fermi surface. Thereby, we gain a comprehensive and realistic overview of the most important contributions to the low-energy plasmon modes in monolayer TMDCs.

4.5.1. Plasmonic Excitations Within the Minimal Model

As mentioned in the beginning, plasmons describe the (quantized) collective oscillations of the Fermi-sea electrons. This leads to two important remarks: First, intra-band plasmonic excitations can be found solely in metallic systems. Second, we need to describe dynamic screening properties. Hence, our task is to derive the Coulomb
4.5. Intra- and Inter-Valley Plasmonic Excitations

interaction

\[ V(q, \omega) = \varepsilon^{-1}(q, \omega)v(q), \]  

(4.29)

which is dynamically screened by the dielectric environment (such as substrates), interband as well as doping induced intra-band transitions. The latter is of main importance for the low-energy dynamical screening properties and thus for plasmonic characteristics of doped MoS\(_2\) monolayers. It can be described by the dynamic dielectric function \( \varepsilon_{dop}(q, \omega) \), while the background screening (due to the dielectric environment and interband transitions) can be reliably approximated to be static. Hence, we refine our task to derive the dynamically screened Coulomb interaction

\[ V(q, \omega) = \varepsilon_{dop}^{-1}(q, \omega)W(q), \]  

(4.30)

from the background screened interaction \( W(q) \), which we have already obtained in section 4.2.2. Now, the dynamic dielectric function implicitly defines the plasmonic dispersions by

\[ \varepsilon_{dop,m}(q, \omega) = 0, \]  

(4.31)

[27, 29, 319] where \( \varepsilon_{dop,m} \) is the macroscopic part of the dynamic dielectric matrix which is defined in the orbital basis, according to section 3.3.2, as the matrix element of \( \varepsilon_{dop}(q, \omega) \) using the eigenfunction \( | v_1(q) \rangle \) corresponding to the leading eigenvalue \( v_1(q) \) of bare Coulomb interaction \( v(q) \)

\[ \varepsilon_{dop,m}(q, \omega) = \langle v_1(q) | \varepsilon(q, \omega) | v_1(q) \rangle. \]  

(4.32)

The most promising experimental method to measure these plasmon modes is electron-energy-loss spectroscopy (EELS), measuring the imaginary part of the inverse macroscopic dielectric function

\[ \text{EELS}(q, \omega) = -\text{Im} \left( \frac{1}{\varepsilon_{dop,m}(q, \omega)} \right), \]  

(4.33)

which is sensitive to both, collective and single-particle excitations (visible as maxima in the EELS spectra) [320].

Up to now, there have been basically two theoretical approaches available to study the plasmonic physics in TMDCs. On the one side there are models combining effective \( k \cdot p \) descriptions of the quadratic electronic bands around the band gap with an evaluation of the dielectric function within the random phase approximation [321, 322]. On the other side, there are RPA descriptions based on full density functional theory calculations, which include realistic single-particle band structures describing the complete Brillouin zone [323, 324, 325, 319, 326, 327].

Here, we add a third approach by utilizing the material-specific low-energy multi-orbital generalized Hubbard model derived from \textit{ab initio} calculations for the undoped
material as introduced in section 4.2. This model serves as the basis for the evaluation of dynamical response functions $\Pi(q, \omega)$ in the electron and hole doped situations. Thereby we gain the possibility to accurately calculate the polarization as well as the screening functions for the whole Brillouin zone, which enables us to study plasmons at arbitrary momenta.

In the orbital basis $(\alpha, \beta \in \{d_x^2, d_{xy}, d_{x^2-y^2}\})$ the density-density polarization function $\Pi_{\alpha\beta}^\sigma(q, \omega)$ for a single spin channel $\sigma$ is given by

$$\Pi_{\alpha\beta}^\sigma(q, \omega) =\sum_{\lambda_1\lambda_2k} \frac{M_{\alpha\beta}^{\lambda_1\lambda_2}(k, q)}{\omega + i\delta + \varepsilon_{\lambda_2}^\sigma(k-q) - \varepsilon_{\lambda_1}^\sigma(k)},$$

(4.34)

where $q$ and $k$ are wave vectors from the first Brillouin zone, $\lambda_i$ band indices, $f_{\lambda_i}^\sigma(k)$ Fermi functions for the energies $\varepsilon_{\lambda_i}^\sigma(k)$ and $i\delta$ a small broadening parameter. The overlap matrix elements are given by

$$M_{\alpha\beta}^{\lambda_1\lambda_2}(k, q) = \bar{c}_{\alpha}^{\lambda_1}(k)c_{\beta}^{\lambda_2}(k)\bar{c}_{\alpha}^{\lambda_2}(k-q)c_{\beta}^{\lambda_2}(k-q),$$

(4.35)

where $c_{\alpha}^{\lambda_i}(k)$ is the expansion coefficient of the eigenfunction corresponding to $\varepsilon_{\lambda_i}^\sigma(k)$ in the orbital basis. A detailed derivation of these formulas is given in section A.6.1.

Here, we already reduced the polarization tensor of 4th order to a matrix to describe density-density correlations only. Hence, we neglect orbital-exchange (Fock-like) matrix elements as well as elements with three or even four different orbital contributions. A detailed analysis of the full background screened Coulomb tensor $W_{\alpha\beta\gamma\delta}$ shows that these elements are in general one order of magnitude smaller or even vanish due to symmetries, which convinces us to stay with density-density like elements (for more details see section A.3.2). Using the full density-density polarization $\Pi(q, \omega) = \Pi^\uparrow(q, \omega) + \Pi^\downarrow(q, \omega)$ the dielectric function is obtained via the following matrix equation

$$\varepsilon(q, \omega)_{\text{dop}} = 1 - W(q)\Pi(q, \omega),$$

(4.36)

where the background screened Coulomb interaction enters via $W(q)$. By including an effective spin-orbit coupling, like introduced in section 4.2.1, the spin degeneracy is removed but time reversal symmetry is preserved. Then, the spin resolved band structure still obeys $\varepsilon_{\uparrow}^\lambda(k) = \varepsilon_{\downarrow}^\lambda(-k)$ and the total polarization including the spin summation can be written as $\Pi(q, \omega) = \Pi^\uparrow(q, \omega) + \Pi^\downarrow(-q, \omega)$.

The combination of our material-realistic description of the undoped system and the very accurate band structure for the RPA evaluation yields indeed quite accurate

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6 Since we will focus on low-energy intra-band transitions in the following the “exact” band gap is not important here. Therefore, we use a Wannier Hamiltonian based on a $G_0W_0$ calculation for an interlayer separation of 35 Å and do not perform the vacuum extrapolation. Furthermore, we neglect the $k$-dependency in $\lambda$ as introduced in Eq. (4.10). Thereby, we end up with a band structure which reproduces the most important characteristics of the Fermi surface reasonably well which allows us to study the universal plasmonic properties arising due to different parts of the Fermi surface.
4.5. Intra- and Inter-Valley Plasmonic Excitations

Figure 4.19.: (a) Plasmon dispersions from our ab initio based model (dots) in comparison with analytic k \cdot p-models by Scholz et al. (blue) [321] and Kechedzhi et al. (red) [322]. In the data by Kechedzhi et al. [322] both spin components (and their coupling) are included while the data of Scholz et al. [321] include a single spin component only. Data shown as red (blue) dots results from the ab initio model by using a simple constantly screened Coulomb interaction and the full (spin resolved) polarization function. The data shown as green dots arise from the complete ab initio model. (b) Plasmon dispersions for undoped NbS$_2$ from (left) full ab initio calculations from Ref. [319] and (right) our ab initio based model. Here, we use the macroscopic dielectric function.

Benchmarks

In Fig. 4.19 (a) we compare the resulting plasmon dispersions\(^7\) of our ab initio based model (dots) to k \cdot p models by Scholz et al. [321] and Kechedzhi et al. [322] (lines) for hole doped MoS$_2$. In these models a simple constantly screened Coulomb interaction of the form $V(q) \propto \frac{1}{\kappa q}$ with $\varepsilon_{\alpha\beta}(q) = \kappa = 5$ is used. As long as we use the same constantly screened Coulomb interaction to evaluate the dielectric function, we end up with nearly identical plasmon dispersions compared to those derived from the k \cdot p-models. However, by including the full ab initio derived $q$-dependent dielectric function for the background screening in the undoped case, which arises due to the two-dimensional geometry and the excluded bands, we find strongly reduced plasmon energies (green dots).

In Fig. 4.19 (b) we compare our method to full ab initio results for NbS$_2$ from Ref. [319] using the parameters given in section A.6.2. NbS$_2$ is a metal in its ground state and thus naturally hosts low-energy plasmonic excitations. In the left panel of Fig. 4.19 (b) we show the EELS spectra as obtained from our model. The plasmonic dispersion is defined by the prominent maxima (bright green). In the right panel we

\(^7\) These dispersions are obtained from corresponding EELS spectra. The dots are extracted by finding the respective maxima for a given $q$ value.
present the corresponding data from full \textit{ab initio} calculations [319]. Although, the resulting dispersions are on an eV range (for which our model is actually not set-up), we find a remarkable agreement with differences on the order of 100 meV to 200 meV ($\approx 10\%$ to $20\%$).

Altogether, we find that the inclusion of static screening effects due to bands at high energies (i.e. background screening) is essential to derive material-realistic plasmonic dispersions upon doping. In contrast to simplified $k \cdot p$ models [321, 322], which utilize \textit{bare} (or constantly screened) Coulomb matrix elements at this stage, our interaction matrix elements are strongly reduced due to $q$-dependent screening effects from the electronic bands which are neglected in the $k \cdot p$ models. As a result of the 2D layer geometry, these dielectric properties cannot be modeled by a simple dielectric \textit{constant} but have to be described as a $q$-dependent dielectric \textit{function} as discussed in section 3.3.

4.5.2. Plasmonic Dispersions Under Electron and Hole Doping

In the following we will consider hole and electron doping scenarios with and without spin-orbit coupling. In order to clarify the differences in these situation we provide in Fig. 4.18 (a) a sketch of all situations. The “hole doping” concentration is chosen in a way that all $K$ and $K'$ (but no $\Gamma$) valleys in the conduction band will be occupied (independently of the in- or exclusion of SOC). In the case of electron doping we will study two different levels: The “low electron doping” case occupies only the $K/K'$ valleys of the conduction band as long as the SOC is excluded and will occupy only one of the $\Sigma/\Sigma'$ valleys upon inclusion of SOC. Within the “high electron doping” scenario all $K/K'$ and $\Sigma/\Sigma'$ valleys are occupied (with or without SOC).

Hole Doping

We fix the chemical potential such that there are holes in the valence band in the $K$ and $K'$ valleys only. The resulting Fermi surfaces consists of circle-like areas around the $K$ points (see Fig. 4.18), which have mainly $d_{xy}/d_{x^2-y^2}$ character and depend on spin-orbit coupling. Hence, we expect low energy plasmon modes for $q \approx \Gamma$ (intra-valley) and $q \approx K$ (inter-valley), which are possibly influenced by SOC.

In Fig. 4.20 (a) we show an intensity plot of the real part of the polarization function for scattering within $d_{xy}$ orbitals along the complete path $\Gamma \rightarrow K$ without SOC. Next to some band-like structures (red) we clearly see the particle-hole continuum (blue).

\cite{footnote:Gamma}

Here we apply $\Gamma$ centered Monkhorst-Pack 720 $\times$ 720 $k$-grids and use a broadening of $\delta = 0.5$ meV. The doping concentration is adjusted by rigid shifts of the Fermi energy, which change the Fermi functions accordingly. All calculations are carried out for $T = 0$ K. Furthermore, we restricted the $\lambda_1$ and $\lambda_2$ summations to the partially occupied band only in order to avoid double counting problems within the definition of the total polarization function and not to overload the resulting plots.

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Figure 4.20.: Real and imaginary parts of the polarization functions ($d_{xy}/d_{xy}$ channel) and EELS spectra for hole doped MoS$_2$ without (left column) and with (right column) spin orbit coupling. The insets in (a) and (d) illustrate the Fermi surface pockets around $K$ and $K'$ in the valence band for a single spin component.
4. Molybdenum Disulfide Monolayers

In comparison to the corresponding EELS data in Fig. 4.20 (c), we see that for higher momentum transfers (away from $\Gamma$) the EELS maxima closely follow the band-like characteristics of the polarization function. For small momenta around $\Gamma$ we find a clearly separated band in the EELS spectra, which can not be seen in the real part of the polarization. This separated band arises from the well known $q$-dispersive intra-valley plasmon mode in 2D [321]. Additionally, we find a linear-dispersive mode around $K$ stemming from an inter-valley plasmon [305]. These activation laws are consistent with the generalized expression for the plasmon dispersion relation defined by Eqs. (4.31) and (4.36) and approximated following Ref. [274]

$$\omega(q) = \hbar v_F q \sqrt{1 + \frac{[N_0 W(q)]^2}{(1/4) + N_0 W(q)}},$$  \hspace{1cm} (4.37)

where $v_F$ is the Fermi velocity, $N_0$ the density of states at the Fermi level and $W(q)$ the macroscopic background screened Coulomb interaction of the undoped system. In the long-wavelength limit ($q \rightarrow 0$) the Coulomb potential remains unscreened, i.e. in leading order $W \propto 1/q$, resulting in a square-root renormalization of the otherwise linear dispersion. However, in the opposite short-range limit, i.e. at the zone boundary, the screened Coulomb potential approaches a constant, and therefore the resulting dispersion of the dielectric function is linear in $q$, which holds for the polarization function itself as well. Thus, for momenta away from $\Gamma$ it is sufficient to study the polarization function to understand how the resulting plasmon dispersion will behave.

