



universität
wien

MASTERARBEIT / MASTER'S THESIS

Titel der Masterarbeit / Title of the Master's Thesis

Radiative Lifetimes of Anisotropic 2D Excitons: A Method Development Applied to ReS₂

verfasst von / submitted by

Richard Bogad, BSc

angestrebter akademischer Grad / in partial fulfilment of the requirements for the degree of

Master of Science (MSc)

Wien, 2018 / Vienna, 2018

Studienkennzahl lt. Studienblatt /
degree programme code as it appears on
the student record sheet:

A 066 876

Studienrichtung lt. Studienblatt /
degree programme as it appears on
the student record sheet:

Physik / Physics

Betreut von / Supervisor:

Assoz. Prof. Dipl.-Ing. Dr. Kerstin Hummer

Acknowledgement

I owe the most profound gratitude to Prof. Kerstin Hummer: for her knowledge, for her time, and for guiding me at every stage of my work. Without her patience and her fast answers to my questions, it would have been impossible to finish this thesis. She encouraged me during difficult times and laboriously corrected my mistakes; this has shown me the proper path to a more educated form of self-criticism. She is an exemplary supervisor.

I would also like to thank: Prof. Georg Kresse for fulfilling my desire to write this thesis in his department; Michael Pörtl for making it possible for me to work from home; and Dr. Menno Bokdam for helping out with a VASP technique that is essential for this thesis.

Of course, my most grateful thanks to my dear family for the ongoing support and for belief—especially during the recent rough years.

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Abbreviations

ch.	chapter
dev.	deviation
eq.	equation
exp.	experimental
fig.	figure
func.	function
imag.	imaginary
lst.	listing
p.	page
ref.	reference
sec.	section
supp.	supplementary paper
tab.	table

Acronymes

BG	band gap 1, 2, 12, 13, 50, 54, 57, 59, 61, 72, 73, 74, 83, 84
BS	band structure 7, 12, 13, 35, 46, 52, 57, 59, 65, 71, 72, 73, 76, 78, 83, 84, 85
BSE	Bethe-Salpeter equation 18, 19, 20, 21, 22, 25, 35, 37, 39, 44, 49, 51, 52, 54, 59, 61, 63, 68, 72, 73, 74, 76, 83, 84, 85
BZ	Brillouin zone 12, 46, 47, 50, 52, 65, 76, 78

DFT	density functional theory 11, 14, 39, 40, 49, 59, 65, 71, 72, 73, 83, 84
HK	Hohenberg-Kohn 11
KS	Kohn-Sham 11, 12, 13, 18, 20, 22, 50
LDA	local density approximation 13, 14
ML	monolayer 1, 2, 40, 44, 46, 47, 49, 50, 52, 53, 57, 59, 61, 63, 70, 71, 72, 74, 75, 76, 78, 79, 80, 83, 84, 85
QP	quasi-particle 18, 20, 22, 23, 50, 51, 59, 61, 73, 74, 83, 84
SE	Schrödinger equation 8, 12
SSP	solid-state physics 7
TMD	transition metal dichalcogenide 1, 7, 13, 18, 25, 39, 44, 46
VASP	Vienna ab initio simulation package ix, 2, 3, 18, 35, 36, 37, 39, 40, 41, 44, 49, 50, 51, 52, 53, 63, 74, 83, 84, 88, 89, 111
WF	Wannier function 12

Notation

$A^\dagger = \bar{A}^T$	conjugate transpose
δ	Kronecker delta, delta distribution
$\hat{O}$	operator
$\hat{x}, \hat{y}, \hat{z}, \hat{q}$	unit vector
$\vec{r}$	vector

Introduction

Atomically thin structures can now be easily produced by using exfoliation methods. The most well-known representative of these two-dimensional monolayer (ML) materials is graphene. Graphene has a high electron mobility, which makes it suitable for high-speed electronic devices operating at room temperature [Net+09]. However, the lack of a band gap (BG) makes graphene useless for digital applications where semiconductors, such as transistors, are needed.

The search for semiconducting 2D materials has led to transition metal dichalcogenides (TMDs) materials, which are easily exfoliated. Molybdenum disulfide (MoS_2), for instance, has a BG; it can, therefore, be used as a transistor for electrical circuits. Since its relatively recent invention, the MoS_2 transistor has already shown features that can compete with commercially established transistors. In contrast to its multi-layer version, the ML MoS_2 structure exhibits a direct BG. This property enables many optical use cases. A combination of high-speed graphene and the digital, semiconducting properties of MoS_2 might help in conceptualizing new forms of flash memory devices. An excellent overview of the possible fields of application has been given in ref. [Lem+15].

Electronic currents or photons with energies in the order of the BG magnitude and higher may cause the formation of electron-hole pairs that have characteristics similar to hydrogen atoms. These "excitons" play a prominent role in the light emission properties of semiconductors. At the end of an exciton lifespan, the recombination process may be radiative through the emission of a photon. More complex radiative mechanisms exist but are not considered in this thesis. Dependent on the recombination time (lifetime), the radiative characteristics of a material may be brighter or darker. Non-radiative recombinations are, for example, caused by lattice defects or by exciton-exciton scattering effects. The formation of different exciton types (states), each with different lifetimes, reveals a complex temperature-dependent interplay between several mechanisms. Furthermore, excitons may annihilate each other, or be trapped in crystal defects. These mechanisms are summarized in ref. [Moo+16].

The recombination process of excitonic states is greatly influenced by impurities, surface effects, and many other factors; and this leads to problematic interpretations of experimental results. In contrast, computational methods are able to simulate perfect crystal structures, and this makes it possible to compute the dynamics of

pure excitonic states. Such results can be useful for interpreting experimental results or for finding new compounds of interest without the need for costly experiments. These results may also promote fundamental research on exciton dynamics.

The computational methods that can compute exciton radiative lifetimes are the subject of the current research. Fundamental computational concepts and methods have been compiled in the book "Many-Body Approach to Electronic Excitations" [Bec15]. The first investigation for calculating exciton radiative lifetimes was limited to 1D structures-carbon nanotubes in particular [Cap+07]. In another recent work, certain formulas were derived that can describe radiative lifetimes for isotropic ML structures [Pal+15, supp.]. This approach was successfully applied to molybdenum and tungsten dichalcogenides, and this method is in accordance with experimental results in ref. [Pal+15].

Isotropic compounds are, of course, a small portion of all possible ML compounds. Anisotropic structures have varying properties for different spatial directions, thereby adding a degree of freedom in designing new devices. The ability to calculate excitonic radiative lifetimes for anisotropic structures would lead to a significant increase in computational possibilities and applications. One particular anisotropic ML compound of current interest is rhenium disulfide (ReS_2), for which several experiments have revealed anisotropic optical and electronic transport features [Cui+15; Rah+17]. The structure of ReS_2 is stable at room temperature and shows direct BG properties in both the ML and the few-layer version. These properties eliminate the necessity to fabricate specific ML structures and, thus, lower the production costs. The initial attempts at measuring the excitonic lifetimes of ReS_2 ML resulted in exceedingly low values [Cui+15]. This is suggestive of non-radiative channels that dominate the decay process; however, little is known about these dynamic properties.

On the basis of the current state of research, the objectives of this thesis can be summarized as follows:

- To construct of a ML rhenium disulfide structure and to examine of its anisotropic optical characteristics by using VASP.
- To derive equations that can calculate radiative lifetimes for anisotropic structures.
- To develop a VASP extension that enables the calculation of excitonic radiative lifetimes.
- To apply this VASP implementation to molybdenum dichalcogenides and to interrogate whether the radiative lifetime results of ref. [Pal+15] can be reproduced.

- To calculate radiative lifetimes for the anisotropic case of ML rhenium disulfide and to gain deeper insights into its exciton dynamics.

With regard to the organization of this thesis, the first part summarizes the theoretical foundations necessary for the aims of this work. In particular, Chapter 2 focuses on the theoretical principles underlying the computational methods of this thesis. Chapter 3 covers the derivation of formulas that can describe radiative lifetimes of anisotropic structures. The second part comprises the application of the developed methods to 2D materials. Subsequently, Chapter 4 describes the steps needed for expanding the functionality of VASP to evaluate radiative lifetimes in anisotropic structures. Chapter 5 covers the computational details that are required to reproduce the results of this thesis. Chapter 6 presents all data along with a discussion on the key points that have been addressed in the thesis.

Part I

Theoretical Foundations

2.1 Introduction

At ambient conditions, TMDs exist in the crystallized phase—that is, as periodic structures. Periodic structure properties like lattice constants, band structures (BSs), absorption spectra, and exciton lifetimes are of central importance to this thesis. Modern methods of computational physics provide powerful tools that enable the accurate calculation of these properties. All of these methods are based on the basic principles of solid-state physics. The computation of optical properties and excitonic lifetimes relies on the "macroscopic dielectric function" (eq. 2.28). Therefore, this chapter mainly discusses the ground-up derivation of this central quantity. The following theory is based on the monograph "Many-Body Approach to Electronic Excitations" [Bec15].

2.2 Quantum Mechanical Solution to Periodic Systems

2.2.1 Periodic Structures

To apply modern computational methods to a crystal structure, it is necessary to describe these structures through the principles of solid-state physics (SSP)s. A set of elemental basis atoms can be duplicated on **periodic lattice** points to result in the whole crystal structure. In TMDs this lattice is usually built up by using three primitive lattice vectors $\vec{u}$, $\vec{v}$ and $\vec{w}$. The lattice grid is then every possible point $\{\vec{R}_n\}$ with $\vec{R}_n = \vec{R}_{n_1, n_2, n_3} = n_1\vec{u} + n_2\vec{v} + n_3\vec{w}$, where $n, n_i \in \mathbb{Z}$. The smallest unit cell contains one lattice point and can always be constructed. Furthermore, it spans the entire space without leaving any holes. The unit cell volume is given by $V = \vec{u} \cdot (\vec{v} \times \vec{w})$. Each basis atom l has a relative position of $\vec{r}_l$ with respect to every grid point. The position of every atom can then be expressed by $\vec{R}_{n,l} = \vec{R}_n + \vec{r}_l$ [Bec15, sec. 1.3].

To deal with the periodicity of the crystal lattice, the **reciprocal lattice** vectors $\vec{u}^*, \vec{v}^*, \vec{w}^*$ are introduced. For any lattice vector $\vec{a} \in \{\vec{u}, \vec{v}, \vec{w}\}$, and any reciprocal lattice vector $\vec{b} \in \{\vec{u}^*, \vec{v}^*, \vec{w}^*\}$, the relation $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$ holds. Just like the lattice in real space, the reciprocal lattice consists of every point $\{\vec{G}_n\}$ with $\vec{G}_n = \vec{G}_{n_1, n_2, n_3} =$

$n_1 \vec{u}^* + n_2 \vec{v}^* + n_3 \vec{w}^*$, where $n, n_i \in \mathbb{Z}$. A primitive unit cell of the reciprocal lattice is called Brillouin zone. Its volume is given by $V_{BZ} = \vec{u}^* \cdot (\vec{v}^* \times \vec{w}^*) = (2\pi)^3 V^{-1}$. Each wavevector $\vec{k}$ of a plane wave ψ that fulfills $\vec{k} = \vec{G}$ reflects the periodicity of the lattice $\psi_{\vec{k}}(\vec{R}) = e^{i\vec{k} \cdot \vec{R}} = e^{i\vec{G} \cdot \vec{R}} = 1$ [Bec15, sec. 1.3].

2.2.2 The Schrödinger Equation for Periodic Electronic Structures

N_n atomic nuclei l at positions $\vec{R}_l$ with mass M_l and charge $Z_l \cdot e$ are now considered. Nuclei spins are ignored. Furthermore there are N electrons i at position x_i charge $-e$ mass m_e and spin $\vec{s}_i = \frac{\hbar}{2} \vec{\sigma}$. Movement is represented by momentum operators $\hat{P}_l$ and $\hat{p}_i$. There is no external perturbation; therefore an explicit dependence on time is omitted in the following.

A charge e at position $\vec{0}$ creates a **coulomb potential** $v(\vec{x})$ at position $\vec{x}$:

$$v(\vec{x}) = \frac{e^2}{4\pi\epsilon_o |\vec{x}|}.$$

The **Hamiltonian of the whole system** $\hat{H}_{\text{sys}}$ can be constructed by taking into account the coulomb potentials of all particles. Without relativistic effects it holds

$$\begin{aligned} \hat{H}_{\text{sys}} = & \frac{1}{2} \sum_{l=1}^{N_n} \frac{1}{M_l} \hat{P}_l^2 + \frac{1}{2} \sum_{i=1}^N \frac{1}{m_e} \hat{p}_i^2 + \frac{1}{2} \sum_{l,l'=1}^{N_n} \quad (l \neq l') \quad Z_l Z_{l'} v(\vec{R}_l - \vec{R}_{l'}) \\ & - \frac{1}{2} \sum_{l=1}^{N_n} \sum_{i=1}^N Z_l v(\vec{x}_i - \vec{R}_l) + \hat{H}_{\text{ee}}. \end{aligned} \quad (2.1)$$

The first two terms represent the kinetic contribution to the system, the third term denotes the nucleus-nucleus interaction, the fourth term the electron-nucleus interaction, and the last expression handles the electron-electron interaction. The time-independent Hamiltonian obeys a stationary Schrödinger equation (SE)

$$\hat{H}_{\text{sys}} \Psi(\vec{x}_1 s_1, \dots, \vec{x}_N s_N) = E_{\Psi} \Psi(\vec{x}_1 s_1, \dots, \vec{x}_N s_N), \quad (2.2)$$

with energy eigenvalues E_{Ψ} and normalized orthogonal N-particle eigenstates $|\Psi\rangle$ defined on a Fock space. Until now, it is impossible to solve the SE with this many-body hamiltonian for extended systems [Bec15, sec. 1.1].

Approximations are made to simplify the problem, and to make a numerical solution for solid-state systems feasible. In the **Born and Oppenheimer approximation** the nuclei motion is decoupled from the electron motion. Atomic nuclei are much more massive compared to electrons. Therefore, electrons can react to changes in nuclei position almost instantaneously. Thus the nuclei can be treated as if an average electronic potential influences them. Once decoupled, it is possible to calculate the system's electronic state as a function of the nuclei positions [Bec15, sec. 1.2].

To this point, only non-relativistic processes have been discussed. The Dirac equation is used for including relativistic effects. This approach exhibits several types of relativistic contributions in addition to the non-relativistic Coulomb interaction for the **electron-electron interaction**. These contributions influence the macroscopic properties of a solid and are therefore taken into account. Further, electrons interact with their own electromagnetic field, requiring a self-consistent solution algorithm. The resulting electron-electron interaction Hamiltonian $\hat{H}_{ee}$ can be split up into different parts:

$$\hat{H}_{ee} = \frac{1}{2} \sum_{i,i'=1}^N (i \neq i') v(\vec{x}_i - \vec{x}_{i'}) + \hat{H}_{sr} + \hat{H}_{so} + \hat{H}_B. \quad (2.3)$$

In eq. 2.3 the electron-electron interaction Hamiltonian consists of the non-relativistic longitudinal electron-electron Coulomb interaction represented by the first term. The second term $\hat{H}_{sr}$ describes the scalar-relativistic Hamiltonian, containing relativistic corrections to the kinetic and potential energies. These corrections can be precalculated by using pseudopotentials, which is of large importance to the computational solution procedure. The third quantity $\hat{H}_{so}$, which describes the interaction between electron spin and orbital momentum, represents the spin-orbit interaction. The last contribution to $\hat{H}_{ee}$ is the Breit interaction Hamiltonian $\hat{H}_B$, which describes the energy of the electron magnetic moments in their own field. It can be shown that for total energy calculations spin-orbit and Breit contributions only have to be taken into account if the material exhibits a specific magnetic ordering, or in the presence of an external magnetic field. The spin-orbit and Breit terms depend on the spin of the electrons and can be calculated with costly non-collinear calculations. In the absence of a magnetic ordering and external magnetic fields, it is sufficient to assume that electron spins are **collinear**, i.e., aligned to the same axis vector, whose specific direction does not influence the result [Bec15, ch. 2].

To gain the **total energy** eigenvalues of a system, the expectation value $E_\Psi = \langle \Psi | \hat{H}_{sys} | \Psi \rangle$ has to be evaluated. This energy can be divided into four different contributions

$$E_\Psi = E_{kin}^\Psi + E_{pot}^\Psi + E_H^\Psi + E_{XC}^\Psi. \quad (2.4)$$

These quantities can be generalized to describe the spin dependence, which is omitted for the sake of clarity.

The terms in eq. 2.4 can be expressed in **second quantization** through the electron creation operator $\hat{\psi}_s^+(\vec{x})$ and the electron annihilation operator $\hat{\psi}_s(\vec{x})$, which create or annihilate an electron with spin s at position $\vec{x}$ [Bec15, sec. 3.1, 3.2].

Similarly the **electron density** n at position $\vec{x}$ can be written in terms of the operators $\hat{\psi}_s^+(\vec{x})$ and $\hat{\psi}_s(\vec{x})$

$$n_\Psi(\vec{x}) = \langle \Psi | \hat{n}(\vec{x}) | \Psi \rangle = \langle \Psi | \sum_s \hat{\psi}_s^+(\vec{x}) \hat{\psi}_s(\vec{x}) | \Psi \rangle ,$$

leading to the conclusion that all quantities in eq. 2.4 can be written in terms of the electron density as follows.

The kinetic energy of the system E_{kin} is

$$E_{\text{kin}}^\Psi = -\frac{\hbar^2}{2m} \int d^3\vec{x} [\Delta_{\vec{x}} n_\Psi(\vec{x}, \vec{x}')]_{\vec{x}' = \vec{x}} , \quad (2.5)$$

with the spin-summed one-particle density matrix $n_\Psi(\vec{x}, \vec{x}') = \langle \Psi | \sum_s \Psi_s^+(\vec{x}) \Psi_s(\vec{x}') | \Psi \rangle$. The potential energy E_{pot} , caused by the total nuclei potential V_n , is

$$E_{\text{pot}}^\Psi = \int d^3\vec{x} V_n(\vec{x}) n_\Psi(\vec{x}) , \quad (2.6)$$

as well as the Hartree energy E_{H} , which describes the classical interaction energy between uncorrelated electrons

$$E_{\text{H}}^\Psi = \frac{1}{2} \int d^3\vec{x} \int d^3\vec{x}' v(\vec{x} - \vec{x}') n_\Psi(\vec{x}') n_\Psi(\vec{x}) , \quad (2.7)$$

and finally the exchange and correlation energy E_{XC} , containing all non-classical electron-electron interactions

$$E_{\text{XC}}^\Psi = \frac{1}{2} \int d^3\vec{x} \int d^3\vec{x}' v(\vec{x} - \vec{x}') n_\Psi(\vec{x}') n_\Psi(\vec{x}) [g_\Psi(\vec{x}, \vec{x}') - 1] . \quad (2.8)$$

In the limit of uncorrelated electrons, the term 2.8 vanishes, therefore $g \rightarrow 1 \Rightarrow E_{\text{XC}}^\Psi = 0$. The exchange energy takes negative values, hence, stabilizing the system from the classical repulsion.

The quantity g is the **pair correlation function**

$$g_\Psi(\vec{x}, \vec{x}') = \frac{n_\Psi(\vec{x}, \vec{x}')}{n_\Psi(\vec{x}) n_\Psi(\vec{x}')} ,$$

with the spin-summed two-particle density matrix

$n_\Psi(\vec{x}, \vec{x}') = \langle \Psi | \sum_{s,s'} \Psi_{s'}^+(\vec{x}') \Psi_s^+(\vec{x}) \psi_s(\vec{x}) \psi_{s'}(\vec{x}') | \Psi \rangle$. The pair correlation function can be interpreted as the probability of finding an electron at position $\vec{x}$ given that there is a second one at position $\vec{x}'$. For uncorrelated electrons, this expression has a value of 1, while it is vanishing for two electrons with the same position (and spin) [Bec15, sec. 3.3].

2.3 Density Functional Theory

2.3.1 Hohenberg-Kohn Theory

Finding the systems' eigenstate $\Psi_0(\vec{x}_1 s_1, \dots, \vec{x}_N s_N)$ with the lowest total energy E^{Ψ_0} is of primary interest. The primary computational challenge is to compute the correlation energy in eq. 2.8, which mostly affects electrons of opposite spin. Despite all approximations, the state Ψ_0 still depends on $3N$ position variables, and even more variables for the electron spins and, thus, is infeasible to solve.

A different concept to the quantum mechanical solution is the **density functional theory (DFT)**, which allows the computation of useful results at lower computational effort. **Hohenberg-Kohn (HK)** showed that for each potential V_{ext} and or nuclei potential V_n there is a surjective map to the ground state $|\Psi_0\rangle$, which implies the existence of a surjective map for an associated electron density n . This insight results in the first HK-theorem, which is the foundation of DFT.

Theorem 1 (Hohenberg-Kohn 1) *The total energy $E = E_{V_{\text{ext}}}(n)$ in the ground state is a universal functional of the corresponding density $n(\vec{x})$.*

The second HK-theorem shows how this ground state density can be calculated in a variational way.

Theorem 2 (Hohenberg-Kohn 2) *For a non-degenerate ground state $|\Psi_0\rangle$ and a given external potential $V_{\text{ext}}(n)$ the energy functional $E_{V_{\text{ext}}}(n)$ assumes its global minimum value E_0 varying the density $n(\vec{x})$ toward the true ground-state density $n_0(\vec{x})$.*

The HK theorems can also be generalized to include spin-dependent quantities. The central statement of the generalized HK theorem 1 is that the ground-state expectation value of any physical observable is a unique functional of the ground-state density $\langle \Psi_0(n) | \hat{O} | \Psi_0(n) \rangle = O(n)$. Therefore the complicated eigenvalue problem (eq. 2.2) with $\geq 3N$ variables may be reduced to a density that depends on only three space coordinates. However, HK do not provide an algorithm on how to do so. [Bec15, sec. 5.2]

2.3.2 Kohn-Sham Scheme

Kohn-Sham (KS) stated that the many-body problem of interacting electrons in a potential of nuclei may be projected onto a gas of non-interacting electrons. The potential acting on the gas may be altered to result in the same electron density as for the system of interacting electrons. The total energy of this system (eq. 2.4) may be written as

$$E(n) = E_{\text{kin}}^S(n) + E_{\text{pot}}(n) + E_{\text{H}}(n) + E_{\text{XC}}(n). \quad (2.9)$$

$E_{\text{kin}}^S(n)$ is the kinetic energy of independent particles, which is calculated by variation with respect to the density. It's important to keep in mind that this expression is just an approximation for the kinetic energy of interacting particles (eq. 2.5). $E_{\text{pot}}(n)$ and $E_{\text{H}}(n)$ can be calculated through eq. 2.6 and 2.7. The exchange-correlation energy will be discussed in the next section.

Further it is possible to assign potentials to the energy (eigen)value contributions in eq. 2.9:

$$V_{\text{KS}}^{m_s}(\vec{x}) = V_n(\vec{x}) + V_{\text{H}}(\vec{x}) + V_{\text{XC}}^{m_s}(\vec{x}).$$

Thus the KS approach can be seen as an eigenvalue problem to the KS Hamilton operator $\hat{H}_{\text{KS}}^{m_s}$, with separate potentials for each possible electron spin m_s :

$$\hat{H}_{\text{KS}}^{m_s} = -\frac{\hbar^2}{2m}\Delta_{\vec{x}} + V_{\text{KS}}^{m_s}(\vec{x}). \quad (2.10)$$

By introducing KS orbitals $\phi_{\lambda m_s}$, which are single-particle wave functions, it is possible to reformulate the many body SE as a set of single-particle SEs. These eigenvalue equations in an effective orbital independent potential $V_{\text{KS}}^{m_s}$ (eq. 2.10) are called **KS equations**

$$\hat{H}_{\text{KS}}^{m_s} \phi_{\lambda m_s}(\vec{x}) = \epsilon_{\lambda m_s} \phi_{\lambda m_s}(\vec{x}), \quad (2.11)$$

where $\phi_{\lambda m_s}(\vec{x})$ are KS eigenorbitals to corresponding eigenvalues ϵ with quantum numbers λm_s [Bec15, ch. 6].

The SE of a periodic potential can be transformed to reciprocal space, where a set of possible wave vectors $\vec{k}$ with solutions $\psi_{\vec{k}}$ and eigenvalues $E_{\vec{k}}$ exists. A basis set of those solutions are called **Bloch waves** $\psi_{\vec{k}}$ with periodic functions $u_{\vec{k}}$:

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}, \quad u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R}).$$

Another basis set for periodic wave functions are **Wannier functions (WFs)** w :

$$\psi(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} w(\vec{r} - \vec{R}), \quad w(\vec{r} - \vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}-\vec{R})} u_{\vec{k}}(\vec{r}). \quad (2.12)$$

Bloch waves are based on plane waves, while WF's use localized wave functions. Often orbital shaped WF's are used to describe crystal states.

For every possible vector $\vec{k}$, there are multiple identical energy solutions $E_n(\vec{k}) = E_n(\vec{k} + \vec{G})$. Due to this fact, the vector $\vec{k}$ is usually restricted to the first Brillouin zone (BZ), where $\vec{G} = 0$. N unit cells result in N possible $\vec{k}$ vectors within the first BZ. Unidentical solutions are enumerated with an index n , which is called band indices. This index is usually ordered in ascending order with respect to energy. All together $E_n(\vec{k})$ is called **BS** or dispersion relation. Dependent on the number, location, and interaction between basis atoms, the BS may differ greatly for various

materials. In the ground state, i.e., at zero temperature, N electrons occupy the lowest N states in the BS. In semiconductors and insulators, there is an energy gap between the highest occupied band and lowest un-occupied band, called BG [GM12, sec. 8.1].

In translationally invariant systems, which is the case for perfect TMDs, **KS eigenfunctions of the Bloch type** $\phi_{n\vec{k}m_s}(\vec{x})$ can be chosen. n now represents the band index, $\vec{k}$ the Bloch wave vector, and m_s the spin channel.

The KS equations are solved iteratively. Its energy eigenvalues have no physical meaning, except for the highest occupied one. This energy can be identified with the negative electron ionization energy. By associating the lowest unoccupied eigenvalue with the electron affinity, the size of the BG is found to be underestimated when compared to experimental results. The reason for this discrepancy can be attributed to the fact that the KS eigenvalues are quantities of the noninteracting reference system. Surprisingly the shape of BS is for many cases close to the experimental findings.

2.3.3 DFT Functionals

Until now details of the exchange-correlation term $E_{\text{XC}}(n)$ in eq. 2.9 have not been discussed. The reason for this is that it is still unknown how to precisely compute this quantity. However, there are many different approaches to calculate an approximation for it.

The very basic approximation for this energy can be understood by formulating a Hamiltonian $\hat{H}_0^\lambda$, where the electron-electron interaction U can be increased gradually with a parameter $\lambda \in [0, 1]$:

$$\hat{H}_0^\lambda = \hat{T} + \hat{V}^\lambda + \lambda \hat{U}.$$

The potential V is replaced by $\hat{V}^\lambda$ to guarantee the same ground state density n for all λ . The exchange-correlation energy can be described by

$$E_{\text{XC}}(n) = \int d^3\vec{x} n(\vec{x}) \epsilon_{\text{XC}}(\vec{x}, n), \quad (2.13)$$

with ϵ_{XC} being the per electron exchange-correlation energy at position $\vec{x}$. After several rearrangements of this formula, it can be shown that the exchange-correlation energy is

$$E_{\text{XC}}(n) = \frac{1}{2} \int d^3\vec{x} \int d^3\vec{x}' v(\vec{x} - \vec{x}') n(\vec{x}) n(\vec{x}') \underbrace{\left(\int_0^1 d\lambda g^\lambda(\vec{x}, \vec{x}', n) - 1 \right)}_{\bar{n}_{\text{XC}}}, \quad (2.14)$$

where g^λ is the pair correlation function, under the influence of the interaction operator $\lambda \hat{U}$. $\bar{n}_{\text{XC}}(\vec{x}, \vec{x}', n)$ is the exchange-correlation hole density, averaged over all

$\lambda \in [0, 1]$. The hole density describes the fact that an electron at position $\vec{x}$ reduces the probability of finding another at position x' . Thus eq. 2.14 can be interpreted as an interaction between electrons and their exchange-correlation holes. This quantity can be approximated by using the energy of a homogeneous electron gas $\epsilon_{\text{XC}}^{\text{hom}}(\vec{x}, n)$ and adding spatial variations to the electron density. This procedure is called **local density approximation (LDA)**.

The DFT+LDA method is able to calculate ground state properties of a system (like the total energy or lattice constants) quite accurately, as long as there are only minor variations in the electron density. In conclusion, the electrons of a structure must not be too localized, which is generally the case for metals. As a consequence, DFT+LDA is not able to provide useful results for surface properties and effects where localized electrons are essential, like in chemical bonding.

The LDA method can be seen as using a zeroth order gradient expansion of the electron density, i.e., the exchange-correlation energy (eq. 2.13) depends on the electron density n only. For improving the accuracy of DFT calculations, one is tempted to include higher order gradients of the density, leading to **Generalized Gradient Approximations** with an exchange-correlation energy term of the form

$$E_{\text{XC}}(n) = \int d^3\vec{x} n(\vec{x}) \epsilon_{\text{XC}}(n, |\nabla n|) .$$

Other established functionals for calculating the XC energy are PBEsol or meta-GGA which will not be discussed any further in this thesis. Many other functionals and methods exist, and they all differ in computational efficiency and accuracy. Each one of them has their very own strengths and impairments. For example, it is not possible to calculate total energy and bond length with the same accuracy by using GGA [Bec15, ch. 7].

2.4 Optical Properties

2.4.1 GW Calculations

A system in its ground state has no excited particles. However, the examination of optical properties requires to describe the interaction between electrons and photons yielding excited particles. To achieve this, the motion, i.e., the time evolution of the particles, has to be considered. This can be achieved by extending the field operators with the **time evolution** operator U_0 , leading to $\psi_s^+(\vec{x}, t) = U_0^+(t) \psi_s^+(\vec{x}) U_0(t)$ and $\psi_s(\vec{x}, t) = U_0^+(t) \psi_s(\vec{x}) U_0(t)$. A time-independent Hamilton operator (like eq. 2.1) now depends on time $H_0(t)$, because every operator can be expressed through field operators [Bec15, ch. 10].

Important correlation functions can be built with these field operators. The hole propagator $G_{ss'}^<$ describes an annihilation of an electron at position $\vec{x}$ and spin s resulting into an hole that propagates to position $\vec{x}'$ and spin s' :

$$G_{ss'}^<(\vec{x}, t, \vec{x}', t') = -\frac{1}{i\hbar} \langle \psi_{s'}^+(\vec{x}', t') \psi_s(\vec{x}, t) \rangle.$$

The electron propagator $G_{ss'}^>$ describes an injection of an electron at position $\vec{x}'$ and spin s' that propagates to position $\vec{x}$ and spin s :

$$G_{ss'}^>(\vec{x}, t, \vec{x}', t') = \frac{1}{i\hbar} \langle \psi_s(\vec{x}, t) \psi_{s'}^+(\vec{x}', t') \rangle.$$

In thermal equilibrium the time dependency of these propagators reduces to the difference of the time arguments $G_{ss'}^<(\vec{x}, t, \vec{x}', t') = G_{ss'}^<(\vec{x}, \vec{x}', t-t')$ and $G_{ss'}^>(\vec{x}, t, \vec{x}', t') = G_{ss'}^>(\vec{x}, \vec{x}', t-t')$.

The **single particle Green function** G unifies electron and hole propagators into one expression. Depending on the time argument this expression acts as either an electron or hole propagator. For real time arguments it has the form

$$\begin{aligned} G_{ss'}(\vec{x}, \vec{x}', t-t') &= \theta(t-t') G_{ss'}^>(\vec{x}, \vec{x}', t-t') + \theta(t'-t) G_{ss'}^<(\vec{x}, \vec{x}', t-t') \\ &= \frac{1}{i\hbar} \langle \hat{T} \psi_s(\vec{x}, t) \psi_{s'}^+(\vec{x}', t') \rangle. \end{aligned}$$

The operator $\hat{T}$ is called 'Wick time-ordering operator', which orders the field operators with real (imaginary) time arguments in a decreasing (increasing) manner. In general, the time arguments of this operator may have complex values. For systems that are in thermodynamic equilibrium the complex time argument corresponds to inverse **temperatures** β . By using a Fourier transform, a **spectral representation** of the Green function $G_{ss'}(\vec{x}, \vec{x}', \omega)$ can be formulated. This function describes either the dynamics of excited single particle states at finite temperatures, or their statistical properties. Due to this fact, propagators and/or Green functions can be used to derive expressions for many physical properties, like the density of states, magnetization, or electron densities.

In the following, the abbreviations that are listed below are used to simplify the expressions.

$$\begin{aligned} \vec{x}_1 t_1 &= 1 \\ v(\vec{x}_1 - \vec{x}_2) \delta(t_1 - t_2) &= v(1-2) \\ \int d^3 \vec{x}_1 \int_0^{-i\hbar\beta} dt_1 &= \int d1 \\ \delta(\vec{x}_1 - \vec{x}_2) \delta(t_1 - t_2) &= \delta(1-2) \\ \vec{x}_1 t_1 \mp i\eta &= 1^\pm, \eta \rightarrow +0 \end{aligned}$$

Using this notation, a **time-ordered two-particle Green function** can be defined as

$$G_{s_1 s_2, s'_1 s'_2}(12, 1'2') = \frac{1}{(i\hbar)^2} \langle \hat{T} \psi_{s_1}(\vec{x}_1, t_1) \psi_{s_2}(\vec{x}_2, t_2) \psi_{s'_1}^\dagger(\vec{x}'_1, t'_1) \psi_{s'_2}^\dagger(\vec{x}'_2, t'_2) \rangle.$$

In the Heisenberg picture, an equation of motion for the Green function can be formulated, which, in principle, is a solution to the problem. However, due to the nature of the Coulomb interaction higher order functions like three-particle, four-particle, etc., Green functions appear, which is unfavorable for computational calculations. For achieving a straightforward solution, further quantities and approximations are required. These are outlined below.