Of special interest are damping effects which are known to attenuate plasmon modes which merge with the particle-hole continuum. Here, the square-root mode around $\Gamma$ behaves in a distinctively different manner compared to the linear modes originating at $K$. At sufficiently small momentum transfers $q < q_c$ the square-root modes are considerably separated from the nearby particle-hole continua [Fig. 4.20 (c) and (f)] and therefore better protected from decomposition via hybridization and Landau damping [expressed as non-vanishing imaginary parts of the polarization as shown in Fig. 4.20 (b) and (e)] compared to the linear modes originating at finite momenta. In contrast, the linear plasmon modes are much closer to their neighbouring continua [Fig. 4.20 (c)], which leads to attenuation effects, reflected in reduced oscillator strength and broadening of the peaks. There is a significant difference in the oscillator strengths of these modes which can be several orders of magnitude apart as can be seen in Fig. 4.20 (c) and (f). Hence, in order to clearly detect these linear plasmon modes in experiments, it may prove practical to use a logarithmic scale to shield the dominant square-root mode around $q = \Gamma$, as it is done in Fig. 4.20 (c) and (f).

When we account for spin-orbit coupling the relative depth of the $K$ and $K'$ pockets shifts. In this case momentum transfer of $q = K$ no longer connects points on the Fermi surface belonging to different hole pockets, which results in two clearly visible characteristics in the polarization of Fig. 4.20 (d): First, at $q = K$ the scattering process is possible only for a finite energy difference, which opens a finite energy gap.
of \( \approx 250 \text{ meV} \). Second, the Fermi surfaces at \( K \) and \( K' \) are now of different sizes but can still be connected with slightly smaller and larger \( q \), resulting in gap-less linear modes originating slightly shifted from \( K \) as seen in Fig. 4.20 (d).

We conclude that the plasmonic features in hole doped MoS\(_2\) are mainly characterized by a square-root mode in the vicinity of the \( \Gamma \) point and additional low contributions at the Brillouin zone edge which disperse linearly when SOC is disregarded. As long as SOC is not taken into account and the \( K \) valley is occupied solely this is qualitatively very similar to the plasmonic properties of doped graphene [305]. Upon inclusion of SOC the linear plasmon mode around \( K \) is \textit{shifted} leading to a gapped excitation spectra at this point.

**Electron Doping**

The lowest conduction band is characterized by two prominent minima around \( K \) and \( \Sigma \). Without SOC these minima are separated by less than 100 meV which is further reduced by considering SOC. Hence, in contrast to the hole doped case, small variations in the electron doping can change the Fermi-surface topology, as shown in the insets of Fig. 4.21 and Fig. 4.22. In order to study these changes, we will neglect the SOC for the beginning and choose two doping levels, resulting in Fermi surfaces comparable to the hole doped case (i.e. \( K \) valley occupation only) and a surface with additional pockets at \( \Sigma \), labeled by low- and high-doping respectively (see Fig. 4.18). Since the \( K \) valley is mainly described by \( d_{z^2} \) orbitals and the \( \Sigma \) valley predominately by \( d_{xy} \) and \( d_{x^2-y^2} \) states, we focus on corresponding diagonal orbital channels in \( \Pi_{\alpha\beta} \) in the following. Off-diagonal elements between \( d_{z^2} \) and \( d_{xy}/d_{x^2-y^2} \) orbitals are negligible here and off-diagonal terms between \( d_{xy}/d_{x^2-y^2} \) states are very similar to diagonal \( d_{xy}/d_{xy} \) and \( d_{x^2-y^2}/d_{x^2-y^2} \) combinations. The corresponding polarization functions are shown along the path \( \Gamma - \Sigma - K - M - \Gamma \) through the whole Brillouin zone in Fig. 4.21 and Fig. 4.22 for \( d_{z^2} \) and \( d_{xy} \) states, respectively.

Analogous to the hole doped case, we observe in all situations (high and low electron doping) around \( q = \Gamma \) the expected plasmonic resonances arising from \textit{intra-valley} scattering (either within the \( K \) or the \( \Sigma \) valleys). The structure of the polarization for larger \( q \) can be understood by inspecting the Fermi surface shown in Fig. 4.18: \textit{Inter-valley} scattering between similar valleys is possible for momentum transfers of \( q = K \) (\( K \leftrightarrow K' \) and \( \Sigma \leftrightarrow \Sigma' \) scattering) and \( q = \Sigma \) and \( M \) (\( \Sigma \leftrightarrow \Sigma' \) scattering). Therefore, we expect additional \textit{inter-valley} plasmon branches close to these momenta. In principle \( K \leftrightarrow \Sigma \) scattering can be found as well (for instance for \( q = \Sigma \) or \( q = M \)), but with strongly decreased amplitudes due to vanishing overlap matrix elements \( M_{d_{z^2}d_{xy}} \).

Indeed, we find at \( q \approx K \) in all situations without SOC possible excitations at zero energy. In Fig. 4.21 (a) and (b) we see the corresponding \( K \leftrightarrow K' \) and in Fig. 4.22 (a) the \( \Sigma \leftrightarrow \Sigma' \) modes. As expected, at momentum transfers of \( q = M \) and \( \Sigma \) we find gap-less linear modes only within the \( d_{xy} \) channel for high doping concentrations.
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Figure 4.21.: Real parts of the polarization functions for $d_{z^2}/d_{z^2}$ scattering at low and high electron doping concentration without SOC. The insets depict the resulting electron pockets within the lowest conduction band.

as shown in Fig. 4.22 corresponding to $\Sigma \leftrightarrow \Sigma'$ excitations. In contrast, within the low doping case [Fig. 4.21 (a)] we observe weak and gapped ($\approx 0.1$ eV) excitations for these momenta originating from $K \leftrightarrow \Sigma$ scattering.

While the SOC has a negligible effect on the $d_{z^2}$ valley at $K$, it splits the $d_{xy}/d_{x^2-y^2}$ valleys at $\Sigma$ resulting in minima at comparable energies. The corresponding Fermi surface for a single spin component is indicated in the inset of Fig. 4.22 (b). The six $\Sigma$ points decompose into two distinct sets, $\Sigma$ and $\Sigma'$. Fermi pockets within each of these subsets are mutually connected by $2\pi/3$ rotations and remain equivalent after inclusion of SOC, while the degeneracy of $\Sigma$ and $\Sigma'$ is lifted by SOC. As a consequence, the phase space for $\Sigma \leftrightarrow \Sigma'$ is lost and the gap-less excitations at $q \approx \Sigma$ and $q \approx K$ must vanish, but $\Sigma \leftrightarrow \Sigma$ scattering processes are still possible. Consequently, we see in the corresponding polarization for the $d_{xy}$ channel with SOC in Fig. 4.22 (b) gap-less modes only at $\Gamma$ and $M$. Since the Fermi surface around $K$ is not changed drastically upon SOC, the corresponding polarization for the $d_{z^2}$ channel is very similar to the one obtained without SOC [see Fig. 4.21 (b)].

Substrate Effects to the Plasmonic Dispersion

After having discussed the details of all relevant scattering channels on the basis of the orbital resolved polarization function we now turn our focus to EELS data in order to study the arising acoustic intra-valley plasmonic branch in the vicinity of the $\Gamma$ point in more detail. Therefore, we investigate how the square-root mode behaves under the influence of different electron-doping levels and by considering varying dielectric
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(a) without SOC

(b) with SOC

Figure 4.22.: Real parts of the polarization functions for $d_{xy}/d_{xy}$ scattering at elevated electron doping concentration ($K$ and $\Sigma$ valleys are partially occupied) without and with SOC. The insets depict the resulting electron pockets within the lowest conduction band for a single spin component.

environments\(^9\). In Fig. 4.23 we present the resulting spectra for increasing doping levels $E_f = -1.20\,\text{eV}$ to $E_f = -1.05\,\text{eV}$ (top to bottom) and increasing dielectric constants of the environment (above and below the layer) from $\varepsilon = 1$ to $\varepsilon = 50$ (left to right). The first three rows belong to doping situations in which the conduction band’s $K/\Gamma$ and only one of the $\Sigma$ valleys are occupied, while the last row corresponds to an occupation of all $K/\Gamma$ and $\Sigma/\Sigma'$ valleys.

In all situations we can clearly identify the electron-hole continua as grey-shaded areas and the plasmonic branch as sharp black lines (in most situations) separated from the continua for $q < 1/2\Gamma\Sigma$. For the free standing layer (i.e. $\varepsilon = 1$) we find strong variations of the plasmonic branch in dependence of the doping-level. For the lowest doping level we find a “shoulder” at about 300 meV which rises in energy and flattens with increasing doping. As soon as the second $\Sigma'$ valley is occupied, we even find a maximum within the former square-root branch close to $\Gamma$. Next to these considerable changes of the acoustic plasmonic branch, we see a broadening of the $K$- and $\Sigma$-valley continua (the former belongs to the “branch” with maxima around $q = 1/2\Gamma\Sigma$ and the latter maxima in the near of $q = \Sigma$) which naturally arise due to increasing Fermi surfaces.

The most prominent effect of the dielectric environment is a considerable reduction of the plasmonic energies for small $q < 1/2\Gamma\Sigma$. Due to its macroscopic nature the environmental screening affects solely these long-wavelength ranges which results in

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\(^9\) The dependence of the dielectric environment is introduced on the level of the underlying Coulomb model which is now describing both, the background screening effects from the neglected inter-band transitions and those stemming from the dielectric environment for the undoped system as explained in section 4.2.2.
4. Molybdenum Disulfide Monolayers

Figure 4.23.: EELS spectra for an increasing doping level (from top to bottom) and an increasing dielectric screening due to the environment (from left to right). On the very right we depict the corresponding Fermi surfaces / electron pockets within the lowest conduction band for a single spin component.

nearly linear (but still separated) modes for small \( q \) and low electron doping levels. For high doping levels the square-root like shape of the acoustic branch is recovered. In all screening scenarios shown here, we find a strong increase of the plasmonic energies at small momenta as soon as the second \( \Sigma \) valley becomes occupied resulting in a significant reshaping of the acoustic plasmonic mode. This finding might be an important observation in order to interpret and understand experimental data since the occupation of distinct electron pockets can now be traced back to corresponding changes in the acoustic plasmonic modes.

4.5.3. Conclusions

We found that the low energy dynamical screening in MoS\(_2\) is controlled by both \textit{inter-} and \textit{intra-valley} scattering processes. These give rise to plasmons with a square root dispersion at small \( q \) and linear dispersion for higher momentum transfers which connect separate valleys on the Fermi surface. In general, inter-valley plasmon modes are observable, although their oscillator strengths are strongly reduced in comparison to zone center modes. Due to the multi-orbital character of the wave functions and spin-orbit coupling, which leads to spin-valley coupling in monolayer TMDCs, not all
inter-valley scattering processes are allowed. As a consequence of spin-valley coupling, some inter-valley plasmon modes are shifted and gapped out, while the $2\pi/3$ rotation symmetry protects certain low energy modes at $\mathbf{M}$. We speculate this selective “gapping out” of collective modes could have consequences for the realization of many-body instabilities towards superconducting or charge-density-wave phases in monolayer TMDCs.
4.6. 2D Heterojunctions From Non-Local Manipulations of the Coulomb Interactions

The following results have been obtained by C. Steinke and myself and have been published in Nano Lett. 16, 2322 (2016). I was responsible for all ab initio calculations, the model derivation, and the supervision of C. Steinke, who performed the Hartree-Fock calculations based on a real-space tight-binding program written by myself. Furthermore, the final manuscript was also prepared by myself considering comments and remarks by M. Lorke, C. Gies, F. Jahnke and T.O. Wehling. Most text of the following paragraphs including its appendix in section A.7 are part of the published article.

Semiconductors play a major role in modern optoelectronics. Particularly heterojunctions, i.e. interfaces of materials with different band gaps, are central building blocks of various applications [328, 329]. Apart from planar junctions, which are the basis of light-emitting diodes and solar cells, more complex structures such as quantum wells [330] or quantum dots [331] hold promises in the context of quantum information processing. In the bulk, e.g. in GaAs / InGaAs material systems, heterojunctions are often fabricated by epitaxy, which can be employed up to industrial scales. In addition to bulk crystals, also monolayer thin two-dimensional materials [2] including semiconducting transition metal dichalcogenides have been assembled into structures like vertical [226, 332, 333, 334, 335, 336, 337] or lateral heterojunctions [338, 339, 340, 341]. All of these systems rely on interfaces of different materials in order to gain spatial band-gap modulations. The epitaxial fabrication of well defined interfaces with the desired electronic properties underlies constraints due to available materials, and can in practice be very challenging.

Here, we propose a scheme to build heterojunctions within a single homogeneous layer of a 2D material based on non-local manipulations of the Coulomb interaction, that is the controlled manipulation of the long-range characteristics of the Coulomb interaction within the layered material. By placing a 2D semiconductor into a laterally structured environment (e.g. a substrate with laterally varying dielectric constants as depicted in Fig. 4.24), the Coulomb interaction within the 2D material changes spatially and with it, the local band gaps are modulated as well. Thus, band-gap variations like in a heterojunction can be induced externally in a homogeneous monolayer by an appropriately structured dielectric environment.

The central quantities that define the possible technical relevance of such externally induced heterojunctions are (i) the size of realistically achievable band-gap modulations and (ii) the length scale over which these modulations take place. In the following we show that changes in the Coulomb interaction can induce band-gap modulations in the range of several 100 meV on the length scale of a few lattice spacings in homogeneous MoS$_2$. To this end, we consider in a first step a free standing MoS$_2$ monolayer and analyze Coulomb interaction effects as manifesting in the electronic self-energy in real space. Based on GW calculations, we demonstrate that the dominant self-energy
4.6. 2D Heterojunctions From Non-Local Manipulations of the Coulomb Interactions

Figure 4.24.: Sketches of a monolayer (blue) in different heterogeneous dielectric environments. (a), (c) and (d) show situations with structured dielectric substrates while in (b) adsorbed polarizable molecules are responsible for the heterogeneous dielectric environment.

...terms are indeed limited to the length scale of a few unit cells. In order to study heterogeneous systems as shown in Fig. 4.24, we switch to a generic 2D semiconductor model that is quantitatively based on our \textit{ab initio} GW results. Using this model, we demonstrate that a spatially inhomogeneous environment allows to \textit{induce externally} a heterojunction of type-II in MoS$_2$.

4.6.1. Locality of the Coulomb Interaction

As described in section 4.1.2, the band gap in MoS$_2$ monolayers arises initially due to strong hybridization of molybdenum $m_l = \{0, \pm 2\}$ states. To investigate the effects of the Coulomb interaction to this hybridization mechanism, we perform $G_0W_0$ (GW) calculations which take these interactions into account. Thereby, we are able to study in detail how the Coulomb interaction affects the band gap. Within a real-space description we are furthermore able to explore the locality of the Coulomb interaction, which is a crucial property to derive spatially sharp band-gap modulations in the new kind of heterojunctions presented in the following section. To this end, we derive the corresponding self-energy in \textit{real space} from a comparison of DFT and $G_0W_0$ calculations utilizing the Dyson equation

\begin{equation}
\Sigma = G_{\text{DFT}}^{-1} - G_{\text{GW}}^{-1},
\end{equation}

where $G_{\text{DFT}}$ and $G_{\text{GW}}$ are the electronic Green functions obtained from corresponding calculations. Within the quasiparticle approximation, the Green functions

\begin{equation}
G_{\text{GW/DFT}}^{-1}(z) = (z + \mu - H_{GW/DFT}),
\end{equation}

follow from the Wannier Hamiltonians $H_{GW}$ and $H_{DFT}$ describing the DFT and $G_0W_0$ band structures, respectively:

\begin{equation}
H^{GW/DFT}_{\alpha\beta}(k) = \sum_{R} e^{ikR} \lambda^{GW/DFT}_{\alpha\beta}(R).
\end{equation}
The quantum numbers $\alpha, \beta \in \{ d_{z^2}, d_{xy}, d_{x^2−y^2} \}$ denote the dominating orbital characters of the wave functions in the Wannier basis. Finally, the real-space self-energy is approximated as

$$\Sigma_{\alpha\beta}^{GW}(\mathbf{R}) = \Sigma_{\alpha\beta}^{GW,0}(\mathbf{R}) + \Delta\mu \delta_{\mathbf{R}0} \delta_{\alpha\beta},$$

(4.41)

where $\Delta\mu$ aligns the Fermi energies between the DFT and $G_0W_0$ calculations which is realized by choosing $\Delta\mu$ such that $\text{Tr} \left[ \Sigma_{\alpha\beta}^{GW}(\mathbf{0}) \right] = 0$.

Fig. 4.25 shows the resulting map of $\Sigma_{\alpha\beta}^{GW}(\mathbf{R})$, which visualizes the $\mathbf{R}$-dependent renormalizations of the tight-binding hopping matrix-elements due to the Coulomb interaction. These elements can be separated into intra- and inter-orbital contributions arising from Coulomb-interaction-induced changes in the intra- ($\alpha \leftrightarrow \alpha$) and inter-orbital ($\alpha \leftrightarrow \beta$) hoppings. In more detail, there are local renormalizations $\Sigma_{\alpha\beta}(\mathbf{R} = \mathbf{0})$, and, more importantly, non-local self-energy terms $\Sigma_{\alpha\beta}(\mathbf{R} \neq \mathbf{0})$ which arise from the non-local character of the Coulomb interaction. These non-local terms in $\Sigma_{\alpha\beta}^{GW}(\mathbf{R})$ can be found in the maps of Fig. 4.25 in the cells around the central unit cells in each panel.

The strongest contributions to the self-energy are non-local inter-orbital exchange terms, which directly increase the hybridization and the resulting band gap. The enhanced band gap in $GW$ calculations therefore results from non-local inter-orbital contributions of the Coulomb interaction. In general, we find non-local contributions to $\Sigma$, as one expects from the long range character of the Coulomb interaction in 2D semiconductors. Nevertheless, the most sizable contributions are clearly localized

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**Figure 4.25:**
Real-space representation of the $GW$ self-energy $\Sigma_{\alpha\beta}^{GW}(\mathbf{R})$ of MoS$_2$ within the minimal Mo $d$ basis. The grey lines mark the hexagonal Wigner-Seitz unit cells of the full lattice with centered Mo atoms.
4.6. 2D Heterojunctions From Non-Local Manipulations of the Coulomb Interactions

within a radius of less than three unit cells. Hence, despite the self-energy being non-local, it could still facilitate sharp band-gap modulations in the case of structured dielectric environments, which will be discussed in the following section.

The real-space structure of $\Sigma_{\alpha\beta}^{GW}(R)$ can be understood by considering the corresponding orbital symmetries. The $d_{z^2}$ orbital is invariant under the operations of the threefold rotation symmetry of the MoS$_2$ lattice, which is reflected in the $d_{z^2}/d_{z^2}$ panel of Fig. 4.25 showing the full symmetry of the lattice. The $d_{xy}$ and $d_{x^2−y^2}$ orbitals belong to a two-dimensional representation of the crystal symmetry point group, which leads to a more complex real-space structure of the corresponding self-energy terms, as seen in the $d_{xy}$ and $d_{x^2−y^2}$ panels in Fig. 4.25.

### 4.6.2. Heterostructures Induced by Heterogeneous Dielectric Environments

Now we turn to structured dielectric environments as depicted in Fig. 4.24. Here, the broken translational symmetry makes $GW$ calculations numerically extremely demanding. As an alternative, we switch to a model system that mimics the essential gap-opening mechanisms and interaction effects present in semiconducting TMDCs.

At the same time it allows us to study the influences of a structured dielectric environment on the local density of states (LDOS) and the resulting spatial variation of the band gap.

**Model Description in the Hartree-Fock Approximation**

In order to model the lowest conduction and the highest valence band of monolayer MoS$_2$ we consider a two-band model in momentum space described by a single-particle Hamiltonian of the form

$$H_{SP}(\mathbf{k}) = \begin{pmatrix} \epsilon_{\parallel=0}(\mathbf{k}) & t_{\perp} \\ t_{\perp} & \epsilon_{\parallel=\pm 2}(\mathbf{k}) \end{pmatrix}. \quad (4.42)$$

Here, $\epsilon_{\parallel=0}(\mathbf{k})$ is meant to describe molybdenum $d_{z^2}$ states and $\epsilon_{\parallel=\pm 2}(\mathbf{k})$ the combined $d_{xy}$ and $d_{x^2−y^2}$ contributions. To simplify the model as much as possible, we approximate $\epsilon_{\parallel=0}(\mathbf{k}) = \epsilon_{\parallel}(\mathbf{k})$ and $\epsilon_{\parallel=\pm 2}(\mathbf{k}) = -\epsilon_{\parallel}(\mathbf{k})$ with the tight-binding dispersions of 2D hexagonal lattices

$$\epsilon_{\parallel}(\mathbf{k}) = t \sum_{j=1}^{6} \exp(i\delta_j \cdot \mathbf{k}), \quad (4.43)$$

where $t$ describes “in-plane” hopping between Mo nearest neighbours which are connected by $\delta_j$. The gap arising in this model is a hybridization gap opened due to $t_{\perp}$. In Fig. 4.26 we show the resulting band-structures [obtained by diagonalization of the
Figure 4.26:
Sketch of the band-gap opening mechanism within the applied model. The dashed lines represent a zoom of the band structure as resulting without any hybridization. The full lines visualize the full band structure, i.e. with hybridization due to $t_\perp$. The region within these dispersions significantly differs is $\delta k$.

Hamiltonian given in Eq. (4.42) for $t_\perp = 0$ (red/blue) and non-zero $t_\perp$ (black). For $t_\perp = 0$ we find two non-hybridized bands with opposite slopes and a crossings between $\Gamma$ and $K$ (in the vicinity of $\Sigma$ point) and between $\Gamma$ and $M$. Upon increasing $t_\perp > 0$ the two bands are shifted by $\pm t_\perp$ (at $\Gamma$) and hybridize at the band crossings. Thereby, a global band gap is opened which is the same mechanism as phenomenologically described in section 4.1.2 for semiconducting TMDC materials\(^{10}\). For the band-structures shown in Fig. 4.26 the hopping parameters are chosen to reproduce the band width ($W \approx 1.0$ eV) and the DFT band gap ($\Delta \approx 2.0$ eV) of MoS\(_2\). In fact, Eq. (4.42) is the most simple description of a 2D semiconductor and thus more generic.

In real-space we realize such a system with the help of two hexagonal lattices with lattice constants $a_0$ which are vertically separated by $c$. These two planes thus represent the $m_l = 0$ and $m_l = \pm 2$ subsystems. The in-plane lattice constants are chosen corresponding to MoS\(_2\) $a_0 = 3.18$ Å and the vertical distance is set to $c = a_0/4$ in the following.

As we show in section A.7.2, the inclusion of the Coulomb interaction gives rise to a real-space self-energy in the Hartree-Fock approximation according to

$$
\Sigma_{ij} = \delta_{ij} \sum_l 2U_{il} \delta m_l - U_{ij} \langle c_j^\dagger c_i \rangle, \quad (4.44)
$$

\(^{10}\) Furthermore, we find comparable variations of the orbital characters throughout the Brillouin zone within the hybridized bands. The direct band gap at $K$ is not reproduced which traces back to the neglect of the second $m_l = \pm 2$ band. The latter can be seen, for instance, in the three-orbital nearest-neighbour TB model by Liu et al. from Ref. [234].
4.6. 2D Heterojunctions From Non-Local Manipulations of the Coulomb Interactions

![Diagram of 2D heterojunctions](image)

Figure 4.27.: Local density of states for unit cells along lines perpendicular to the dielectric interfaces. Negative unit-cell numbers correspond to areas with $\varepsilon_1$ and positive numbers to $\varepsilon_2$. In all panels $\varepsilon_2$ is fixed to 15 while $\varepsilon_1$ is decreased from 15 to 5 from left to right.

where $\delta n_l = \langle \hat{n}_l \rangle - \bar{n}$ is the deviation from the average occupation $\bar{n}$, $U_{ij} = U(r_i, r_j)$ is the interaction energy between electrons or ions at sites $r_i$ and $r_j$ and $c_i^\dagger (c_i)$ are the corresponding electronic creation (annihilation) operators. Spin indices are suppressed as $\Sigma_{ij}$ is spin diagonal. The structured dielectric environments, as depicted in Fig. 4.24, enter the model via the interaction matrix elements $U_{ij}$ which are correspondingly screened by the dielectric function $\varepsilon_{ij}$ resulting in

$$U_{ij} = \int \varepsilon^{-1}(r_i, r_j) \nu(n_i, r_j) d^3 r_i. \quad (4.45)$$

For heterogeneous environments the corresponding background-screened Coulomb interaction can be obtained from a solution of the Poisson equation. In general, numerical schemes need to be employed for this purpose, although analytical results exist for simplified situations. For instance, the potential for a setup as shown in Fig. 4.24 (c) with zero layer height can be analytically derived, as we sketch out in section A.7.3. For such a scenario we are now able to (self-consistently) calculate $\Sigma_{ij}$ and the resulting LDOS for arbitrary $\varepsilon_1$ and $\varepsilon_2$.