The **complete self-energy** $\hat{\Sigma}$ (also mass operator) is introduced, which allows to calculate the Green function self-consistently by using a **Dyson equation**

$$G_{s_1 s'_1}(11') = G_{s_1 s'_1}^0(11') + \sum_{s_2, s_3} \int d2 \int d3 G_{s_1 s_2}^0(12) \hat{\Sigma}_{s_2 s_3}(23) G_{s_3 s'_1}(31'), \quad (2.15)$$

where G^0 denotes the Green function of the system with non-interacting electrons, which can be easily calculated. The complete self-energy contains all of the electron-electron interaction and can be split up into the Hartree self-energy, which can be calculated directly, and the exchange correlation self-energy [Bec15, ch. 11]:

$$\hat{\Sigma}_{s_1 s_2}(12) = \hat{\Sigma}_{s_1 s_2}^H(12) + \hat{\Sigma}_{s_1 s_2}^{XC}(12) = \delta(1-2) \delta_{s_1 s_2} V_H(\vec{x}_1) + \hat{\Sigma}_{s_1 s_2}^{XC}(12).$$

By using perturbation theory, a spin-dependent **density correlation function** L can be introduced. It describes the expectation value of the fluctuations of spin densities

$$L_{s_1 s'_1, s_2 s'_2}(12) = -i\hbar (G_{s_1 s'_1}(11^+) G_{s_2 s'_2}(22^+) - G_{s_1 s_2, s'_1 s'_2}(12, 1^+ 2^+)).$$

In the limit of a small external potential ϕ and independent electrons, the **density correlation of independent particles** is given by

$$L_{s_1 s'_1, s_2 s'_2}^0(12) = -i\hbar G_{s_1 s'_1}(12') G_{s_2 s'_2}(21').$$

The **polarization function** P describes the response of the system to external perturbations. This quantity allows to calculate the dielectric function, and furthermore the optical properties of a system

$$P_{s_1 s'_1, s_2 s'_2}(12) = - \sum_{s_3, s_4} \int d3 \int d4 L_{s_1 s'_1, s_4 s_3}^0(11^+, 43) \Gamma_{s_3 s_4, s_2 s'_2}(34, 2). \quad (2.16)$$

The **vertex function** Γ in eq. 2.16 mediates between the interacting system and the independent particle system on the two-particle level. It is given by

$$\Gamma_{s_1 s_2, s_3 s'_3}(12, 3) = -\delta(1-2)\delta(1-3)\delta_{s_1 s'_3}\delta_{s_2 s_3} + \frac{1}{i\hbar} \sum_{s_4, s_5} \int d4 \int d5 \frac{\delta \Sigma_{s_1, s_2}(12 | \phi)}{\delta G_{s_4, s_5}(45 | \phi)} \bigg|_{\phi=0} P_{s_4 s_5, s_3 s'_3}(45, 33+). \quad (2.17)$$

The **dynamically screened potential** W can be also written in the form of a Dyson equation

$$W(11') = v(1-1') + \sum_{s_3, s_4} \int d3 \int d4 v(1-3) P_{s_3 s_3, s_4 s_4}(34) W(41').$$

With all these expressions the complete self-energy $\hat{\Sigma}_{s_1 s_2}$ (eq. 2.15) can be simplified to

$$\hat{\Sigma}_{s_1 s_2}(12) = \hat{\Sigma}^H - i\hbar \sum_{s_4, s_5, s'_5} \int d4 \int d5 G_{s_1 s_4}(14) \Gamma_{s_4 s_2, s_5 s'_5}(42, 5) \delta_{s_5 s'_5} W(1^+ 5). \quad (2.18)$$

The coupled equations 2.15 and 2.16-2.18 are called **Hedin's equations**. These are to be solved self-consistently, along with the lines of the so-called Hedin's pentagon (fig. 2.1).

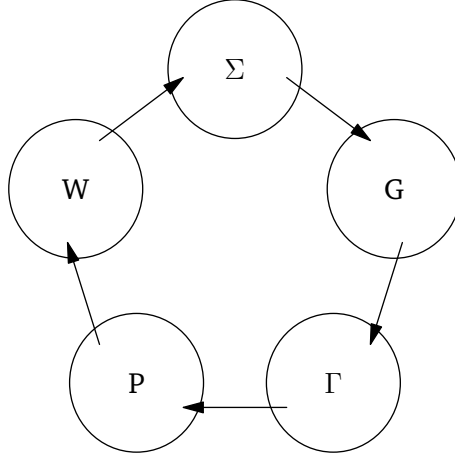


Figure 2.1.: Hedin's pentagon - Iterative update procedure of the quantities in the Hedin equations.

This procedure can be approximated further, by initially setting the exchange correlation self-energy $\hat{\Sigma}$ to zero. Thereby eq. 2.17 is simplified to

$$\Gamma_{s_1 s_2, s_3 s'_3}(12, 3) = -\delta(1-2)\delta(1-3)\delta_{s_1 s'_3}\delta_{s_2 s_3},$$

and eq. 2.18 is reduced to

$$\hat{\Sigma}_{s_1 s_2}(12) = \hat{\Sigma}^H + i\hbar G_{s_1 s_2}(12) W(1^+ 2). \quad (2.19)$$

This form is the **GW approximation** to the self-energy.

In this thesis, only the first iteration of 2.15 is calculated. This approach is called **single shot G_0W_0** , where the KS eigenenergies $\epsilon_{\lambda m_s}$ (eq. 2.11) are updated to $\epsilon_{\lambda m_s}^{\text{QP}}$, to include quasi-particle (QP) effects [Bec15, ch. 12].

Once the Green function has been calculated, it can be expressed as an expansion in Fourier space z . In translationally invariant systems, this is the case for perfect TMDs, the KS orbitals (eq. 2.11) may be chosen as basis functions

$$\tilde{G}_{ss'}(\vec{x}\vec{x}', z) = \sum_{n, n', \vec{k}, m_s, m'_s} \frac{\delta_{nn'} \delta_{m_s m'_s}}{\hbar z - \epsilon_{nm_s}^{\text{QP}}(\vec{k})} \phi_{n\vec{k}m_s}(\vec{x}) \phi_{n'\vec{k}'m'_s}^\dagger(\vec{x}') \chi_{\frac{1}{2}m_s}(s) \chi_{\frac{1}{2}m'_s}^\dagger(s'),$$

where $\phi_{n\vec{k}m_s}$ are the KS orbitals with band index n , Bloch wave vector $\vec{k}$, spin z -component quantum number m_s , spin-function χ with spin s , and the updated QP eigenenergies $\epsilon_{nm_s}^{\text{QP}}(\vec{k})$. The GW approximation takes into account that an excited electron attracts a positive charge cloud (screening cloud). This screening charge weakens the Coulomb interaction of the electron. The same principle applies to the positive hole that is left behind by the electron. The particle together with its screening charge is called **QP**. QPs interact with their surroundings through their **screened interaction** represented by the quantity W [Bec15, sec. 14.1, 14.3].

2.4.2 BSE Calculations

The GW approximation describes single QP excitations; however when a photon excites an electron out of its ground state it then propagates to its destination. At the same time the remaining hole interacts with the excited electron, leading to a different behaviour in comparison to two independent QPs. Thus it is even more revealing to consider the motion of an electron and its residual hole at the same time. The Bethe-Salpeter equation (BSE) for the **two-particle polarization function** $P_{s_1 s'_1, s_2 s'_2}$ describes such a process:

$$P_{s_1 s'_1, s_2 s'_2}(11', 22') = L_{s_1 s'_1, s_2 s'_2}^0(11', 22') + \sum_{s_3, s_4, s_5, s_6} \int d3 \int d4 \int d5 \int d6 L_{s_1 s'_1, s_3 s_4}^0(11', 34) \Xi_{s_3 s_4, s_5 s_6}(34, 56) P_{s_5 s_6, s_2 s'_2}(56, 22'). \quad (2.20)$$

Its derivation can be accomplished by using the polarization function 2.16 along with the vertex function 2.17. The calculation of the **interaction kernel** Ξ is based on the single-particle self-energy and contains the full two-particle interactions:

$$\Xi_{s_3 s_4, s_5 s_6}(34, 56) = -\frac{1}{i\hbar} \frac{\delta \hat{\Sigma}_{s_4 s_3}^{XC}(43)}{\delta G_{s_5 s_6}(56)}.$$

Various approximations can be made to find a computationally useful expression for the kernel. The simplest one is called the **random phase approximation**, where

$\hat{\Sigma}^{XC} = 0$ is set. Another approximation is the **GW approximation for $\hat{\Sigma}$** (eq. 2.19), taken from a preceding GW calculation. The latter is used by VASP [Bec15, sec. 18.1].

2.4.3 Dielectric Function

The **dielectric function** describes the optical response of extended systems. It is defined by

$$\epsilon(12) = \delta(1-2) - \sum_{s_2, s_3} \int d^3v (1-3) P_{s_3 s_3, s_2 s_2}(33^+, 22^+).$$

This function is transformed to momentum space with wave vector $\vec{q}$, and a complex (frequency) parameter z $\epsilon(12) \rightarrow \epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}', z)$, resulting in the frequency dependent dielectric function.

Optical excitations usually involve photons with long wavelength resp. small momenta. These properties are macroscopic optical properties. A corresponding **macroscopic dielectric function** ϵ^M is defined in the limit of vanishing $\vec{G}$ vectors:

$$\epsilon^M(\vec{q}, z) = \frac{1}{\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}', z) |_{\vec{G}, \vec{G}' = \vec{0}}}. \quad (2.21)$$

The dielectric function is related to the **dielectric tensor** $\epsilon_{ij}(z)$ through the photon propagation direction vector $\hat{q} = \frac{\vec{q}}{|\vec{q}|}$:

$$\epsilon^M(\hat{q}, z) = \sum_{ij} \hat{q}_i \epsilon_{ij}^M(z) \hat{q}_j. \quad (2.22)$$

The computational evaluation of the complete macroscopic dielectric tensor (eq. 2.21) is exceedingly demanding. Thus a macroscopic polarization function ϵ^M for small $\vec{q}$ is introduced, along with the Coulomb potential in frequency space $\tilde{v}$

$$\epsilon^M(\hat{q}, z) = 1 - \lim_{\vec{q} \rightarrow 0} 2\tilde{v}(|\vec{q}|) P^M(\vec{q}, \vec{q}, z). \quad (2.23)$$

In order to derive the macroscopic version of the polarization function in eq. 2.23, a change to another base of states is introduced. An excited pair-state α now describes an excited electron and its residual hole. This state either represents a singlet state $\alpha = 1$ or one of three triplet states $\alpha \in \{2, 3, 4\}$. The two-particle polarization function (eq. 2.20) can be expressed as a tensor depending on singlet and triplet states $P_{\alpha\beta}$, where $\alpha, \beta \in \{1, 2, 3, 4\}$. This transformation leads to a significant simplification in all non-spin-polarized cases due to numerous vanishing matrix elements. Furthermore it can be shown that only singlet states with a total spin quantum number $S = 0$ and spin z-component of $M_S = 0$ contribute to (macroscopic) optical properties through the polarization function P_{11} . These insights

can be used to derive the **macroscopic version of the two-particle polarization function** P^M , which has the form of a BSE:

$$P_{s_1 s'_1, s_2 s'_2}^M(11', 22') = L_{s_1 s'_1, s_2 s'_2}^0(11', 22') + \sum_{s_3, s_4, s_5, s_6} \int d3 \int d4 \int d5 \int d6 L_{s_1 s'_1, s_3 s_4}^0(11', 34) \Xi_{s_3 s_4, s_5 s_6}^M(34, 56) P_{s_5 s_6, s_2 s'_2}^M(56, 22'). \quad (2.24)$$

Hence, the macroscopic version looks identical to the complete polarization function P (eq. 2.20) and all its coupled expressions. However, the great difference between these equations is the replacement of the (Fourier transformed) Coulomb potential $\tilde{v}$ with the **truncated short-range coulomb potential** $\tilde{\tilde{v}}$, which reduces the computational effort significantly [Bec15, sec. 18.2, 18.3]:

$$\tilde{\tilde{v}}(|\vec{q} + \vec{G}|) = \begin{cases} 0 & \text{for } \vec{G} = 0 \\ \tilde{v}(|\vec{q} + \vec{G}|) & \text{for } \vec{G} \neq 0 \end{cases}.$$

To compute the macroscopic dielectric function (eq. 2.23), the macroscopic version of the polarization function P^M (eq. 2.24) is transformed to frequency space with frequency z . It can be shown that in the basis of KS eigenfunctions (eq. 2.11) $\phi_{\lambda m_s}$, along with corresponding GW QP energies $\epsilon_{\lambda m_s}^{\text{QP}}$, P^M takes the form

$$P_{m_{s_1} m_{s'_1}, m_{s_2} m_{s'_2}}^M(\lambda_1 \lambda'_1, \lambda_2 \lambda'_2, z) = \frac{f(\epsilon_{\lambda_1 m_{s_1}}^{\text{QP}}) - f(\epsilon_{\lambda'_1 m_{s'_1}}^{\text{QP}})}{\epsilon_{\lambda_1 m_{s_1}}^{\text{QP}} - \epsilon_{\lambda'_1 m_{s'_1}}^{\text{QP}} - \hbar z} \times \left(\delta_{m_{s_1} m_{s'_1}} \delta_{\lambda_1 \lambda'_1} \delta_{m_{s_2} m_{s'_2}} \delta_{\lambda_2 \lambda'_2} + \sum_{\substack{\lambda_3, \lambda_4 \\ m_{s_3}, m_{s_4}}} \Xi_{m_{s'_1} m_{s_1}, m_{s_3} m_{s_4}}^M(\lambda'_1 \lambda_1, \lambda_3 \lambda_4, z) P_{m_{s_3} m_{s_4}, m_{s_2} m_{s'_2}}^M(\lambda_3 \lambda_4, \lambda_2 \lambda'_2, z) \right), \quad (2.25)$$

where the f represent Fermi-distribution functions.

Eq. 2.25 can be transformed into a homogenous BSE. Photonic excitations from valence band state $|v\vec{k}\rangle$ to conduction band state $|c\vec{k}\rangle$ are now considered. $\vec{k}$ has the same value for both states because in the long wavelength limit $\vec{q} \rightarrow 0$ only vertical transitions are relevant. In the product basis of two single-particle states, e.g. $|v\vec{k}m_s\rangle |c\vec{k}m_s\rangle = |vc\vec{k}m_{s_1}m_{s_2}\rangle$, the homogenous BSE is of the form

$$\hat{F}\hat{H}|\phi_\Lambda\rangle = E_\Lambda|\phi_\Lambda\rangle. \quad (2.26)$$

The operator $\hat{F}\hat{H}$ in eq. 2.26 can be simplified by using the **Tamm-Dancoff approximation**, where the off-diagonal elements of the matrix are neglected

$$\hat{F}\hat{H} = \begin{pmatrix} \hat{H} & \hat{\Xi}^M \\ -(\hat{\Xi}^M)^\dagger & -\hat{H}^\dagger \end{pmatrix} \rightarrow \begin{pmatrix} \hat{H} & 0 \\ 0 & -\hat{H}^\dagger \end{pmatrix}.$$

The **resonant electron-hole-pair Hamiltonian** $\hat{H}$ is the most important part of the matrix. In terms of KS Bloch functions $\phi_{v\vec{k}m_s}$ and GW QP energies $\epsilon_{v\vec{k}m_s}^{\text{QP}}(\vec{k})$, this Hamiltonian has the form

$$\hat{H}_{\substack{c\vec{k}m_{sc}v\vec{k}m_{sv} \\ c'\vec{k}'m_{s'_c}v'\vec{k}'m_{s'_v}}} = \left(\epsilon_{cm_{sc}}^{\text{QP}}(\vec{k}) - \epsilon_{vm_{sv}}^{\text{QP}}(\vec{k}) \right) \delta_{cc'} \delta_{vv'} \delta_{\vec{k}\vec{k}'} \delta_{m_{sc}m_{s'_c}} \delta_{m_{sv}m_{s'_v}} \\ - \delta_{m_{sc}m_{s'_c}} \delta_{m_{sv}m_{s'_v}} W_{\substack{\vec{k},\vec{k}' \\ m_{sc},m_{sv} \\ c,c' \\ v,v'}} + \delta_{m_{sc}m_{s'_c}} \delta_{m_{sv}m_{s'_v}} \bar{v}_{\substack{\vec{k},\vec{k}' \\ m_{sc},m_{sv} \\ c,v \\ v',c'}} ,$$

where W represents the screened Coulomb potential between an electron and a hole, and $\bar{v}$, a short ranged unscreened Coulomb repulsion. The exact form of W and $\bar{v}$ may not be discussed in detail here. This resonant Hamiltonian fullfills an eigenvalue problem with eigenvalues E_Λ and eigenvectors, or **electron-hole-pair amplitudes**, A_Λ , where Λ represents the quantum numbers of the electron-hole excitations

$$\sum_{c',v',m_{s'_c},m_{s'_v},\vec{k}'} \hat{H}_{\substack{c\vec{k}m_{sc}v\vec{k}m_{sv} \\ c'\vec{k}'m_{s'_c}v'\vec{k}'m_{s'_v}}} A_\Lambda^{c'\vec{k}'m_{s'_c}v'\vec{k}'m_{s'_v}} = E_\Lambda A_\Lambda^{c\vec{k}m_{sc}v\vec{k}m_{sv}} . \quad (2.27)$$

In the following, eq. 2.27 is called **BSE**. Its solution (E_Λ and A_Λ) can be used for evaluating the **macroscopic dielectric function** ϵ^M

$$\epsilon^M(\hat{q}, \omega) = 1 + \frac{4\pi}{\Omega} \sum_{\Lambda} \left| \sum_{m_s, c, v, \vec{k}} M_{\vec{k}, \vec{k}, c, v}^{m_s}(\hat{q})^\dagger A_\Lambda^{c\vec{k}m_s, v\vec{k}m_s} \right|^2 \sum_{\beta=\pm 1} \frac{1}{E_\Lambda - \beta\hbar(\omega + i\eta)} , \quad (2.28)$$

where Ω represents the total system volume and $z \rightarrow \omega + i\eta$.

The **optical transition matrix elements** $M_{\vec{k}, \vec{k}, c, v}^{m_s}(\hat{q})$ describe the probability amplitude of a radiative single particle transition. It is calculated by using the **dipole operator** components $(M_{\vec{k}, \vec{k}, c, v}^{m_s})_j$ along with the photon propagation vector $\hat{q}$

$$M_{\vec{k}, \vec{k}, c, v}^{m_s}(\hat{q}) = \sum_j \hat{q}_j (M_{\vec{k}, \vec{k}, c, v}^{m_s})_j = \sum_j \hat{q}_j \frac{e \langle c\vec{k}m_s | \hat{x}_j | v\vec{k}m_s \rangle}{\sqrt{4\pi\epsilon_0}} \delta_{\vec{k}\vec{k}'} .$$

The **interband Bloch matrix element** of the position operator $\langle c\vec{k}m_s | \hat{x} | v\vec{k}m_s \rangle$ relates to the momentum operator $\hat{p}$ through

$$\langle c\vec{k}m_s | \hat{x} | v\vec{k}m_s \rangle = -\frac{i\hbar}{m_e} \frac{\langle c\vec{k}m_s | \hat{p} | v\vec{k}m_s \rangle}{\epsilon_{cm_s}(\vec{k}) - \epsilon_{vm_s}(\vec{k})} . \quad (2.29)$$

The **weighted dipole operator** for state Λ and cartesian component j is defined by

$$\langle M_j | A_\Lambda \rangle = \sum_{m_s, c, v, \vec{k}} (M_{\vec{k}, \vec{k}, c, v}^{m_s})_j^\dagger A_\Lambda^{c\vec{k}m_s, v\vec{k}m_s} . \quad (2.30)$$

Eq. 2.28 can be reformulated into an expression for the dielectric tensor by using the j -th component of the dipole operator $(M_{\vec{k},\vec{k},c,v}^{m_s})_j$:

$$\epsilon_{jj}^M(\hat{q}, \omega) = 1 + \frac{4\pi}{\Omega} \sum_{\Lambda} |\langle M_j | A_{\Lambda} \rangle|^2 \sum_{\beta=\pm 1} \frac{1}{E_{\Lambda} - \beta \hbar(\omega + i\eta)}.$$

From this expression for the dielectric function, various optical properties of solids, including electron-hole interactions are obtained. For example, absorption, reflection, and transmission spectra [Bec15, ch. 19].

2.5 Electron-Hole Pairs

2.5.1 Excitons

When a photon excites an electron into an unoccupied state, a QP electron, and a QP hole forms. Their surrounding screening charges lead to a weak attraction between these two particles. Stable bound states called **excitons** may form, which are the most important many-body effect apart from the recombination of an electron with a hole. The solution of the BSE (eq. 2.26) is able to describe the interaction between the two QPs.

The solution determines the coefficients A_{Λ} that are needed to express an exciton state Λ in terms of two-particle KS Bloch functions:

$$|\Phi_{\Lambda}\rangle = \sum_{v,c,\vec{k}} A_{\Lambda}^{v,c,\vec{k}} |v, \vec{k}\rangle |c, \vec{k}\rangle. \quad (2.31)$$

This superposition of states can be expressed in position space through a wave function with an electron at position $\vec{x}_e$ and a hole at position $\vec{x}_h$ [Bec15, ch. 21]:

$$\Phi_{\Lambda}(\vec{x}_e, \vec{x}_h) = \sum_{v,c,\vec{k}} A_{\Lambda}^{v,c,\vec{k}} \phi_{c\vec{k}}^{\dagger}(\vec{x}_e) \phi_{v\vec{k}}(\vec{x}_h).$$

As a generalization of eq. 2.31 an exciton Λ may have a center of mass momentum $\hbar\vec{Q}$ with wave vector $\vec{Q}$. The excitation energy is $E_{\Lambda}(\vec{Q})$. Again, this exciton state can be written in terms of KS functions [Pal+15, supp.]:

$$|\Phi_{\Lambda}(\vec{Q})\rangle = \sum_{v,c,\vec{k}} A_{\Lambda}^{v,c,\vec{k}}(\vec{Q}) |v, \vec{k}\rangle |c, \vec{k} + \vec{Q}\rangle. \quad (2.32)$$

The probability of a photonic interaction with exciton Λ correlates with the weighted dipole operator (eq. 2.28). The **oscillator strength** of state Λ for Cartesian coordinate j is proportional to

$$f_j^\Lambda \propto E_\Lambda |\langle M_j | A_\Lambda \rangle|^2 .$$

In this thesis excitonic states with large (small) interaction probabilities are called bright (dark) excitons [Fuc+08, p. 3].

2.5.2 Effective Masses

The bandstructure $E_n(k)$ of a parabolic band n in the vicinity of k-point k_0 may be approximated by using an **effective mass** $m_n^*(\vec{k}_0)$:

$$E_n(k) = E_n(k_0) + \frac{\hbar^2}{2} \frac{(k - k_0)^2}{m_n^*(\vec{k}_0)} .$$

Deriving this equation with respect to k gives an expression for calculating the effective mass through a parabolic fit of the bandstructure, where the negative (positive) sign is used for holes (electrons):

$$\left. \frac{\partial^2 E_n(k)}{\partial k^2} \right|_{k=k_0} = \frac{\hbar^2}{m_n^*(\vec{k}_0)} \Rightarrow m_n^*(\vec{k}_0) = \pm \frac{\hbar^2}{\left. \frac{\partial^2 E_n(k)}{\partial k^2} \right|_{k=k_0}} . \quad (2.33)$$

In anisotropic structures, the effective mass has different values for different directions in k-space. The effective mass is then described through an **effective mass tensor** $m_{n,ij}$

$$m_{n,ij}^{-1}(\vec{k}_0) = \pm \frac{1}{\hbar^2} \left. \frac{\partial^2 E_n(k)}{\partial k_i \partial k_j} \right|_{k=k_0} .$$

The energy of a QP in energy band n in the vicinity of k-point $\vec{k}_0$ is given by

$$E(\vec{k}) = E(\vec{k}_0) + \frac{\hbar^2}{2} (\vec{k} - \vec{k}_0)^T m_n^{-1}(\vec{k}_0) (\vec{k} - \vec{k}_0) .$$

Some properties of an exciton Λ , which is centered on k-point $\vec{k}_0$, can be described through the **reduced effective mass tensor** M_Λ . It is calculated with the effective mass of the QP electron in the conduction band m_c , and the QP hole in the valence band m_v :

$$M_{\Lambda,ij}^{-1}(\vec{k}_0) = m_{c,ij}^{-1}(\vec{k}_0) + m_{v,ij}^{-1}(\vec{k}_0) .$$

The approximation of the total excitation energy for an exciton Λ with momentum $\hbar\vec{Q}$ and energy E_Λ is [Ash+77, p. 228][Bec15, p. 504]:

$$E_\Lambda(\vec{Q}) = E_\Lambda(\vec{0}) + \frac{\hbar^2}{2} \vec{Q}^T M_\Lambda^{-1} \vec{Q} . \quad (2.34)$$

2.5.3 Exciton Radiative Lifetimes

An excitonic state with a center of mass momentum $\hbar\vec{Q}$ (eq. 2.32) decays into the electronic ground state with one **photon** of wave vector $q = |\vec{q}| = |(q_x, q_y, q_z)|$. The polarization of this photon is described by two polarization vectors $\vec{e}_{\vec{q},\lambda}$, where $\lambda = 1, 2$. This process is noted as $|\Phi_\Lambda(\vec{Q}), 0\rangle \rightarrow |G, 1_{\vec{q},\lambda}\rangle$.

The **radiative decay rate** $\gamma_\Lambda^{\text{rad}}$ resp. (inverse) **radiative lifetime** $\tau_\Lambda^{\text{rad}}$ for a population of a particular excitonic state Λ is defined by

$$\gamma_\Lambda^{\text{rad}}(\vec{Q}) = \tau_\Lambda^{\text{rad}}(\vec{Q})^{-1} = \frac{2\pi}{\hbar} \sum_{\vec{q},\lambda} \left| \langle G, 1_{\vec{q},\lambda} | \hat{H} | \Phi_\Lambda(\vec{Q}), 0 \rangle \right|^2 \delta(E_\Lambda(\vec{Q}) - \hbar c_0 q). \quad (2.35)$$

$E_\Lambda(\vec{Q})$ represents the excitation energy, $\hat{H}$ the photon-electron interaction Hamiltonian of the system, and c_0 the vacuum speed of light [Pal+15, supp. eq. 2].

Eq. 2.35 is a function that depends on the momentum of the exciton. In thermal equilibrium, this momentum is statistically distributed depending on the thermal energy $k_B T$. Therefore, the **thermally averaged radiative decay rate** can be expressed in terms of temperature $\gamma_\Lambda^{\text{rad}}(\vec{Q}) \rightarrow \gamma_\Lambda^{\text{rad}}(T)$.

In thermal equilibrium a crystal structure forms excitons of multiple states. The thermally averaged radiative rates are statistically averaged over the lowest excitonic states. The resulting **effective radiative decay rate** $\gamma_{\text{eff}}^{\text{rad}}$ or (inverse) **effective radiative lifetime** $\tau_{\text{eff}}^{\text{rad}}$ at temperature T is the main quantity that can be compared to experimental results [Pal+15]:

$$\gamma_{\text{eff}}^{\text{rad}}(T) = \tau_{\text{eff}}^{\text{rad}}(T)^{-1} = \frac{\sum_\Lambda \gamma_\Lambda^{\text{rad}}(T) e^{-\frac{E_\Lambda}{k_B T}}}{\sum_\Lambda e^{-\frac{E_\Lambda}{k_B T}}}. \quad (2.36)$$

An exciton population of density N not only decays through a radiative channel. Crystal defects are responsible for a different nonradiative recombination lifetime τ^{norad} . Furthermore, excitons may annihilate each other with a rate of γ^{ee} . The change of exciton density N with respect to time is then given by [Rob+16]:

$$\frac{dN}{dt} = -\frac{N}{\tau_{\text{eff}}^{\text{rad}}} - \frac{N}{\tau^{\text{norad}}} - \gamma^{\text{ee}} \frac{N^2}{2}. \quad (2.37)$$

Derivation of the 2D Anisotropic Exciton Lifetimes Formulas

3.1 Introduction

As explained in sec. 2.5.3, excitonic states (eq. 2.31) undergo different processes of decay and thus exhibit finite lifetimes. In this chapter, the main expressions for describing the radiative decay process are derived. The first formula allows the calculation of the "radiative lifetime for zero momentum" (eq. 3.8). It is an intrinsic constant value that describes the statistical lifetime for an excitonic population of a particular state. From the second formula, the "thermally averaged lifetime" (eq. 3.11) is obtained. The formula describes the statistical lifetime of a particular excitonic state population at a specific temperature. When comparing to experiment, one has to evaluate the "effective lifetime" formula (eq. 2.36) that combines all excitonic states. These quantities have been calculated for isotropic TMDs such as MoS₂ and MoSe₂ in ref. [Pal+15]. The formula that was derived for these systems takes advantage of the structures' isotropy and can, therefore, only be applied to isotropic structures. In this thesis, exciton lifetimes for anisotropic 2D structures (such as ReS₂) are of primary importance; in particular, this chapter derives the corresponding formulas for calculating exciton lifetimes in anisotropic 2D materials.

3.2 Radiative Decay Rate

Similar to sec. 2.5 an **exciton state** Λ with a center of mass momentum $\hbar\vec{Q}$ and a wave vector $\vec{Q}$ is considered (eq. 2.32). Without any momentum, the excitation energy is abbreviated by $E_{\Lambda}(\vec{0}) = E_{\Lambda}$. This photon-less state decays into the electronic ground state with one **photon** of wave vector $q = |\vec{q}| = |(q_x, q_y, q_z)|$ and two-photon polarization vectors $\vec{e}_{\vec{q},\lambda}$, where $\lambda = 1, 2$.

The **radiative decay rate** $\gamma_{\Lambda}^{\text{rad}}$ resp. (inverse) **radiative lifetime** $\tau_{\Lambda}^{\text{rad}}$ (eq. 2.35) can be reformulated by using results of BSE calculations (ref. [Pal+15, supp. eq. 2]):

$$\begin{aligned} \gamma_{\Lambda}^{\text{rad}}(\vec{Q}) &= \tau_{\Lambda}^{\text{rad}}(\vec{Q})^{-1} = \frac{2\pi}{\hbar} \frac{e^2}{m_e^2 c_0^2} \frac{2\pi}{V} \times \\ &\quad \left(\sum_{\vec{q}, \lambda} \frac{1}{q} \left| \vec{e}_{\vec{q}, \lambda} \cdot \sum_{v, c, \vec{k}} A_{\Lambda}^{v, c, \vec{k}}(\vec{Q}) \langle v, \vec{k} | e^{-i\vec{q} \cdot \vec{r}} \hat{p} | c, \vec{k} + \vec{Q} \rangle \right|^2 \right) \delta \left(\frac{E_{\Lambda}(\vec{Q})}{\hbar c_0} - q \right) \quad (3.1) \\ &= \frac{2\pi}{\hbar} \frac{e^2}{m_e^2 c_0^2} \frac{2\pi}{V} I_{\Lambda}(\vec{Q}). \quad (3.2) \end{aligned}$$

As indicated by eq. 3.2, $I_{\Lambda}(\vec{Q})$ denotes the sum term, which will be solved in this chapter. As usual v labels the valence bands, c the conduction bands, and $\vec{k}$ the Bloch wave vectors. $A_{\Lambda}^{v, c, \vec{k}}$ are the expansion coefficients retrieved by solving the BSE (eq. 2.27). m_e is the electron mass, c_0 the vacuum speed of light, and e the unit charge. $\hat{p} = \hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z$ is the momentum operator, with $\hat{x}, \hat{y}, \hat{z}$ representing the Cartesian unit vectors. The volume of the structure is given by $V = A_{\text{uc}} N_k L_z$, with A_{uc} denoting the 2D area of the unit cell, and N_k the number of k-points used within that area, according to ref. [Pal+15, p. 4].

Analogous to eq. 2.30, the **weighted interband matrix elements** $d_{\Lambda i}^Q$ are introduced in the next step:

$$d_{\Lambda i}^Q = \sum_{v, c, \vec{k}} A_{\Lambda}^{v, c, \vec{k}}(\vec{Q}) \langle v, \vec{k} | \hat{p}_i | c, \vec{k} + \vec{Q} \rangle. \quad (3.3)$$

The sum term I_{Λ} 3.2 can be rewritten by applying the sum rule for expectation values

$$\begin{aligned} &\vec{e}_{\vec{q}, \lambda} \cdot \sum_{v, c, \vec{k}} A_{\Lambda}^{v, c, \vec{k}}(\vec{Q}) \langle v, \vec{k} | e^{-i\vec{q} \cdot \vec{r}} (\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z) | c, \vec{k} + \vec{Q} \rangle \\ &= \vec{e}_{\vec{q}, \lambda} \cdot \left(\hat{x} d_{\Lambda x}^Q + \hat{y} d_{\Lambda y}^Q + \hat{z} d_{\Lambda z}^Q \right) \\ &\Rightarrow I_{\Lambda}(\vec{Q}) = \sum_{\vec{q}, \lambda} \frac{1}{q} \left| \vec{e}_{\vec{q}, \lambda} \cdot \left(\hat{x} d_{\Lambda x}^Q + \hat{y} d_{\Lambda y}^Q + \hat{z} d_{\Lambda z}^Q \right) \right|^2. \quad (3.4) \end{aligned}$$

The 2D system can be aligned to the $\hat{x}, \hat{y}$ -plane. When this is done, the weighted interband matrix element for the $\hat{z}$ -axis becomes negligible small, leading to a simplification of the calculation:

$$d_{\Lambda z}^Q \stackrel{!}{=} 0.$$

Due to this alignment, the movement of the exciton is restricted to the $\hat{x}, \hat{y}$ -plane; therefore the exciton wave vector can be written as $\vec{Q} = (Q_x, Q_y, 0)$. Furthermore

the photon decay must conserve the in-plane components of the exciton wave vector. With these restrictions the sum in eq. 3.4 can be reformulated to:

$$\sum_{\vec{q}, \lambda} \rightarrow \frac{L_z}{2\pi} \sum_{\lambda} \int_{-\infty}^{\infty} dq_z \sum_{q_x} \sum_{q_y} \delta_{q_x, Q_x} \delta_{q_y, Q_y},$$

or

$$\vec{q} = (q_x, q_y, q_z) \rightarrow (Q_x, Q_y, q_z) \text{ and } \sum_{\vec{q}, \lambda} \rightarrow \frac{L_z}{2\pi} \sum_{\lambda} \int_{-\infty}^{\infty} dq_z.$$

These substitutions lead to a new expression for the radiative decay rate:

$$\gamma_{\Lambda}^{\text{rad}}(\vec{Q}) = \frac{2\pi}{\hbar} \frac{e^2}{m_e^2 c_0^2} \frac{1}{A_{\text{uc}} N_k} \left(\sum_{\lambda} \int_{-\infty}^{\infty} dq_z \frac{1}{q} \left| \vec{e}_{\vec{q}, \lambda} \cdot (\hat{x} \mathbf{d}_{\Lambda x}^Q + \hat{y} \mathbf{d}_{\Lambda y}^Q) \right|^2 \right) \delta \left(\frac{E_{\Lambda}(\vec{Q})}{\hbar c_0} - q \right).$$

In the next steps the photon polarization vectors $\vec{e}_{\vec{q}, \lambda}$ are generalized to an arbitrary angle α . It is further shown that the derived formulas are independent of this angle. An initial photon polarization vector can be aligned to the $\hat{x}, \hat{y}$ -plane. This vector represents the arbitrary polarization vector at zero angle $\vec{e}_{\vec{q}, 1}(0) = \vec{e}_{\vec{q}, xy}$

$$\vec{e}_{\vec{q}, xy} = \frac{\vec{q} \times \hat{z}}{|\vec{q} \times \hat{z}|} = \left(\frac{Q_y}{\sqrt{\vec{Q}^2}}, -\frac{Q_x}{\sqrt{\vec{Q}^2}}, 0 \right).$$

To obtain the first photon polarization $e_{\vec{q}, 1}(\alpha)$ vector, $\vec{e}_{\vec{q}, xy}$ is now rotated by an arbitrary angle α with respect to an rotation axis pointing into the direction of the photon wave vector $\vec{q}$. The second polarization vector $e_{\vec{q}, 2}(\alpha)$ is defined as being perpendicular to the first polarization vector and the photon wave vector:

$$\begin{aligned} e_{\vec{q}, 1}(\alpha) &= \begin{pmatrix} \frac{Q_y \cos(\alpha) |\vec{q}| + Q_x q_z \sin(\alpha)}{\sqrt{\vec{Q}^2 \vec{q}^2}} \\ \frac{Q_y q_z \sin(\alpha) - Q_x \cos(\alpha) |\vec{q}|}{\sqrt{\vec{Q}^2 \vec{q}^2}} \\ \sin(\alpha) \left(-\sqrt{\frac{\vec{Q}^2}{\vec{q}^2}} \right) \end{pmatrix}, \\ \vec{e}_{\vec{q}, 2}(\alpha) &= e_{\vec{q}, 1} \times \frac{\vec{q}}{|\vec{q}|} = \begin{pmatrix} \frac{Q_y \sin(\alpha) |\vec{q}| - Q_x q_z \cos(\alpha)}{\sqrt{\vec{Q}^2 \vec{q}^2}} \\ -\frac{Q_x \sin(\alpha) |\vec{q}| + Q_y q_z \cos(\alpha)}{\sqrt{\vec{Q}^2 \vec{q}^2}} \\ \cos(\alpha) \sqrt{\frac{\vec{Q}^2}{\vec{q}^2}} \end{pmatrix}. \end{aligned} \quad (3.5)$$

These two vectors are visualized in fig. 3.1.

The polarization vectors (eq. 3.5) represent all polarizations that are possible in the model for the radiative decay process. With these vectors it is possible to carry

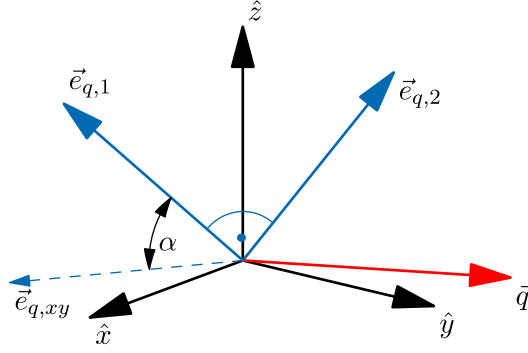


Figure 3.1.: Photon vectors during radiative decay - Vector $\vec{q}$ is the photon wave vector, vectors $\vec{e}_{q,1}$ and $\vec{e}_{q,2}$ represent the polarization vectors. $\vec{e}_{q,1}$ is rotated out of the in-plane vector $\vec{e}_{q,xy}$ by an arbitrary angle α .

out the dot product with the weighted interband matrix element terms in eq. 3.4, leading to a new expression for the sum term

$$\begin{aligned}
 I_{\Lambda}(\vec{Q}) &= \sum_{\lambda} \int_{-\infty}^{\infty} dq_z \frac{1}{q} \left| \vec{e}_{\vec{q},\lambda} \cdot (\hat{x} d_{\Lambda x}^Q + \hat{y} d_{\Lambda y}^Q) \right|^2 \\
 &= \int_{-\infty}^{\infty} dq_z \frac{\left| (d_{\Lambda y}^Q Q_x - d_{\Lambda x}^Q Q_y) |\vec{q}| \cos(\alpha) - (d_{\Lambda x}^Q Q_x + d_{\Lambda y}^Q Q_y) q_z \sin(\alpha) \right|^2}{\vec{Q}^2 (\vec{q}^2)^{3/2}} \delta \left(\frac{E_{\Lambda}(\vec{Q})}{\hbar c_0} - q \right) \\
 &+ \int_{-\infty}^{\infty} dq_z \frac{\left| (d_{\Lambda x}^Q Q_x + d_{\Lambda y}^Q Q_y) q_z \cos(\alpha) + (d_{\Lambda y}^Q Q_x - d_{\Lambda x}^Q Q_y) |\vec{q}| \sin(\alpha) \right|^2}{\vec{Q}^2 (\vec{q}^2)^{3/2}} \delta \left(\frac{E_{\Lambda}(\vec{Q})}{\hbar c_0} - q \right) \\
 &= \int_{-\infty}^{\infty} dq_z \frac{d_{\Lambda y}^{Q\dagger} (d_{\Lambda y}^Q (Q_x^2 + q_z^2) - d_{\Lambda x}^Q Q_x Q_y) + d_{\Lambda x}^{Q\dagger} (d_{\Lambda x}^Q (Q_y^2 + q_z^2) - d_{\Lambda y}^Q Q_x Q_y)}{(\vec{q}^2)^{3/2}} \delta(\dots) .
 \end{aligned}$$

Carrying out the integration, the sum term in eq. 3.2 now reads

$$\begin{aligned}
 I_{\Lambda}(\vec{Q}) &= \frac{2c_0^2 \hbar^2 d_{\Lambda x}^{Q\dagger} \left(\frac{d_{\Lambda x}^Q E_{\Lambda}^2(\vec{Q})}{c_0^2 \hbar^2} - Q_x (d_{\Lambda x}^Q Q_x + d_{\Lambda y}^Q Q_y) \right)}{E_{\Lambda}^2(\vec{Q}) \sqrt{\frac{E_{\Lambda}^2(\vec{Q})}{c_0^2 \hbar^2} - \vec{Q}^2}} + \\
 &\frac{2c_0^2 \hbar^2 d_{\Lambda y}^{Q\dagger} \left(\frac{d_{\Lambda y}^Q E_{\Lambda}^2(\vec{Q})}{c_0^2 \hbar^2} - Q_y (d_{\Lambda x}^Q Q_x + d_{\Lambda y}^Q Q_y) \right)}{E_{\Lambda}^2(\vec{Q}) \sqrt{\frac{E_{\Lambda}^2(\vec{Q})}{c_0^2 \hbar^2} - \vec{Q}^2}} . \quad (3.6)
 \end{aligned}$$

In the following, the radiative decay rate $\gamma_{\Lambda}^{\text{rad}}(\vec{Q})$ for zero exciton wave vector is of interest. Hence, it is required to analyze the limit of vanishing values for Q_x and Q_y

$$I_{\Lambda}(\vec{0}) = \lim_{Q_x \rightarrow 0, Q_y \rightarrow 0} (I_{\Lambda}(\vec{Q})) = \frac{2c_0 \hbar \left(|d_{\Lambda x}^0|^2 + |d_{\Lambda y}^0|^2 \right)}{E_{\Lambda}(\vec{0})} .$$

Substituting this result into eq. 3.2 gives the radiative decay rate for zero exciton wave vector

$$\gamma_{\Lambda}^{\text{rad}}(\vec{0}) = \frac{2\pi}{\hbar} \frac{e^2}{m_e^2 c_0^2} \frac{1}{A_{\text{uc}} N_k} \frac{2c_0 \hbar \left(|d_{\Lambda x}^0|^2 + |d_{\Lambda y}^0|^2 \right)}{E_{\Lambda}(\vec{0})}. \quad (3.7)$$

The final expression of the **radiative decay rate for anisotropic 2D structures** $\gamma_{\Lambda}^{\text{rad}}$, resp. (inverse) **radiative lifetime for anisotropic 2D structures** $\tau_{\Lambda}^{\text{rad}}$, can be obtained by rearranging eq. 3.7. It will be used for the thermal lifetime formulas and is therefore essential. Analogous to ref. [Pal+15, eq. 9] a quantity μ^2 is introduced

$$\gamma_{\Lambda}^{\text{rad}}(\vec{0}) = \tau_{\Lambda}^{\text{rad}}(\vec{0})^{-1} = \frac{8\pi e^2 E_{\Lambda}(\vec{0})}{A_{\text{uc}} \hbar^2 c_0} \frac{\mu_{\Lambda x}^2 + \mu_{\Lambda y}^2}{2}, \quad \mu_{\Lambda i}^2 = \frac{\hbar^2}{m_e^2 E_{\Lambda}^2(\vec{0})} \frac{|d_{\Lambda i}^0|^2}{N_k}. \quad (3.8)$$

This result shows that in anisotropic structures both quantities $\mu_{\Lambda x}^2$ and $\mu_{\Lambda y}^2$ have to be averaged.

In the case of isotropic 2D structures it holds $|d_{\Lambda x}^0|^2 = |d_{\Lambda y}^0|^2 = |d_{\Lambda||}^0|^2$, thus eq. 3.8 simplifies to the same formula that was derived in ref. [Pal+15, supp. eq. 14]

$$\gamma_{\Lambda}^{\text{rad}}(\vec{0}) = \frac{8\pi e^2 E_{\Lambda}(\vec{0})}{A_{\text{uc}} \hbar^2 c_0} \frac{\hbar^2}{m_e^2 E_{\Lambda}^2(\vec{0})} \frac{|d_{\Lambda||}^0|^2}{N_k} = \frac{8\pi e^2 E_{\Lambda}(\vec{0})}{A_{\text{uc}} \hbar^2 c_0} \mu_{\Lambda}^2.$$

3.3 Thermally Averaged Radiative Decay Rate

The radiative decay rate (eq. 3.8) holds for zero exciton momenta. To describe the decay rate for an exciton Λ at temperature T , a thermally averaged radiative decay rate $\gamma_{\Lambda}^{\text{rad}}(T)$ has to be derived. This can be done with eq. 16 of ref. [Pal+15, supp.]:

$$\gamma_{\Lambda}^{\text{rad}}(T) = \frac{\int_0^{2\pi} d\phi \int_0^{Q_0} dQ Q \gamma(Q, \phi) e^{-\frac{\Gamma_{\Lambda}(\vec{Q})}{k_B T}}}{\int_0^{2\pi} d\phi \int_0^{Q_0} dQ Q e^{-\frac{\Gamma_{\Lambda}(\vec{Q})}{k_B T}}}. \quad (3.9)$$

Where $\Gamma_{\Lambda}(\vec{Q}) = E_{\Lambda}(\vec{Q}) - E_{\Lambda}$ is the **exciton kinetic energy**.

To simplify eq. 3.9, a transformation of the exciton wave vector to polar coordinates is introduced:

$$Q_x = Q \cos \phi, \quad Q_y = Q \sin \phi, \quad Q = |\vec{Q}| = Q_x^2 + Q_y^2.$$

The kinetic energy of the exciton is reformulated by using the reduced **effective exciton mass tensor** M_{Λ} (eq. 2.34), along with polar coordinates. The coordinate

system is rotated to diagonalize the mass tensor in the **denominator** of eq. 3.9, leading to

$$\begin{aligned}\Gamma_{\Lambda}(\vec{Q}) &= \frac{\hbar^2 \vec{Q}^2}{2} \begin{pmatrix} \cos(\phi) & \sin(\phi) & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{M_{\Lambda xx}} & 0 & 0 \\ 0 & \frac{1}{M_{\Lambda yy}} & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \cos(\phi) \\ \sin(\phi) \\ 0 \end{pmatrix} \\ &= \frac{\hbar^2 \vec{Q}^2}{2} \left(\frac{\cos^2(\phi)}{M_{\Lambda xx}} + \frac{\sin^2(\phi)}{M_{\Lambda yy}} \right).\end{aligned}$$

Integrating out the denominator (eq. 3.9) results in a constant value similar to ref. [Pal+15, supp. p. 7]:

$$\int_0^{2\pi} d\phi \int_0^{Q_0} dQ Q e^{-\frac{\Gamma_{\Lambda}(\vec{Q})}{k_B T}} = \frac{2\pi \sqrt{M_{\Lambda x} M_{\Lambda y}} k_B T}{\hbar^2}. \quad (3.10)$$

In order to calculate the **nominator** the polar coordinate transformation is applied to the integral term (eq. 3.6), giving the **radiative decay rate in polar coordinates**

$$\begin{aligned}\gamma_{\Lambda}^{\text{rad}}(Q, \phi) &= \frac{2\pi}{\hbar} \frac{e^2}{m_e^2 c_0^2} \frac{2c_0 \hbar}{A_{\text{uc}} N_k} \left(\frac{d_{\Lambda x}^{Q\dagger} \left(d_{\Lambda x}^Q E_{\Lambda}^2(\vec{Q}) - c_0^2 \hbar^2 \vec{Q}^2 \cos(\phi) (d_{\Lambda x}^Q \cos(\phi) + d_{\Lambda y}^Q \sin(\phi)) \right)}{E_{\Lambda}^2(\vec{Q}) \sqrt{E_{\Lambda}^2(\vec{Q}) - c_0^2 \hbar^2 \vec{Q}^2}} \right. \\ &\quad \left. + \frac{d_{\Lambda y}^{Q\dagger} \left(d_{\Lambda y}^Q E_{\Lambda}^2(\vec{Q}) - c_0^2 \hbar^2 \vec{Q}^2 \sin(\phi) (d_{\Lambda x}^Q \cos(\phi) + d_{\Lambda y}^Q \sin(\phi)) \right)}{E_{\Lambda}^2(\vec{Q}) \sqrt{E_{\Lambda}^2(\vec{Q}) - c_0^2 \hbar^2 \vec{Q}^2}} \right).\end{aligned}$$

In ref. [Pal+15, supp. p. 7], the exponential function in the nominator (eq. 3.9) is approximated by a Taylor expansion. Instead of this approach, a **mean effective exciton mass** approximation is introduced in this thesis, which is obtained by the comparison of the effective mass quantity in eq. 3.10 with the isotropic case. This results in a new expression for the kinetic energy of the exciton:

$$\bar{M}_{\Lambda} = \sqrt{M_{\Lambda xx} M_{\Lambda yy}} \Rightarrow \Gamma_{\Lambda}(\vec{Q}) = \frac{\hbar^2 \vec{Q}^2}{2\bar{M}_{\Lambda}}.$$

Furthermore it is assumed that for small exciton momenta $\vec{Q}$ the weighted interband matrix elements are identical to the ones at zero wave vector $d_{\Lambda z}^Q \approx d_{\Lambda z}^0$, as it was concluded in the derivation of ref. [Pal+15, eq. 13]. With this assumption, the integration over ϕ in the nominator of eq. 3.9 gives:

$$\begin{aligned}\int_0^{2\pi} d\phi \int_0^{Q_0} dQ Q \gamma_{\Lambda}^{\text{rad}}(Q, \phi) e^{-\frac{\Gamma_{\Lambda}(\vec{Q})}{k_B T}} &= \frac{16\pi^2 e^2 \bar{M}_{\Lambda} \left(|d_{\Lambda x}^Q|^2 + |d_{\Lambda y}^Q|^2 \right)}{A_{\text{uc}} c_0 m_e^2 n} \\ &\times \int_0^{Q_0} dQ \frac{e^{-\frac{\hbar^2 \vec{Q}^2}{2k_B \bar{M}_{\Lambda} T}} |\vec{Q}| \left(-2\hbar^2 \bar{M}_{\Lambda} \vec{Q}^2 (c_0^2 \bar{M}_{\Lambda} - 2E_{\Lambda}(\vec{0})) + 4E_{\Lambda}(\vec{0})^2 \bar{M}_{\Lambda}^2 + \hbar^4 |\vec{Q}|^4 \right)}{\left(2E_{\Lambda}(\vec{0}) \bar{M}_{\Lambda} + \hbar^2 \vec{Q}^2 \right)^2 \sqrt{4\hbar^2 \bar{M}_{\Lambda} \vec{Q}^2 (E_{\Lambda}(\vec{0}) - c_0^2 \bar{M}_{\Lambda}) + 4E_{\Lambda}(\vec{0})^2 \bar{M}_{\Lambda}^2 + \hbar^4 |\vec{Q}|^4}}.\end{aligned}$$

This result makes it clearly visible that the anisotropic part of the calculation $\left(|d_{\Lambda x}^Q|^2 + |d_{\Lambda y}^Q|^2 \right)$ can be factored out of the complicated integration over Q . There-

fore, it is also possible to factor $\gamma_{\Lambda}^{\text{rad}}(\vec{0})$ out of the thermally averaged radiative decay rate

$$\gamma_{\Lambda}^{\text{rad}}(T) = \gamma_{\Lambda}^{\text{rad}}(\vec{0}) \int_0^{Q_0} dQ \times \frac{2\pi|\vec{Q}| \left(-2\hbar^2 \bar{M}_{\Lambda} \vec{Q}^2 (c_0^2 \bar{M}_{\Lambda} - 2E_{\Lambda}(\vec{0})) + 4E_{\Lambda}(\vec{0})^2 \bar{M}_{\Lambda}^2 + \hbar^4 |\vec{Q}|^4 \right) e^{-\frac{\hbar^2 \vec{Q}^2}{2k_B \bar{M}_{\Lambda} T}}}{\left(2E_{\Lambda}(\vec{0}) \bar{M}_{\Lambda} + \hbar^2 \vec{Q}^2 \right) \sqrt{4\hbar^2 \bar{M}_{\Lambda} \vec{Q}^2 (E_{\Lambda}(\vec{0}) - c_0^2 \bar{M}_{\Lambda}) + 4E_{\Lambda}(\vec{0})^2 \bar{M}_{\Lambda}^2 + \hbar^4 |\vec{Q}|^4}}.$$

The geometry of the structure only depends on the factor outside the integral, this integral must be the same for both cases, anisotropic and isotropic. It follows that the integral must be equal to the integral which was solved in ref. [Pal+15, supp. eq. 17]. Hence the rest of the derivation must be identical to the derivation in ref. [Pal+15].

The final formula for the **thermally averaged radiative decay rate** $\gamma_{\Lambda}^{\text{rad}}(T)$, resp. (inverse) **thermally averaged lifetime** $\tau_{\Lambda}^{\text{rad}}(T)$, is:

$$\gamma_{\Lambda}^{\text{rad}}(T) = \tau_{\Lambda}^{\text{rad}}(T)^{-1} = \gamma_{\Lambda}^{\text{rad}}(\vec{0}) \frac{4}{3} \left(\frac{E_{\Lambda}^2}{2\sqrt{M_{\Lambda xx} M_{\Lambda yy}} c^2 k_B T} \right). \quad (3.11)$$

Part II

Application to 2D Materials

VASP Adaptions for Excitonic Lifetime Calculations

4.1 Introduction

The VASP version 5.4.4 was used to calculate ground state lattice constants BSs, and optical properties such as absorption spectra. In its BSE module, VASP calculates the dielectric function according to eq. 2.28. The calculation of the radiative lifetime (eq. 3.8) requires a quantity that is calculated but not exported in the distributed version of VASP. This chapter examines the source code changes of VASP that are necessary for calculating excitonic lifetimes.

4.2 VASP Quantities

The radiative decay rate (eq. 3.8) requires the computation of weighted interband matrix elements (eq. 3.3)

$$d_{\Lambda i}^0 = \sum_{v,c,\vec{k}} A_{\Lambda}^{v,c,\vec{k}}(\vec{0}) \langle v, \vec{k} | \hat{p}_i | c, \vec{k} \rangle. \quad (4.1)$$

For every vector $\vec{k}$, valence band v , and conduction band c , the corresponding interband Bloch matrix element (eq. 2.29) is multiplied by the coefficient $A_{\Lambda}^{v,c,\vec{k}}(\vec{0})$, which is obtained from the BSE eigenvalue problem (eq. 2.27).

VASP computes this quantity in its subroutine CALCULATE_BSE_OSZI_SCALE, which is located in the Fortran source code file BSE.F. This routine implements the calculation of the dielectric function (eq. 2.28), where the interband Bloch matrix elements are multiplied by the BSE eigenvector coefficients. The result is assigned to the variable CTRANS, which stores a complex number for each axis $\hat{x}$, $\hat{y}$, $\hat{z}$. A copy of this quantity, called ATRANSEL, is introduced for increasing code flexibility. In this subroutine, the position space version of the interband Bloch matrix elements (eq. 2.29) is used. VASP uses position space units of angstroem; therefore, a constant factor of 10^{-10} has to be added for the conversion to SI-units:

$$\left| \sum_{v,c,\vec{k}} A_{\Lambda}^{v,c,\vec{k}}(\vec{0}) \langle v, \vec{k} | \hat{r}_i | c, \vec{k} \rangle \right|^2 = 10^{-10} |\text{ATRANSEL}_i|^2.$$

According to ref. [Cap+07, eq. 11], it holds

$$|d_{\Lambda i}^0|^2 = \frac{m_e^2 E_{\Lambda}^2(\vec{0})}{\hbar^2} \left| \sum_{v,c,\vec{k}} A_{\Lambda}^{v,c,\vec{k}}(0) \langle v, \vec{k} | \hat{r}_i | c, \vec{k} \rangle \right|^2.$$

Thus the calculation of μ_{Λ}^2 for eq. 3.8 leads to

$$\mu_{\Lambda i}^2 = \frac{\hbar^2}{m_e^2 E_{\Lambda}^2(\vec{0})} \frac{|d_{\Lambda i}^0|^2}{N_k} = \frac{|\sum_{v,c,\vec{k}} A_{\Lambda}^{v,c,\vec{k}}(\vec{0}) \langle v, \vec{k} | \hat{r}_i | c, \vec{k} \rangle|^2}{N_k} = 10^{-10} \frac{|\text{ATRANSEL}_i|^2}{N_k}.$$

The final formula for the **anisotropic radiative decay rate** in terms of VASP quantities is

$$\gamma_{\Lambda}^{\text{rad}}(\vec{0}) = \frac{8\pi e^2 E_{\Lambda}(\vec{0})}{A_{\text{uc}} \hbar^2 c_0} \frac{|\text{ATRANSEL}_x|^2 + |\text{ATRANSEL}_y|^2}{2 \cdot 10^{10} N_k}.$$

4.3 VASP Source Code Changes

In lst. 4.1, the changes to the source code of VASP are shown.

Listing 4.1: Changes to the VASP BSE.F file - The character combination `!rb` marks the lines that have been added to the code, where `[..]` represent code lines that have been left unchanged.

```

1  SUBROUTINE CALCULATE_BSE_OSZI_SCALE(WHF, NQPOINT, KPOINT_BSE, LATT_CUR, ISP_LOW, ISP_HIGH, &
2  SHIFT, BD, BSE_INDEX, R, AMAT, NCV, ANTIRESP, NOMEGA_DIM, OMEGAMAX, IU6)
3  [..]
4  GDEF      :: CDER_BETWEEN_STATE(3)
5  COMPLEX(q) :: CTRANS(3)
6  COMPLEX(q) :: CTRANS_SQUARE(3,3)
7  COMPLEX(q) :: ATRANSEL(3) !rb
8  REAL(q)    :: E_AND_ATRANSEL(7,SIZE(R)) !rb
9  INTEGER    :: Q_IS_ZERO, N, M !rb
10 [..]
11 IF (ABS(WHF%WDES%VKPT(1,NQPOINT)+KPOINT_BSE(1))<=1E-6_q .AND. & !rb
12 ABS(WHF%WDES%VKPT(2,NQPOINT)+KPOINT_BSE(2))<=1E-6_q .AND. & !rb
13 ABS(WHF%WDES%VKPT(3,NQPOINT)+KPOINT_BSE(3))<=1E-6_q) THEN !rb
14   Q_IS_ZERO = 1 !rb
15 ELSE !rb
16   Q_IS_ZERO = 0 !rb
17 ENDIF !rb
18
19 DO LAMBDA=1, NCV
20   ATRANSEL=0 !rb
21 [..]
22   DO I1=1,NP,DESCSTD(MB_)
23 [..]
24   DO I2=1,I1RES
25 [..]
26     WEIGHT=(WHF%FERTOT(NB1_INTOT_TOT,K1,ISP)-WHF%FERTOT(NB3_INTOT_TOT, K3, ISP))
27     CALL CDER_BETWEEN_STATES_ROTATED(CDER_BETWEEN_STATE,LATT_CUR, NK1_IN_KPPOINTS_FULL_ORIG,
28     ISP, NB1_INTOT_TOT, NB3_INTOT_TOT)
29     CTRANS=CTrans+CDER_BETWEEN_STATE*AMAT(IROW+(JCOL-1)*DESCSTD(LLD_*WEIGHT
30     IF (Q_IS_ZERO==1) THEN !rb
31       ATRANSEL=ATRANSEL+CDER_BETWEEN_STATE*AMAT(IROW+(JCOL-1)*DESCSTD(LLD_*WEIGHT !rb
32     ENDIF !rb
33   ENDDO
34 [..]
35   CALLMPI( M_sum_z(WHF%WDES%COMM, CTRANS, 3))
36   CALLMPI( M_sum_z(WHF%WDES%COMM, ATRANSEL, 3)) !rb
37
38   E_AND_ATRANSEL(1,LAMBDA)= R(LAMBDA) !rb

```

```

39      DO I=1,3 !rb
40        M = 1+I !rb
41        N = 1+I+3 !rb
42        E_AND_ATRANSEL(M,LAMBDA)= REAL(ATRANSEL(I)) !rb
43        E_AND_ATRANSEL(N,LAMBDA)= AIMAG(ATRANSEL(I)) !rb
44      ENDDO !rb
45    [..]
46  ENDDO
47  [..]
48  CALL XML_VECARRAY("transmatel") !rb
49  CALL XML_FIELD("energy",type="float") !rb
50  CALL XML_FIELD("x_re", type="float") !rb
51  CALL XML_FIELD("y_re", type="float") !rb
52  CALL XML_FIELD("z_re", type="float") !rb
53  CALL XML_FIELD("x_im", type="float") !rb
54  CALL XML_FIELD("y_im", type="float") !rb
55  CALL XML_FIELD("z_im", type="float") !rb
56  CALL XML_ARRAY_REAL(E_AND_ATRANSEL,"(F10.5,'_')") !rb
57  CALL XML_CLOSE_TAG("varray") !rb
58  END SUBROUTINE CALCULATE_BSE_OSZI_SCALA

```

Q_IS_ZERO (line 9 and 11-17) detects, whether the current calculation is done in the long photon wavelength limit or not. The loops over I1 and I2 (line 22 and 24) represent the sum over $\vec{k}$, v and c (eq. 4.1). ATRANSEL is defined in line 7. It is identical to CTRANS and stores one complex value for each Cartesian axis. Lines 29-31 are the actual computation of this quantity. The parallelization of VASP requires the summation of all CPU-node results (line 36). The two dimensional array E_AND_ATRANSEL (line 8, and 38-44) stores the values of ATRANSEL for each BSE eigenvalue E_Λ . These eigenvalues are stored in the array R(LAMBDA). The loop over Λ is implemented in line 19. The output is written to the XML file vasprun.xml by the lines 48-57.

VASP was compiled with the makefile makefile.include, which is listed in lst. A.36. An example output of the file vasprun.xml is shown in lst. 4.2.

Listing 4.2: Modified VASP example XML output - This output shows the new 'transmatel' XML section containing the weighted interband matrix elements.

```

[..  

<varray name="transmatel" >  

  <field>energy</field>  

  <field>x_re</field>  

  <field>y_re</field>  

  <field>z_re</field>  

  <field>x_im</field>  

  <field>y_im</field>  

  <field>z_im</field>  

  <v> 1.91717 0.00993 -0.01739 0.00003 0.06571 -0.11360 -0.00003 </v>  

  <v> 1.91727 -0.11218 -0.06458 0.02101 0.03054 0.01811 -0.02170 </v>  

  <v> 1.92575 -0.30983 -0.36867 0.00034 4.98522 1.40784 0.00073 </v>  

[..  


```


Computational Details

5.1 Introduction

In this chapter, the computational details for the investigation of the TMDs MoS₂, MoSe₂, MoTe₂ (abbreviated by MoX₂), and ReS₂ with the VASP are summarized. First, there is an outline of the structure optimization that uses the methods of DFT. This step is necessary to prepare the unit cells for the study of their optical properties with the G₀W₀ and BSE calculations. This chapter contains all the information needed for reproducing the data that is used in the results and discussion parts of this thesis. Some of the following results are demonstrated for MoS₂ only; in these cases, the corresponding data for MoSe₂ and MoTe₂ can be found in Appendix A.

5.2 General Notes

All diagrams in this thesis were programmed and generated with the vector graphics language Asymptote (ref. [asy]). The 3D graphics can be viewed interactively by using a compatible PDF viewer. VASP data was evaluated with Linux shell scripts.

The MPI version of VASP was used for enabling parallel processing. The MPI version, with spin-orbit coupling enabled, required the non-collinear version of VASP. It is, however, not possible to calculate Van-der-Waals forces with the non-collinear version. As stated in sec. 2.2.2, spin-orbit coupling is not necessary for the structural relaxation of MoX₂ and ReS₂. Therefore, DFT calculations were performed with the MPI version of VASP. In addition, G₀W₀ and BSE based calculations were performed with the MPI-NCL version, where spin-orbit coupling is activated with the LSORBIT and MAGMOM flags.

5.3 DFT Lattice Relaxation

This section concerns the structural relaxation, which was performed to find the unit cell parameters that minimize the total energy of the MoX₂ and ReS₂ structures. The geometric results could then be analyzed regarding a property of interest.

5.3.1 Molybdenum Dichalcogenides ML

The MoX_2 TMDs form structures that are described by the space group $\text{P6}_3/\text{mmc}$. The hexagonal unit cell of this space group can be uniquely defined with two parameters a and c . In their natural bulk state, all three compounds have two molybdenum (Mo) atoms located on the Wyckoff c positions. Four sulfur (S), selenium (Se) or tellurium (Te) atoms are located on Wyckoff f positions, defined by a parameter z . The chosen basis vectors of this unit cell are listed in tab. 5.1, along with the atomic positions r_i .

Table 5.1.: MoX_2 bulk: generic unit cell - X represents a chalcogenide atom.

$$\vec{u} = \begin{pmatrix} \frac{1}{2}a \\ -\frac{\sqrt{3}}{2}a \\ 0 \end{pmatrix} \quad \vec{v} = \begin{pmatrix} \frac{1}{2}a \\ \frac{\sqrt{3}}{2}a \\ 0 \end{pmatrix} \quad \vec{w} = \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix}$$

$$\begin{aligned} \vec{r}_1 &= \frac{1}{3} \cdot \vec{u} + \frac{2}{3} \cdot \vec{v} + \frac{1}{4} \cdot \vec{w} \quad (\text{Mo}) \\ \vec{r}_2 &= \frac{2}{3} \cdot \vec{u} + \frac{1}{3} \cdot \vec{v} + \frac{3}{4} \cdot \vec{w} \quad (\text{Mo}) \\ \vec{r}_3 &= \frac{1}{3} \cdot \vec{u} + \frac{2}{3} \cdot \vec{v} + z \cdot \vec{w} \quad (\text{X}) \\ \vec{r}_4 &= \frac{2}{3} \cdot \vec{u} + \frac{1}{3} \cdot \vec{v} + z + \frac{1}{2} \cdot \vec{w} \quad (\text{X}) \\ \vec{r}_5 &= \frac{2}{3} \cdot \vec{u} + \frac{1}{3} \cdot \vec{v} - z \cdot \vec{w} \quad (\text{X}) \\ \vec{r}_6 &= \frac{1}{3} \cdot \vec{u} + \frac{2}{3} \cdot \vec{v} - z + \frac{1}{2} \cdot \vec{w} \quad (\text{X}) \end{aligned}$$

As a starting point, the experimentally determined unit cell parameters a , c , and z , as listed in tab. 5.2, were used.