In Fig. 4.27 we present the LDOS along lines perpendicular to the dielectric interfaces for situations with varying $\varepsilon_2/\varepsilon_1$ ratios and fixed $\varepsilon_2 = 15$ (thus decreasing $\varepsilon_1$). The very left panel of Fig. 4.27 corresponds to a homogeneous dielectric environment, while the very right panel shows the LDOS for a strongly heterogeneous situation. In all panels, two main characteristics can be clearly seen: The van-Hove singularities (from the $M$ point, see Fig. 4.26) as maxima in the LDOS, and spatially dependent band gaps $E_{\text{gap}}(\mathbf{r})$ as energy ranges where the LDOS vanishes between the singularities\footnote{Since an artificial broadening $\delta = 5 \text{ meV}$ is involved in the evaluation of the LDOS it never vanishes.}.
$E_{\text{gap}}(r)$ is clearly reduced in the $\varepsilon_2$ regions (on the right hand side of each panel) compared to the $\varepsilon_1$ area (left hand side) as a result of stronger external screening effects of the $\varepsilon_2$ substrate and correspondingly reduced Coulomb interaction. For all given $\varepsilon_2/\varepsilon_1$ ratios, we find a nearly vanishing conduction-band offset (CBO) between both regions, while the corresponding band gaps can be tuned precisely. Thus, the ratio between the CBO and the band gaps can be controlled in these kind of heterostructure, allowing e.g. for optimal solar cell setups [342, 343]. For all heterogeneous situations ($\varepsilon_2/\varepsilon_1 > 1$), the overall variation of the band gaps along the spatial direction is reminiscent of a heterojunction band diagram of type-II.

This kind of band diagram will arise in all systems shown in Fig. 4.24, although the effect of the structured environment is strongest in the setups corresponding to the panels Fig. 4.24 (a) and Fig. 4.24 (c). In order to obtain strong effects in the other situations the substrate $\varepsilon$ in Fig. 4.24 (b) or capping layer $\varepsilon_3$ in Fig. 4.24 (d) should have a small polarizability compared to the adsorbed molecules or $\varepsilon_1$, respectively.

Most importantly for electronic functionalities and particularly regarding electronic transport in these heterojunctions, the band-gap changes within less than 5 unit cells around the interface, which holds for the whole range of $\varepsilon_2/\varepsilon_1$ ratios shown in Fig. 4.27. In lateral heterojunctions made from stitching together different TMDCs, a comparable length-scale has been reported [339]. Thus, we find a similar behaviour with the difference, that here the heterojunction does not arise from different materials, but is induced externally by structuring the dielectric substrate.

There are intrinsic and extrinsic factors limiting the length scale over which band-gap variations in dielectrically induced heterojunctions can be realized. The major extrinsic factor determining the sharpness of the induced band-gap variation, is the length-scale on which the dielectric environment changes, which depends on experimental substrate or adsorbate preparation procedures. There are several experimental ways to realize nearly atomically sharp variations of the dielectric polarizability of the environment of a 2D material. Examples range from the extreme case of substrates containing holes [344, 345, 193], patterned adsorption of polarizable molecules [346, 347, 348, 349], and intercalation or adsorption of atoms [350, 351] to self-organized growth of structured dielectrics by epitaxial means [352, 353, 354, 355].

A lower intrinsic bound $\delta r$ for the length scale, on which the band-gap variation takes place is defined by the spatial extent of the self-energy which can be deduced qualitatively from the underlying model. According to Eq. (4.44) the range of the self-energy is limited by the real-space decay range of the correlation functions $\langle c_j^\dagger c_i \rangle$. In reciprocal space this extent translates to the region $\delta k$ (see right panel of Fig. 4.26) in which we find significant hybridization between the two layers which we can approximate on the basis of the Wannier Hamiltonian from Eq. (4.42). Using this Hamiltonian we find a hybridization gap of the order $\sim t_\perp$ around $\epsilon_k(k) = 0$, as illustrated in the right panel of Fig. 4.26. Thus, the single-particle band structure is completely. Therefore we consider values smaller than 0.02 as zero.
4.6. 2D Heterojunctions From Non-Local Manipulations of the Coulomb Interactions

Figure 4.28.: Real-space representation of the Hartree-Fock self-energy $\Sigma_{ij}$ in the $\varepsilon_1 = 5$ area of the system shown in Fig. 4.27 (unit cell “$10$”). The grey lines mark the hexagonal Wigner-Seitz unit cells. Note, the diagonal elements were enhanced by a factor of 5.

significantly changed due to the hybridization in a region extending about $\delta k = t_1/v_F$ (see right panel of Fig. 4.26) with $v_F$ being the Fermi velocity which is proportional to the band width $W \propto t$. By the uncertainty principle, the momentum-space extent $\delta k$ translates into a range $\delta r \propto 1/\delta k \approx t/t_1$ of the correlation functions $\langle c_i^\dagger c_j \rangle$ in real space. As a consequence, $\Sigma_{ij}$ is generically limited to the scale of a few unit cells as long as hybridization ($t_1$) and band width ($W \propto t$) are similar in size.

This finding is reflected in the numerical data for the non-local real-space self-energy $\Sigma_{ij}$ depicted in Fig. 4.28. In analogy to the discussion of the MoS$_2$ GW self-energy in the homogeneous case, we show in Fig. 4.28 the self-energy in the middle of the $\varepsilon_1 = 5$ area of the heterostructure (unit cell “$10$” in the right most panel of Fig. 4.27). Here, the local dielectric environment is essentially homogeneous and thus comparable to the fully homogeneous case. The off-diagonal self-energy terms shown in Fig. 4.28 are by definition non-local, as they describe modulations of interlayer couplings (separated by $R_z = c$), but significant contributions are limited to a single unit cell. For orbitals in the same layer (diagonal panels in Fig. 4.28), the self-energy is smaller, and substantial contributions are limited to about two unit cells. Hence, the real-space structure of the model self-energy in this homogeneous-like area of the system is quite similar to the self-energy in MoS$_2$ obtained from full ab initio calculations (see Fig. 4.28).

More specifically, the Hartree contribution of the self-energy $\Sigma^H$ [see Eq. (4.44)] is diagonal and has hardly any effect on the band structure. Especially the non-local Fock terms $\Sigma^F$, as we show in more detail in section A.7.4, increase the band gap by modifying the hybridization (as seen in $\Sigma_{AB}/\Sigma_{BA}$ in Fig. 4.28). This tendency is independent of the dielectric constant and inherent to all semiconducting 2D materials in which band gaps result from hybridization effects. Consequently, in all materials of this kind, heterojunctions can be induced by an external manipulation of the Coulomb interaction.
4.6.3. Conclusions

For heterojunctions obtained from non-local manipulations of interactions we expect that screening and exchange-interaction induced confinement potentials affect uncorrelated electrons and holes quite differently compared to correlated electron-hole pairs. For instance, optical absorption energies related to the excitation of correlated electron-hole pairs (i.e. excitons) depend on the quasiparticle band gaps but also on the excitonic binding energies which are both decreased by a highly polarizable dielectric environment. Hence, the excitonic absorption energies will change less by external manipulations of the Coulomb interaction [242] than the single-particle properties, which are most relevant for electronic transport. As a consequence, the relation between optical and transport properties in the kind of heterojunctions proposed here will likely differ from heterojunctions created by stitching different materials together.

We have demonstrated that in MoS$_2$, as a typical 2D TMDC semiconductor, heterostructures can be formed by means of spatially structured dielectric environments. For this purpose, we have used ab initio calculations and a generic 2D semiconductor model, to show that the external manipulation of the Coulomb interaction allows for sharp, spatially modulated band gaps. Hence, new kinds of heterojunctions can be constructed by placing semiconducting 2D materials on appropriately structured substrates. Similarly, polarizable molecules could be deposited on top of 2D materials to cover parts of the surface to form heterojunctions. Such heterojunctions bring the advantage that only the environment of the active material but not the material itself needs to be structured during the fabrication process. One could thus add the active 2D semiconducting layer to independently pre-structured dielectric layers which is very attractive from a fabrication point of view.

While we have considered a single interface in this section, our findings can be generalized to more complex structures. One can for instance use two parallel interfaces to realize a quantum wire-like structure. Finally, with four interfaces (two in the $x$- and two in the $y$-direction) or also partial coverage of finite areas with adsorbates quantum dots could be externally induced in monolayers of homogeneous 2D materials.
5. Conclusions and Outlook

By combining material-realistic low-energy models that we derived from *ab initio* calculations with high-level many-body or multi-scale approaches, we were able to get deep insights into the electronic and optical properties of novel two-dimensional materials. Depending on the material property under consideration, we chose models which are capable of hosting the corresponding physics and combined them with appropriate many-body or multi-scale methods. Thereby, we have shown that the accuracy of the resulting properties such as exciton binding energies, critical temperatures or optical conductivities directly depends on the precision of the underlying model ingredients. Those comprise the electronic and phononic dispersions and the electron-phonon as well as the electron-electron interactions.

Regarding the electronic properties, we have seen in the case of partially fluorinated graphene that a proper description of both dispersions (pristine graphene’s and fluorographene’s) is needed to describe the disordered systems as closely as possible. Moreover, in the case of molybdenum disulfide monolayers we found that a precise description of the $K$ and $\Sigma$ valleys in the lowest conduction band is absolutely necessary in order to accurately describe the multifaceted physics of excitonic and plasmonic excitations as well as the details of the superconducting state under electron doping. For the interaction matrix elements we were able to show that, among others, the physical details of the superconducting state of doped MoS$_2$ strongly depends on details of the electron-phonon coupling. Furthermore, we revealed that the in general increased Coulomb interactions in two-dimensional materials strongly enhances band-gaps and exciton binding energies. Thus, accurate descriptions of these interactions are absolutely necessary as soon as optical properties shall be described. Thereby, a proper inclusion of screening effects due to those parts of the system which are excluded from the low-energy model is of outstanding importance. Otherwise the Coulomb interaction would be overestimated, resulting in poor agreement with experimental data.

Having settled the model-derivation schemes and their interfaces to subsequent approaches, we were able to study a large variety of electronic and optical properties of functionalized graphene and graphene heterostructures in chapter 3 as well as doped or optically excited MoS$_2$ monolayers in chapter 4.

In section 3.2 we showed that disorder effects alone are not sufficient to explain the significantly reduced optical band gap of fluorographene. However, we found specific “finger prints” in the optical spectra resulting from different kinds of disorder which might form the basis for more realistic considerations including broadening effects due to phonons and/or excitonic effects. We also showed that the transition from a
perfectly flat to a buckled structure due to partial fluorination can be measured by polarization rotations of passing polarized light. This finding might be a powerful tool to distinguish between $sp^2$- and $sp^3$ hybridized areas.

By introducing in section 3.3 a novel scheme to describe Coulomb interactions of layered heterostructures in the Wannier basis, we gained a deep understanding of the nature of these interactions. Using this approach (with the help of recently derived phase diagrams), we found the ground state of bilayer graphene being in the near of the phase transition between an antiferromagnetic spin-density wave phase and a quantum-spin-hall state. Additionally, we showed that the antiferromagnetic ground state is stabilized by an increasing external screening.

In section 4.3 we showed that the phase diagram of electron-doped MoS$_2$ monolayers includes a metallic, a superconducting and a charge-density-wave phase. We presented a detailed analysis of the superconducting dome and found that the occupation of the $\Sigma$ valley is of prime importance to enhance the corresponding critical temperature. Additionally, we analyzed in detail the super-cell band structure within the newly found charge-density-wave phase regime and disclosed a possible coexistence of the superconducting and CDW phases.

Regarding the excitonic effects which arise in optically excited MoS$_2$ monolayers, we were able to predict in section 4.4 a significant redshift of the $A$ and $B$ transitions with increasing excitation densities, which have been measured shortly after. The solution of the semiconductor Bloch equations based on our material-realistic model allowed us to disentangle band-gap shifts and changes in the exciton binding energies, yielding an in-depth understanding of the underlying physics. Furthermore, we showed how biaxial strain, acting mainly on the electronic dispersion, influences the absorption spectra.

In section 4.5 we studied in detail plasmonic excitations under electron and hole doping and found the well known intra-valley plasmonic branches as well as clear hints for arising inter-valley excitations. Once again, all observations could be explained upon taking the band-structure details and (properly screened) Coulomb interactions into account. By introducing additional screening channels to the latter, which arise for example due to dielectric substrates, we were able to show how the intra-valley plasmon mode can be tuned on demand using different dielectric environments.

Besides these considerations of translationally invariant systems, we focused in section 4.6 on systems with broken translational symmetry due to spatial modulations of the Coulomb interaction. Here, we were able to show that in these kind of systems a type-II band diagram can be induced externally. Thus, we proposed to build new kinds of heterojunctions by placing a homogeneous semiconducting layered material on a heterogeneous dielectric substrate.
Outlook

Although we have made some progress, it is still a long way to a complete and universal understanding of layered heterostructures. However, we believe that the adopted strategy is promising due to its versatile extension opportunities.

On the model level, the biggest drawbacks so far are the non-inclusion of non-density-density Coulomb matrix elements and missing efficient analytic expressions for the electron-phonon couplings. In principle, both of these problems can be overcome using the Wannier basis. Thereby, the long-term objective should be to introduce generalized Wannier-interpolations for all model ingredients based on real-space representations of the latter ones. Doing so, we would be able to evaluate each matrix element for arbitrary points in momentum space. Furthermore, it remains to be seen whether the presented down folding scheme based on Wannier constructions for the low-energy states is always suitable. As far as we know today, monolayers of transition metal dichalcogenides seem to be “well-behaved” in this context. For multilayers or very different layered systems the situation is not clear and has to be checked carefully. Additionally, we need to extend our modeling scheme to describe the dynamical and non-local effects of substrates not only to the Coulomb interactions but also to the electron-phonon couplings.

On the side of the “many-body approaches”, we need to extend our methods to deal with all important ingredients at the same time, that are the electronic and phononic dispersions and the electron-electron and electron-phonon interactions, in order to understand their interplay. Furthermore, we need to extend the methods in order to treat dynamical processes and to include higher-order diagrams.

Doing so, it will be possible to gain a unified understanding of many-body instabilities and excitations as well as their interplay in layered heterostructures. For instance, in the field of optical properties we will be able to study time-resolved electron-electron and electron-phonon scattering processes (indeed first results for the former are already available [356]) under the influence of the dielectric environment. Furthermore, taking higher-order diagrams into account, we will be able to describe trions or other multi-exciton processes.

Especially regarding the description of superconducting phases within these layered materials, we will be able to make progress upon application of these extensions. Indeed, this is necessary as recent experiments on the dependence of the critical temperature to the number of involved layers demonstrate: While Cao et al. and Costanzo et al. found a decreasing $T_c$ towards the monolayer limit in TMDCs [6, 357], Ge et al. report a substantially enhanced $T_c$ in FeSe films in this limit (on the order of 100K) [358]. To understand these contradicting trends, we can apply our modeling scheme in combination with full solutions to the Eliashberg equations in order to take simultaneously external effects (like substrates, applied pressure or strain) and internal details (band structure effects, screened interaction matrix elements, etc.) into account. This scheme can additionally be extended to include dynamical properties of the Coulomb
5. Conclusions and Outlook

interaction [in contrast to the formulation in Eq. (2.221)]. Thus, we will be able to study the influence of plasmons to the superconducting state, which might introduce additional coupling channels for the Cooper pairing as discussed by Takada, Akashi and Arita [359, 360, 361]. The latter might also be a promising direction to study effects that arise from external bosonic modes provided by the environment as it has already been suggested by Ginzburg and Kirzhnits [362] and Little [363] in 1964 or Allender [364] in 1973. Also, it is important to note that the Eliashberg theory is a diagrammatic approach which neglects specific classes of diagrams. Whether or not this is appropriate for the system under consideration remains to be checked by evaluating higher-order diagrams or by benchmarking the Eliashberg results to those gained from quantum Monte-Carlo (QMC) approaches which are in principle exact (if it is possible to find a solution).

Using appropriate QMC schemes in combination with our material-realistic models we might also gain deeper insights into the physics taking place in the near of quantum phase transitions or into the interplay of different phases like it was already speculated in the case of electron doped MoS$_2$. Here, it will be extremely interesting to see if coexisting phases increase or decrease specific critical temperatures and how this behaviour might be tuned from the outside.

Thus, in a final conclusion, layered materials exhibit a large variety of many-body effects which need to be explored in more detail in order to gain full control of artificial layered heterostructures. Therefore, it seems to be appropriate to bring together the best of both worlds, namely ab initio calculations and model descriptions, as we have shown for some specific examples.
A. Model Parameters and Calculations Details

A.1. Optical Properties of Fluorographene

A.1.1. Ab Initio Details

We use the PAW method as implemented in the VASP code [365, 366, 65] to obtain converged GGA (PBE) DFT results as starting points for the $G_0W_0$ [124, 123, 117, 116] calculations. In all cases a $8 \times 8 \times 1$ $k$-mesh and an energy cut-off of 400 eV is used. For pristine graphene we use a lattice constant of $a_0 = 2.47$ Å. The geometry of fluorographene in the chair configuration [see Fig. 3.3 (a)] has been optimized yielding a lattice constant of $a_0 = 2.62$ Å, an out-of-plane displacement of $\Delta z = \pm 0.21$ Å for each carbon atom and a fluorine-carbon distance of $c = 1.38$ Å. The $G_0W_0$ calculations included Bloch states up to an energy of 120 eV in all calculations.

A.1.2. Tight-Binding Model Details

Our tight-binding model is parametrized using two-center integrals within the Slater-Koster scheme [367]. Thus, the hopping matrix elements used in Eq. (3.10) are defined as combinations of Slater-Koster parameters $V$ and direction cosines $l$, $m$ and $n$ (see Tab. A.1) which are given in Tab. A.3 and Tab. A.2, respectively. The direction cosines are calculated based on the geometrical relaxations and the Slater-Koster parameters are fitted to $G_0W_0$ quasiparticle band structures. As mentioned in section 3.2 three different carbon-carbon hopping combinations arise: (i) nearest neighbour hopping between pristine carbon atoms, (ii) hopping between two fluorinated carbon atoms and (iii) hopping between a pristine and a fluorinated carbon atom (CF$_x$). The corresponding carbon-carbon hoppings for the pristine materials are given in the upper part of Tab. A.3. To describe a hopping matrix element between a fluorinated and an fluorinated carbon atom we take the arithmetic mean value of the corresponding values from the “graphene” and “fluorographene” columns from Tab. A.3 together with the CF$_x$ direction cosines from Tab. A.2. The carbon on-site energies for a partially fluorinated system are chosen depending on whether the carbon atom is fluorinated or not. In the lower part of Tab. A.3 fluorine on-site matrix elements and fluorine-carbon hopping matrix elements are given. Thus, there is no direct fluorine-fluorine hopping.
### A. Model Parameters and Calculations Details

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<td>$t_{pzpy}$</td>
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Table A.1.: Definition of Slater-Koster parameters.

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</tr>
<tr>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
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</tr>
</tbody>
</table>

Table A.2.: Direction cosines. Here $\delta_F$ denotes the vector of the adjacent upper F atom of the central C atom.

| $\varepsilon_s$ | -2.85 | -5.54 |
| $\varepsilon_{p_{xy}}$ | +3.20 | +2.31 |
| $\varepsilon_{p_z}$ | +0.00 | +4.92 |
| $V_{ss\sigma}$ | -5.34 | -3.65 |
| $V_{sp\sigma}$ | +6.40 | +7.20 |
| $V_{pp\sigma}$ | +7.65 | +7.65 |
| $V_{pp\pi}$ | +0.00 | +2.20 |
| $V_{pzpz}$ | -2.80 | -2.64 |
| $V_{pzpy}$ | +0.00 | -2.80 |
| $V_{pzpz}$ | -2.80 | -1.87 |

Table A.3.: Two-center integrals involved in the definition of the Slater-Koster parameters for graphene and fluorographene. The upper panel shows the carbon on-site energies as well as the carbon-carbon hoppings, while the lower panel shows the fluorine on-site energies and the corresponding carbon-fluorine hoppings. All values are given in eV.
A.1. Optical Properties of Fluorographene

A.1.3. Tight-Biding Propagation Method

In the following we briefly discuss the main ideas of the tight-binding propagation method. For more details the reader is referred to the Refs. [368, 189].

In order to apply the so-called tight-binding propagation method to calculate the total density of state, the latter is written as the Fourier transform of the overlap between the time-evolved state $|\phi_s(t)\rangle$ and the initial (random) state $|\phi_s(0)\rangle$:

$$D_s(E) = \sum_i \delta(E - E_i) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ Tr \left\{ e^{iHt} \right\} e^{iEt} \quad (A.1)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \langle \phi_s(0) | \phi_s(t) \rangle e^{iEt},$$

where the time evolution is given by

$$|\phi_s(t)\rangle = e^{iHt} |\phi_s(0)\rangle. \quad (A.2)$$

By averaging over a variety of randomly initialized states $|\phi(0)\rangle = \sum_i a_i |i\rangle$ the total density of states is obtained according to

$$D(E) = \lim_{s \rightarrow \infty} \frac{1}{s} \sum_s D_s(E). \quad (A.3)$$

From a numerical point of view this scheme is quite advantageous, since the “partial” density of states $D_s(E)$ can be obtained efficiently by evaluating the time evolution within a Chebychev polynomial decomposition and the Fourier transformation with the help of fast Fourier transform algorithms. Thereby, huge real-space super cells can be simulated without the need of a full diagonalization. Furthermore, it has been shown that for large systems it is often enough to use just a single initial random state [368, 189].

Based on the same concepts, the optical conductivity according to Kubo’s formula [29, 24] can be efficiently evaluated for arbitrary frequencies $\omega$ and spatial directions $\alpha, \beta \in \{x, y, z\}$

$$\sigma_{\alpha\beta}(\omega) = \lim_{\epsilon \rightarrow 0^+} \frac{1}{(\omega + i\epsilon)\Omega} \left( \int_0^\infty dt \langle [J_\alpha(t), J_\beta]\rangle e^{i(\omega + i\epsilon)t} - i \langle [P_\alpha, J_\beta]\rangle \right) \quad (A.4)$$

using the polarization $P$ and the current $J$ operators

$$P = eR \quad \text{and} \quad J = e\dot{R} = \frac{ie}{\hbar} [H, R]. \quad (A.5)$$

Within the tight-binding formalism the dipole operator can be separated $R = R_1 + R_2$ into a regular (or envelope) term and an inter-orbital (or intra-atomic) term yielding

$$R_1 = \sum_{i\alpha} r_i c_{ia}^\dagger c_{i\alpha} \quad \text{and} \quad R_2 = \sum_{i\alpha\beta} \langle i\alpha | \delta r | i\beta \rangle c_{i\alpha}^\dagger c_{i\beta}; \quad (A.6)$$
A. Model Parameters and Calculations Details

where \( r \) and \( \delta r \) denote the atomic positions and the positions within a unit cell, respectively \([369]\). These contributions can in turn be used to evaluate the commutator which is involved in the definition of the current operator (see Ref. \([189]\) for more details). Hence, as soon as the matrix elements \( \langle i\alpha | \delta r | i\beta \rangle \) are known, the optical conductivity can readily be evaluated within the tight-binding propagation method.
A.2. Coulomb-Interaction Matrix Elements for Graphene Heterostructures

We start with DFT calculations employing the Fleur code [370, 371] to obtain the corresponding ground states within the FLAPW method based on the generalized gradient approximation (PBE) [48]. Afterwards, we use the SPEX code [121, 122] to calculate the bare and screened Coulomb matrix elements in the constrained random phase approximation (for more details on the cRPA method see section 2.3.2).

In the case of carbon atoms we use an angular momentum cut-off of $l_{\text{cut}} = 6$ and $l_{\text{cut}} = 8$ for iridium. The plane-wave cut-off is set to $4.5 a_0^{-1}$, where $a_0$ is the Bohr radius. The involved $k$ meshes and the energy cut-offs for the polarization function are shown in Tab. A.4. The energy cut-off corresponds to the energy of the highest, unoccupied band (and thus to the total number of empty bands) involved in the calculation of the polarization function. Since in the case of MLG and BLG several “vacuum distances” (see below) have been used, the number of empty bands had to be adjusted for each vacuum height (corresponding to the given energy cut-off).

A “vacuum distance” $h_{\text{vac}}$ (the distance between adjacent layers) is introduced, since we embed the mono- or bilayer in a three-dimensional unit cell. Thereby, we produce, due to the periodic boundaries, an infinite stack of mono- or bilayers separated by the unit-cell height. The freestanding situation is obtained in the limit of $h_{\text{vac}} \to \infty$. To approximate this limit, we do several calculations for different vacuum distances (ranging from $h_{\text{vac}} \approx 15 \text{Å}$ to $h_{\text{vac}} \approx 30 \text{Å}$) and extrapolate the freestanding value $U_{\alpha\beta}(q, \infty)$ by fitting the results to

$$U_{\alpha\beta}(q, h_{\text{vac}}) = U_{\alpha\beta}(q, \infty) + \frac{b_{\alpha\beta}(q)}{h_{\text{vac}}}$$

(A.7)

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<th>system</th>
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<th>cRPA $k$ mesh</th>
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<td>$16 \times 16 \times 5$</td>
<td>$\approx 180 \text{eV}$</td>
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</table>

Table A.4.: 
*Ab initio* details for each system. The polarization energy cut-offs are given relative to the graphene Dirac-cone position.
A. Model Parameters and Calculations Details

Figure A.1: Band gap at $K$ as a function of the $GW$ parameters. All calculations have been done for the unstrained lattice constant of $a_0 = 3.18\,\text{Å}$. If not declared otherwise, an intermediate vacuum distance of $h = 35\,\text{Å}$, 200 bands and a $GW$ energy cut-off of 150 eV have been used on a $18 \times 18 \times 1$ $k$-mesh.