Table 5.2.: MoX_2 bulk: crystallographic data - MoX_2 bulk: crystallographic data

Compound	a [Å]	c [Å]	z [Å]	V [Å ³]
MoS_2	3.149	12.250	0.618	105.20
MoSe_2	3.288	12.931	0.625	121.07
MoTe_2	3.519	13.964	0.625	149.75

The bulk unit cell contains two mirrored layers, which are stacked along the $\hat{z}$ -axis. The structures of primary interest are ML structures. MLs MoX_2 can be modeled by discarding one of the two layers, e.g. by removing atoms $\vec{r}_2$, $\vec{r}_3$ and $\vec{r}_6$, and by creating a large vacuum gap between two layers. In order to create such a gap, the unit cell was stretched to a length of $25\text{\AA}$, while keeping the (absolute) atomic positions fixed. This value was chosen in accordance with the relaxation of MoX_2 structures in ref. [Lia+13, p. 2], along with a k-point grid of $12 \times 12 \times 1$.

The lattice optimization requires to find the unit cell shape and atomic positions that result in the lowest total lattice energy. As a DFT functional, the meta-GGA SCAN was chosen (ref. [Sun+16]). The lattice constant a was multiplied by a factor

$x \in [0.9, 1.1]$ in increments of $\Delta x = 0.01$. For every value of x an ionic relaxation was performed (ISIF=2), with the VASP settings that are listed in tab. A.1. POSCAR files for VASP were computed with the bash script listed in lst. A.31.

The value of x (and therefore a), which minimizes the total energy, was determined by using a quadratic fit. The fit functions and results for MoS₂, MoSe₂, MoTe₂ are shown in fig. 5.3 and A.12.

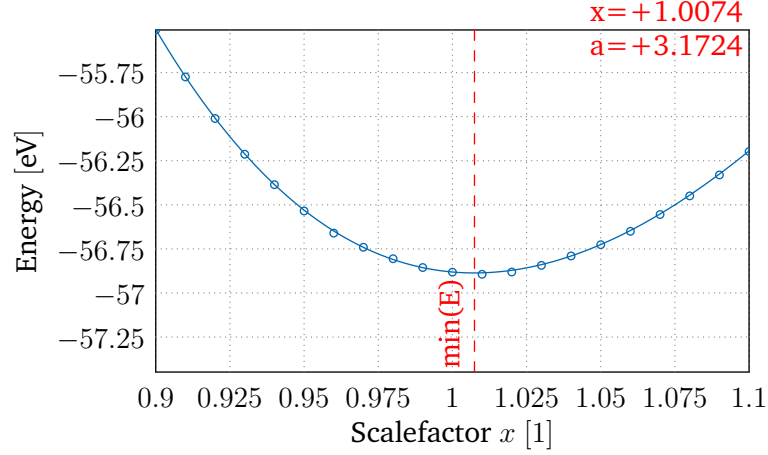


Figure 5.3.: MoS₂ ML: relaxation data and fit function - The optimized lattice constant a is in unit of Å

The obtained value of a , for which the total energy is minimized, was used for a final relaxation of the atomic positions with the VASP settings listed in tab. A.1. The relaxed values of the basis vectors and atomic positions are listed in tab. A.13, A.14 and A.15. The unit cells are visualized in fig. 5.4 and A.16.

5.3.2 Rhenium Disulfide bulk

The bulk structure of ReS₂ is described by the space group $P\bar{1}$ (no.2) through a triclinic unit cell. Experimental lattice constants and angles are listed in tab. 5.5.

This experimental unit cell contains one layer of ReS₂, which is coplanar to the basis vectors that have the length a and b . To align the layer structure to the $\hat{x}, \hat{y}$ -plane, lattice constants a and c , as well as angles α and γ , were interchanged. The basis vectors of the trinlinic unit cell were calculated according to ref. [SC10, p. 307]:

$$\vec{u} = \begin{pmatrix} c \\ 0 \\ 0 \end{pmatrix}, \quad \vec{v} = b \begin{pmatrix} \cos \alpha \\ \sin \alpha \\ 0 \end{pmatrix}, \quad \vec{w} = \begin{pmatrix} a \cos \beta \\ a \frac{\cos \gamma - \cos \beta \cos \alpha}{\sin \alpha} \\ \sqrt{a^2 - w_x^2 - w_y^2} \end{pmatrix}.$$

Lattice vectors $\vec{u}$ and $\vec{v}$ represent the layer plane. The full experimental structure of the unit cell is listed in tab. A.11. This data was converted to a VASP POSCAR file by using the bash script listed in lst. A.32.

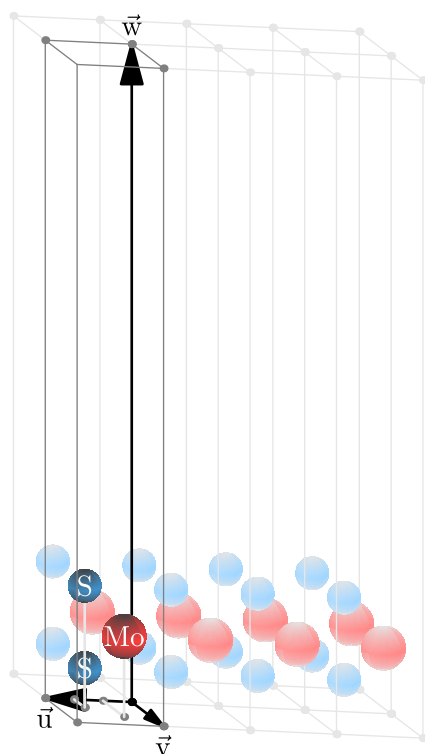


Figure 5.4.: MoS₂ ML: 3D lattice visualization

Table 5.5.: ReS₂ bulk: crystallographic data - ReS₂ bulk: crystallographic data

	a [Å]	b [Å]	c [Å]	V [Å ³]	α [deg]	β [deg]	γ [deg]
ReS ₂	6.417	6.510	6.461	219.300	121.10	88.38	106.47

In the ReS_2 bulk structure, Van-der-Waals forces may not be neglected due to their large contribution to the interaction between layers. To ensure a consensus with the previous MoX_2 calculations, it was initially planned to use the SCAN functional for the ReS_2 structure. However, when the simulations were carried out, the SCAN+rVV10 functional (ref. [Pen+16]), which implements Van-der-Waals effects, was not yet available. Therefore the optB86b GGA functional with PAW PBE potentials was used. Van-der-Waals forces were included through the VASP flags LUSE_VDW, AGGAC, GGA, PARAM1 and PARAM2. The VASP simulation settings are listed in tab. A.5.

Due to the anisotropy of this triclinic structure, the cell shape, its volume, and all atomic positions were allowed to relax (ISIF=3). When the volume is relaxed, the ENMAX flag has to be at least 30% larger than the highest ENMAX value of all POTCAR files. In tab. 5.6, the resulting total energy values vs. k-point grid densities are compared for ensuring convergence.

Table 5.6.: ReS_2 bulk: total energy vs. k-point grid densities

k-Point Grid	$3 \times 3 \times 3$	$6 \times 6 \times 6$	$9 \times 9 \times 9$
total energy [eV]	-67.215	-67.235	-67.235

The relaxed ReS_2 bulk unit cell is visualized in fig. 5.7 and listed in tab. A.17.

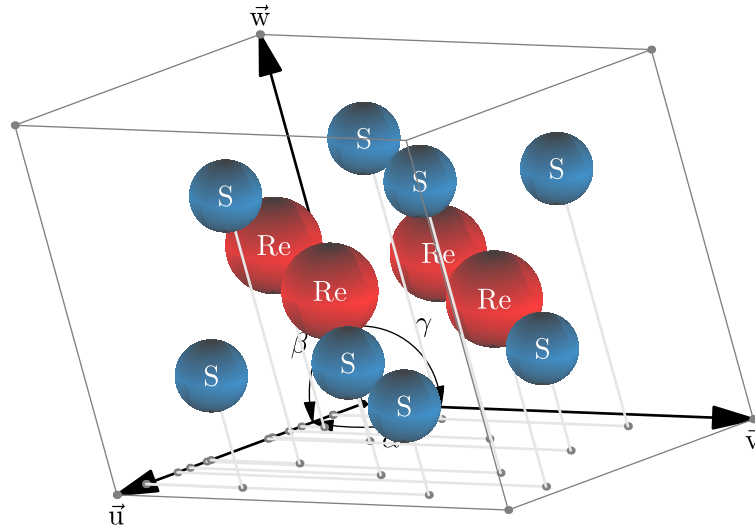


Figure 5.7.: ReS_2 bulk: 3D lattice visualization

The relaxation of the ReS_2 bulk unit cell led to a modified cell shape. Its displaced basis vectors rotated the $\vec{u}$ - $\vec{v}$ layer out of the $\hat{x}$, $\hat{y}$ -plane. In ch. 3, the derivation of the anisotropic lifetime formulas requires an alignment of the layer structure (tab. A.17) to the $\hat{x}$, $\hat{y}$ -plane. Therefore the unit cell was realigned as follows.

Initially the $\vec{u}, \vec{v}$ -plane was rotated to be perpendicular to the $\hat{z}$ -axis. A rotation matrix R_1 was used for this step:

$$(\vec{u} \times \vec{v})R_1 = \lambda_1 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad \vec{u}_1 = \vec{u}R_1, \quad \vec{v}_1 = \vec{v}R_1, \quad \vec{w}_1 = \vec{w}R_1.$$

The next step rotated the new basis vectors $\vec{u}_1, \vec{v}_1, \vec{w}_1$ around the $\hat{z}$ -axis so that vector $\vec{u}_2$ points in the same direction as $\hat{x}$ -axis. For this step, a second rotation matrix R_2 was used:

$$\vec{u}_1R_2 = \lambda_2 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \vec{u}_2 = \vec{u}_1R_2, \quad \vec{v}_2 = \vec{v}_1R_2, \quad \vec{w}_2 = \vec{w}_1R_2.$$

In the following, the resulting vectors $\vec{u}_2, \vec{v}_2, \vec{w}_2$ are renamed to $\vec{u}, \vec{v}, \vec{w}$. The rotated and relaxed ReS₂ bulk unit cell is listed in tab. A.18.

5.3.3 Rhenium Disulfide ML

A MoX₂ unit cell contains two stacked layers, and on the contrary, the ReS₂ structure already consists of only one layer per unit cell. To convert the structure to a ML structure, only the lattice vector $\vec{w}$ has to be stretched, while keeping atomic positions fixed. This procedure creates a vacuum space between two layers. Previous TMD simulations (such as ref. [Lia+13]) have shown that a unit cell height of 25Å is sufficient to ensure minimal interaction between two layers. However, the subsequent G₀W₀ and BSE calculations led to "out of memory" abortions due to the complexity of the ReS₂ structure. Therefore the length of $\vec{w}$ was set to 20Å. Due to the stretching of vector $\vec{w}$, the corresponding reciprocal vector $\vec{w}^*$ in k-space has become shorter. Therefore the k-point grid was accommodated to $9 \times 9 \times 1$.

In the next relaxation step, all atomic positions were allowed to relax while the cell shape was kept fixed (ISIF=2). The absolute (Cartesian) atomic positions from the relaxed bulk structure (tab. A.18) were used. The corresponding VASP settings are listed in tab. A.6. The triclinic ReS₂ ML unit cell is visualized in fig. 5.8 and listed in tab. A.19.

The obtained ML structure still has a triclinic geometry. Its unit cell may be simplified to a monoclinic unit cell by altering the basis vector $\vec{w}$ in a way, such that it is pointing to the direction of the $\hat{z}$ -axis. This procedure is visualized in fig. 5.9a. The Cartesian positions of the basis atoms from the result of the previous simulation run (tab. A.19) were kept fix during this step. The relaxation was executed once more with the settings listed in tab. A.6. The resulting monoclinic ReS₂ ML unit cell is shown in fig. 5.9b and listed in tab. A.20.

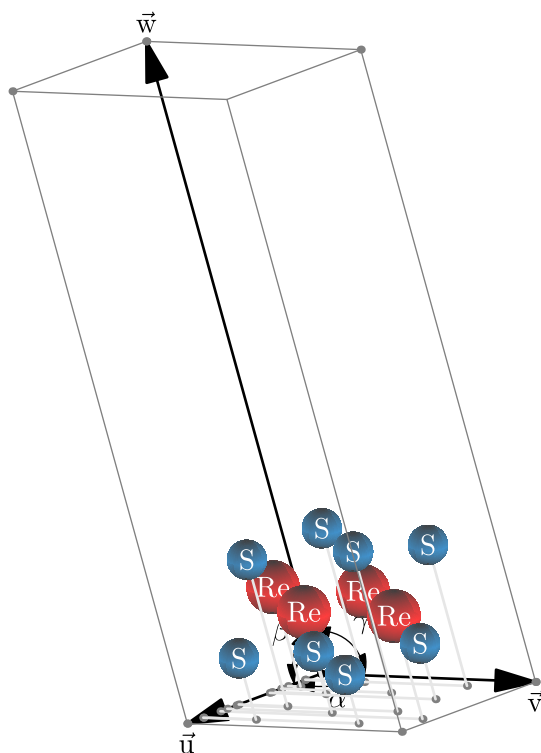


Figure 5.8.: ReS₂ ML: 3D lattice visualization of the triclinic version

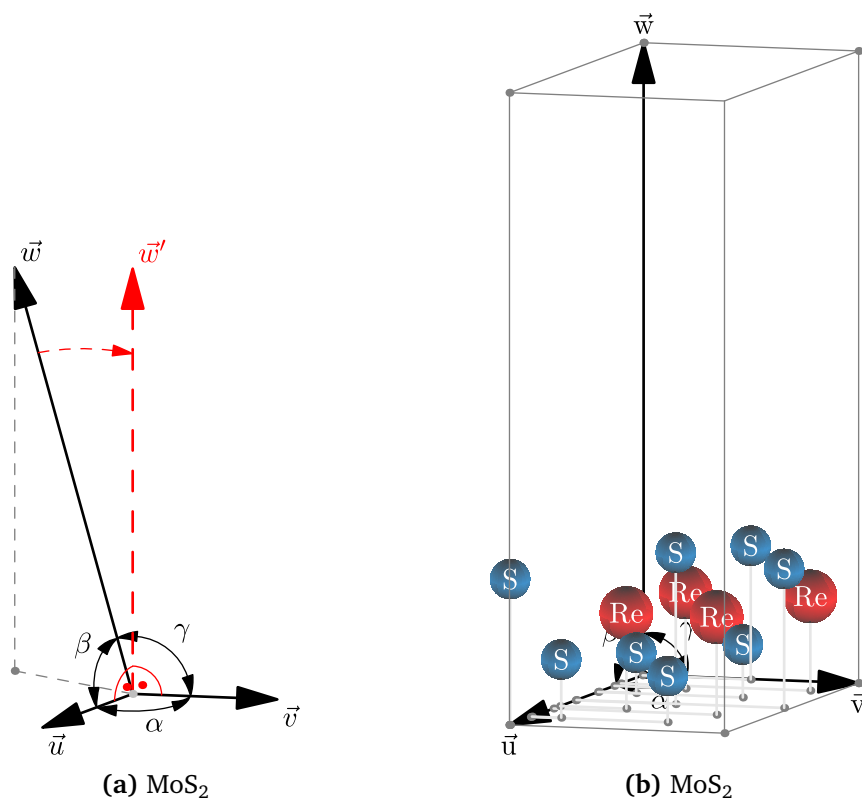


Figure 5.9.: ReS₂ ML: monoclinic to triclinic lattice transformation - (a) The transformation from a triclinic lattice into a monoclinic lattice by altering lattice vector $\vec{w}$. (b) 3D lattice visualization of the monoclinic version.

The relaxed, monoclinic atomic positions have to be compared with the triclinic ones, to ensure that the structures are equivalent. The properties of a lattice structure stay the same when all atoms are dislocated by the same vector. Therefore the (relative) distance vectors $\vec{r}_{1,j}$ between basis atom 1 and all other basis atoms j for both structures (tab. A.19 and tab. A.20) were calculated. The resulting distances (tab. A.21 and A.22) were compared and show a deviation of only $< 5 \cdot 10^{-4} \text{\AA}$. The large difference in distance vectors $\vec{r}_{1,8}$ and $\vec{r}_{1,12}$ were caused by the skewed unit cell walls, which fold back the affected basis atoms to the other sides of the unit cell. It was therefore concluded that the monoclinic ReS₂ ML structure is identical to the triclinic ReS₂ ML structure. The increase in structures' symmetry enables a faster computation in VASP.

5.4 Symmetry Points and Reciprocal Path

5.4.1 Molybdenum Dichalcogenides ML

The space group P6₃/mmc has a center of inversion symmetry which is located between the two layers of the unit cell. The removal of one layer breaks this inversion symmetry (ref. [Mak+12]). In reciprocal space, this leads to a split up of the high symmetry point K into two separate points K and K'. The BS plot in the vicinity of point K remains identical to the one at the K' point. Since spin-resolved BSs are not relevant for this thesis, only the K point was included in the BSs. Nevertheless, interband electron transitions from the valence band to the conduction band at the symmetry point K (K') can only be induced by left (right) circularly polarized photons. Hence, it is important to keep in mind that the valence and conduction band, as well as the allowed transitions, have opposite spin values at both symmetry points.

For the ML TMDs BS plots the standard path for hexagonal structures was chosen:

$$\Gamma(0, 0, 0) \rightarrow M(1/2, 0, 0) \rightarrow K(1/3, 1/3, 0) \rightarrow \Gamma(0, 0, 0).$$

Fig. 5.10 shows the BZ for ML MoS₂, along with the path for the band structure. The BZs and band structure path of ML MoSe₂ and ML MoTe₂ look similar to fig. 5.10 and are therefore not visualized separately.

5.4.2 Rhenium Disulfide bulk

The ReS₂ bulk structure was mainly used for deriving a ML structure. Excitonic lifetimes and optical spectra of the bulk structure are not of interest in this thesis. A

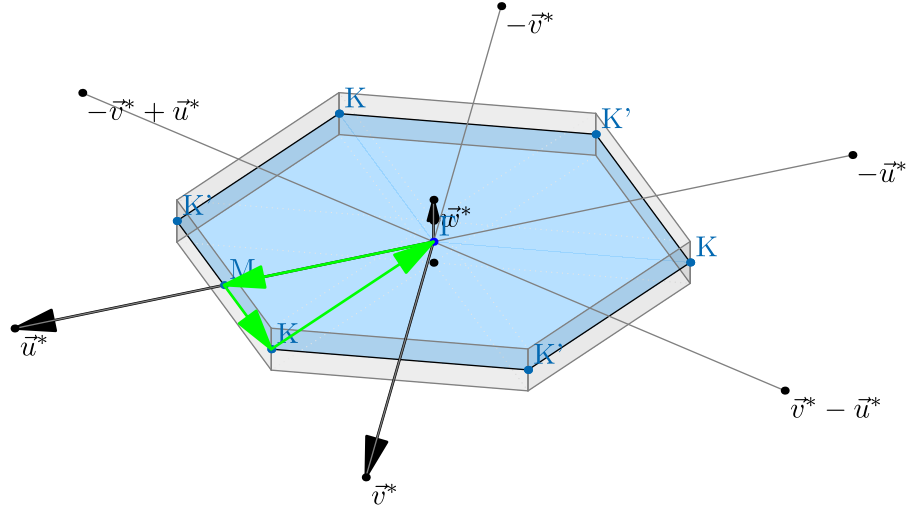


Figure 5.10.: MoS₂ ML: Brillouin zone - The green arrows represent the path for the band structure. Symmetry points K and K' result from the broken inversion symmetry.

reciprocal space path through all high symmetry points with $\vec{w}^* = 0$ was chosen, for allowing a discussion about general properties:

$$\Gamma(0, 0, 0) \rightarrow Y(0, 1/2, 0) \rightarrow V(1/2, 1/2, 0) \rightarrow X(1/2, 0, 0) \rightarrow \Gamma(0, 0, 0) .$$

5.4.3 Rhenium Disulfide ML

The monoclinic structure of ML ReS₂ comes close to a hexagonal unit cell due to the similar values for lattice constants c and b (tab. 5.5). These constants define the length of lattice vectors $\vec{u}$ and $\vec{v}$. Also, the angle between these two lattice vectors ($\alpha = 121.1\text{deg}$) is close to a hexagonal structure. Due to this similarity, the reciprocal space points K and M are introduced for the band structure. The anisotropy of the structure causes three different sets of K and M points, one set for each non-equivalent direction (ref. [Har+17]). The BZ of the ReS₂ ML structure is visualized in fig. 5.11 along with the introduced symmetry points.

The symmetry points M1, M2 and M3 have coordinates that can be calculated easily with linear combinations of half the reciprocal lattice vectors. In contrast to the K point of a hexagonal system, the coordinates of the points K1, K2, and K3 have to be calculated in a more complex way. These points were calculated by using linear combinations of basis vectors with a modified length of $|\vec{c}_u^*| = c_{u^*}$ and c_{v^*} (fig. 5.11). These constants can be calculated trigonometrically by using

$$c_1 = \frac{|\vec{u}^*|/2}{\cos \alpha}, \quad c_2 = c_1 - \frac{|\vec{v}^*|}{2}, \quad c_3 = \frac{c_2}{\tan \alpha}, \quad c_5 = \frac{c_3}{\tan \alpha},$$

$$c_{u^*} = \frac{c_3}{\sin \alpha} \Rightarrow c_{u^*} = \frac{\frac{|\vec{u}^*|}{2 \cos \alpha} - \frac{|\vec{v}^*|}{2}}{\tan \alpha \sin \alpha}, \quad c_{v^*} = \frac{|\vec{v}^*|}{2} - c_5 = \frac{|\vec{v}^*|}{2} - \frac{\frac{|\vec{u}^*|}{2 \cos \alpha} - \frac{|\vec{v}^*|}{2}}{\tan^2 \alpha}.$$

The final values of the reciprocal space coordinates are listed in table 5.12.

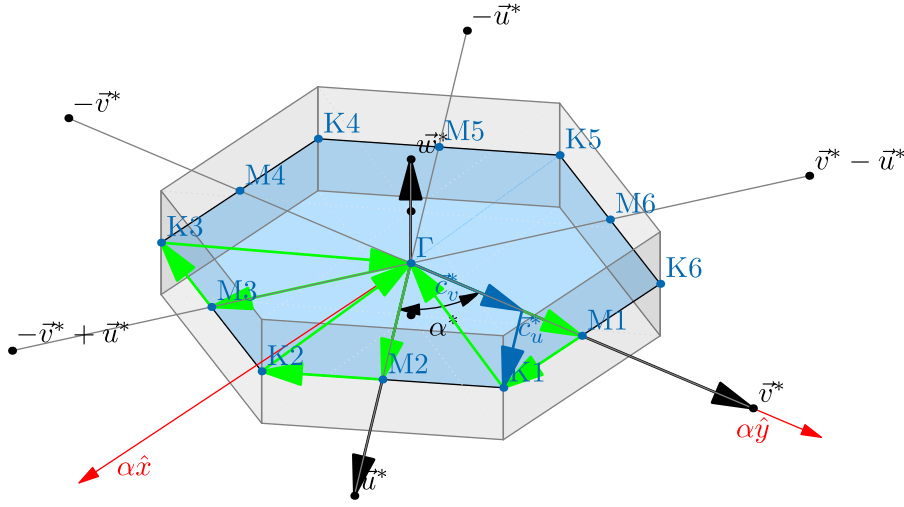


Figure 5.11.: ReS₂ ML: Brillouin zone - The green arrows represent the path for the band structure. The vectors $\vec{c}_u^*$ and $\vec{c}_v^*$ are used to calculate the coordinates of the symmetry points K1, K2 and K3.

Table 5.12.: ReS₂ ML: symmetry point coordinates in the BZ

k-Point	Vector Value	Multiple of $\vec{u}^*$		Multiple of $\vec{v}^*$	
K1	$\frac{c_{u^*}}{ \vec{u}^* } \vec{u}^* + \frac{c_{v^*}}{ \vec{v}^* } \vec{v}^*$	$\frac{c_{u^*}}{ \vec{u}^* } =$	0.332 25	$\frac{c_{v^*}}{ \vec{v}^* } =$	0.325 50
K2	$+\vec{u}^* - \frac{c_{u^*}}{ \vec{u}^* } - \frac{c_{v^*}}{ \vec{v}^* }$	$\frac{1-c_{u^*}}{ \vec{u}^* } =$	0.667 75	$-\frac{c_{v^*}}{ \vec{v}^* } =$	-0.325 50
K3	$\frac{c_{u^*}}{ \vec{u}^* } + \frac{c_{v^*}}{ \vec{v}^* } - \vec{v}^*$	$\frac{c_{u^*}}{ \vec{u}^* } =$	0.332 25	$\frac{c_{v^*}-1}{ \vec{v}^* } =$	-0.674 50
M1	$\frac{1}{2} \vec{v}^*$	$0 =$	0.000 00	$\frac{1}{2} =$	0.500 00
M2	$\frac{1}{2} \vec{u}^*$	$\frac{1}{2} =$	0.500 00	$0 =$	0.000 00
M3	$\frac{1}{2} \vec{u}^* - \frac{1}{2} \vec{v}^*$	$\frac{1}{2} =$	0.500 00	$-\frac{1}{2} =$	-0.500 00

A band structure path for ML ReS₂ was chosen for enabling the calculation of effective masses at the Γ -point for various directions,

$$\begin{aligned} &\Gamma(0, 0, 0) \rightarrow \text{M1}(0, 1/2, 0) \rightarrow \text{K1}(0.33225, 0.32550, 0) \\ &\rightarrow \Gamma(0, 0, 0) \rightarrow \text{M2}(1/2, 0, 0) \rightarrow \text{K2}(0.66775, -0.32550, 0) \\ &\rightarrow \Gamma(0, 0, 0) \rightarrow \text{M3}(1/2, -1/2, 0) \rightarrow \text{K3}(0.33224, -0.67450, 0) \rightarrow \Gamma(0, 0, 0). \end{aligned}$$

5.5 DFT Band Structures

The calculations of DFT band structures were realized in three steps. The previous relaxation results were initially used to generate the converged electronic wave functions and charge densities. A second step increased the k-point resolution for the resulting charge density (ICHARG flag). The third step calculated the band structure for a given path in the reciprocal space, which had been specified in the KPOINTS file.

The VASP settings for calculating the band structures of ML MoX₂, ReS₂ bulk, and ML ReS₂ are listed in tab. A.2, A.7, and A.8.

5.6 Effective Masses

In this thesis, the DFT band structures of MoX₂ and ReS₂ were used to calculate the effective masses according to sec. 2.5.2. The effective masses for particles on band v in the vicinity of k-point k_0 were obtained through a quadratic fit function for the band structure

$$E_v(k) = a + \frac{b}{2}(k - k_0)^2 \Rightarrow \frac{\partial^2 E_v(k)}{\partial k^2} = b.$$

The evaluated fit constants b were used to calculate the relative effective masses by using eq. 2.33

$$m_v^*(\vec{k}_0) = \pm \frac{\hbar^2}{b \cdot 1,60218 \cdot 10^{-19} 10^{-10.2}}.$$

The negative (positive) sign were used for holes (electrons). The constants in the denominator are required for a unit conversion from electronvolt to joule and angstroem to meter.

If not stated separately, three data points were used to calculate the parameters for one side of a fit function.

5.7 G_0W_0 Calculations

G_0W_0 calculations are required for the BSE computations. These calculations were performed for the molybdenum and rhenium ML structures.

Previous work shows that the settings for the grid density (NOMEGA=64) and maximum frequency (OMEGAMAX=10) are sufficient for converging the G_0W_0 computations in the low energetic spectrum (ref. [Mav16]). Furthermore, the number of bands has to be increased with the NBANDS flag. For most structures, it is assumed that 2048 empty conduction bands are sufficient for calculating the BG energy with a precision in the meV range (ref. [Pee+11]). However, the calculation of the ML ReS_2 structure only allowed 512 bands due to the large memory consumption of the fairly complex unit cell. Fortunately, the magnitude of the G_0W_0 BG is not of large interest in this thesis. Previous work suggests that with 512 bands the G_0W_0 calculation should be accurate for most applications other than the BG energy. For example, only “up to 300 empty bands” were used for calculating excitonic lifetimes, as stated in ref. [Pal+15, p. 2799].

The k-point grid density is also crucial for converging the G_0W_0 computations. In tab. 5.13 and 5.14, the BG energies are compared for different k-point grids for evaluating the impact of varying grid densities.

Table 5.13.: MoX_2 ML: G_0W_0 band gap energies vs. k-point grid densities

k-Point Grid	$12 \times 12 \times 1$	$15 \times 15 \times 1$	$18 \times 18 \times 1$
MoS_2 band gap [eV]	2.568	2.517	2.498
MoSe_2 band gap [eV]	2.193	2.154	2.133
MoTe_2 band gap [eV]	1.680	1.633	1.629

Table 5.14.: ReS_2 ML: G_0W_0 band gap energy vs. k-point grid densities

k-Point Grid	$6 \times 6 \times 1$	$9 \times 9 \times 1$	$12 \times 12 \times 1$
ReS_2 band gap [eV]	2.318	2.260	2.236

The difference in the resulting BG energies for ML MoX_2 are $\leq 21\text{meV}$ between the grids $15 \times 15 \times 1$ and $18 \times 18 \times 1$. For ML ReS_2 the difference is $\leq 23\text{meV}$ between the grids $9 \times 9 \times 1$ and $12 \times 12 \times 1$. It was concluded that the grid densities are sufficient for converging the G_0W_0 QP energies with an uncertainty of less than 25meV .

The VASP settings for the G_0W_0 calculations of the ML MoX_2 and ML ReS_2 structures are listed in tab. A.3 and A.9.

5.7.1 Wannier Interpolation

The G_0W_0 solution includes the dispersion relation for all k-points within the BZ. However, the specified grid densities would not result in a band structure with a useful resolution. The results can be interpolated to a finer grid by using a transformation from the KS Bloch eigenfunctions to a basis of Wannier functions (eq. 2.12). This basis typically consists of wave functions that mimic the orbital wave function of all involved atoms. Orbitals that do not participate in bonding are usually neglected from the calculations. All filled inner shells were therefore ignored in the process of wannierization. Furthermore all s-orbitals (Mo 4s, Re 5s, S 3s, Se 4s, Te 5s) and metal p-orbitals (Mo 4p, Re 5p) were not considered. Therefore, only Mo 4d, S 3p, Se 4p and Te 5p (Re 5d, S 3p) orbitals were taken into account in the case of MoX_2 ML (ReS_2 ML) structures. More details on this band selection are given in tab. 5.15 and 5.16.

Table 5.15.: MoS_2 ML: band inclusion details for the wannierization step - MoS_2 ML: band inclusion details for the wannierization step

Orbital	E (POTCAR)	Bands	Occupation	Atoms	Inclusion	Band Range
Mo 4s	-62.1983	2	2	1	no	1-2
Mo 4p	-36.4414	6	6	1	no	3-8
S 3s	-17.2562	2	2	2	no	9-12
S 3p	-7.0085	6	4	2	yes	13-24
Mo 4d	-2.3086	10	6	1	yes	25-34
various					no	>35

Table 5.16.: ReS_2 ML: band inclusion details for the wannierization step

Orbital	E (POTCAR)	Bands	Occupation	Atoms	Inclusion	Band Range
Re 5s	-81.2979	2	2	4	no	1-8
Re 5p	-43.3311	6	6	8	no	9-32
S 3s	-17.2562	2	2	8	no	33-48
S 3p	-7.0085	6	4	4	yes	49-96
Re 5d	-2.9212	10	7	4	yes	97-136
various					no	>137

The software Wannier90 version 2.1.0 (ref. [wan]) was compiled and included in the VASP makefile, which is listed in lst. A.36. After a successful G_0W_0 calculation, Wannier90 was launched with the VASP INCAR file flags `LWANNIER90=.TRUE.` and `ALGO=None`. The wannier90.win configuration files for MoX_2 and ReS_2 are listed in lst. A.34 and A.35.

5.8 BSE Calculations

The G_0W_0 QP energies and orbitals were used as a starting point for the BSE computations. The number of occupied and virtual states (NBANDSO and NBANDSV flags) are crucial for the accuracy of the BSE results. For MoX_2 both values were set to 16 in accordance with ref. [Mav16]. For ReS_2 this setting was reduced to 8 because otherwise, the required memory would have exceeded the available memory capacity. The calculation of excitonic lifetimes requires accurate results for the lowest excitonic states (eq. 2.36) only, because at room temperature only the lowest four excitons were found to dominate the effective radiative lifetime. In ref. [Mav16] it is also shown that eight occupied and virtual bands are sufficient for converging the result in the low energy range. Therefore this setting was adopted.

The VASP settings for the BSE calculations of ML MoX_2 and ML ReS_2 are listed in tab. A.4 and A.10. The BSE-related methods are discussed in the following subsections.

5.8.1 Excitonic Composition

The evaluation of the excitonic lifetime for an exciton state Λ requires the calculation of the exciton reduced effective mass (eq. 3.11). This involves the determination of effective masses on either the valence and conduction bands in the vicinity of the largest excitonic contribution in k-space, i.e., the largest coefficient $|A_{\Lambda}^{v,c,\vec{k}}|$ (eq. 2.31). Therefore the composition of the lowest excitonic states was analyzed with the NBSEEIG=32 VASP flag. This setting enables the export of detailed information about (the lowest 32) excitonic states to the BSEFATBAND file.

An excitonic state can be visualized in reciprocal space, where each pair of valence and conduction bands v, c at vector $\vec{k}$ has a specific electron-hole-pair amplitude $A_{\Lambda}^{v,c,\vec{k}}$. These quantities are usually drawn by applying their magnitudes to radii of circles, which are placed on the corresponding states in the BS. The disadvantage of this method is that outside of the BS path there could exist larger amplitudes to the excitonic state. Furthermore, all data in the BSEFATBAND file is presented with the density of the k-point grid used by the BSE calculation. Therefore, it is a common practice to interpolate this data to the desired density of the band structure, by using further calculations. Hence, the content of the BSEFATBAND file was visualized directly in the 2D BZ of the structures to avoid subsequent costly computations. In fig. 5.17, a visualization example is shown.

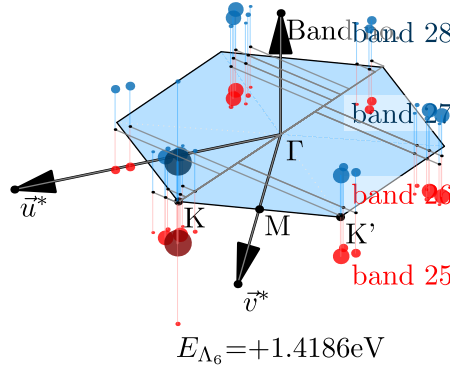


Figure 5.17.: Visualization example of the contributions to exciton 6 in MoTe_2

In fig. 5.17, different bands are represented by separate flat layers, which are stacked along the $\hat{z}$ -axis. The largest electron-hole-pair amplitudes are visualized with darker red (blue) spheres of a predefined maximum radius. All other spheres have a brighter color and smaller radii, which are interpolated according to their corresponding amplitudes.

5.8.2 Optical spectra

The probability of an interaction with photons can be assigned to each excitonic state Λ . VASP exports this data to the `opticaltransitions` section of the `vasprun.xml` file. This quantity is proportional to the Cartesian sum of the squared weighted dipole operators (eq. 2.30),

$$I_{\Lambda} \propto |\langle M_x | A_{\Lambda} \rangle|^2 + |\langle M_y | A_{\Lambda} \rangle|^2 + |\langle M_z | A_{\Lambda} \rangle|^2.$$

In this thesis, these probabilities I_{Λ} are visualized with respect to the exciton energies E_{Λ} . Orange color, `RGB[1.0,0.75,0.0]`, was assigned to the state with the highest probability of photon interaction within the arbitrary energy plot range. All other state colors were linearly interpolated to the color gray with respect to the corresponding transition probability. The color gray, `RGB[0.5,0.5,0.5]`, represents states without any photonic interaction probabilities.

Another way to visualize the optical properties of a structure is the absorption spectrum, which is calculated through the macroscopic dielectric tensor. This tensor is exported to the `dielectricfunction` section of the `vasprun.xml` file. The bash script `extract_optics.sh` (listed in A.33) was used to extract the real and imaginary part of the dielectric tensor into the files `REAL.IN` and `IMAG.IN`. These files were then read by the software VASPKIT (ref. [kit]), which calculated the extinction coefficient tensor κ_{ij} and other optical data. The absorption coefficient tensor α_{ij} could be calculated with the extinction coefficient tensor (ref. [Bec15, p. 433])

$$\alpha_{ij}(\omega) = \frac{2\omega}{c} \kappa_{ij}(\omega).$$

Thus, the `linearoptics.f90` file of VASPKIT was modified for calculating the absorption coefficient tensor directly (lst. A.37). The absorbance tensor A_{ij} for MLs was then calculated by using the Beer–Lambert law, along with the height h of the unit cell,

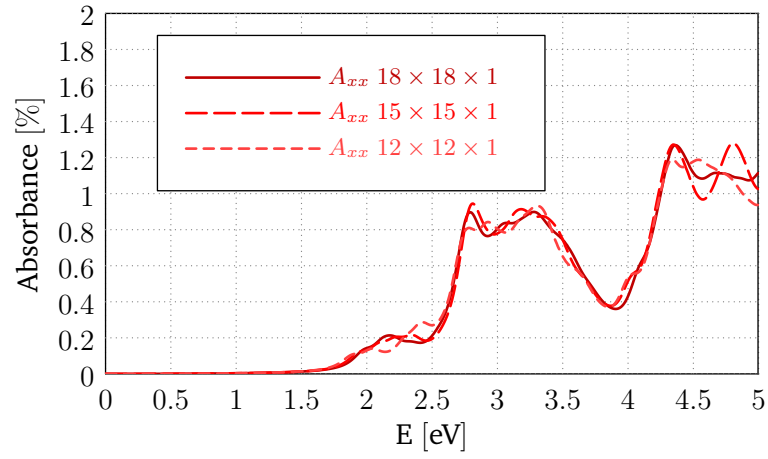
$$\frac{I}{I_0} = 10^{-\alpha_{ij} \cdot h} \Rightarrow A_{ij} = \alpha_{ij}(\omega) \frac{h}{\log_{10} e}.$$

In few-layer structures, it is common practice to visualize the imaginary part of the dielectric function ϵ_2 with respect to photon energy for a photon propagation direction $\hat{q}$ of interest. The dielectric function can be calculated for a particular direction by using its relationship to the dielectric tensor eq. 2.22.

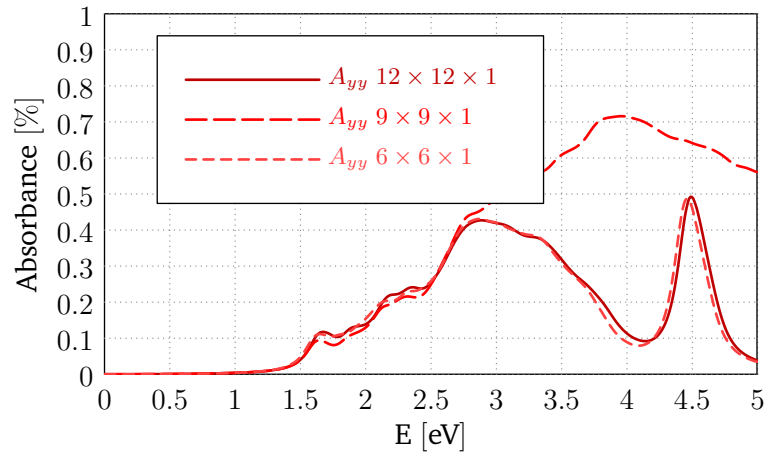
5.8.3 Grid Density

Another critical parameter to the convergence of the BSE calculation is the k-point grid density. Thus, the absorbance spectra for various k-points grid densities were compared for each structure. The available memory capacity limited the calculations to a $12 \times 12 \times 1$ ($18 \times 18 \times 1$) grid for ReS_2 (MoX_2) structures. The absorbance spectra below the largest BG energy ($\approx 2.6\text{eV}$ for MoS_2) showed only minor differences between the two most dense grids. Therefore the highest available densities were considered as being sufficient for describing bound excitonic states. The comparisons of absorbance spectra for various grid densities are visualized in fig. 5.18 and A.28.

The grid density is incorporated in the formula for the radiative decay rate (eq. 3.8). The number of k-points in the layer plane was set to $N_k = 18^2$ for the MoX_2 structures and $N_k = 12^2$ for the ReS_2 structure.



(a) MoS₂



(b) ReS₂

Figure 5.18.: MoS₂ ML and ReS₂ ML: absorbance spectrum vs. k-point densities
- The reader is referred to sec. 5.8.2 for a detailed explanation on how the data is visualized.

Results and Discussion

6.1 Introduction

In this chapter, the mathematical derivation, computational development, and methods (ch. 3, 4, and 5) are applied to the well-known MoX₂ structures. The resulting BSs, BG energies, optical spectra, excitonic amplitudes, and radiative lifetimes are compared to what is presented in the existing literature. After successful validation, the same methods are applied to the anisotropic ReS₂ structure, where new results are expected and discussed.

6.2 Molybdenum Dichalcogenides Monolayer

6.2.1 Structure Relaxation

The first step for all subsequent calculations was to obtain the relaxed ML MoX₂ structures. In tab. 6.1 the relaxation results for the ML MoX₂ structures with the SCAN functional are summarized together with DFT-PBE results of ref. [Lia+13].

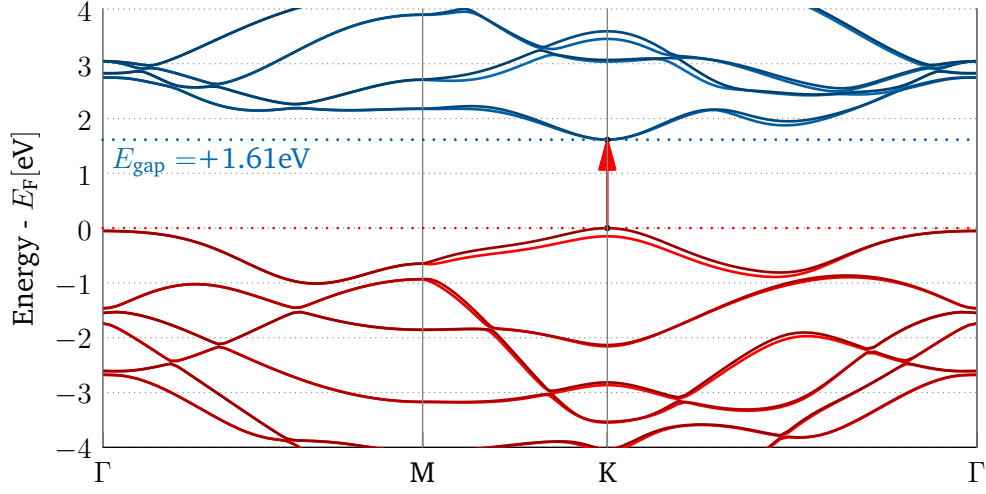
Table 6.1.: MoX₂ ML: relaxation results and comparison - MoX₂ ML: relaxation results and comparison

Structure	a [Å]	Ref. DFT [Å]	Dev. to Ref. DFT [%]
MoS ₂	3.172	3.18	-0.24
MoSe ₂	3.300	3.31	-0.30
MoTe ₂	3.514	3.51	+0.11

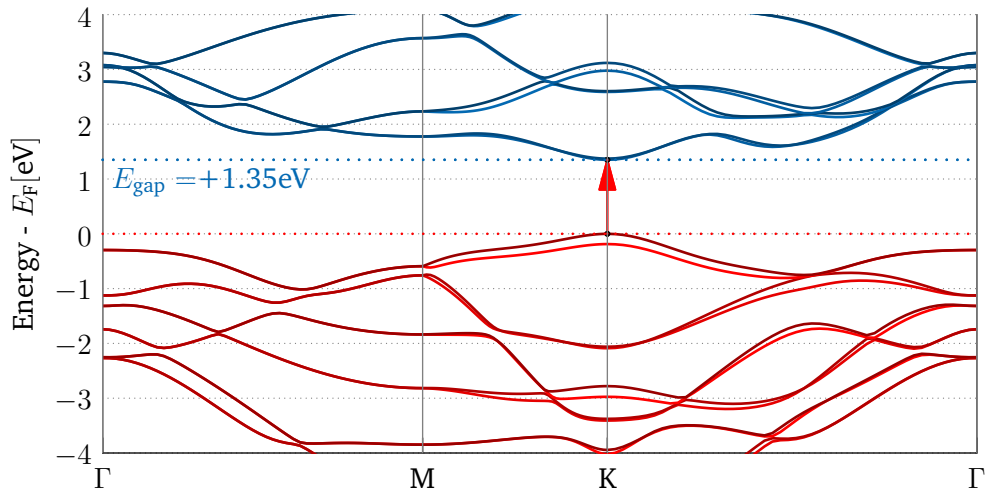
The SCAN functional performed comparably as well as the DFT-PBE functional, and it performed even better for MoS₂ and MoSe₂, where the overestimation of the lattice parameter a compared to experiment was smaller ($a_{\text{MoS}_2}^{\text{exp}} = 3.149$, $a_{\text{MoSe}_2}^{\text{exp}} = 3.288$).

6.2.2 DFT Band Structures

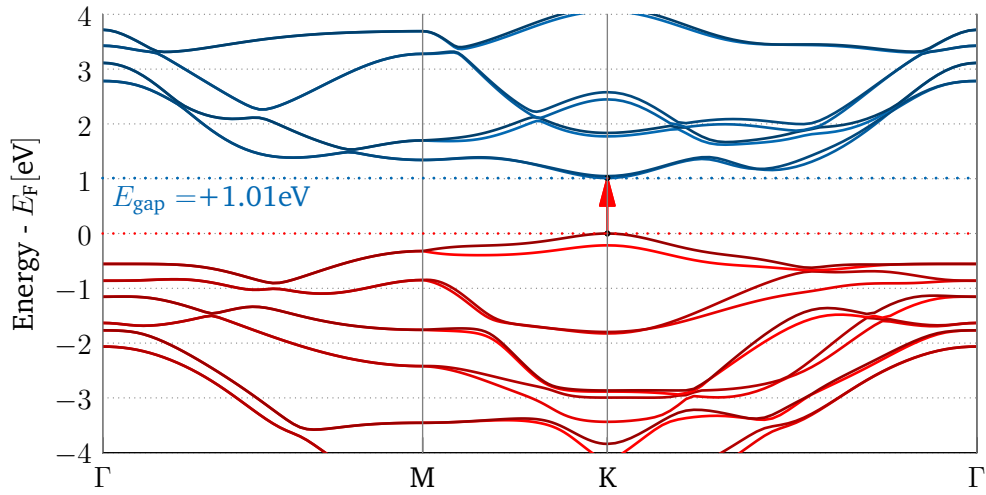
The SCAN functional was further used to calculate the BSs, which were needed to obtain the effective masses for particular excitonic states. The results are condensed in fig. 6.2, tab. 6.3, and 6.4, where the BSs are depicted and analyzed concerning BG energies and spin-orbit splittings, in comparison to reference values, respectively.



(a) MoS₂



(b) MoSe₂



(c) MoTe₂

Figure 6.2.: MoX₂ ML: DFT band structures - SOC effects are included. The red arrow visualizes the band gap. The valence band maximum is set to zero energy. The reader is referred to sec. 5.4 and 5.5 for a detailed explanation on how the data is visualized.

Table 6.3.: MoX₂ ML: DFT band gap energy results and comparison - MoX₂ ML: DFT band gap energy results and comparison

Structure	DFT BG [eV]	DFT BG Ref. 1 [eV]	DFT BG Ref. 2 [eV]
MoS ₂	1.61	1.58	1.69
MoSe ₂	1.35	1.32	1.43
MoTe ₂	1.01	0.93	1.10

Table 6.4.: MoX₂ ML: DFT SOC splitting of valence and conduction bands - MoX₂ ML: DFT SOC splitting of valence and conduction bands

Structure	Δ_v [meV]	Δ_c [meV]	Δ_v Ref. [meV]	Δ_c Ref. [meV]
MoS ₂	149	3	150	0
MoSe ₂	187	22	190	20
MoTe ₂	216	36	230	40

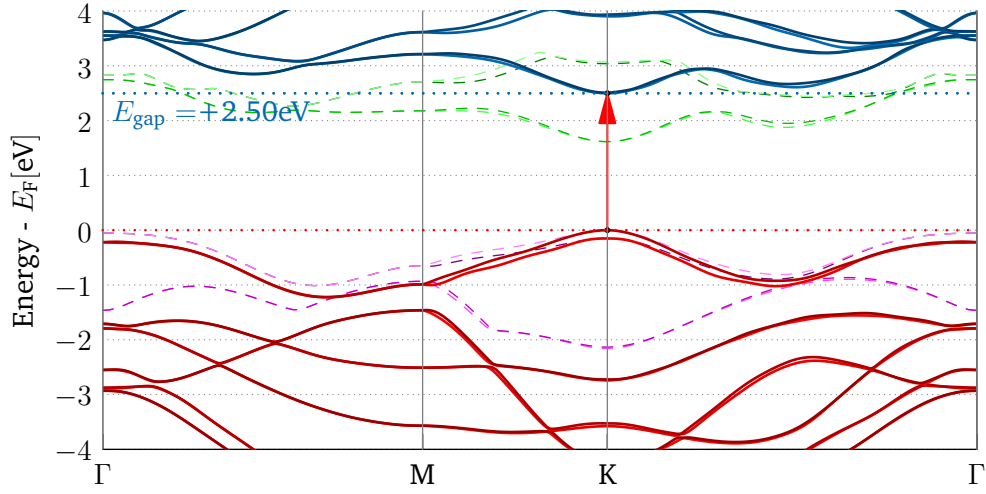
It is a well-known feature of ML molybdenum dichalcogenides to exhibit direct BGs. This property is found in all resulting band structures at the expected K point in reciprocal space. The BG energies decrease with increasing period of the chalcogenide, and are found to be in good agreement to ref. [RT15] resp. [Lia+13], where DFT-LDA resp. DFT-PBE functionals were used. Since relativistic effects are increasingly pronounced in more massive ions, the spin-orbit coupling induced splittings of the valence and conduction bands at point K increase with increasing period of the chalcogenide atom. Similar results are found in ref. [RT15]. The SCAN functional and its resulting structures were therefore considered as good starting points for further investigations.

6.2.3 G_0W_0 Band Structures

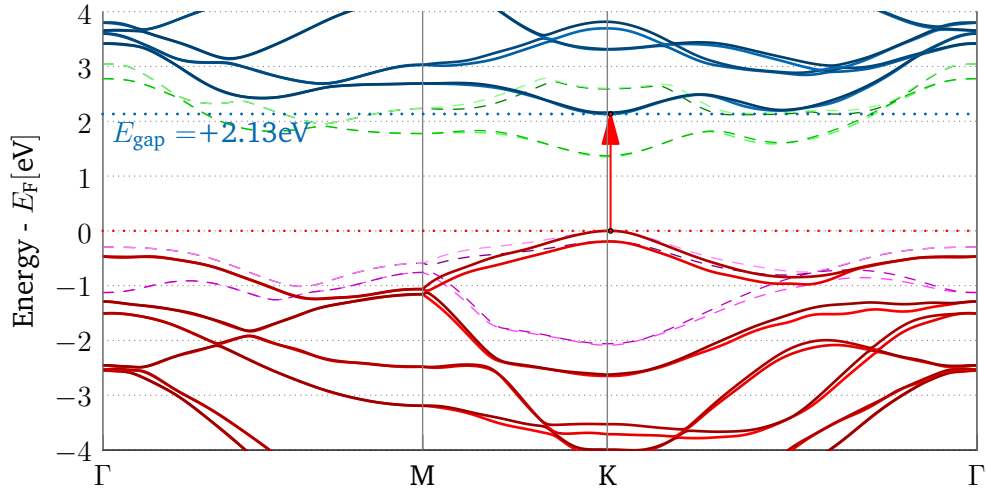
The excitonic effects gained by the BSE, like radiative lifetimes, are premised on QP corrections. G_0W_0 calculations were performed in a preceding step to include screening effects. In fig. 6.5, the G_0W_0 BSs, which were obtained via wannierization, are visualized. In tab. 6.6 the G_0W_0 BG energies are compared to literature results.

A comparison of fig. 6.5 with the DFT BSs and BGs shows that the BGs opened up by mainly shifting the conduction bands upwards in energy. These shifts are due to the QP screening effects, which are taken into account through the GW approximation. Moreover, the curvature of the BSs shows great similarities to the DFT results in the vicinity of the relevant symmetry points Γ and K. Thus effective masses were calculated from DFT BSs.

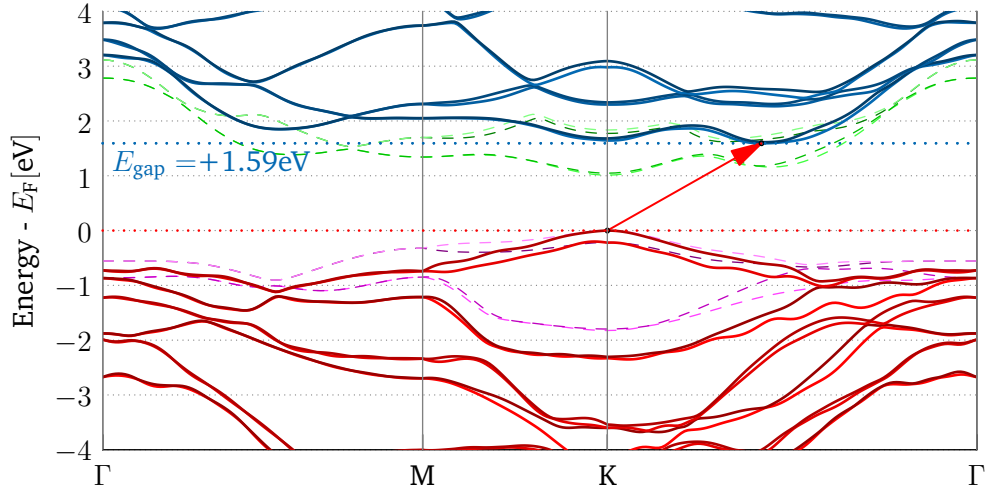
When comparing the resulting G_0W_0 BGs to literature values, it turns out that the results are smaller by roughly 0.2eV. This discrepancy is probably due to the lower number of virtual states taken into account for calculating the screening effects in



(a) MoS₂



(b) MoSe₂



(c) MoTe₂

Figure 6.5.: MoX₂ ML: G₀W₀ band structure - SOC effects are included. The red arrow visualizes the band gap. The valence band maximum is set to zero energy. The dashed lines represent the corresponding DFT band structure. The reader is referred to sec. 5.4 and 5.7 for a detailed explanation on how the data is visualized.

Table 6.6.: MoX₂ ML: G₀W₀ band gap energy results and comparison - MoX₂ ML: G₀W₀ band gap energy results and comparison

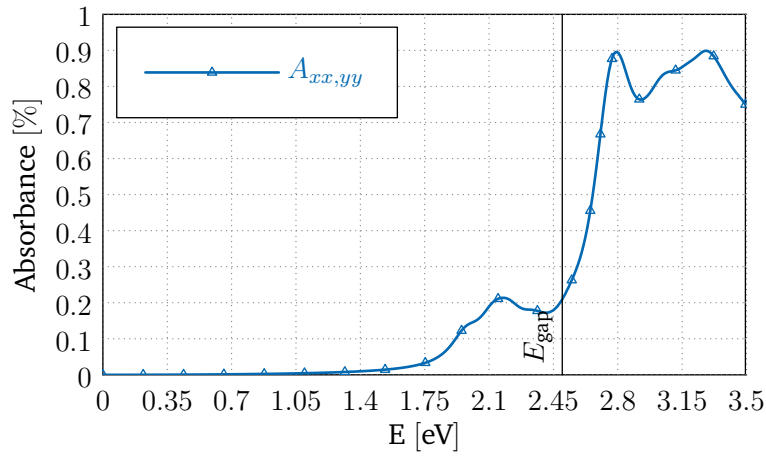
Structure	G ₀ W ₀ BG [eV]	Ref. G ₀ W ₀ BG [eV]
MoS ₂	2.50	2.75
MoSe ₂	2.13	2.33
MoTe ₂	1.59	1.82

the present case. Due to hardware limitations, only 512 bands in total were used, whereas in ref. [Lia+13, p. 2] 1500 conduction bands were included. Convergence issues are present in the case of MoTe₂, where the G₀W₀ corrections shifted the conduction band minimum at point K slightly higher up in energy than the second minimum along K- Γ . As a consequence, ML MoTe₂ became an indirect semiconductor, which is not the case in ref. [Lia+13, p. 2]. Nevertheless, the computations were continued with 512 bands for allowing a comparison of the subsequent BSE results with literature. In the case of the MoTe₂ G₀W₀ BS one remark is necessary regarding the oscillatory disturbances in the valence band region between the points K and Γ . The same process of wannierization was applied to all MoX₂. However, in the case of MoTe₂ the set of local Wannier functions is insufficient for a converged BS. Hence, these bands are not further used.

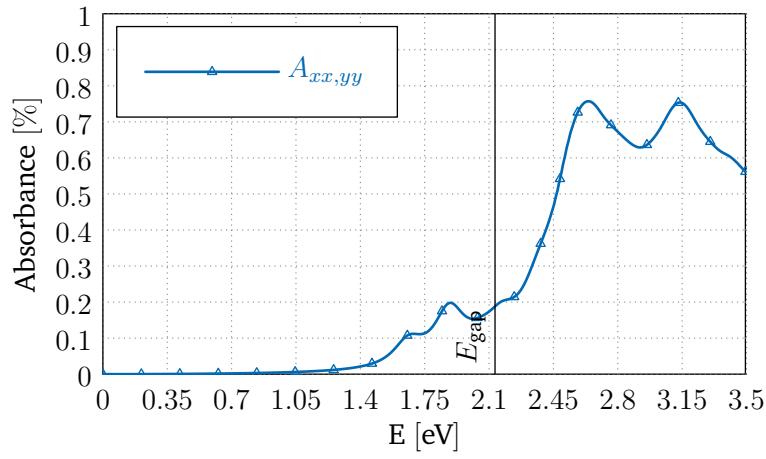
6.2.4 Absorption Spectrum

With the knowledge of the QP energies, the BSE can be calculated. From these results, the optical properties, including excitonic effects, can be investigated. In fig. 6.7 absorbance spectra for ML MoX₂ structures are shown.

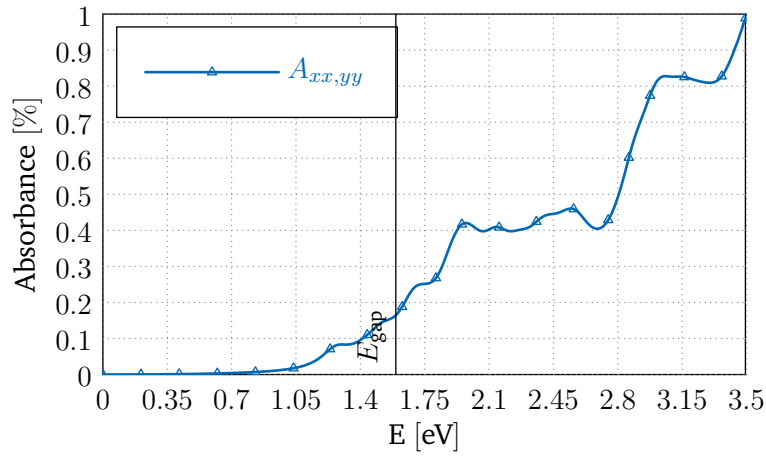
In all MoX₂ structures, the absorbance tensor matrix elements A_{xx} and A_{yy} show an almost identical spectrum. Therefore, the simulated structures reveal isotropic optical properties as expected. Furthermore, the ML structures show a negligible A_{zz} matrix element, confirming the fact, that there is almost zero interaction for photon momenta perpendicular to the thin ML structure. Furthermore, the absorbance spectra show peaks below the BG energy which can be attributed to absorption processes that lead to the formation of excitons.



(a) MoS₂



(b) MoSe₂



(c) MoTe₂

Figure 6.7.: MoX₂ ML: absorbance spectra - The reader is referred to sec. 5.8.2 for a detailed explanation on how the data is visualized.

6.2.5 Excitonic States

The evaluation of radiative lifetimes requires to analyze excitonic states in more detail. In tab. A.25, A.26, and A.27, the BSE output of the modified VASP code (ch. 4) is listed. In fig. 6.8, the photon interaction probabilities, with respect to the exciton energies, are visualized.

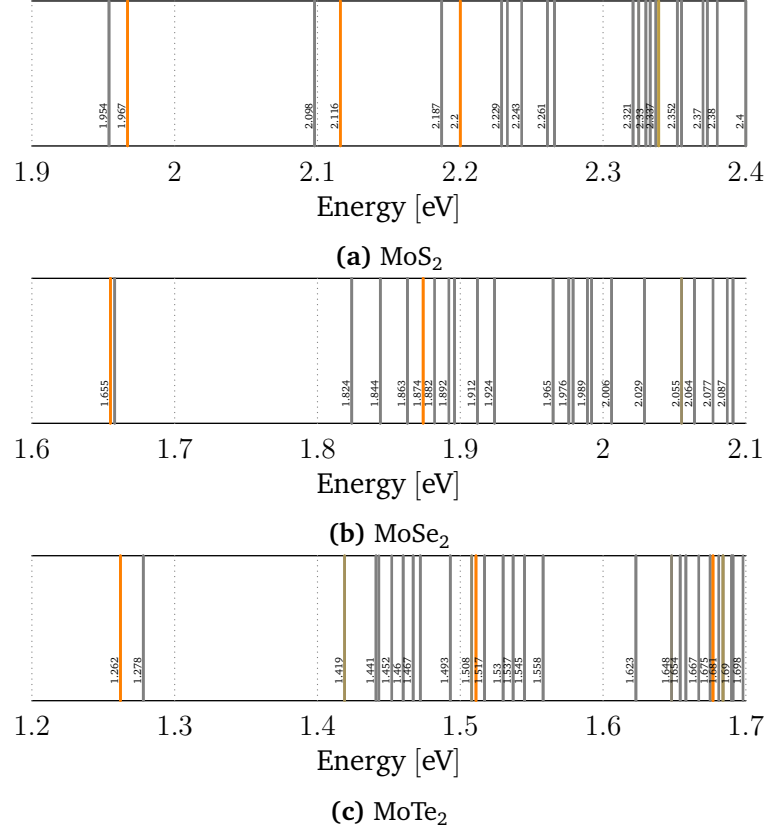


Figure 6.8.: MoX₂ ML: exciton energies vs. interaction probabilities - The reader is referred to sec. 5.8.2 for a detailed explanation on how the data is visualized.

The BSE results show exciton state pairs with degenerate energies. It was expected to find excitonic state pairs due to the broken inversion symmetry in ML structures, as addressed in sec. 5.4.1. To confirm this, the composition of these degenerate states will be examined later in this chapter in more detail.

The resulting energies of the lowest two state pairs for MoS₂ lie closer together (fig. 6.8a) than in the ref. [Pal+15, fig. 2]. The lowest state pair are dark states and the second lowest are bright, in accordance with the reference. In MoSe₂ the energies of the two lowest state pairs are even closer together (fig. 6.8b). The lowest state pair is bright and the second lowest one are dark states. However, opposite behavior, i.e., the same as for MoS₂, is reported in ref. [Pal+15].

For allowing to relate all subsequent results to the reference, an explanation of this discrepancy had to be found. Hence, this issue might be explained as follows. The

k-point grid density is primarily suspected to have the greatest impact on the energy difference between the excitonic states. Hence, in fig. 6.9, the exciton energies for different k-point grid densities are compared to the ref. [Pal+15].

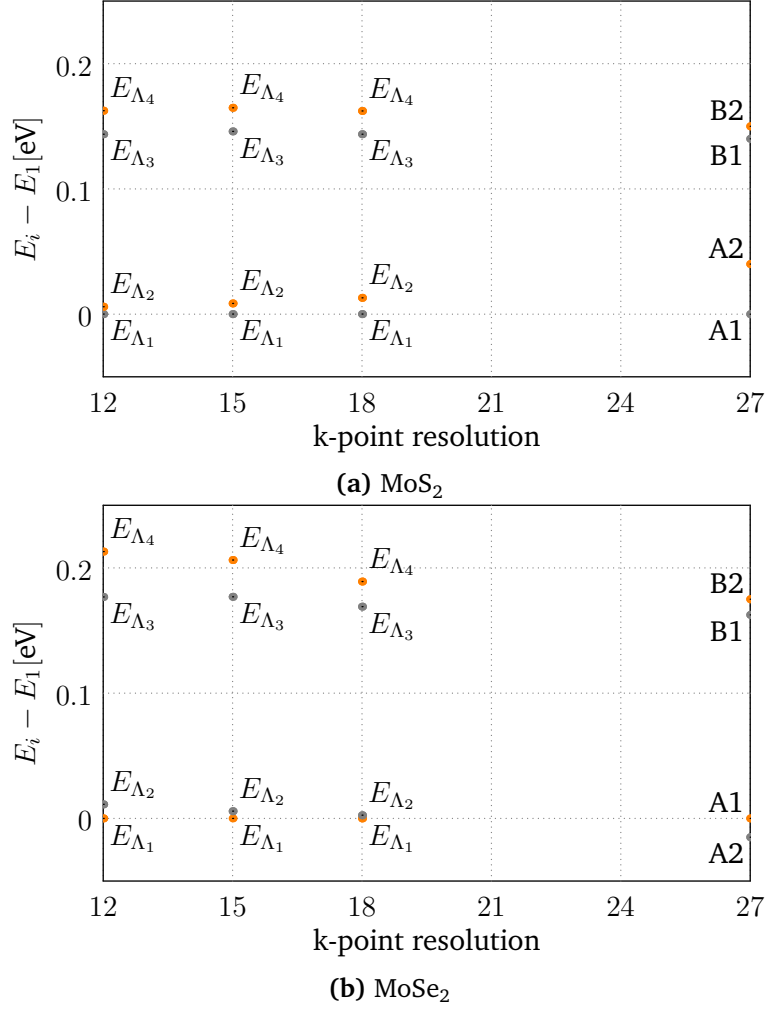


Figure 6.9.: MoX₂ ML: exciton energies vs. k-point grid densities - Energy differences are presented with respect to the lowest excitonic state pair of each density. Data for grid density 12, 15 and 18 are results of this thesis, data for density 27 is taken from ref. [Pal+15, fig. 2].