A.3. Generalized Hubbard Model for MoS$_2$ Monolayers

A.3.1. $GW$-based Three-band Tight-Binding Hamiltonian

In order to obtain the three-band tight-binding Hamiltonian we perform $G_0W_0$ [124, 123, 117, 116] calculations within the PAW method as implemented in the VASP code [365, 366, 65]. As a starting point, we use the Kohn-Sham eigenstates and energies obtained from GGA (PBE) [48] calculations on $18 \times 18 \times 1$ $k$-meshes with a plane wave cut-off of 280 eV. The sulfur $z$-displacements are optimized until the force acting on each S atom is smaller than $10^{-5}\,\text{eV}/\text{Å}$. In the $G_0W_0$ calculations the same $k$-mesh is used together with 200 bands and an energy cut-off of 150 eV for the response function to obtain quasiparticle energies. The converged results (see next section) are projected onto Mo $d_{z^2}$, $d_{xy}$ and $d_{x^2-y^2}$ states using the Wannier90 package [69].
A.3. Generalized Hubbard Model for MoS$_2$ Monolayers

Convergence

Fig. A.1 shows the convergence behaviour of the $G_0W_0$ calculations concerning the $k$-point sampling and height extrapolations. Regarding the $k$-point sampling we find that using a $18 \times 18 \times 1$ $k$-mesh overestimates the resulting band gap of a truly converged $k$-mesh by roughly 100 to 150 meV, see Fig. A.1 (c). Fig. A.1 (d) shows the linearly extrapolated band gaps (dashed lines) for different $k$-meshes in dependence of the vacuum height. In this plot the $1/h = 0$ value corresponds to the limit of a freestanding monolayer. Here, we see that the slope of the linear extrapolation decreases with the $k$-mesh.

Strictly speaking, for each vacuum distance the $GW$ energy cutoff and the number of bands must be chosen individually to reach convergence. For $h = 35$ Å we have verified that the band-gap dependence on both parameters is at least one order of magnitude smaller in comparison to the $k$-point sampling, see Fig. A.1 (a) and (b). For a detailed analysis of the $GW$ parameters on the convergence properties we refer to Refs. [197] and [194]. We note, however, that full optimization of the band gap is not a central purpose of this thesis, since we are most interested in relative trends and not absolute numbers. In addition, MoS$_2$ will be in the most experimental setups subject to some environmental screening effects, which will additionally change (decrease) the band gap.

A.3.2. Coulomb-Interaction Matrix Elements

Here, we briefly describe how the ab initio data from Fig. 4.7 is obtained. To this end we proceed in a similar way as described in section A.2. Hence, we use the Fleur code [370, 371] to obtain electronic ground-state densities which are used in the SPEX code [121, 122] to calculate the bare $W_{\alpha\beta}(q)$ and screened $v_{\alpha\beta}(q)$ Coulomb matrix elements in the random phase approximation (note, that we use the fully screened version of the RPA and that the $k$ and $k'$ dependencies have been traced out) in the effective Mo $\{d_{x^2}, d_{xy}, d_{x^2-y^2}\}$ basis. In all calculations we use the unstrained geometry (e.g. $a = 3.18$ Å). In order to obtain matrix elements for the free standing layer we have to apply the extrapolation scheme as described in section A.2. The vacuum distances have been varied between 20 and 31 Å. For the DFT calculations we use $16 \times 16 \times 1$ $k$-meshes and angular momentum cut-offs of $l_{\text{cut}} = 10$ and $l_{\text{cut}} = 8$ for molybdenum and sulfur, respectively. The $k$-meshes are increased to $32 \times 32 \times 1$ for the evaluation of the polarization in order to get highly resolved interaction matrix elements in momentum space. Furthermore, we use 200 Bloch states to obtain converged dielectric functions which are calculated element wise via the inversion of Eq. (4.12).

In Tab. A.5 we list all resulting bare $v_{\alpha\beta\gamma\delta}$ and screened $W_{\alpha\beta\gamma\delta}$ real-space Coulomb matrix elements for $R = 0$.\footnote{Here, we show the real part of each element up to the second decimal place. We note, that some elements have a finite but small imaginary part (two to three orders of magnitude smaller than...} Density-density and exchange matrix elements (i.e. ele-
A. Model Parameters and Calculations Details

bare Coulomb interaction $v$

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screened Coulomb interaction $W$

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</table>

Table A.5.: Real parts of the bare $v$ and screened $W$ Coulomb matrix elements of monolayer MoS$_2$ in real-space for $R = 0$. These values are obtained via height-extrapolated calculations on $16 \times 16 \times 1$ $k$-meshes using 200 bands.

...ments which involve only two different orbital characters) are the biggest contributions. In more detail, homogeneous density-density elements show the biggest contributions of $v_{\alpha \alpha \alpha \alpha} \approx 10 – 8.9$ eV and $W_{\alpha \alpha \alpha \alpha} \approx 2.1 – 1.9$ eV, followed by mixed density-density elements with $v_{\alpha \beta \beta \alpha} \approx 8.7 – 8.5$ eV and $W_{\alpha \beta \beta \alpha} \approx 1.5 – 1.6$ eV, while the smallest contributions arise due to exchange elements of the type $v_{\alpha \alpha \beta} \approx 0.4 – 0.2$ eV and $W_{\alpha \alpha \beta} \approx 0.3 – 0.2$ eV. All other elements are essentially (within the shown accuracy) zero. Based on the observation that the exchange Coulomb matrix elements are at least one order of magnitude smaller than the density-density elements we conclude that the most important contributions of the Coulomb interaction arise due to the latter and the former are neglected in the following. 

the real part) which is not shown here.

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A.3. Generalized Hubbard Model for MoS$_2$ Monolayers

Convergence

In Fig. A.2 we show the bare and screened Coulomb interaction in dependence on the number of bands and the $k$-mesh. Since the number of bands mainly influences the polarization function and thus the screened Coulomb interaction, the bare Coulomb interaction is unaffected by this parameter. Even the screened matrix elements differ by less than 1%. The use of different $k$-meshes ($16 \times 16 \times 1$ and $32 \times 32 \times 1$) also results in deviations of less than 1%. Thus, the RPA calculations for the Coulomb matrix elements are clearly converged.

Figure A.2.: Bare (green) and screened (red) Coulomb matrix elements between $d_{z^2}$ orbitals for different $k$-meshes and number of bands for a vacuum height of $\sim 30$ Å.

![Figure A.2.](image-url)
A.4. Superconductivity and Charge-Density Waves in MoS$_2$ Monolayers

A.4.1. Computational Details

The results presented in section 4.3.2 are gained by using the VASP [365, 366, 65] and Quantum Espresso [372] packages for the density functional theory based self-consistent evaluation of the electronic and phononic band structures. The DFT calculations are performed within the LDA using norm-conserving pseudo potentials. For the electronic calculations a $32 \times 32 \times 1$ $k$-mesh is used ($64 \times 64 \times 1$ for the calculation of $N_F$), in combination with a Methfessel-Paxton smearing (0.0075 Ry). The lattice parameter is chosen to be 3.122 Å and adjacent layers are separated by $\approx 13$ Å. The geometry (S positions) of the simple unit cell is optimized for each electron doping. The phonon band structures as well as electron-phonon coupling matrix elements are calculated within the density functional perturbation theory based on the evaluation of the dynamical matrices on a $8 \times 8 \times 1$ $q$-mesh using the phonon package of Quantum Espresso. The relaxed structures and the total energies of $1 \times 1$ and $2 \times 1$ super-cells for several doping concentrations are calculated within the LDA. Both calculations are performed on $32 \times 32 \times 1$ $k$-meshes ($16 \times 32 \times 1$ in the latter case). The tetrahedron method is applied to obtain accurate total energies. While all other electronic band structures are calculated within Quantum Espresso the results shown in Fig. 4.13 (c) and Fig. 4.14 are obtained using the PAW method in the LDA as implemented in VASP code.

A.4.2. Renormalization of the Phononic Dispersion upon Doping

As discussed in section 2.4.4 and section 4.3.2, the phononic energies are renormalized by the real part of the phonon self-energy $\Sigma_{ph}$ which can be approximated in metals [27] via

$$\text{Re} \{\Sigma_{ph}\} = \text{Re} \left\{ \frac{|g_{qp}^{(0)}| \Pi(q, \omega = 0)}{\varepsilon(q, \omega = 0)} \right\} = \text{Re} \left\{ |g_{qp}^{(0)}| \chi(q, \omega = 0) \right\}. \quad (A.8)$$

This approximation is in fact valid only for a simple metal. Since a realistic description of electron-doped MoS$_2$ needs to be based on a multi-band (multi-orbital) electronic structure in combination with three acoustic and six optical phonon modes and their mutual couplings, Eq. (A.8) can be used solely to derive qualitative statements.

Doing so by using the evaluation of the macroscopic polarization and the macroscopic dielectric function within the random phase approximation as introduced in section 4.4, we can readily calculate an educated guess to $\text{Re} \chi \approx \text{Re} \Pi/\text{Re} \varepsilon$. In Fig. A.3 we show the corresponding results for a “low” and a “high” doping level, which correspond to
Figure A.3.: Quotient of the real parts of the electronic polarization and dielectric functions of an electron doped MoS$_2$ monolayer along a path through the whole Brillouin zone. The black line corresponds to a “low doping level” for which just the $K$ valley is occupied, while the red curve corresponds to an increased doping level which occupies the $\Sigma$ valleys as well.

$\Gamma$ or $K$ and $\Sigma$ occupations. Since the dielectric function for small $q$ is sufficiently described here by the Thomas-Fermi approximation $\varepsilon(q, \omega = 0) \approx 1 + q_{TF}/q$ there is no renormalization in the vicinity of $\Gamma$. In the rest of the Brillouin zone we find an overall reduction of $\chi$ upon electron doping. Due to the fact that there are no particular features visible around $M$ or $K$, which might explain the Kohn anomalies in Fig. 4.9 (b), the latter seem to trace back to efficient bare couplings $g^{(0)}_{q}$ at those points.

A.4.3. Optical Electron-Phonon Coupling Matrix Elements

In analogy to the maps of the electron-phonon coupling arising due to the acoustic phonon branches we present in Fig. A.4 the corresponding maps arising due to optical phonons. Most importantly, we see that the *summed contribution* of all six optical phonon modes is throughout the Brillouin zone smaller. Hence, the average contribution of a single optical mode is much smaller compared to these of the acoustic branches. Furthermore, we see less structure and nearly no doping dependence. However, there is finite electron-phonon coupling arising due to these phonon modes [as it can also be seen in the Eliashberg functions presented in Fig. 4.10 (b)] which enhances $T_c$, but is less effected by the doping.
Figure A.4.: Electron-phonon coupling matrix elements $|g_{K-c_1}^{\nu}|$ with $k = K$ (left column) and $k = \Sigma$ (right column) for the lowest conduction bands ($n = n' = c_1$). The maps represent the $q$-dependencies of the sum of all optical branches. Green lines indicate the $k$-Brillouin zones while the red lines define the $q$-Brillouin zones. From the top to the bottom row the electron doping is increased from $x = 0.0$, $x = 0.05$ ($K$ occ.) to $x = 0.1$ ($K$ and $\Sigma$ occ.).
A.5. Optical Properties of MoS\textsubscript{2} Monolayers

A.5.1. Semiconductor Bloch Equation

In the following we briefly discuss all details and necessary ingredients to solve the Semiconductor Bloch equation as given in Eq. 4.21. For more details see Ref. [373].

Basic Parameters

The semiconductor Bloch equation is solved by sampling the irreducible part of the first Brillouin zone by 60 grid points in \( \Gamma M \) direction and 120 points in the \( KK' \) direction. For all results presented in section 4.4.1 direct transitions between the two highest valence bands and the four lowest conduction bands (including SOC) in the electron-hole picture are included.

We use an electric field with circular polarization

\[
E_\pm(t) = E \frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ \pm i \end{array} \right) e^{i\omega t},
\]

on which the dipole matrix elements (see next section) are projected. Hence, they exhibit a threefold rotational symmetry, allowing for the reduction of the \( k \)-space to one sixth of the first Brillouin zone.

Transition Dipole Matrix Elements

From the tight-binding Hamiltonian we calculate direct dipole transition matrix elements using Peierl’s approximation [374]

\[
d_{\lambda\lambda'}(k) = e \langle \psi_{\lambda}(k) | \hat{r} | \psi_{\lambda'}(k) \rangle = \frac{1}{i} \frac{1}{\epsilon_{\lambda}(k) - \epsilon_{\lambda'}(k)} \sum_{\alpha} \epsilon^*_{\lambda\alpha}(k) c_{\lambda\alpha'}(k) \hat{c}_{\beta\lambda}(k). \tag{A.10}
\]

The involved derivative can be analytically evaluated by utilizing the tight-binding descriptions of the Hamiltonian from Eq. (2.79).