These findings show an almost linear dependence between the energy differences of the lowest excitonic states and the k-point density. In ref. [Pal+15, fig. 2] a dense k-mesh of $27 \times 27 \times 1$ is used. A linear extrapolation of the simulated data results in a similar state pair ordering as found in the reference. With the gained insight, that the two lowest excitonic states in MoSe₂ are inversely ordered, it was now possible to compare all subsequent results to the results in ref. [Pal+15].

6.2.6 Excitonic Compositions

The determination of the radiative lifetimes requires to calculate effective masses, for which the electron-hole pair amplitudes on every band of the BS has to be analyzed. These excitonic compositions are visualized in fig. 6.10, resp. A.29, and A.30, for the MoS₂, MoSe₂, and MoTe₂ structures.

These visualizations show that all excitonic states are highly localized in the BZ or delocalized in real space. Either of the two excitonic states of the pairs (1&2, 3&4, 5&6, and 7&8) have electron-hole-pair amplitudes on the same bands, where the k-point K is more pronounced in one state and K' in the other state. It was therefore concluded, that these degenerate states are in fact the result of the broken inversion symmetry (ref. [Mak+12]). In contrast to the field of valleytronics, it was assumed, that radiative lifetime experiments are carried out with photonic states, that are described by a perfect superposition of left/right circularly polarized states (e.g. $\frac{1}{\sqrt{2}}(|l\rangle + |r\rangle)$). In this case, one-half of the photons participate in excitations at the K point, and the other half in excitations at the K' point of the BZ. Due to the similar BS in the vicinity of these two symmetry points, the values for the radiative lifetimes were arithmetically averaged over the corresponding excitonic states of a pair.

6.2.7 Effective Masses

According to sec. 6.2.3, the reduced effective exciton masses were deduced from the DFT BSs, by using the methods of sec. 5.6. Due to the symmetry of the hexagonal unit cell at point K, the effective masses could be averaged over the two directions $K \rightarrow M$ and $K \rightarrow \Gamma$, for increasing the precision of the quantities (ref. [RT15, sec. 3.5]). In fig. 6.11, resp. A.23, the parabolic fit functions are depicted. In tab. A.24, the resulting electron and hole masses, for either valence and conduction bands, are listed. From these quantities, the reduced effective masses for the lowest eight excitonic states were calculated (tab. 6.12).

The comparison of the resulting effective masses with the DFT-PBE+G₀W₀ results of ref. [RT15, tab. 5] shows a deviation of less than 20%. The effective masses are found to increase with increasing period of the chalcogenide atom. Given the fact that the accuracy of the effective masses is restricted by many evaluation steps, the obtained DFT SCAN values conform well with the DFT-PBE+G₀W₀ results.

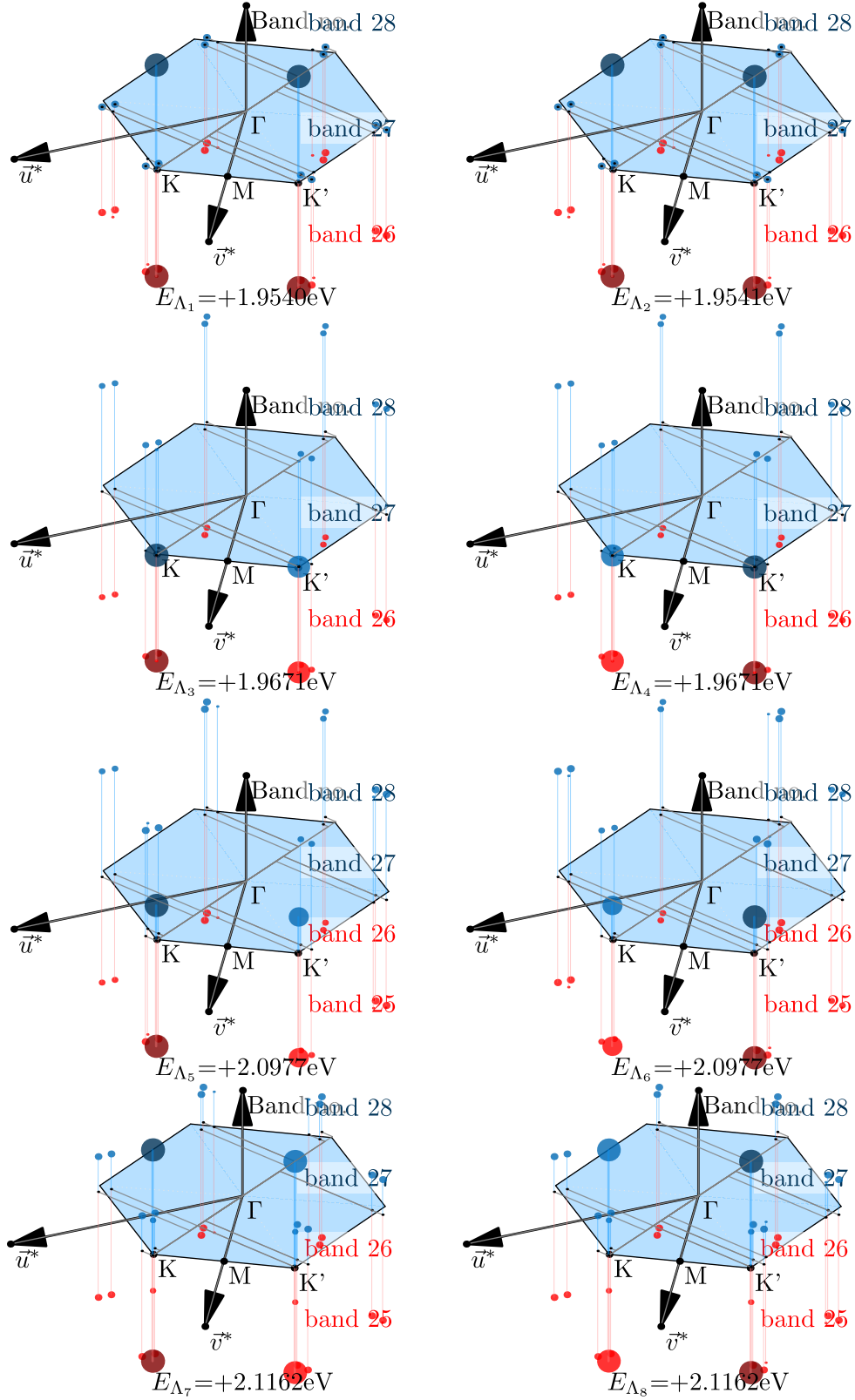


Figure 6.10.: MoS₂ ML: contributions to excitons 1-8 - The reader is referred to sec. 5.8.1 for a detailed explanation on how the data is visualized.

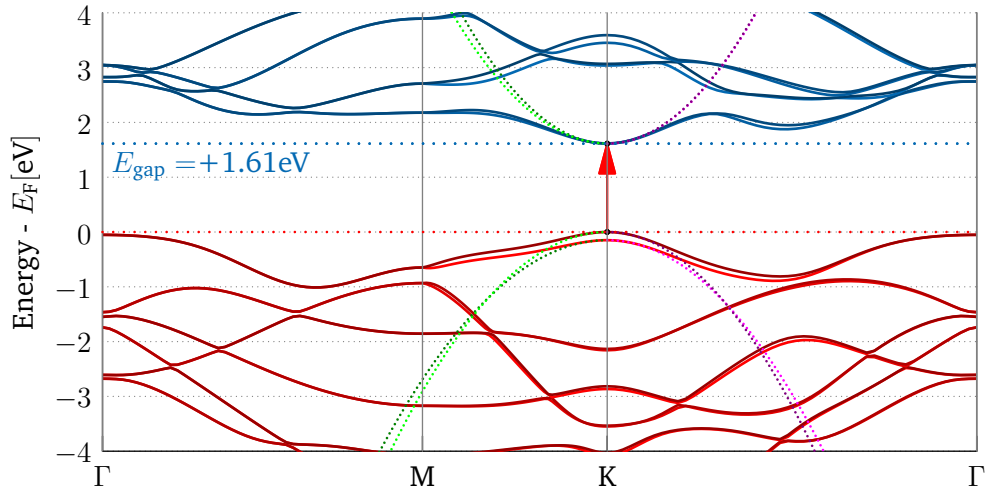


Figure 6.11.: MoS₂ ML: fit functions for the effective mass approximation - The reader is referred to sec. 5.6 for a detailed explanation on how the data is visualized.

Table 6.12.: MoX₂ ML: exciton reduced masses - MoX₂ ML: exciton reduced masses

Exciton	Val. Band	Cond. Band	m_{hole}	m_{e-}	M_{Λ}
MoS ₂ 1, 2	26	28	0.55	0.47	0.25
MoS ₂ 3, 4	26	27	0.55	0.44	0.25
MoS ₂ 5, 6	25	27	0.62	0.44	0.26
MoS ₂ 7, 8	25	28	0.62	0.47	0.27
MoSe ₂ 1, 2	26	27	0.59	0.48	0.26
MoSe ₂ 3, 4	26	28	0.59	0.55	0.28
MoSe ₂ 5, 6	25	27	0.69	0.48	0.28
MoSe ₂ 7, 8	26	27	0.59	0.48	0.26
MoTe ₂ 1, 2	26	27	0.63	0.51	0.28
MoTe ₂ 3, 4	26	28	0.63	0.59	0.31
MoTe ₂ 5, 6	26	27	0.63	0.51	0.28
MoTe ₂ 7, 8	26	28	0.63	0.59	0.31

6.2.8 Exciton Radiative Lifetimes

The weighted interband matrix elements of the BSE results (lst. A.25, A.26, A.27), along with the exciton reduced masses (tab. 6.12), were used for the calculation of the the radiative lifetime $\tau_{\Lambda}^{\text{rad}}(0)$ (eq. 3.8) and the thermally averaged lifetime $\tau_{\Lambda}^{\text{rad}}(300)$ (eq. 3.11). Due to the symmetry of the hexagonal unit cell at k-point K it holds $\sqrt{M_{\Lambda xx}M_{\Lambda yy}} = M_{\Lambda}$. These quantities were calculated for the lowest eight excitonic state pairs of all three materials. The effective lifetime $\gamma_{\text{eff}}^{\text{rad}}(300)$ was calculated according to eq. 2.36. State pairs beyond the lowest eight ones had changed the effective lifetime less than 1%, and were therefore neglected. In tab. 6.13, 6.14, 6.15, and 6.16 the final results of the radiative lifetime calculations are listed, along with a comparison to the values taken from ref. [Pal+15, p. 2796].

Table 6.13.: MoS₂ ML: radiative lifetimes - MoS₂ ML: radiative lifetimes

Exciton	$\tau_{\Lambda}^{\text{rad}}(0)$ [s]	$\tau_{\Lambda}^{\text{rad}}(300)$ [s]	Exciton ^{ref}	$\tau_{\Lambda}^{\text{rad}}(0)$ [s]	$\tau_{\Lambda}^{\text{rad}}(300)$ [s]
E_{Λ_1}	170×10^{-12}	230×10^{-9}			
E_{Λ_2}	170×10^{-12}	230×10^{-9}			
$E_{\Lambda_{1,2}}$ (dark)	170×10^{-12}	230×10^{-9}	A_1	$59 \cdot 10^{-3}$	
E_{Λ_3}	220×10^{-15}	270×10^{-12}			
E_{Λ_4}	220×10^{-15}	270×10^{-12}			
$E_{\Lambda_{3,4}}$ (bright)	220×10^{-15}	270×10^{-12}	A_2	$230 \cdot 10^{-15}$	$270 \cdot 10^{-12}$
E_{Λ_5}	310×10^{-12}	370×10^{-9}			
E_{Λ_6}	320×10^{-12}	370×10^{-9}			
$E_{\Lambda_{5,6}}$ (dark)	310×10^{-12}	370×10^{-9}	B_1	$81 \cdot 10^{-6}$	
E_{Λ_7}	170×10^{-15}	210×10^{-12}			
E_{Λ_8}	170×10^{-15}	210×10^{-12}			
$E_{\Lambda_{7,8}}$ (bright)	170×10^{-15}	210×10^{-12}	B_2	$140 \cdot 10^{-15}$	

Table 6.14.: MoSe₂ ML: radiative lifetimes - MoSe₂ ML: radiative lifetimes

Exciton	$\tau_{\Lambda}^{\text{rad}}(0)$ [s]	$\tau_{\Lambda}^{\text{rad}}(300)$ [s]	Exciton ^{ref}	$\tau_{\Lambda}^{\text{rad}}(0)$ [s]	$\tau_{\Lambda}^{\text{rad}}(300)$ [s]
E_{Λ_1}	230×10^{-15}	430×10^{-12}			
E_{Λ_2}	230×10^{-15}	430×10^{-12}			
$E_{\Lambda_{1,2}}$ (bright)	230×10^{-15}	430×10^{-12}	A_2	$240 \cdot 10^{-15}$	$380 \cdot 10^{-12}$
E_{Λ_3}	1.3×10^{-9}	2.7×10^{-6}			
E_{Λ_4}	1.5×10^{-9}	3.0×10^{-6}			
$E_{\Lambda_{3,4}}$ (dark)	1.4×10^{-9}	2.9×10^{-6}	A_1	$72 \cdot 10^{-6}$	
E_{Λ_5}	180×10^{-9}	300×10^{-6}			
E_{Λ_6}	180×10^{-9}	310×10^{-6}			
$E_{\Lambda_{5,6}}$ (dark)	180×10^{-9}	310×10^{-6}	B_1	$180 \cdot 10^{-6}$	
E_{Λ_7}	18×10^{-12}	28×10^{-9}			
E_{Λ_8}	17×10^{-12}	27×10^{-9}			
$E_{\Lambda_{7,8}}$ (bright)	18×10^{-12}	27×10^{-9}	B_2	$145 \cdot 10^{-12}$	

Table 6.15.: MoTe₂ ML: radiative lifetimes at 0K and 300K

Exciton	$\tau_{\Lambda}^{\text{rad}}(0)$ [s]	$\tau_{\Lambda}^{\text{rad}}(300)$ [s]
E_{Λ_1}	290×10^{-15}	1.0×10^{-9}
E_{Λ_2}	290×10^{-15}	1.0×10^{-9}
$E_{\Lambda_{1,2}}$ (bright)	290×10^{-15}	1.0×10^{-9}
E_{Λ_3}	68×10^{-9}	250×10^{-6}
E_{Λ_4}	70×10^{-9}	260×10^{-6}
$E_{\Lambda_{3,4}}$ (dark)	69×10^{-9}	260×10^{-6}
E_{Λ_5}	700×10^{-15}	2.0×10^{-9}
E_{Λ_6}	710×10^{-15}	2.0×10^{-9}
$E_{\Lambda_{5,6}}$ (bright)	700×10^{-15}	2.0×10^{-9}
E_{Λ_7}	78×10^{-6}	230×10^{-3}
E_{Λ_8}	79×10^{-6}	230×10^{-3}
$E_{\Lambda_{7,8}}$ (dark)	78×10^{-6}	230×10^{-3}

Table 6.16.: MoX₂ ML: effective radiative lifetimes - MoX₂ ML: effective radiative lifetimes

Structure	$\gamma_{\text{eff}}^{\text{rad}}(300)$ [s]	$\gamma_{\text{eff,ref}}^{\text{rad}}(300)$ [s]	$\gamma_{\text{eff,exp}}^{\text{rad}}(300)$ [s]
MoS ₂	$0.72 \cdot 10^{-9}$	$0.82 \cdot 10^{-9}$	$0.85 \cdot 10^{-9}$
MoSe ₂	$0.83 \cdot 10^{-9}$	$0.80 \cdot 10^{-9}$	$0.90 \cdot 10^{-9}$
MoTe ₂	$1.5 \cdot 10^{-9}$		

Compared to the ref. [Pal+15, p. 2799], all radiative lifetime results show a good consensus for bright excitons and a large deviation between the values for dark excitons. To understand this deviation, further tests are necessary. However, one main difference in the GW approximation between ref. [Pal+15] and the present work is that the plasmon-pole model was applied in case of the former. Nevertheless, dark states have negligible influence on the effective radiative lifetimes. The resulting effective radiative lifetimes (0.72ns for MoS₂ and 0.83ns for MoSe₂) are close to the reference values (0.85ns for MoS₂ and 0.90ns for MoSe₂). Within the series of MoX₂, the effective radiative lifetime increases with increasing period of the chalcogenide atom, resulting in 1.5ns for MoTe₂.

The experimental results stated in ref. [Pal+15], as well as in ref. [Moo+16, tab. 1], exhibit exciton effective radiative lifetime values ranging from 300ps to 850ps for MoS₂. In particular, various lower radiative lifetimes are reported (300ps, 360ps and 469ps). The large discrepancy may be caused by the dependence on the substrate type. Moreover, competitive interactions between radiative, non-radiative and annihilation processes of decay according to eq. 2.37 are possible.

To explain the possible overestimation of the calculated value, the influence of the k-point grid density on the result was analyzed. In tab. 6.17, the dependence of the MoS₂ effective radiative lifetime on the k-point grid is shown.

Table 6.17.: MoS₂ ML: effective radiative lifetimes vs. grid densities - MoS₂ ML: effective radiative lifetimes vs. grid densities

	$12 \times 12 \times 1$	$15 \times 15 \times 1$	$18 \times 18 \times 1$	Exponential Fit
MoS ₂ $\gamma_{\text{eff}}^{\text{rad}}(300)$	0.83	0.76	0.72	0.66

With increasing grid density the lifetime decreases. In order to estimate the converged value for $\gamma_{\text{eff}}^{\text{rad}}(300)$, an exponential fit was applied, yielding a result of 660ps.

It can be concluded, that for ML MoS₂ an effective radiative lifetime of 660ps seems plausible, given the fact that many other measurements result in values well below 850ps.

6.3 Rhenium Disulfide Bulk

To construct a ML ReS_2 structure, a bulk structure was created from experimental data taken from ref. [Mur+94]. Lattice parameters were obtained from the relaxation step and compared to reference data. The results are listed in tab. 6.18.

Table 6.18.: ReS_2 bulk: relaxation result and comparison - ReS_2 bulk: relaxation result and comparison

	a [Å]	b [Å]	c [Å]	V [Å ³]	α [deg]	β [deg]	γ [deg]
Result	6.402	6.546	6.484	220.169	121.35	88.28	106.54
Exp.	6.461	6.510	6.417	219.300	121.10	88.38	106.47
Dev. exp. [%]	-0.23	+0.55	+0.36	+0.40	+0.21	-0.12	+0.06

The comparison between the present data, obtained with the VdW-DFT functional, and experimental values, yields a good agreement. This emphasizes the importance of using functionals including VdW interactions for computing the structural properties of such materials.

6.3.1 DFT Band Structure

The BS of the bulk version of ReS_2 was evaluated to ensure a successful relaxation. In fig. 6.19, the DFT BS is depicted.

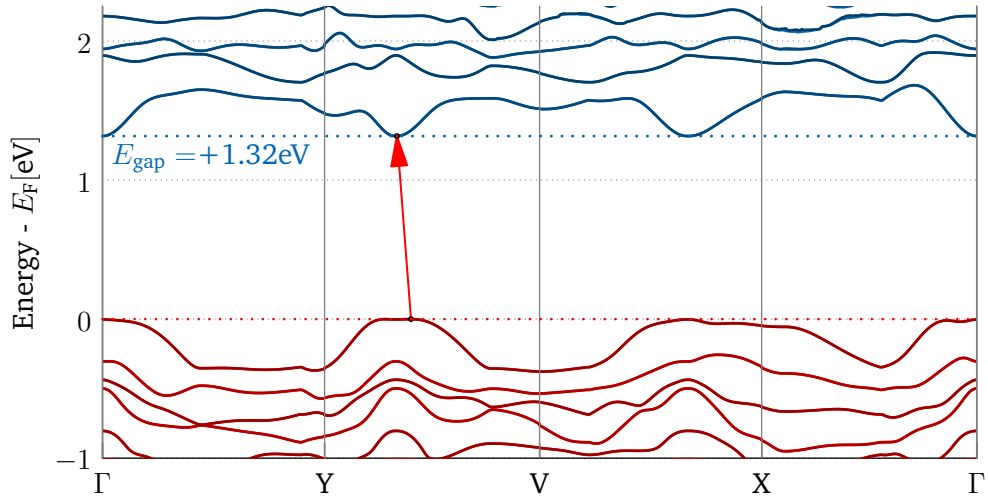


Figure 6.19.: ReS_2 bulk: DFT band structure - SOC effects are included. The red arrow visualizes the band gap. The valence band maximum is set to zero energy. The reader is referred to sec. 5.4 and 5.5 for a detailed explanation on how the data is visualized.

When focusing on the valence band region, the anisotropy of the system is clearly manifested along the Γ -Y and Γ -X directions.

The BS is compared with figure 4d of ref. [Geh+17]. The plane of the chosen BS path is coplanar to the Γ point. The dark blue lines in the figure of the reference

represent the same plane in reciprocal space. The reference symmetry point $\overline{M}'$ equals symmetry point Y. A good consensus between the BS section $\Gamma\text{-}\overline{M}'$ and $\Gamma\text{-Y}$ is found. Therefore the ML ReS_2 structure was built by using this bulk geometry as a starting point.

6.4 Rhenium Disulfide Monolayer

6.4.1 DFT Band Structure

The bulk structure was converted to a ML according to sec. 5.3.3. The DFT BS was then calculated for evaluating the electronic properties of the ML structure. Furthermore, the result was also used in the calculation of the effective masses. In fig. 6.20, the DFT BS is visualized.

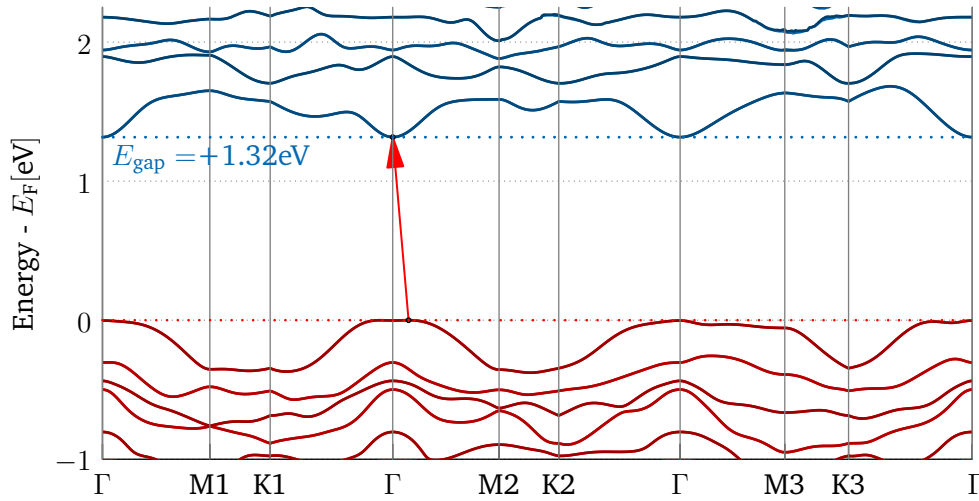


Figure 6.20.: ReS_2 ML: DFT band structure - SOC effects are included. The red arrow visualizes the band gap. The valence band maximum is set to zero energy. The reader is referred to sec. 5.4 and 5.5 for a detailed explanation on how the data is visualized.

All states at the band edges are found to be doubly degenerate.

The BS of the ReS_2 ML structure reveals an indirect BG, with a conduction band minimum located at the Γ point. The valence band maximum is located between the Γ and M2 points, often labeled as Z in literature. The energy of these valence band states differs marginally from the values at the Γ point. This little energy difference is the explanation for either direct and indirect experimental BG measurement results. In ref. [Geh+17, p. 5190], the BG was therefore considered as being a direct BG. The DFT BG energy of 1.32eV conforms well to the result of 1.36eV in ref. [Zho+15], where the DFT-PBE functional was used.

6.4.2 G_0W_0 Band Structure

Screening effects were included for the subsequent BSE calculations. Furthermore, the BS, obtained with wannierization, was compared to the DFT BS. In fig. 6.21, the G_0W_0 BS is visualized .

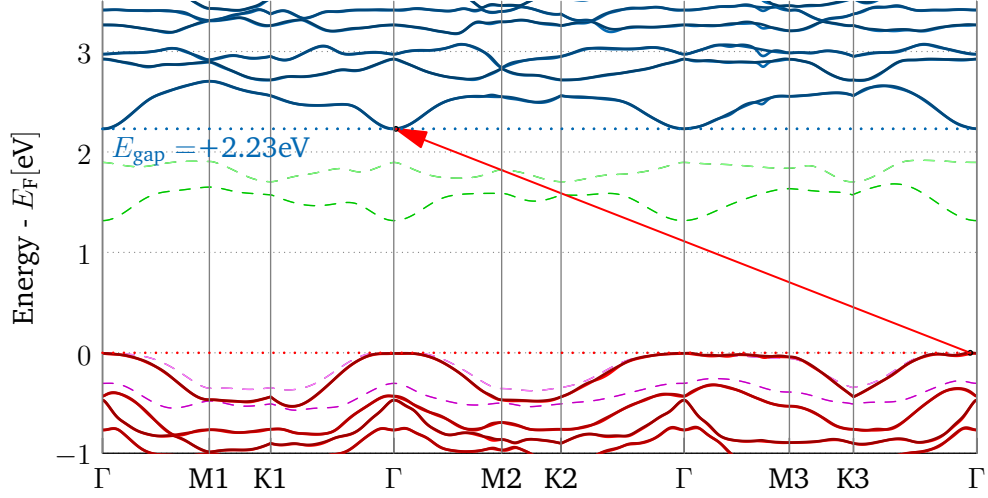


Figure 6.21.: ReS₂ ML: G_0W_0 band structure - Calculations are SOC enabled. The red arrow visualizes the band gap. The valence band maximum is set to zero energy. The dashed lines represent the corresponding DFT band structure. The reader is referred to sec. 5.4 and 5.7 for a detailed explanation on how the data is visualized.

As expected, the BG magnitude was increased by applying QP corrections. The BG energy of the G_0W_0 result is 2.23eV. Compared to ref. [Zho+15], where a G_0W_0 BG energy of 2.38eV is reported, the present result is slightly underestimated. This small discrepancy is probably due to different computational settings (e.g. number of virtual states, grid density).

A comparison with the DFT BS shows that the G_0W_0 screening effects decrease the valence band energy difference between the points Γ and Z, resulting in an almost flat dispersion relation on the path between these points. An explanation for this finding is found in ref. [Zho+15, p.8], where it is stated, that the self-energy depends on the spatial localization of the states. The valence states at point Z have a higher contribution of d-orbitals than the states at the Γ point, thus leading to a different self-energy correction in those two points.

Calculations beyond single shot G_0W_0 revealed no significant changes of the BS in ref. [Zho+15]. Therefore the G_0W_0 QP orbitals were employed for the subsequent BSE calculation.

Oscillatory disturbances are seen in the wannierization result, similar to the MoX₂ structures. The curvature of the DFT BS appears to be equivalent to the result of the G_0W_0 calculation in the vicinity of the relevant symmetry point Γ . Therefore the DFT BS was used for the calculation of the effective masses.

6.4.3 Excitonic States

The QP corrections of the G_0W_0 calculation were used as a starting point for the BSE calculation. The inclusion of excitonic effects is crucial for the calculation of accurate optical spectra, and necessary for the computation of radiative lifetimes. The output of the modified VASP BSE code, as listed in lst. 6.22, was further analyzed to discuss the excitonic effects in ReS_2 ML. In fig. 6.23, the obtained transitions probabilities with respect to excitonic energies are visualized.

Listing 6.22: ReS_2 ML: BSE output of the modified VASP - This output shows the energies and weighted interband matrix elements for the lowest eight excitonic states. The VASP modification is described in ch. 4.

[..]								
<v>	1.60934	-0.21397	0.00072	-0.06513	0.20288	-0.00279	0.06195	</v>
<v>	1.62351	-0.01591	0.90252	-0.31626	-0.02658	2.57424	-0.88336	</v>
<v>	1.62426	-2.71632	-6.79535	-0.29980	1.53665	3.83790	0.17176	</v>
<v>	1.70706	-1.92939	3.99363	0.20843	-1.58205	3.27474	0.17079	</v>
<v>	1.79989	0.00000	0.00015	0.00000	-0.00000	0.00004	0.00000	</v>
<v>	1.80005	-0.00004	0.00000	0.00001	0.00005	0.00001	-0.00001	</v>
<v>	1.80926	-0.00004	-0.00001	-0.00000	-0.00002	-0.00001	-0.00000	</v>
<v>	1.81594	0.00001	-0.00000	-0.00000	0.00002	-0.00000	-0.00000	</v>
[..]								

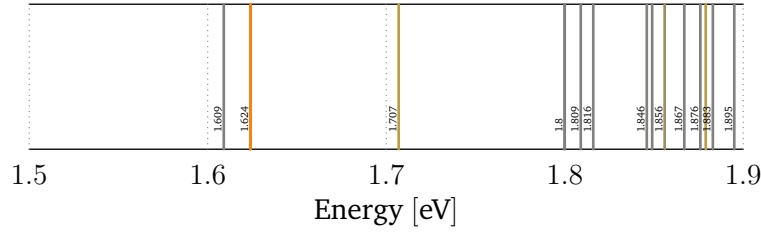


Figure 6.23.: ReS_2 ML: exciton energies vs. interaction probability - The reader is referred to sec. 5.8.2 for a detailed explanation on how the data is visualized.

Below the BG magnitude, the largest photon interaction probabilities for excitons are found at the energies $E_{\Lambda_3} = 1.624$, $E_{\Lambda_4} = 1.707$, $E_{\Lambda_{11}} = 1.856$, $E_{\Lambda_{14}} = 1.879$ and $E_{\Lambda_{19}} = 1.951$ eV. Below the bright exciton $E_{\Lambda_3} = 1.624$ eV, there exists a dark state with $E_{\Lambda_1} = 1.609$ eV. In ref. [Zho+15], only the lowest excitonic peak of $E_{\Lambda_1}^{\text{ref}} = 1.63$ eV is mentioned. This energy, however, suggests a very good agreement.

6.4.4 Absorption Spectrum

The absorption spectrum was calculated including excitonic effects. Furthermore, the influence of different excitons on the spectrum was analyzed. Therefore, the imaginary part of the dielectric function ϵ_2 was diagonalized at the energy of the

lowest bright state $E_{\Lambda_3} = 1.624\text{eV}$. The resulting eigenvectors $\bar{x}$ and $\bar{y}$ represent the principal axes of anisotropy, which relate closely to the Cartesian axes $\hat{x}$ and $\hat{y}$.

$$\bar{x} = \begin{pmatrix} -0.9705 \\ -0.2404 \\ 0.0191 \end{pmatrix} \quad \bar{y} = \begin{pmatrix} 0.2411 \\ -0.9689 \\ 0.0550 \end{pmatrix}$$

In fig. 6.24 the imaginary parts of the dielectric function for the two in-plane directions $\bar{x}$ and $\bar{y}$ are shown.

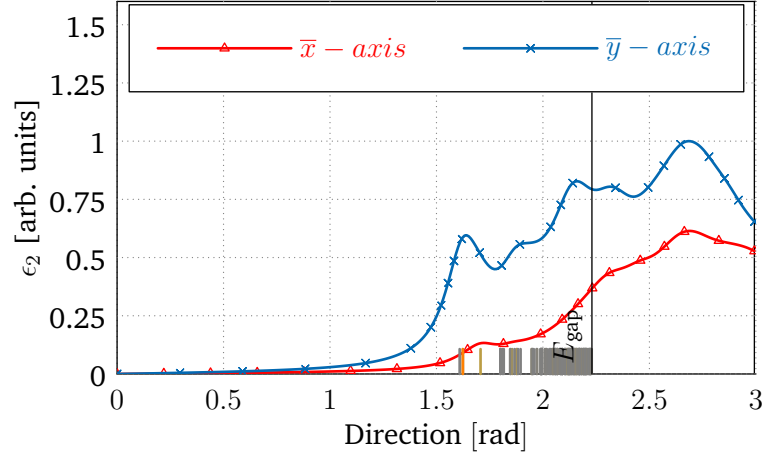


Figure 6.24.: ReS₂ ML: imag. dielectric func. for the principal axis of anisotropy - The bars at the horizontal axis represent the excitonic states according to fig. 6.23. The reader is referred to sec. 5.8.2 for a detailed explanation on how the data is visualized.

Subsequently, ϵ_2 with respect to all in-plane directions, was visualized for the lowest bright excitonic states. The results are shown in fig. 6.25.

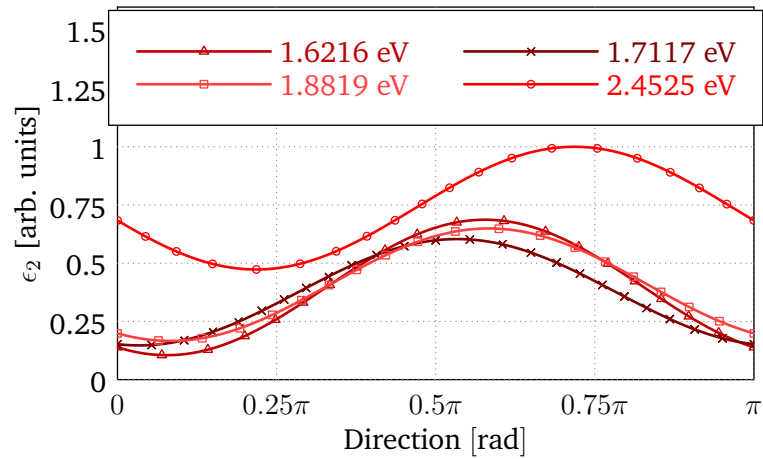


Figure 6.25.: ReS₂ ML: imag. dielectric func. vs. photon propagation direction - 0deg points into direction $\hat{x}$, while 0.5π points to $\hat{y}$. The reader is referred to sec. 5.8.2 for a detailed explanation on how the data is visualized.

As indicated by the bars in fig. 6.24, ϵ_2 shows a peak at $\approx 1.62\text{eV}$ in $\bar{y}$ -direction. This peak corresponds to the exciton state Λ_3 , which has a high photon interaction probability. On the contrary, exciton state Λ_4 affects the $\bar{x}$ -direction at $\approx 1.71\text{eV}$. These findings confirm the anisotropy of the optical response of ML ReS₂ consistent with the computational results in ref. [Zho+15].

Fig. 6.25 shows, that for lower photon energies the imaginary part of the dielectric function is larger in $\bar{y}$ -direction when compared to the $\bar{x}$ -direction. At the energy of the lowest bright excitonic state E_{Λ_3} , a minimum relative absorption of 0.105 close to the Cartesian $\hat{x}$ -direction is found, and a maximum absorption of 0.687 close to the Cartesian $\hat{y}$ -direction. Therefore, the anisotropy magnitude of the absorption coefficient shows a factor of 6.54. Experimentally a factor of 7 in the change of the laser-induced pump and probe signal was found (ref. [Cui+15]). Hence, the simulation results conform well with experimental results. For energies of about 2.5eV, the principal axes of anisotropy are rotated by approximately 45deg. At even higher energies the absorption profile is inverted, leading to a weak absorption in $\bar{y}$ -direction and a strong absorption in $\bar{x}$ -direction. However, precise results for higher energies were not available due to current hardware limitations of the GW and BSE calculations.

6.4.5 Excitonic Compositions

Deeper insights into the anisotropic optical effects can be expected by analyzing the exciton states concerning their electron-hole-pair amplitudes in k-space. These data are also necessary for the calculation of the effective masses. The visualizations are presented in fig. 6.26.

All visualized excitonic states have relatively large amplitudes on four bands of the BS. This is caused by the double degeneracy of states at the valence and conduction band edges.

Excitons 1-4 are centered on the Γ point of the BZ. The electron-hole-pair amplitudes in direction Γ -K2 are scattered differently throughout the BZ for different excitons. This direction is close to the Cartesian $\hat{x}$ -axis (fig. 5.11). The amount of scattering seems to be less and equal in the perpendicular direction Γ -M1 in all excitons 1-4, which is close to Cartesian $\hat{y}$ -axis.

Excitons 5-8 are not centered on the Γ point of the BZ. A similar non- Γ -centered exciton amplitude distribution is seen in ML ReSe₂ (ref. [Zho+15, fig. 4]). These states were neglected for further analysis due to their vanishing photon interaction probabilities.

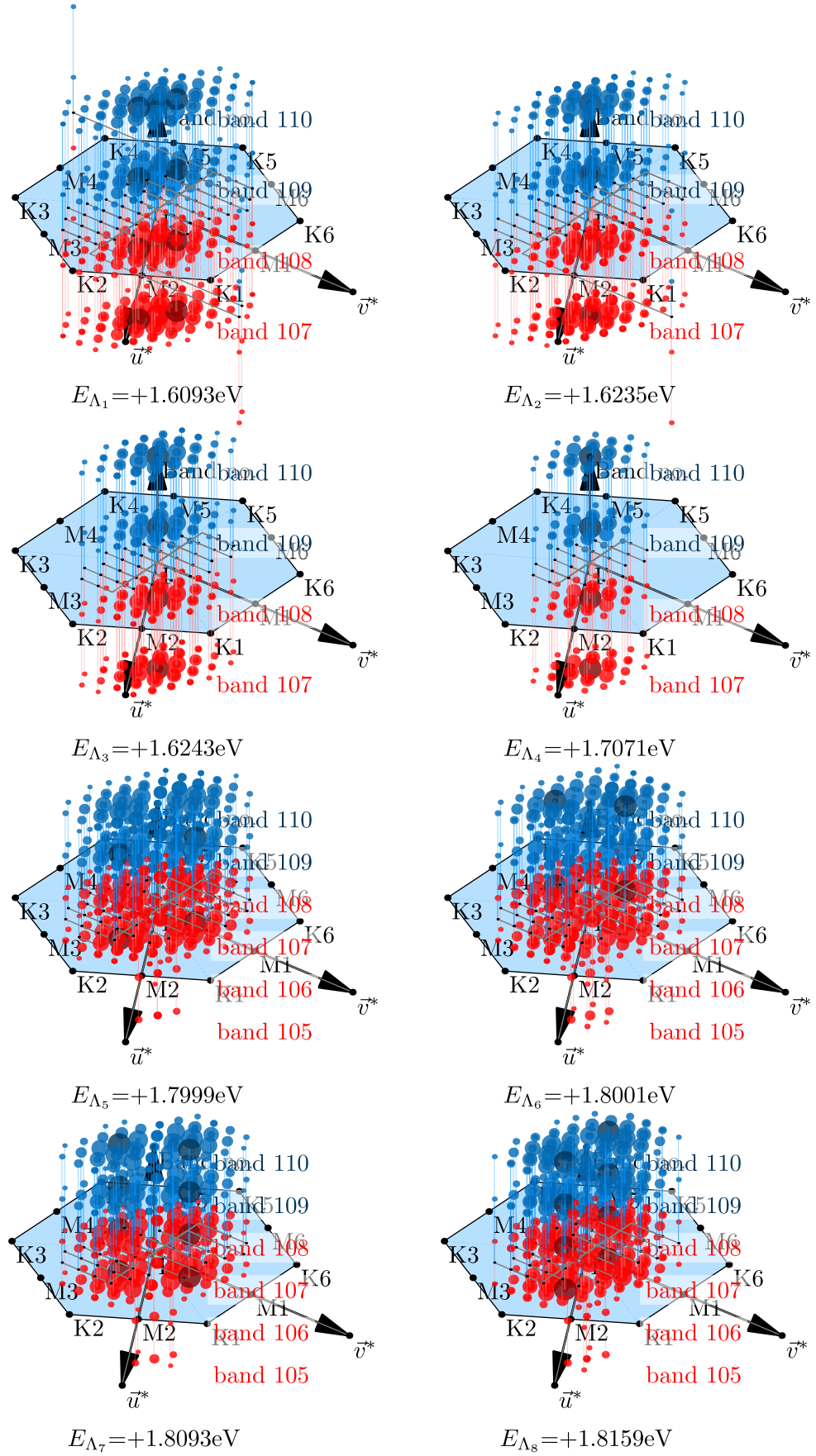


Figure 6.26.: ReS₂ ML: contributions to excitons 1-8 - The reader is referred to sec. 5.8.1 for a detailed explanation on how the data is visualized.

Together with the insights from the dielectric function (fig. 6.24) it can be concluded, that excitons delocalized in k-space, or localized in real space, exhibit smaller photon interaction probabilities.

6.4.6 Effective Masses

The electron-hole-pair amplitudes show that excitons 1-4 are all centered around the Γ point. Some excitons are more scattered throughout the BZ than other ones. Visual examination revealed that their amplitudes have axes of symmetry, which are close to the directions Γ -K2 and Γ -M1. These are the principal directions in the BS, for which the reduced effective masses $M_{\Lambda xx}$ and $M_{\Lambda yy}$ had to be calculated. The first, respectively second, third, and fourth exciton was considered to extend $1/4$, $1/6$, $1/6$, and $1/12$, into the path from Γ to K2. In direction Γ -M1 a factor of $1/12$ was used for all excitons 1-4, because of the small amplitude scattering. Effective masses that were calculated with the scattering factors $1/4$, resp. $1/6$, and $1/12$ are labelled 'wide', 'medium' and 'narrow'. These factors, multiplied by the BS section resolution (i.e. 48), define the number of data points that were used for the effective mass fit functions.

In fig. 6.27 the fit functions are presented. In tab. 6.28 and 6.29, the resulting effective masses and reduced effective masses are listed.

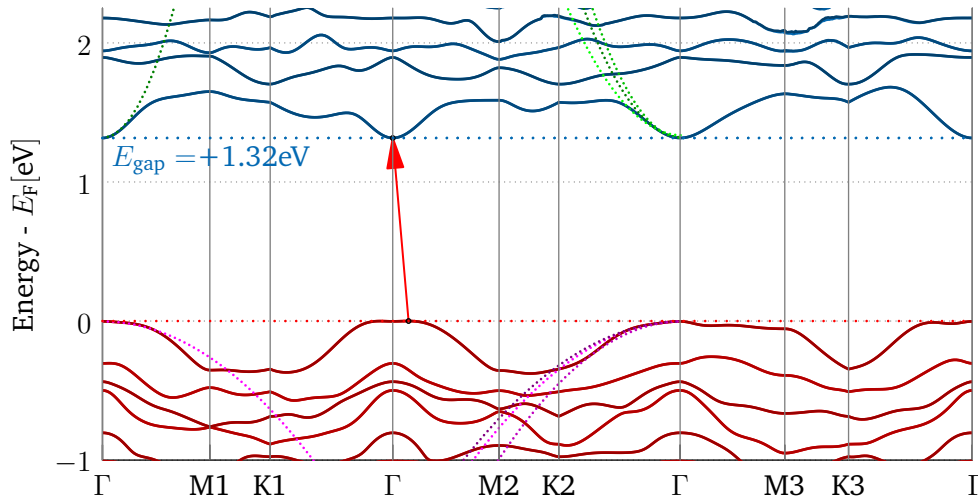


Figure 6.27.: ReS₂ ML: fit functions for the effective mass approx. - The reader is referred to sec. 5.6 for a detailed explanation on how the data is visualized

Table 6.28.: ReS₂ ML: effective masses at the Γ point - ReS₂ ML: effective masses at the Γ point

Band	Type	$m_{\Gamma \rightarrow K2}^{\text{wide}}$	$m_{\Gamma \rightarrow K2}^{\text{medium}}$	$m_{\Gamma \rightarrow K2}^{\text{narrow}}$	$m_{\Gamma \rightarrow M1}^{\text{narrow}}$
ReS ₂ 107,108	hole	4.62	5.07	3.57	4.73
ReS ₂ 109,110	electron	1.51	1.10	0.90	0.58
ReS ₂ Ref.	electron	-	-	0.92	0.53

Table 6.29.: ReS₂ ML: exciton reduced masses - ReS₂ ML: exciton reduced masses

Exciton	$M_{\Lambda xx}$ EH-Masses	$M_{\Lambda yy}$ EH-Masses	$M_{\Lambda xx}$	$M_{\Lambda yy}$
E_{Λ_1}	$m_{\Gamma \rightarrow K2}^{\text{wide}}$	$m_{\Gamma \rightarrow M1}^{\text{narrow}}$	1.14	0.52
E_{Λ_2}	$m_{\Gamma \rightarrow K2}^{\text{medium}}$	$m_{\Gamma \rightarrow M1}^{\text{narrow}}$	0.90	0.52
E_{Λ_3}	$m_{\Gamma \rightarrow K2}^{\text{medium}}$	$m_{\Gamma \rightarrow M1}^{\text{narrow}}$	0.90	0.52
E_{Λ_4}	$m_{\Gamma \rightarrow K2}^{\text{narrow}}$	$m_{\Gamma \rightarrow M1}^{\text{narrow}}$	0.72	0.52

Effective masses for anisotropic structures are usually obtained by calculating all combinations of the second derivatives on dense k-point meshes, as stated in ref. [Ovc+16, supp. p.11]. The resulting mass tensor is then diagonalized for retrieving the effective masses for all principal axes. The approach that was used in this thesis is less accurate but saves computational effort. Nevertheless, the resulting effective masses for the conduction band (tab. 6.28) are close to the reference values in ref. [Ovc+16, supp. p.11]. However, the concept of effective masses is only applicable to extremal states in the BS that exhibit a parabolic band shape in their vicinity. Consequently, it is questionable, whether the effective mass concept is applicable to excitons that are highly distributed in k-space. In the case of ML ReS₂ the band structure exhibits at least three different in-plane effective masses, which cannot be described by a rank three tensor.

The resulting reduced effective masses for excitons 1-4 clearly show larger values for one principal axis of anisotropy ($0.72m_e$, $0.90m_e$, and $1.14m_e$) when compared to the other axis ($0.52m_e$).

6.4.7 Exciton Radiative Lifetimes

The reduced effective masses summarized in tab. 6.29, were used for the calculation of the radiative lifetimes $\tau_{\Lambda}^{\text{rad}}(0)$ (eq. 3.8) and the thermally averaged lifetimes $\tau_{\Lambda}^{\text{rad}}(300)$ (eq. 3.11). The results are listed in tab. 6.30.

Table 6.30.: ReS₂ ML: exciton radiative lifetimes at 0K and 300K - ReS₂ ML: exciton radiative lifetimes at 0K and 300K

Exciton	Type	$\tau_{\Lambda}^{\text{rad}}(0)$ [s]	$\tau_{\Lambda}^{\text{rad}}(300)$ [s]
E_{Λ_1}	dark	240×10^{-12}	1.4×10^{-6}
E_{Λ_2}	bright	2.8×10^{-12}	14.0×10^{-9}
E_{Λ_3}	bright	290×10^{-15}	1.5×10^{-9}
E_{Λ_4}	bright	600×10^{-15}	2.5×10^{-9}

The effective radiative lifetime $\gamma_{\text{eff}}^{\text{rad}}(300)$ was calculated by using eq. 2.36. Excitonic states beyond the lowest four ones had changed the effective lifetime less than 1%,

and are therefore neglected. Hence, the final value that was computed for ML ReS₂ is:

$$\gamma_{\text{eff}}^{\text{rad}}(300) = 5.1 \times 10^{-9} \text{ s}.$$

This result for ML ReS₂ is larger than the ones for ML MoX₂ materials (tab. 6.16), suggesting an increase of radiative lifetimes with increasing period of the metal respective chalcogenide atom.

For comparison with experiment, only few data is available. In ref. [Cui+15], the experimental results of excitonic lifetimes for ML ReS₂ are reported, where the structures' photoluminescence under the influence of a 405nm laserbeam was measured at room temperature. From the sample response, it was concluded that the exciton dynamics are independent of polarization and sample orientations. This is in perfect agreement with the derivation in ch. 4. However, the experimental exciton lifetime of $40 \pm 2 \text{ ps}$ is much shorter than the predicted effective radiative lifetime of 5.1ns. A possible reason for this discrepancy is that the non-radiative decay channel $\tau_{\text{eff}}^{\text{norad}}$ dominates all other decay channels (ref. [Cui+15, p. 55689]). This relation is described by eq. 2.37. At lower temperatures, radiative effects usually outweigh non-radiative effects, and thus low-temperature experiments should agree with the computed results presented in this thesis. To support this assumption, the effective radiative lifetime of ML ReS₂ with respect to temperature $\gamma_{\text{eff}}^{\text{rad}}(T)$ is plotted in fig. 6.31.

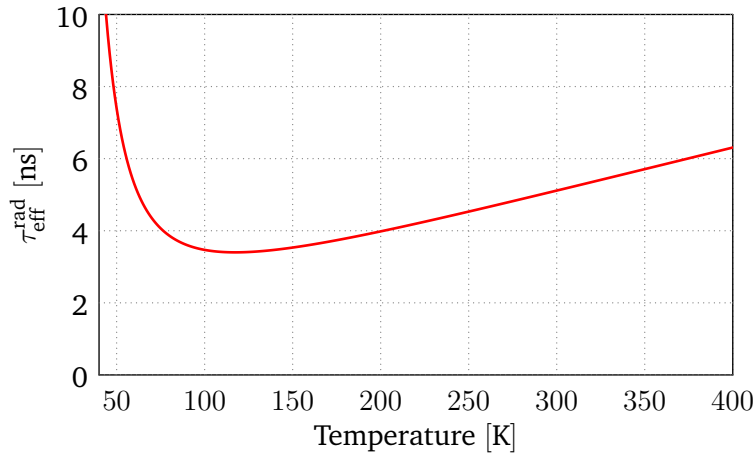


Figure 6.31.: ReS₂ ML: effective radiative lifetimes vs. temperature

For temperatures above 150°K, the $\gamma_{\text{eff}}^{\text{rad}}$ depends linearly on temperature. At lower temperatures, the formation of bright excitonic states is decreased, due to the reduced thermal energy. The lowest (dark) excitonic state then becomes the dominating state of the exciton population. This state has a diminishing photon interaction probability, which results in a high radiative lifetime.

In tab. 6.32, the influence of the k-point grid density on the result is presented.

Table 6.32.: ReS₂ ML: effective radiative lifetimes vs. grid densities - ReS₂ ML: effective radiative lifetimes vs. grid densities

Structure	$6 \times 6 \times 1$	$9 \times 9 \times 1$	$12 \times 12 \times 1$
ReS ₂ $\gamma_{\text{eff}}^{\text{rad}}(300)$	5.8	6.1	5.1

These values do not drop monotonically; therefore it is not meaningful to apply a fit function. The absorption spectrum (fig. 5.18) was used to estimate the value of the converged result. The higher energy range of this spectrum looks similarly for the densities $6 \times 6 \times 1$ and $12 \times 12 \times 1$ but different for $9 \times 9 \times 1$. The downward trend in the $6 \times 6 \times 1$ and $12 \times 12 \times 1$ grids, together with the results for MoS₂, allows a rough assumption, that the converged effective radiative lifetimes may lie 20% below the results.

Conclusion and Outlook

In this thesis, it was shown that the radiative lifetime formulas can be extended from the isotropic to the anisotropic case. The derived formulas can be evaluated without additional computational costs for the BSE routine. In the limit of isotropic structures, the equations simplify to the formulas of the ref. [Pal+15]. The derivation uses an effective mass approximation that bypasses the solution of a complicated integral. By using this approximation, radiative lifetimes turn out to be isotropic quantities with respect to emissive photon polarization. It is possible that this approximation is identical to the analytical solution. If this is not the case, the error of the approximation must be related to the magnitude of anisotropy—this would require further work to evaluate the exact form of this relation.

After the theoretical derivation of the exciton radiative lifetime in anisotropic systems, VASP was extended to evaluate these formulas. The BSE routine of VASP already computed the interband matrix elements needed for calculating lifetimes, but source code changes were necessary to obtain a respective output for further evaluation of the lifetimes.

To verify the VASP implementations, the radiative exciton lifetimes of ML MoX₂ systems were investigated first since computational results were available for comparison. Prior to the computation of the optical properties, the structures were relaxed by means of the recently implemented SCAN functional. It was confirmed that the SCAN functional performs slightly better than the standard DFT-PBE functional. In all three ML systems, a direct BG at the K point was obtained, and with the increasing period of the chalcogenide atom, the BG decreased. Moreover, the computed BSs and BGs are consistent with previous DFT-LDA and DFT-PBE calculations of ref. [RT15] and [Lia+13]. The spin-orbit coupling induced splittings of the valence band and conduction band at the band extrema. The magnitude of both splittings increased within the series of MoX₂. These results adequately reproduce the DFT-LDA results of ref. [RT15].

On the basis of these DFT-SCAN results, the electronic and optical properties of ML MoX₂, including QP screening and excitonic effects, were studied by performing G₀W₀ and BSE calculations. In the present work, QP BGs of 2.50eV, 2.13eV and 1.59eV were obtained for ML MoS₂, ML MoSe₂, and ML MoTe₂, respectively. Considering that G₀W₀ calculations are difficult to converge for ML structures, it was found that these values deviate less than 10% to literature data (ref. [Lia+13, p. 2]).

The effective masses of ML MoX₂, deduced from the BSs, are in concordance with the findings of ref. [RT15, tab. 5], and they thus confirm the quality of the present calculations. The QP energies and orbitals were applied to the BSE for investigating excitonic effects in ML MoX₂. The lowest two bound excitons were found at energies of 1.95eV and 1.97eV in ML MoS₂, 1.665eV and 1.667eV in ML MoSe₂, and 1.26eV and 1.28eV in ML MoTe₂. In ML MoS₂ the lowest excitonic state was a dark state, and the second lowest one was a bright state. For ML MoSe₂ and ML MoTe₂, the opposite result was obtained.

In order to test the VASP extension, the effective radiative lifetimes of ML MoX₂ were evaluated. With a fairly low density k-point grid of $12 \times 12 \times 1$, the resulting effective radiative lifetimes were 720ps for ML MoS₂, 830ps for ML MoSe₂, and 1500ps for ML MoTe₂. The first two were also calculated in ref. [Pal+15] to which they conform well. In contrast, the calculated lifetimes for particular dark excitonic states deviated by three orders of magnitude to those obtained in ref. [Pal+15]. Currently, the reasons for this discrepancy are not fully understood. The extrapolation of the effective radiative lifetime for ML MoS₂ to higher k-point grid densities suggests a $\approx 10\%$ lower value of 660ps. This finding is supported by various experimental results that are tendentially smaller (300ps, 360ps, 469ps, and 850ps), as listed in ref. [Moo+16]. Within the series of MoX₂, the effective excitonic radiative lifetimes increased with the increasing period of the chalcogenide atom.

In addition to ML MoX₂, low dimensional ReS₂ was investigated through the same approach. This system is particularly interesting since it exhibited anisotropic optical properties, and, moreover, less information about the excitonic lifetimes is currently available. The bulk ReS₂ structure was optimized with DFT-VdW (optB86b functional) to account for the VdW forces governing the distance between the two ReS₂ layers in the unit cell. The resulting lattice parameters were in excellent agreement with crystallographic data in ref. [Mur+94] and were used to set up the ML structure. The original triclinic structure was converted to a monoclinic one so as to take advantage of the higher symmetry; this was relevant for the computationally demanding G₀W₀ and BSE calculations. ML ReS₂ exhibited a BG of 1.32eV, which is in good agreement with the DFT-PBE results in ref. [Zho+15]. Due to the extremely flat dispersion of the valence band at the Γ -point, the valence band maximum could not be conclusively assigned to the Γ -point within the range of computational uncertainty. Therefore, it is not clear, if ML ReS₂ is a direct or an indirect semiconductor. The inclusion of QP screening increased the BG to 2.23eV, which is also in good agreement with ref. [Zho+15]. The anisotropy of the system was manifested in the BS as well as in the absorption spectra. The BSE calculation revealed a dark exciton state at 1.61eV and a bright one at 1.62eV deep inside the QP gap. Moreover, a strong anisotropy of the in-plane absorption with respect to the response to parallel and perpendicular polarized photons was observed. The

magnitude of this anisotropy was determined from the dielectric function. A value of 6.5 was obtained, which reproduces the experimental finding of approximately 7 in ref. [Cui+15].

For the determination of the excitonic lifetimes of ML ReS₂, a detailed analysis of the excitonic contributions at various k-points was required. With this analysis, the anisotropic effective masses were obtained from the BS, and they conformed to the masses in ref. [Ovc+16, supp. p.11]. The effective masses for excitons 1-4 exhibited varying larger values for one principal axis of anisotropy ($0.72m_e$, $0.90m_e$, $0.90m_e$, and $1.14m_e$) when compared to the other axis ($0.52m_e$ for all four excitons). With this data, a thermally averaged radiative lifetime of 5.1ns at 300K was obtained. It was estimated that the converged value was lower by approximately 20%. In the existing literature, experimental results have shown a substantially shorter lifetime of 40ps (ref. [Cui+15]). This mismatch is most likely caused by non-radiative mechanisms that are not covered in this thesis. Further experiments with ML ReS₂ are needed to gain more information about its exciton dynamics. These experiments might be carried out at lower temperatures, where radiative decay processes play a larger role. To facilitate such a data comparison in future research, the effective radiative lifetime with respect to temperature was provided in this work. This data shows an almost linear dependence at temperatures above approximately 150°K. Below this temperature, the effective lifetime rises quickly because the thermal distribution of exciton formation favors the lowest dark states, which have a long radiative lifetime.

For further work, it is recommended that this thesis' methods are applied to other anisotropic ML structures, for which experimental results are available. It is also suggested that the convergence of radiative lifetime calculations are analyzed with large-scale computer systems. It is assumed that the resulting accuracy strongly depends on GW and BSE parameters that are already known to have a substantial impact on optical properties; in particular, these are the k-point density and the number of virtual states.

Excitonic states in ReS₂ are found to be highly distributed in k-space. The concept of effective masses is, thus, questionable, and its use for radiative lifetime calculations has to be re-evaluated. Further work could dismiss this concept altogether by directly evaluating the "raw" lifetime formula (eq. 3.1) during the execution of the BSE routine. This would lead to a fully automated algorithm without the need for manual BS evaluations.

Appendix

A

A.1 VASP Settings

Table A.1.: MoX₂ ML: lattice relaxation VASP settings

File	Description
INCAR	METAGGA=SCAN, ISMEAR=0, EDIFF=10E-8, ISIF=2, EDIFFG=10E-7
KPOINTS	12 × 12 × 1, gamma centered
SCRIPT	variation of lattice constant a
POTCAR	PAW_PBE Mo_pv 04Feb2005, PAW_PBE S 08Apr2002, PAW_PBE Se 08Apr2002, PAW_PBE Te 08Apr2002

Table A.2.: MoX₂ ML: DFT band structure VASP settings

File	Description
1.POSCAR	tab. A.13, A.14, A.15
1.INCAR	METAGGA=SCAN, ISMEAR=-5, EDIFF=10E-8, LSORBIT=.TRUE., MAGMOM=3*3*0
1.KPOINTS	12 × 12 × 1, gamma centered
2.INCAR	ISMEAR=2, EDIFF=10E-8, LSEPB=.TRUE., ICHARG=11, NEDOS=2048, LORBIT=11, LSORBIT=.TRUE., MAGMOM=3*3*0
2.KPOINTS	32 × 32 × 1, gamma centered
3.KPOINTS	G-M-K-G, 48 steps
POTCAR	PAW_PBE Mo_pv 04Feb2005, PAW_PBE S 08Apr2002, PAW_PBE Se 08Apr2002, PAW_PBE Te 08Apr2002

Table A.3.: MoX₂ ML: GW calculation VASP settings

File	Description
1.POSCAR	tab. A.13, A.14, A.15
1.INCAR	ISMEAR=-5, EDIFF=10E-6, METAGGA=SCAN, LSORBIT=.TRUE., MAGMOM=3*3*0
1.KPOINTS	18 × 18 × 1, gamma centered
2.INCAR	NBANDS=512, ALGO=NORMAL, EDIFF=10E-6, NELM=1, ISMEAR=0, SIGMA=0.01, METAGGA=SCAN, LOPTICS=.TRUE., LCHARG=.FALSE., LSORBIT=.TRUE., MAGMOM=3*3*0
2.KPOINTS	18 × 18 × 1, gamma centered
3.INCAR	NBANDS=512, ALGO=GW0, ISMEAR=0, SIGMA=0.01, METAGGA=SCAN, NELM=1, NOMEGA=64, LWAVE=.TRUE., PRECFOCK=Fast, OMEGAMAX=10, LSORBIT=.TRUE., MAGMOM=3*3*0
3.KPOINTS	18 × 18 × 1, gamma centered
POTCAR	PAW_PBE Mo_sv_GW 05Dec2013, PAW_PBE S_GW 19Mar2012, PAW_PBE Se_GW 20Mar2012, PAW_PBE Te_GW 22Mar2012

Table A.4.: MoX₂ ML: BSE VASP settings

File	Description
1.POSCAR	tab. A.13, A.14, A.15
1.INCAR	ALGO=Nothing, NELM=1, EDIFF=1.E-6, NBANDS=512, LWAVE=.FALSE., LOPTICS=.TRUE., LPEAD=.TRUE., OMEGAMAX=10, LSORBIT=.TRUE., MAGMOM=3*3*0
1.KPOINTS	18 × 18 × 1, gamma centered
2.INCAR	ALGO=BSE, ISMEAR=0, SIGMA=0.01, EDIFF=1.E-6, NBANDS=512, NBANDSO=16, NBANDSV=16, NOMEGA=56, OMEGAMAX=10, LSORBIT=.TRUE., MAGMOM=3*3*0, NBSEEIG=32
2.KPOINTS	18 × 18 × 1, gamma centered
POTCAR	PAW_PBE Mo_sv_GW 05Dec2013, PAW_PBE S_GW 19Mar2012, PAW_PBE Se_GW 20Mar2012, PAW_PBE Te_GW 22Mar2012

Table A.5.: ReS₂ bulk: lattice relaxation VASP settings

File	Description
INCAR	ISMear=0, EDIFF=10E-6, EDIFFG=-10E-3, ISIF=3, LUSE_VDW=.TRUE., AGGAC=0.0000, GGA=MK, PARAM1=0.1234, PARAM2=1.0000, ENMAX=340.0
KPOINTS	$x \times x \times x$, gamma centered
SCRIPT	variation of k-point density $x \in \{3, 6, 9\}$
POTCAR	PAW_PBE Re_pv 06Sep2000, PAW_PBE S 06Sep2000

Table A.6.: ReS₂ ML: lattice relaxation VASP settings

File	Description
INCAR	ISMear=0, EDIFF=10E-6, EDIFFG=-10E-3, ISIF=2, LUSE_VDW=.TRUE., AGGAC=0.0000, GGA=MK, PARAM1=0.1234, PARAM2=1.0000, ENMAX=340.0
KPOINTS	$9 \times 9 \times 1$, gamma centered
POTCAR	PAW_PBE Re_pv 06Sep2000, PAW_PBE S 06Sep2000

Table A.7.: ReS₂ bulk: DFT band structure VASP settings

File	Description
1.POSCAR	tab. A.18
1.INCAR	ISMear=-5, EDIFF=10E-6, LSORBIT=.TRUE., MAG- MOM=3*12*0
1.KPOINTS	$9 \times 9 \times 9$, gamma centered
2.INCAR	ISMear=2, EDIFF=10E-6, LSEPB=.TRUE., ICHARG=11, NEDOS=2048, LORBIT=11, LSORBIT=.TRUE., MAG- MOM=3*12*0
2.KPOINTS	$24 \times 24 \times 24$, gamma centered
3.KPOINTS	G-YV-X-G, 48 steps
POTCAR	PAW_PBE Re_pv 06Sep2000, PAW_PBE S 06Sep2000

Table A.8.: ReS₂ ML: DFT band structure VASP settings

File	Description
1.POSCAR	tab. A.19
1.INCAR	ISMEAR=-5, EDIFF=10E-6, LSORBIT=.TRUE., MAGMOM=3*12*0
1.KPOINTS	9 × 9 × 1, gamma centered
2.INCAR	ISMEAR=2, EDIFF=10E-6, LSEPB=.TRUE., ICHARG=11, NEDOS=2048, LORBIT=11, LSORBIT=.TRUE., MAGMOM=3*12*0
2.KPOINTS	24 × 24 × 1, gamma centered
3.KPOINTS	G-M1-K1-G-M2-K2-G-M3-K3-G, 48 steps
POTCAR	PAW_PBE Re_pv 06Sep2000, PAW_PBE S 06Sep2000

Table A.9.: ReS₂ ML: GW calculation VASP settings

File	Description
1.POSCAR	tab. A.19
1.INCAR	ISMEAR=-5, EDIFF=10E-6, CSHIFT=0.3, LSORBIT=.TRUE., MAGMOM=3*12*0
1.KPOINTS	12 × 12 × 1, gamma centered
2.INCAR	NBANDS=512, ALGO=NORMAL, EDIFF=10E-6, NELM=1, ISMEAR=0, SIGMA=0.01, CSHIFT=0.3, LOPTICS=.TRUE., LCHARG=.FALSE., LSORBIT=.TRUE., MAGMOM=3*12*0
2.KPOINTS	12 × 12 × 1, gamma centered
3.INCAR	NBANDS=512, ALGO=GW0, ISMEAR=0, SIGMA=0.01, CSHIFT=0.3, NELM=1, NOMEGA=64, LWAVE=.TRUE., PRECFOCK=Fast, OMEGAMAX=10, LSORBIT=.TRUE., MAGMOM=3*12*0
3.KPOINTS	12 × 12 × 1, gamma centered
POTCAR	PAW_PBE Re_sv_GW 23Mar2010, PAW_PBE S_GW 19Mar2012

Table A.10.: ReS₂ ML: BSE VASP settings

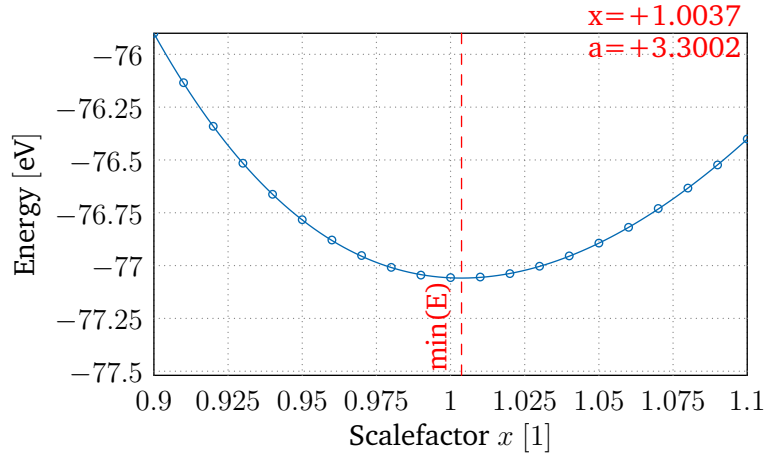
File	Description
1.INCAR	ALGO=Nothing, NELM=1, EDIFF=1.E-6, NBANDS=512, LWAVE=.FALSE., LOPTICS=.TRUE., LPEAD=.TRUE., OMEGAMAX=10, LSORBIT=.TRUE., MAGMOM=3*12*0
1.KPOINTS	18 × 18 × 1, gamma centered
2.INCAR	ALGO=BSE, ISMEAR=0, SIGMA=0.01, EDIFF=1.E-6, NBANDS=512, NBANDSO=8, NBANDSV=8, NOMEGA=56, OMEGAMAX=10, LSORBIT=.TRUE., MAGMOM=3*3*0, NBSEEIG=32
2.KPOINTS	12 × 12 × 1, gamma centered
POTCAR	PAW_PBE Re_sv_GW 23Mar2010, PAW_PBE S_GW 19Mar2012