Plasma Screened Coulomb Matrix Elements in the Band Basis

The Coulomb matrix elements of the minimal model [as described by Eq. (4.12)] are given in the orbital basis \( |k\alpha\rangle \), but the SBE is formulated within the band or eigenbasis. Therefore, we need to apply a corresponding basis transformation using the eigensystem of the Wannier Hamiltonian (see section 2.2.2). Using this eigensystem the density-density Coulomb matrix elements in the orbital basis are transformed to Hartree-like inter-band density-density matrix elements via

\[
W^{\lambda\lambda'\lambda\lambda'}_{kk'k'k} = \sum_{\alpha\beta} c^*_{\alpha\lambda}(k) c^*_{\beta\lambda'}(k') c_{\beta\lambda'}(k') c_{\alpha\lambda}(k) W_{\alpha\beta}(q = 0) \tag{A.11}
\]
A. Model Parameters and Calculations Details

<table>
<thead>
<tr>
<th></th>
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<th>a = 3.18Å</th>
<th>a = 3.20Å</th>
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<td>0.60</td>
<td>0.59</td>
<td>0.57</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.51</td>
<td>0.51</td>
<td>0.49</td>
</tr>
<tr>
<td>$K_{3/4}$</td>
<td>0.61</td>
<td>0.59</td>
<td>0.54</td>
</tr>
<tr>
<td>$\Sigma_3$</td>
<td>0.78</td>
<td>0.64</td>
<td>0.70</td>
</tr>
<tr>
<td>$\Sigma_4$</td>
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<td>0.69</td>
<td>0.75</td>
</tr>
<tr>
<td>$\Gamma_{1/2}$</td>
<td>5.5</td>
<td>4.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table A.6.: Effective electron and hole masses in units of $m_0$ at the relevant symmetry points $K$, $\Sigma$ and $\Gamma$. The subscripts denote the band index in energetic order.

with zero momentum transfer and Fock-like *inter-band exchange* matrix elements via

$$W_{kk'kk''}^{\lambda\lambda'} = \sum_{\alpha\beta} c_{\alpha\lambda}^*(k)c_{\beta\lambda'}^*(k')c_{\beta\lambda}(k)c_{\alpha\lambda'}(k')W_{\alpha\beta}(q = |k - k'|) \quad (A.12)$$

with finite momentum transfer $q = |k - k'|$ which *exchanges* the momenta $k$ and $k'$. As explained in section 4.4.1, additional finite charge-carrier distributions in the valence or conduction band lead to additional (plasma) screening effects which decrease the background screened Coulomb interaction $W$ and thus renormalizes excitonic binding energies as well as the quasiparticle band structure as obtained in the $GW$ approximation for the ground state. These additional screening effects are described according to Eq. (4.28) by the dielectric function $\varepsilon_{\text{plasma}}(q)$ which can be obtained within the random phase approximation (see section 2.3.1). Here, we use its long-wavelength static limit (Thomas-Fermi screening) arising due to carrier populations in all relevant valleys $v \in \{K, K', \Sigma, \Sigma', \Gamma\}$. To this end we describe each valley (at $v$ and band $\lambda$) for each lattice constant in the effective mass approximation ($m_{v\lambda}^*$) and calculate the total plasma screening function as

$$\varepsilon_{\text{plasma}}(q) = 1 - \sum_{\lambda} \sum_v W_{\lambda\lambda'}^{v,v,q,v,q} \Pi_{\text{TF}}(v, \lambda) \quad (A.13)$$

with the valley and band resolved Thomas-Fermi polarizations

$$\Pi_{\text{TF}}(v, \lambda) = -N_F(v, \lambda) = -\frac{m_{v\lambda}^*}{2\pi\hbar^2}f_\lambda(v). \quad (A.14)$$

The Fermi functions in Eq. (A.14) are included in order to properly account for each valley occupation. The involved effective masses are given in Tab. A.6.

**Renormalized Band Energies**

Next to additional screening, the presence of the excited electron-hole plasma leads to further renormalization effects to the band structure and the Rabi frequency. Here, we
use the Coulomb-hole plus screened exchange (COHSEX) approximation to deduce the arising effects. As briefly discussed in section 2.3.4 within the COHSEX approximation the self-energy is divided into an exchange and a correlation term. While the former depends solely on (plasma) screened Coulomb interactions $V$, the latter involves bare (but screened by the background) interactions $W$ as well. A systematic derivation of these self-energy terms yield the following COHSEX-renormalized electron energies

$$\tilde{\varepsilon}_e(k) = \varepsilon_e(k) + \frac{1}{A} \sum_{k',e'} \left( W_{kk'kk'}^{e'e'} - V_{kk'kk'}^{e'e'} \right) f_{e'}(k') + \frac{1}{2} \left[ V_{kk'kk'}^{e'e'e'e'} - W_{kk'kk'}^{e'e'e'e'} \right]$$ (A.15)

$$- \frac{1}{A} \sum_{k',h'} \left( W_{kk'kk'}^{hh'h'h'} - V_{kk'kk'}^{hh'h'h'} \right) f_{h'}(k') + \frac{1}{2} \left[ V_{kk'kk'}^{hh'h'h'} - W_{kk'kk'}^{hh'h'h'} \right].$$

The corresponding expression for the hole energies is gained via simple permutation of all $e$ and $h$ indices.

### A.5.2. Finite-Density Results Under Strain

In the strained case ($a_0 = 3.20 \text{Å}$) the conduction band minimum at $\Sigma$ is energetically significantly higher than that at $K$ (see inset of Fig. 4.15), which, however, does not change the density-dependent behaviour of the optical spectra drastically, as shown in Fig. A.5. The positions of $A$ and $B$ transitions exhibit a redshift from 2.02 to 1.98 eV and from 2.15 to 2.12 eV, respectively. Hence, the redshift is smaller in the strained case (40 instead of 70 meV). The reason is that more population is building up in the conduction band minima at $K$ and $K'$ in this case. This leads to stronger Hartree shifts of $K$ and $K'$ that counteract the band-gap shrinkage caused by the COHSEX renormalizations due to the excited carriers.
A. Model Parameters and Calculations Details

Figure A.5.:  
**Left**: Monolayer MoS$_2$ optical absorption spectra for carrier densities from 0 to $10^{13}$/cm$^2$ and 300 K. Calculations are shown for the strained structure ($a_0 = 3.20$ Å). **Right**: Gap shifts and binding energies belonging to the A (solid line) and B (dashed line) exciton transitions for increasing carrier densities.
A.6. Plasmonic Excitations in Doped MoS$_2$ Monolayers

A.6.1. Polarization Function Within the Orbital Basis

\[
\begin{align*}
\alpha_{k-q} & \quad \beta_{k'+q} \quad \alpha_{k-q} \\
\delta_k & \quad \gamma_{k'} \
\end{align*}
\]

Figure A.6.: Dyson equation for screened Coulomb matrix elements in the orbital basis using Feynman diagrams. Straight lines correspond to unrenormalized Green functions and (double) wiggly lines to (screened) Coulomb interactions.

In Fig. A.6 we show the Dyson equation for the screened Coulomb matrix elements in the orbital basis. In the following we will derive the corresponding density-density polarization function as used in section 4.5.

In its most general form the RPA polarization function is given by the inner bubble diagram of Fig. A.6 which translates into

\[
\Pi^\alpha_{k-k'}(i\Omega) = \frac{1}{i\sum_{i\omega_n} \langle \tilde{\beta}k' + q | G_0(i\omega_n + i\Omega) | \tilde{\delta}k \rangle \langle \tilde{\alpha}k-q | \tilde{G}_0(i\omega_n) | \tilde{\gamma}k' \rangle}
\]

(A.16)

using fermionic Matsubara frequencies $i\omega_n$ and the corresponding unrenormalized Green function $G_0(i\omega_n)$. The Lehmann representation of $G_0$ reads in the band basis

\[
G_0(i\omega_n) = \sum_{k\lambda} |k\lambda\rangle \langle k\lambda| \frac{1}{i\omega_n - \epsilon_\lambda(k)}.
\]

(A.17)

By plugging Eq. (A.17) into Eq. (A.16) matrix elements of the form $\langle \tilde{\alpha}k | k\lambda \rangle$ will arise, which can be readily evaluated using the eigencoefficients of our tight-binding Hamiltonian (see section 2.2.2)

\[
\langle \tilde{\alpha}k | k\lambda \rangle = \sum_{\alpha} c_{\alpha}(k) \langle \tilde{\alpha}k | \alpha k \rangle = c_{\alpha}(k) \delta_{kk'}. \]

(A.18)
Thereby Eq. (A.16) becomes

$$
\Pi^{k'k}_{\alpha\beta\gamma\delta}(i\Omega) = \frac{1}{\beta} \sum_{i\omega_n} \sum_{k_1 \lambda_1} \sum_{k_2 \lambda_2} \left\langle \beta \tilde{\kappa} + q \right| k_1 \lambda_1 \left| k_1 \lambda_1 \right. \left. \right| \tilde{\kappa} \right\rangle \frac{1}{i\omega_n + i\Omega - \varepsilon_{\lambda_1}(k_1)}
$$

(A.19)

$$
= \frac{1}{\beta} \sum_{i\omega_n} \sum_{k_1 \lambda_1} \sum_{k_2 \lambda_2} C^{\lambda_1}_{\beta}(k_1) \delta_{k^{'},k} \tilde{\kappa}_\delta(k_1) \delta_{k,k_1} \frac{1}{i\omega_n + i\Omega - \varepsilon_{\lambda_1}(k_1)}
$$

(A.20)

$$
= \frac{1}{\beta} \sum_{i\omega_n} \sum_{k_1 \lambda_1} \sum_{k_2 \lambda_2} C^{\lambda_1}_{\beta}(k_2) \delta_{k,k_2} \tilde{\kappa}^{\lambda_2}_{\delta}(k_2) \delta_{k^{'},k_2} \frac{1}{i\omega_n + i\Omega - \varepsilon_{\lambda_2}(k_2)}
$$

(A.21)

which can in principle be used to solve the Dyson equations as given in Fig. A.6. Since we will use the analytic fits to the background screened Coulomb interaction $W_q$ from section 4.2.2, the interaction lines in Fig. A.6 depend solely on the momenta $q$ which allows us to carry out the summation over the inner momenta $\tilde{k}$ and $\tilde{k}'$ yielding

$$
\Pi_{\alpha\beta\gamma\delta}(q, i\Omega) = \sum_{k'} \Pi^{k'k}_{\alpha\beta\gamma\delta}(i\Omega)
$$

(A.22)

Finally, we can carry out the summation over the inner Matsubara frequencies $i\omega_n$ (see e.g. [27]) in order to introduce the well known “RPA quotient”

$$
\Pi_{\alpha\beta\gamma\delta}(q, i\Omega) = \frac{1}{\beta} \sum_{k} C^{\lambda_1}_{\beta}(k) C^{\lambda_2}_{\gamma}(k) C^{\lambda_1}_{\delta}(k) \frac{1}{i\omega_n + i\Omega - \varepsilon_{\lambda_1}(k)}
$$

(A.23)

The density-density Coulomb matrix elements belong to situations in which the orbital character at each vertex is the same for the in- and outgoing Green functions. Hence, it is given by

$$
\Pi_{\alpha\beta\alpha\alpha}(q, \omega) = \sum_{k} \sum_{\lambda_1 \lambda_2} M^{\lambda_1 \lambda_2}_{\alpha\beta} \frac{f_{\lambda_1}(k - q) - f_{\lambda_1}(k)}{\omega + i\delta + \varepsilon_{\lambda_2}(k - q) - \varepsilon_{\lambda_1}(k)}
$$

(A.24)
in real frequencies with the matrix elements
\[ M_{\lambda_1 \lambda_2}^{\lambda_3 \lambda_4} = c^{\lambda_2}_{\alpha}(k-q)c^{\lambda_1}_{\beta}(k)c^{\lambda_2}_{\beta}(k-q)c^{\lambda_3}_{\alpha}(k). \] (A.25)

**A.6.2. Coulomb-Interaction Model Parametrization for NbS\textsubscript{2} Monolayers**

In Tab. A.7 we summarize the parameters\textsuperscript{2} to describe the density-density Coulomb-interaction matrix elements of monolayer NbS\textsubscript{2} according to Eqs. (4.11)–(4.13). In principle these values are obtained like described in section A.3.2. However, here we applied the constrained random phase approximation in order to neglect screening effects of the half-filled highest valence band. The intra-band screening effects due to the half-filled band are afterwards properly described within the RPA treatment as described in section 4.5.1.

<table>
<thead>
<tr>
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<th>(d) (Å)</th>
<th>(\epsilon^\infty)</th>
<th>(\gamma) (Å)</th>
</tr>
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<td>5.41</td>
<td>1.27</td>
</tr>
<tr>
<td>(d_x^2)</td>
<td>3.91</td>
<td>10.86</td>
<td>1.89</td>
</tr>
<tr>
<td>(d_{x^2-y^2})</td>
<td>3.96</td>
<td>10.75</td>
<td>1.86</td>
</tr>
<tr>
<td>(d_{xy})</td>
<td>10.25</td>
<td>5.31</td>
<td>1.79</td>
</tr>
<tr>
<td>(d_{xy})</td>
<td>6.23</td>
<td>7.58</td>
<td>1.99</td>
</tr>
<tr>
<td>(d_{x^2-y^2})</td>
<td>10.22</td>
<td>5.32</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table A.7.: Parametrization of the orbitally-resolved screened Coulomb matrix elements for freestanding, unstrained NbS\textsubscript{2} from cRPA \textit{ab initio} calculations.

\textsuperscript{2}These parameters have been derived by Gunnar Schönhoff under my supervision.
A.7. 2D Heterojunctions From Non-Local Manipulations of the Coulomb Interactions

A.7.1. Ab Initio Details

The DFT and $G_0W_0$ Wannier Hamiltonians are obtained as described in section A.3.1. While the band gap at the $K$ point can be easily and reliably extrapolated on the basis of $G_0W_0$ calculations, as discussed in section 4.2.1, this scheme can not be applied to each element $t^{GW}_{\alpha\beta}$ of the resulting Wannier Hamiltonian. Therefore, we calculate the self-energy in Eq. (4.41) based on hopping matrix elements $t^{GW}_{\alpha\beta}$ which are obtained from $G_0W_0$ calculations with an interlayer separation of $55\,\text{Å}$. Hence, no vacuum extrapolations is performed here.

A.7.2. Real-Space Hartree-Fock Approximation

As discussed in section 2.1, the Coulomb interaction gives rise to electron-electron, electron-ion and ion-ion interaction terms: $H_{\text{Coulomb}} = H_{\text{ee}} + H_{\text{ei}} + H_{\text{ii}}$. Here, the ions are assumed to have a fixed positive charge $Ze = +1e$ to ensure charge neutrality of the whole system, i.e. $Z = 2\bar{n}$, where $\bar{n}$ is the average electron occupation per spin and orbital. The ionic positions are assumed to be fixed. Thus, $H_{\text{ii}}$ leads to a constant shift of the total energy, which will be neglected in the following. The remaining Coulomb terms (we use density-density elements only) read [27, 29]

\begin{equation}
H_{\text{ee}} = \frac{1}{2} \sum_{ij\sigma\sigma'} U_{ij} c^{\dagger}_{i\sigma} c_{j\sigma'} c_{j\sigma'} c^{\dagger}_{i\sigma},
\end{equation}

\begin{equation}
H_{\text{ei}} = -\sum_{ij\sigma} U_{ij} \hat{n}_{i\sigma} Z,
\end{equation}

where $U_{ij} = U(r_i, r_j)$ is the interaction energy between electrons or ions at sites $r_i$ and $r_j$, $\sigma$ labels the electron spin, $c^{\dagger}_{i\sigma}$ ($c_{i\sigma}$) are the corresponding electronic creation (annihilation) operators, and $\hat{n}_{i\sigma} = c^{\dagger}_{i\sigma} c_{i\sigma}$ are electron occupation operators. In the Hartree-Fock approximation $H_{\text{ee}}$ becomes

\begin{align}
H_{\text{ee}}^{\text{HF}} &= \sum_{ij\sigma\sigma'} U_{ij} (c^{\dagger}_{i\sigma} c_{j\sigma'} \langle c_{j\sigma'} c^{\dagger}_{i\sigma} c_{j\sigma'} c^{\dagger}_{i\sigma} \rangle - c^{\dagger}_{i\sigma} c_{j\sigma'} \langle c^{\dagger}_{j\sigma'} c_{i\sigma} \rangle) \\
&= \sum_{ij\sigma\sigma'} U_{ij} \langle \hat{n}_{i\sigma} \hat{n}_{j\sigma'} \rangle - c^{\dagger}_{i\sigma} c_{j\sigma'} \langle c^{\dagger}_{j\sigma'} c_{i\sigma} \rangle \\
&= \sum_{ij\sigma} U_{ij} \left( 2\hat{n}_{i\sigma} \langle \hat{n}_{j\sigma} \rangle - c^{\dagger}_{i\sigma} c_{j\sigma} \langle c^{\dagger}_{j\sigma} c_{i\sigma} \rangle \right),
\end{align}

where we used the symmetry $U_{ij} = U_{ji}$ in the second row and assumed a non-magnetic system, i.e. $\langle \hat{n}_{j\sigma} \rangle = \langle \hat{n}_{j\sigma'} \rangle \equiv \langle \hat{n}_{j} \rangle$ and $\langle c^{\dagger}_{j\sigma} c_{i\sigma} \rangle \equiv \delta_{\sigma'\sigma} \langle c^{\dagger}_{j} c_{i} \rangle$, in the third row.
factor of 2 in the Hartree term (first term) accounts for spin-degeneracy. Together with the electron-ion interaction \( H_{ei} = -\sum_{ij\sigma} U_{ij} \hat{n}_{i\sigma} Z \) from Eq. (A.27) and the charge-neutrality condition \( Z = 2\bar{n} \) we arrive at

\[
H_{ee}^{\text{HF}} + H_{ei} = \sum_{ij\sigma} U_{ij} \left( 2\hat{n}_{i\sigma} \langle \hat{n}_{j\sigma} \rangle - \langle \hat{c}^+_i c_j \rangle \right) \\
= \sum_{ij\sigma} U_{ij} \left( 2\hat{n}_{i\sigma} \delta n_{j\sigma} - \langle \hat{c}_i^+ c_j \rangle \right),
\]

where we used the deviation from the average occupation \( \delta n_{j\sigma} = \langle \hat{n}_{j\sigma} \rangle - \bar{n} \). Eq. (A.28) can be also expressed according to

\[
H_{ee}^{\text{HF}} + H_{ei} = \sum_{ij\sigma} \Sigma_{ij} c_j^\dagger c_i 
\]

with the self-energy

\[
\Sigma_{ij} = \delta_{ij} \sum_l 2U_{il} \delta n_l - U_{ij} \langle \hat{c}_j^\dagger c_i \rangle
\]

as given in Eq. (4.44).

The corresponding self-consistent evaluations of \( \Sigma_{ij} \) are performed using non-primitive rectangular unit cells, which involve 4 atoms. All super cells consist of 50 × 30 non-primitive unit cells with periodic boundary conditions in the \( y \)-direction and fixed boundaries in the \( x \)-direction. In the case of the heterostructures, the plane, which separates the different dielectric areas from each other, is chosen to be parallel to the \( y \)-axis and is placed between the 25th and 26th unit cells on the \( x \)-axis.

### A.7.3. Screening Model

As described in section 4.6.2, in general the Poisson equation has to be solved numerically to obtain the screened Coulomb interaction within the two-dimensional layer. Nevertheless, there are situations in which the resulting problem can be solved analytically, for instance, in the case of two half spaces with different dielectric constants \( \varepsilon_1 \) and \( \varepsilon_2 \) and zero film thickness. In this situation, the screened Coulomb potential can be obtained analytically using the method of image charges (see for instance Ref. [89]).

Therefore, the electrostatic potential \( \phi_{r_i}(r_i) = U_{ij}/e \) at position \( r_i \) resulting from a source electron with charge \( q_j \) at \( r_j \) is calculated as a superposition of the potential of the source charge \( q_j \) and its corresponding image charge \( q_m \). If \( r_i \) and \( r_j \) are in the same subspace, the image charge \( q_m \) is placed at \( r_m \), which is the mirrored position of \( r_j \) with respect to the plane separating the dielectrics yielding the total potential

\[
\phi_{r_i}(r_i) = \frac{q_j}{\sqrt{|r_i - r_j|^2 + \delta^2}} + \frac{q_m}{\sqrt{|r_i - r_m|^2 + \delta^2}}.
\]
A. Model Parameters and Calculations Details

Otherwise, the image charge $q'_m$ is positioned at $r_j$ and the total potential is given by

$$\phi_{r_j}(r_i) = \frac{q'_m}{\sqrt{|r_i - r_j|^2 + \delta^2}}. \quad (A.33)$$

Using the continuity conditions (assuming for simplicity that the separating interfaces is located at $x = 0$ and infinitely extends in $y$- and $z$-direction)

$$\lim_{x \to 0^+} \varepsilon_1 E_x = \lim_{x \to 0^-} \varepsilon_2 E_x, \quad E_y = E_y \quad \text{and} \quad E_z = E_z \quad (A.34)$$

we can define the mirror charges $q_m$ and $q'_m$

$$q_m = \pm \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} q_j \quad \text{and} \quad q'_m = \frac{2}{\varepsilon_1 + \varepsilon_2} q_j \quad (A.35)$$

which finally yields the potential:

$$U_{ij} = \begin{cases} \frac{1}{\varepsilon_1} \left( v_{ij} + \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} v_{im} \right) & i, j \in R_{\varepsilon_1} \\ \frac{1}{\varepsilon_2} \left( v_{ij} + \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2} v_{im} \right) & i, j \in R_{\varepsilon_2} \\ \frac{2}{\varepsilon_1 + \varepsilon_2} v_{ij} & \text{otherwise.} \end{cases} \quad (A.36)$$

Here, $R_{\varepsilon_1}$ ($R_{\varepsilon_2}$) is the set of lattice vectors in the area with the dielectric constant $\varepsilon_1$ ($\varepsilon_2$). $v_{ij}$ is an unscreened (bare) Coulomb potential of the form

$$v_{ij} = \frac{e^2}{\sqrt{|r_i - r_j|^2 + \delta^2}}, \quad (A.37)$$

with $e$ being the elementary charge and $\delta$ accounting for the finite spread of the electronic orbitals [375].

If $\varepsilon_1 = \varepsilon_2 = \varepsilon$, we end up with a homogeneous environment and the Coulomb interaction reduces to

$$U_{ij} = \frac{1}{\varepsilon} v_{ij}. \quad (A.38)$$

In order to implement a situation that is similar to MoS$_2$, we set $\delta = 1.5$ Å which leads to a bare on-site potential $U_{ii} \approx 9.6$ eV (i.e. for $\varepsilon = 1$) and (roughly) corresponds to a bare density-density matrix element of the Coulomb interaction for the $d_{z^2}$ orbitals of MoS$_2$ (see Tab. A.5).
A.7. Hartree-Fock self-energy contributions to the density of states in an homogeneous dielectric environment. (a) Influence of the Hartree and full Fock terms. (b) Local and non-local contributions of the Fock term.

A.7.4. Hartree and Fock Contributions to the Band Gap

In Fig. A.7 we show the electronic density of states obtained by including different parts of the self-energy using the generic model within a homogeneous dielectric environment ($\varepsilon = 5$) for a $50 \times 30$ super cell. Fig. A.7 (a) shows the evolution of the band gap by subsequent inclusion of the Hartree ($\Sigma_H$) and Fock ($\Sigma_F$) terms. The local Hartree contribution to the tight-binding gap is negligible, while the Fock terms cause a drastic increase. In more detail, we see in Fig. A.7 (b) that this increase is due to the non-local Fock contribution only, while the local Fock terms just broaden the bands. Thus, the drastic increase of the band gap within the Hartree-Fock treatment of the model results from a modified hybridization due to non-local interactions as it has been observed in the \textit{ab initio} data as well.
Bibliography


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Own Publications

Most parts of the results presented in chapter 3 and chapter 4 have already been published. The corresponding article titles are underlined.

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11. *Strain in Epitaxial Graphene Visualized by Intercalation*
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**Under review**

1. *Interplay of screening and superconductivity in low-dimensional materials*
   G. Schönhoff, M. Rösner, R. E. Groenewald, S. Haas, and T. O. Wehling

2. *Nonequilibrium Carrier Dynamics in Transition Metal Dichalcogenide Semiconductors*
   A. Steinhoff, M. Florian, M. Rösner, M. Lorke, T. O. Wehling, C. Gies, F. Jahnke
Conference Contributions

1. Talk: *Electronic excitations in transition metal dichalcogenides under the influence of dielectric environments*
   M. Rösner, R. Groenewald, G. Schönhoff, S. Haas T. O. Wehling  
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2. Talk: *Description and Tuning of Many-Body Effects*
   M. Rösner, C. Steinke, G. Schönhoff, A. Schulz, T. O. Wehling  
   Workshop of the WP3 of the “Graphene Flagship” program, Zürich (2016)

3. Talk: *Many-body and disorder effects: The role of fluorination and dielectric substrates*
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4. Poster: *From optics to superconductivity: Many body effects in transition metal dichalcogenides*
   M. Rösner, A. Steinhoff, G. Schönhoff, E. Şaşıoğlu, C. Friedrich, S. Blügel, F. Jahnke, C. Gies, T. O. Wehling  

5. Talk: *Presentation of the WP3 (University of Bremen) Progress*
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6. Talk: *From Three to two Dimensions: The Effect on the Coulomb Interaction*
   M. Rösner, E. Şaşıoğlu, C. Friedrich, S. Blügel, A. Lichtenstein, M. I. Katsnelson, T. O. Wehling  
   DPG-Frühjahrstagung, Dresden (2014)

7. Poster: *Generalized Hubbard models for two dimensional hybrid materials*
   M. Rösner, E. Şaşıoğlu, C. Friedrich, S. Blügel, A. Lichtenstein, M. I. Katsnelson, T. O. Wehling  

8. Talk: *Generalized Hubbard models for two dimensional hybrid materials*
   M. Rösner, E. Şaşıoğlu, C. Friedrich, S. Blügel, A. Lichtenstein, M. I. Katsnelson, T. O. Wehling  
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