A.2 Miscellaneous

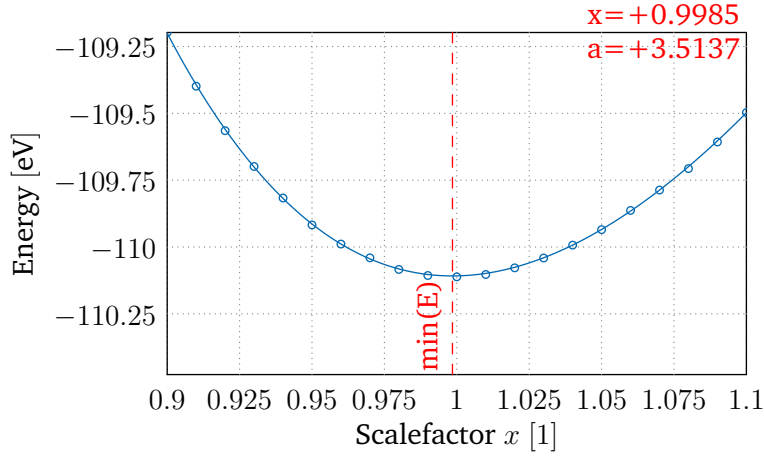
Table A.11.: ReS₂ bulk: experimental unit cell parameters - quantities are in unit of Å

$$\vec{u} = \begin{pmatrix} +6.4610 \\ 0.0000 \\ 0.0000 \end{pmatrix} \quad \vec{v} = \begin{pmatrix} -3.3626 \\ +5.5743 \\ 0.0000 \end{pmatrix} \quad \vec{w} = \begin{pmatrix} +0.1814 \\ -2.0153 \\ +6.0896 \end{pmatrix}$$

$$\begin{aligned} \vec{r}_1 &= +1.5001 \cdot \hat{x} - 0.6781 \cdot \hat{y} + 2.9991 \cdot \hat{z} \quad (\text{Re}) \\ \vec{r}_2 &= +0.2937 \cdot \hat{x} + 1.8367 \cdot \hat{y} + 3.0607 \cdot \hat{z} \quad (\text{Re}) \\ \vec{r}_3 &= -1.3187 \cdot \hat{x} - 1.3371 \cdot \hat{y} + 3.0905 \cdot \hat{z} \quad (\text{Re}) \\ \vec{r}_4 &= -0.1123 \cdot \hat{x} - 3.8520 \cdot \hat{y} + 3.0290 \cdot \hat{z} \quad (\text{Re}) \\ \vec{r}_5 &= +1.5745 \cdot \hat{x} + 0.9543 \cdot \hat{y} + 1.3239 \cdot \hat{z} \quad (\text{S}) \\ \vec{r}_6 &= -0.0732 \cdot \hat{x} + 3.7370 \cdot \hat{y} + 1.6862 \cdot \hat{z} \quad (\text{S}) \\ \vec{r}_7 &= -0.0194 \cdot \hat{x} - 0.0027 \cdot \hat{y} + 4.6050 \cdot \hat{z} \quad (\text{S}) \\ \vec{r}_8 &= -1.6489 \cdot \hat{x} + 2.7896 \cdot \hat{y} + 4.2475 \cdot \hat{z} \quad (\text{S}) \\ \vec{r}_9 &= -1.3931 \cdot \hat{x} - 2.9696 \cdot \hat{y} + 4.7658 \cdot \hat{z} \quad (\text{S}) \\ \vec{r}_{10} &= +0.2546 \cdot \hat{x} - 5.7522 \cdot \hat{y} + 4.4034 \cdot \hat{z} \quad (\text{S}) \\ \vec{r}_{11} &= +0.2008 \cdot \hat{x} - 2.0125 \cdot \hat{y} + 1.4847 \cdot \hat{z} \quad (\text{S}) \\ \vec{r}_{12} &= +1.8303 \cdot \hat{x} - 4.8048 \cdot \hat{y} + 1.8421 \cdot \hat{z} \quad (\text{S}) \end{aligned}$$



(a) MoSe₂



(b) MoTe₂

Figure A.12.: MoSe₂, MoTe₂ ML: relaxation data and fit function - The optimized lattice constant a is in unit of Å

Table A.13.: MoS₂ ML: relaxed unit cell parameters - quantities are in unit of Å

$$\vec{u} = \begin{pmatrix} +1.5862 \\ -2.7474 \\ 0.0000 \end{pmatrix} \quad \vec{v} = \begin{pmatrix} +1.5862 \\ +2.7474 \\ 0.0000 \end{pmatrix} \quad \vec{w} = \begin{pmatrix} 0.0000 \\ 0.0000 \\ +25.0000 \end{pmatrix}$$

$$\begin{aligned} \vec{r}_1 &= +0.3333 \cdot \vec{u} + 0.6667 \cdot \vec{v} + 0.1225 \cdot \vec{w} \quad (\text{Mo}) \\ \vec{r}_2 &= +0.6667 \cdot \vec{u} + 0.3333 \cdot \vec{v} + 0.0600 \cdot \vec{w} \quad (\text{S}) \\ \vec{r}_3 &= +0.6667 \cdot \vec{u} + 0.3333 \cdot \vec{v} + 0.1850 \cdot \vec{w} \quad (\text{S}) \end{aligned}$$

Table A.14.: MoSe₂ ML: relaxed unit cell parameters - quantities are in unit of Å

$$\vec{u} = \begin{pmatrix} +1.6501 \\ -2.8580 \\ 0.0000 \end{pmatrix} \quad \vec{v} = \begin{pmatrix} +1.6501 \\ +2.8580 \\ 0.0000 \end{pmatrix} \quad \vec{w} = \begin{pmatrix} 0.0000 \\ 0.0000 \\ +25.0000 \end{pmatrix}$$

$$\begin{aligned} \vec{r}_1 &= +0.3333 \cdot \vec{u} + 0.6667 \cdot \vec{v} + 0.1293 \cdot \vec{w} \quad (\text{Mo}) \\ \vec{r}_2 &= +0.6667 \cdot \vec{u} + 0.3333 \cdot \vec{v} + 0.0630 \cdot \vec{w} \quad (\text{Se}) \\ \vec{r}_3 &= +0.6667 \cdot \vec{u} + 0.3333 \cdot \vec{v} + 0.1956 \cdot \vec{w} \quad (\text{Se}) \end{aligned}$$

Table A.15.: MoTe₂ ML: relaxed unit cell parameters - quantities are in unit of Å

$$\vec{u} = \begin{pmatrix} +1.7569 \\ -3.0430 \\ 0.0000 \end{pmatrix} \quad \vec{v} = \begin{pmatrix} +1.7569 \\ +3.0430 \\ 0.0000 \end{pmatrix} \quad \vec{w} = \begin{pmatrix} 0.0000 \\ 0.0000 \\ +25.0000 \end{pmatrix}$$

$$\begin{aligned} \vec{r}_1 &= +0.3333 \cdot \vec{u} + 0.6667 \cdot \vec{v} + 0.1396 \cdot \vec{w} \quad (\text{Mo}) \\ \vec{r}_2 &= +0.6667 \cdot \vec{u} + 0.3333 \cdot \vec{v} + 0.0678 \cdot \vec{w} \quad (\text{Te}) \\ \vec{r}_3 &= +0.6667 \cdot \vec{u} + 0.3333 \cdot \vec{v} + 0.2115 \cdot \vec{w} \quad (\text{Te}) \end{aligned}$$

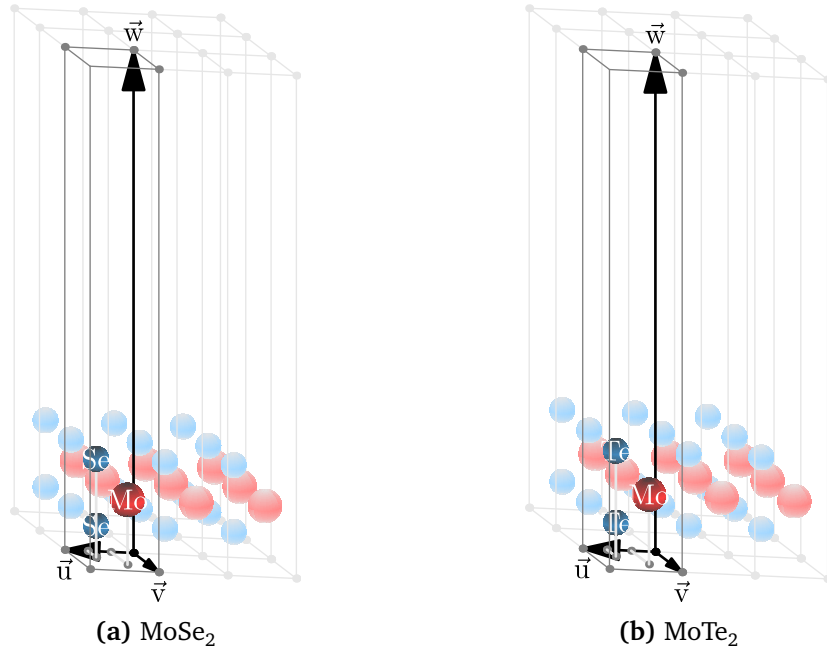


Figure A.16.: MoSe₂, MoTe₂ ML: 3D lattice visualization

Table A.17.: ReS₂ bulk: relaxed unit cell parameters - quantities are in unit of Å
$$\vec{u} = \begin{pmatrix} +6.4844 \\ -0.0179 \\ -0.0004 \end{pmatrix} \quad \vec{v} = \begin{pmatrix} -3.3903 \\ +5.5998 \\ +0.0023 \end{pmatrix} \quad \vec{w} = \begin{pmatrix} +0.1873 \\ -2.0193 \\ +6.0728 \end{pmatrix}$$

$\vec{r}_1 =$	+0.2475	$\cdot \vec{u}$	+0.0583	$\cdot \vec{v}$	+0.4924	$\cdot \vec{w}$	(Re)
$\vec{r}_2 =$	+0.2982	$\cdot \vec{u}$	+0.5127	$\cdot \vec{v}$	+0.5023	$\cdot \vec{w}$	(Re)
$\vec{r}_3 =$	+0.7525	$\cdot \vec{u}$	+0.9417	$\cdot \vec{v}$	+0.5076	$\cdot \vec{w}$	(Re)
$\vec{r}_4 =$	+0.7018	$\cdot \vec{u}$	+0.4873	$\cdot \vec{v}$	+0.4977	$\cdot \vec{w}$	(Re)
$\vec{r}_5 =$	+0.3668	$\cdot \vec{u}$	+0.2492	$\cdot \vec{v}$	+0.2112	$\cdot \vec{w}$	(S)
$\vec{r}_6 =$	+0.3832	$\cdot \vec{u}$	+0.7734	$\cdot \vec{v}$	+0.2763	$\cdot \vec{w}$	(S)
$\vec{r}_7 =$	+0.1191	$\cdot \vec{u}$	+0.2777	$\cdot \vec{v}$	+0.7594	$\cdot \vec{w}$	(S)
$\vec{r}_8 =$	+0.1188	$\cdot \vec{u}$	+0.7540	$\cdot \vec{v}$	+0.6972	$\cdot \vec{w}$	(S)
$\vec{r}_9 =$	+0.6332	$\cdot \vec{u}$	+0.7508	$\cdot \vec{v}$	+0.7888	$\cdot \vec{w}$	(S)
$\vec{r}_{10} =$	+0.6168	$\cdot \vec{u}$	+0.2266	$\cdot \vec{v}$	+0.7237	$\cdot \vec{w}$	(S)
$\vec{r}_{11} =$	+0.8809	$\cdot \vec{u}$	+0.7223	$\cdot \vec{v}$	+0.2406	$\cdot \vec{w}$	(S)
$\vec{r}_{12} =$	+0.8812	$\cdot \vec{u}$	+0.2460	$\cdot \vec{v}$	+0.3028	$\cdot \vec{w}$	(S)

Table A.18.: ReS₂ bulk (rotated): relaxed unit cell parameters - quantities are in unit of Å
$$\vec{u} = \begin{pmatrix} +6.4844 \\ 0.0000 \\ 0.0000 \end{pmatrix} \quad \vec{v} = \begin{pmatrix} -3.4057 \\ +5.5904 \\ 0.0000 \end{pmatrix} \quad \vec{w} = \begin{pmatrix} +0.1924 \\ -2.0164 \\ +6.0735 \end{pmatrix}$$

$\vec{r}_1 =$	+0.2475	$\cdot \vec{u}$	+0.0583	$\cdot \vec{v}$	+0.4923	$\cdot \vec{w}$	(Re)
$\vec{r}_2 =$	+0.2982	$\cdot \vec{u}$	+0.5127	$\cdot \vec{v}$	+0.5023	$\cdot \vec{w}$	(Re)
$\vec{r}_3 =$	+0.7525	$\cdot \vec{u}$	+0.9417	$\cdot \vec{v}$	+0.5077	$\cdot \vec{w}$	(Re)
$\vec{r}_4 =$	+0.7018	$\cdot \vec{u}$	+0.4873	$\cdot \vec{v}$	+0.4977	$\cdot \vec{w}$	(Re)
$\vec{r}_5 =$	+0.3668	$\cdot \vec{u}$	+0.2493	$\cdot \vec{v}$	+0.2112	$\cdot \vec{w}$	(S)
$\vec{r}_6 =$	+0.3832	$\cdot \vec{u}$	+0.7734	$\cdot \vec{v}$	+0.2763	$\cdot \vec{w}$	(S)
$\vec{r}_7 =$	+0.1191	$\cdot \vec{u}$	+0.2777	$\cdot \vec{v}$	+0.7594	$\cdot \vec{w}$	(S)
$\vec{r}_8 =$	+0.1187	$\cdot \vec{u}$	+0.7540	$\cdot \vec{v}$	+0.6972	$\cdot \vec{w}$	(S)
$\vec{r}_9 =$	+0.6332	$\cdot \vec{u}$	+0.7507	$\cdot \vec{v}$	+0.7888	$\cdot \vec{w}$	(S)
$\vec{r}_{10} =$	+0.6168	$\cdot \vec{u}$	+0.2266	$\cdot \vec{v}$	+0.7237	$\cdot \vec{w}$	(S)
$\vec{r}_{11} =$	+0.8809	$\cdot \vec{u}$	+0.7223	$\cdot \vec{v}$	+0.2406	$\cdot \vec{w}$	(S)
$\vec{r}_{12} =$	+0.8813	$\cdot \vec{u}$	+0.2460	$\cdot \vec{v}$	+0.3028	$\cdot \vec{w}$	(S)

Table A.19.: ReS₂ ML (triclinic): unit cell parameters - quantities are in unit of Å

$$\vec{u} = \begin{pmatrix} +6.4844 \\ 0.0000 \\ 0.0000 \end{pmatrix} \quad \vec{v} = \begin{pmatrix} -3.4057 \\ +5.5904 \\ 0.0000 \end{pmatrix} \quad \vec{w} = \begin{pmatrix} +0.6012 \\ -6.2990 \\ +18.9726 \end{pmatrix}$$

$\vec{r}_1 =$	+0.2476	$\cdot \vec{u}$	+0.0581	$\cdot \vec{v}$	+0.1572	$\cdot \vec{w}$	(Re)
$\vec{r}_2 =$	+0.2982	$\cdot \vec{u}$	+0.5124	$\cdot \vec{v}$	+0.1608	$\cdot \vec{w}$	(Re)
$\vec{r}_3 =$	+0.7524	$\cdot \vec{u}$	+0.9419	$\cdot \vec{v}$	+0.1629	$\cdot \vec{w}$	(Re)
$\vec{r}_4 =$	+0.7018	$\cdot \vec{u}$	+0.4876	$\cdot \vec{v}$	+0.1594	$\cdot \vec{w}$	(Re)
$\vec{r}_5 =$	+0.3674	$\cdot \vec{u}$	+0.2499	$\cdot \vec{v}$	+0.0675	$\cdot \vec{w}$	(S)
$\vec{r}_6 =$	+0.3839	$\cdot \vec{u}$	+0.7729	$\cdot \vec{v}$	+0.0883	$\cdot \vec{w}$	(S)
$\vec{r}_7 =$	+0.1207	$\cdot \vec{u}$	+0.2769	$\cdot \vec{v}$	+0.2432	$\cdot \vec{w}$	(S)
$\vec{r}_8 =$	+0.1189	$\cdot \vec{u}$	+0.7543	$\cdot \vec{v}$	+0.2230	$\cdot \vec{w}$	(S)
$\vec{r}_9 =$	+0.6326	$\cdot \vec{u}$	+0.7501	$\cdot \vec{v}$	+0.2527	$\cdot \vec{w}$	(S)
$\vec{r}_{10} =$	+0.6161	$\cdot \vec{u}$	+0.2271	$\cdot \vec{v}$	+0.2319	$\cdot \vec{w}$	(S)
$\vec{r}_{11} =$	+0.8793	$\cdot \vec{u}$	+0.7231	$\cdot \vec{v}$	+0.0770	$\cdot \vec{w}$	(S)
$\vec{r}_{12} =$	+0.8811	$\cdot \vec{u}$	+0.2457	$\cdot \vec{v}$	+0.0971	$\cdot \vec{w}$	(S)

Table A.20.: ReS₂ ML (monoclinic): unit cell parameters - quantities are in unit of Å

$$\vec{u} = \begin{pmatrix} +6.4844 \\ 0.0000 \\ 0.0000 \end{pmatrix} \quad \vec{v} = \begin{pmatrix} -3.4057 \\ +5.5904 \\ 0.0000 \end{pmatrix} \quad \vec{w} = \begin{pmatrix} 0.0000 \\ 0.0000 \\ +20.0000 \end{pmatrix}$$

$\vec{r}_1 =$	+0.1691	$\cdot \vec{u}$	+0.8809	$\cdot \vec{v}$	+0.1491	$\cdot \vec{w}$	(Re)
$\vec{r}_2 =$	+0.2179	$\cdot \vec{u}$	+0.3313	$\cdot \vec{v}$	+0.1525	$\cdot \vec{w}$	(Re)
$\vec{r}_3 =$	+0.6711	$\cdot \vec{u}$	+0.7584	$\cdot \vec{v}$	+0.1545	$\cdot \vec{w}$	(Re)
$\vec{r}_4 =$	+0.6223	$\cdot \vec{u}$	+0.3080	$\cdot \vec{v}$	+0.1512	$\cdot \vec{w}$	(Re)
$\vec{r}_5 =$	+0.3338	$\cdot \vec{u}$	+0.1739	$\cdot \vec{v}$	+0.0640	$\cdot \vec{w}$	(S)
$\vec{r}_6 =$	+0.3398	$\cdot \vec{u}$	+0.6735	$\cdot \vec{v}$	+0.0837	$\cdot \vec{w}$	(S)
$\vec{r}_7 =$	+0.9994	$\cdot \vec{u}$	+0.0028	$\cdot \vec{v}$	+0.2307	$\cdot \vec{w}$	(S)
$\vec{r}_8 =$	+0.0076	$\cdot \vec{u}$	+0.5029	$\cdot \vec{v}$	+0.2116	$\cdot \vec{w}$	(S)
$\vec{r}_9 =$	+0.5064	$\cdot \vec{u}$	+0.4654	$\cdot \vec{v}$	+0.2397	$\cdot \vec{w}$	(S)
$\vec{r}_{10} =$	+0.5004	$\cdot \vec{u}$	+0.9658	$\cdot \vec{v}$	+0.2199	$\cdot \vec{w}$	(S)
$\vec{r}_{11} =$	+0.8409	$\cdot \vec{u}$	+0.6365	$\cdot \vec{v}$	+0.0730	$\cdot \vec{w}$	(S)
$\vec{r}_{12} =$	+0.8327	$\cdot \vec{u}$	+0.1364	$\cdot \vec{v}$	+0.0921	$\cdot \vec{w}$	(S)

Table A.21.: ReS₂ ML (triclinic): distance vectors between atoms

$\vec{r}_{1,2} = \begin{pmatrix} -1.5153 \\ +0.6815 \\ +1.6307 \end{pmatrix}$	$\vec{r}_{1,3} = \begin{pmatrix} +0.0701 \\ +1.6381 \\ -1.7031 \end{pmatrix}$	$\vec{r}_{1,4} = \begin{pmatrix} -4.6255 \\ +0.4746 \\ +1.4163 \end{pmatrix}$
$\vec{r}_{1,5} = \begin{pmatrix} -1.2963 \\ -1.3667 \\ -1.5229 \end{pmatrix}$	$\vec{r}_{1,6} = \begin{pmatrix} +0.2400 \\ -2.1128 \\ +1.2482 \end{pmatrix}$	$\vec{r}_{1,7} = \begin{pmatrix} +1.8139 \\ -1.1599 \\ -1.3085 \end{pmatrix}$
$\vec{r}_{1,8} = \begin{pmatrix} +2.1885 \\ -3.0728 \\ +0.0673 \end{pmatrix}$	$\vec{r}_{1,9} = \begin{pmatrix} -5.0001 \\ +2.3875 \\ +0.0406 \end{pmatrix}$	$\vec{r}_{1,10} = \begin{pmatrix} -2.8116 \\ -0.6852 \\ +0.1079 \end{pmatrix}$
$\vec{r}_{1,11} = \begin{pmatrix} -3.0516 \\ +1.4276 \\ -1.1404 \end{pmatrix}$	$\vec{r}_{1,12} = \begin{pmatrix} -2.8817 \\ -2.3233 \\ +1.8109 \end{pmatrix}$	

Table A.22.: ReS₂ ML (monoclinic): distance vectors between atoms

$\vec{r}_{1,2} = \begin{pmatrix} -1.5155 \\ +0.6814 \\ +1.6307 \end{pmatrix}$	$\vec{r}_{1,3} = \begin{pmatrix} +0.0700 \\ +1.6383 \\ -1.7029 \end{pmatrix}$	$\vec{r}_{1,4} = \begin{pmatrix} -4.6255 \\ +0.4747 \\ +1.4159 \end{pmatrix}$
$\vec{r}_{1,5} = \begin{pmatrix} -1.2965 \\ -1.3664 \\ -1.5225 \end{pmatrix}$	$\vec{r}_{1,6} = \begin{pmatrix} +0.2399 \\ -2.1130 \\ +1.2483 \end{pmatrix}$	$\vec{r}_{1,7} = \begin{pmatrix} +1.8136 \\ -1.1597 \\ -1.3077 \end{pmatrix}$
$\vec{r}_{1,8} = \begin{pmatrix} -1.2175 \\ +2.5178 \\ +0.0674 \end{pmatrix}$	$\vec{r}_{1,9} = \begin{pmatrix} -5.0002 \\ +2.3877 \\ +0.0408 \end{pmatrix}$	$\vec{r}_{1,10} = \begin{pmatrix} -2.8119 \\ -0.6849 \\ +0.1082 \end{pmatrix}$
$\vec{r}_{1,11} = \begin{pmatrix} -3.0518 \\ +1.4281 \\ -1.1401 \end{pmatrix}$	$\vec{r}_{1,12} = \begin{pmatrix} -6.2877 \\ +3.2671 \\ +1.8111 \end{pmatrix}$	

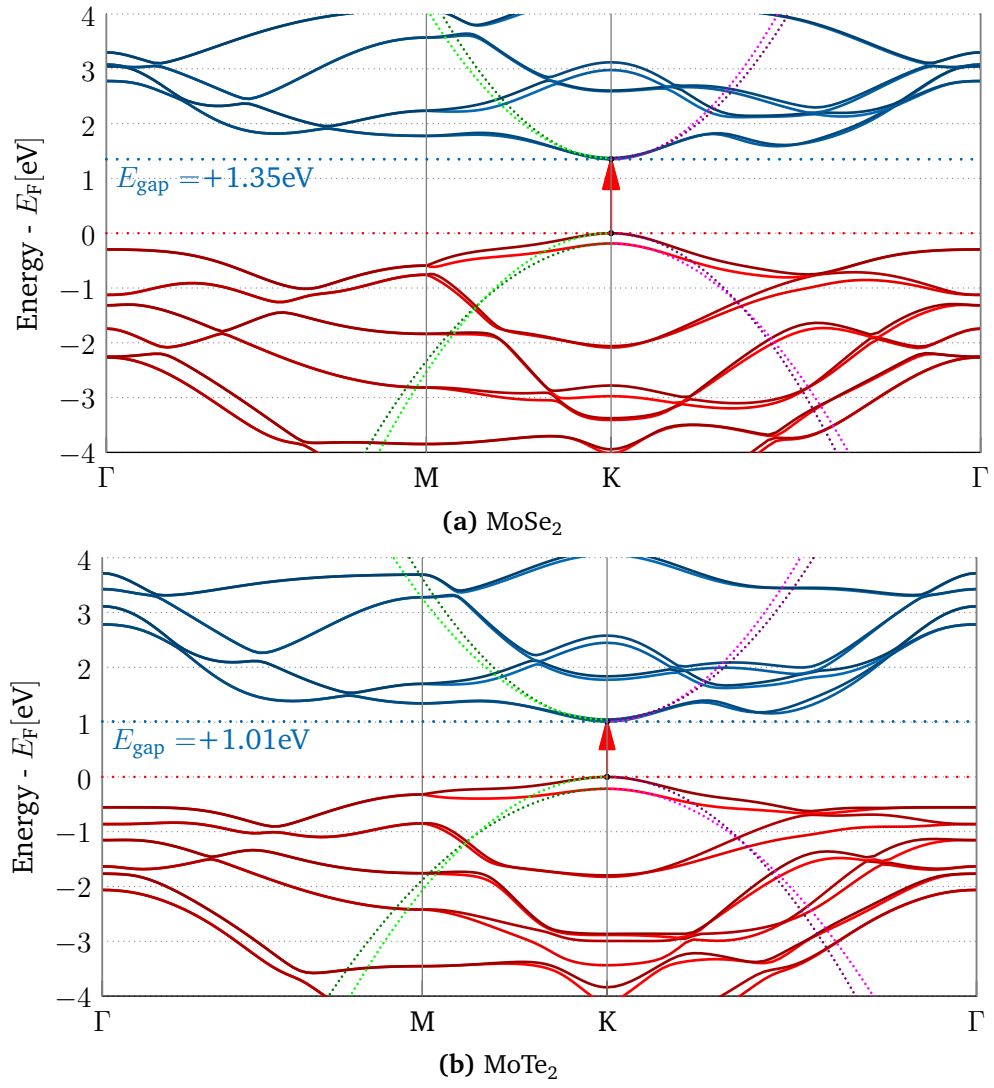


Figure A.23.: MoSe₂, MoTe₂ ML: fit functions for the effective mass approx. - The reader is referred to sec. 5.6 for a detailed explanation on how the data is visualized

Table A.24.: MoX₂ ML: effective masses at the K point - MoX₂ ML: effective masses at the K point

Band	Type	$m_{K \rightarrow \Gamma}$	$m_{K \rightarrow M}$	m_{mean}	Ref.
MoS ₂ 25	hole	0.59	0.65	0.62	-
MoS ₂ 26	hole	0.52	0.57	0.55	0.56
MoS ₂ 27	electron	0.45	0.44	0.44	0.55
MoS ₂ 28	electron	0.45	0.49	0.47	-
MoSe ₂ 25	hole	0.67	0.72	0.69	-
MoSe ₂ 26	hole	0.57	0.61	0.59	0.61
MoSe ₂ 27	electron	0.47	0.49	0.48	0.49
MoSe ₂ 28	electron	0.54	0.56	0.55	-
MoTe ₂ 25	hole	0.74	0.81	0.78	-
MoTe ₂ 26	hole	0.61	0.65	0.63	0.64
MoTe ₂ 27	electron	0.50	0.52	0.51	0.65
MoTe ₂ 28	electron	0.57	0.61	0.59	-

Listing A.25: MoS₂ ML: BSE output of the modified VASP - This output shows the energies and weighted interband matrix elements for the lowest eight excitonic states. The VASP modification is described in ch. 4.

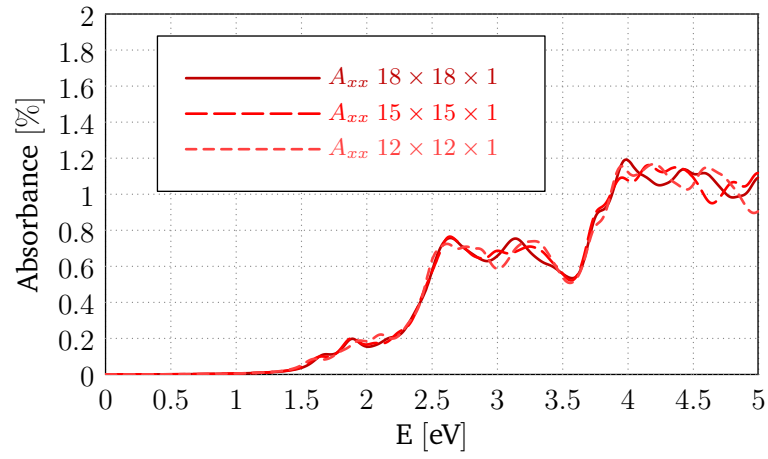
```
[..]
<v> 1.95400 0.05810 -0.10001 -0.00001 0.09987 -0.17345 0.00000 </v>
<v> 1.95411 -0.16471 -0.09483 -0.01639 0.11698 0.06784 0.03522 </v>
<v> 1.96705 -5.47716 -1.28163 0.00070 3.28987 0.56529 -0.00121 </v>
<v> 1.96705 1.37836 -6.04448 0.00045 0.26540 -2.06969 -0.00005 </v>
<v> 2.09768 -0.00017 0.12947 -0.00000 -0.09579 0.04166 -0.00000 </v>
<v> 2.09768 0.10025 0.08280 -0.00002 0.09110 -0.04782 0.00002 </v>
<v> 2.11625 6.79801 1.51438 -0.00002 -1.03863 -0.15985 0.00001 </v>
<v> 2.11625 -1.43586 6.42336 -0.00001 -0.49467 2.44021 0.00000 </v>
[..]
```

Listing A.26: MoSe₂ ML: BSE output of the modified VASP

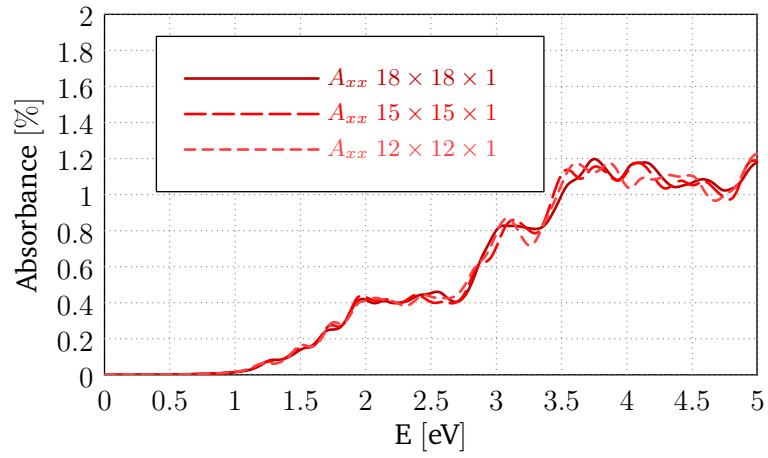
```
[..]
<v> 1.65506 2.74702 1.67016 0.00004 -5.63605 -3.21080 0.00057 </v>
<v> 1.65506 -3.11620 5.28195 0.00000 -1.84442 3.38272 -0.00001 </v>
<v> 1.65751 0.00093 -0.00121 0.00001 0.04718 -0.08173 -0.00000 </v>
<v> 1.65765 -0.07749 -0.04474 -0.04034 -0.00052 -0.00012 0.02420 </v>
<v> 1.82413 0.00409 0.00486 0.00000 -0.00043 0.00444 -0.00000 </v>
<v> 1.82413 -0.00114 0.00353 0.00000 0.00641 -0.00197 -0.00000 </v>
<v> 1.84417 -0.56012 -0.04632 -0.00000 0.42559 0.29720 0.00000 </v>
<v> 1.84417 0.21595 -0.71261 -0.00000 0.24409 0.01529 0.00000 </v>
[..]
```

Listing A.27: MoTe₂ ML: BSE output of the modified VASP

```
[..]
<v> 1.26169 -1.95582 -1.24228 0.00003 6.47289 3.76907 0.00012 </v>
<v> 1.26169 -3.37692 5.59427 -0.00000 -2.09593 3.81324 0.00000 </v>
<v> 1.27800 0.00750 -0.01304 -0.00001 -0.00275 0.00466 -0.00001 </v>
<v> 1.27822 -0.00465 -0.00275 0.05403 -0.01292 -0.00743 0.04288 </v>
<v> 1.41859 2.16374 -3.59591 -0.00000 0.92681 -1.97268 -0.00000 </v>
<v> 1.41859 -1.70031 -1.10168 0.00000 3.73221 2.07618 0.00004 </v>
<v> 1.44068 0.00001 0.00000 -0.00001 0.00025 -0.00037 -0.00001 </v>
<v> 1.44078 -0.00037 -0.00024 0.03820 0.00003 0.00003 0.03033 </v>
[..]
```



(a) MoSe₂



(b) MoTe₂

Figure A.28.: MoSe₂, MoTe₂ ML: absorbance spectrum vs. k-point densities - The reader is referred to sec. 5.8.2 for a detailed explanation on how the data is visualized.

A.3 Excitonic Compositions

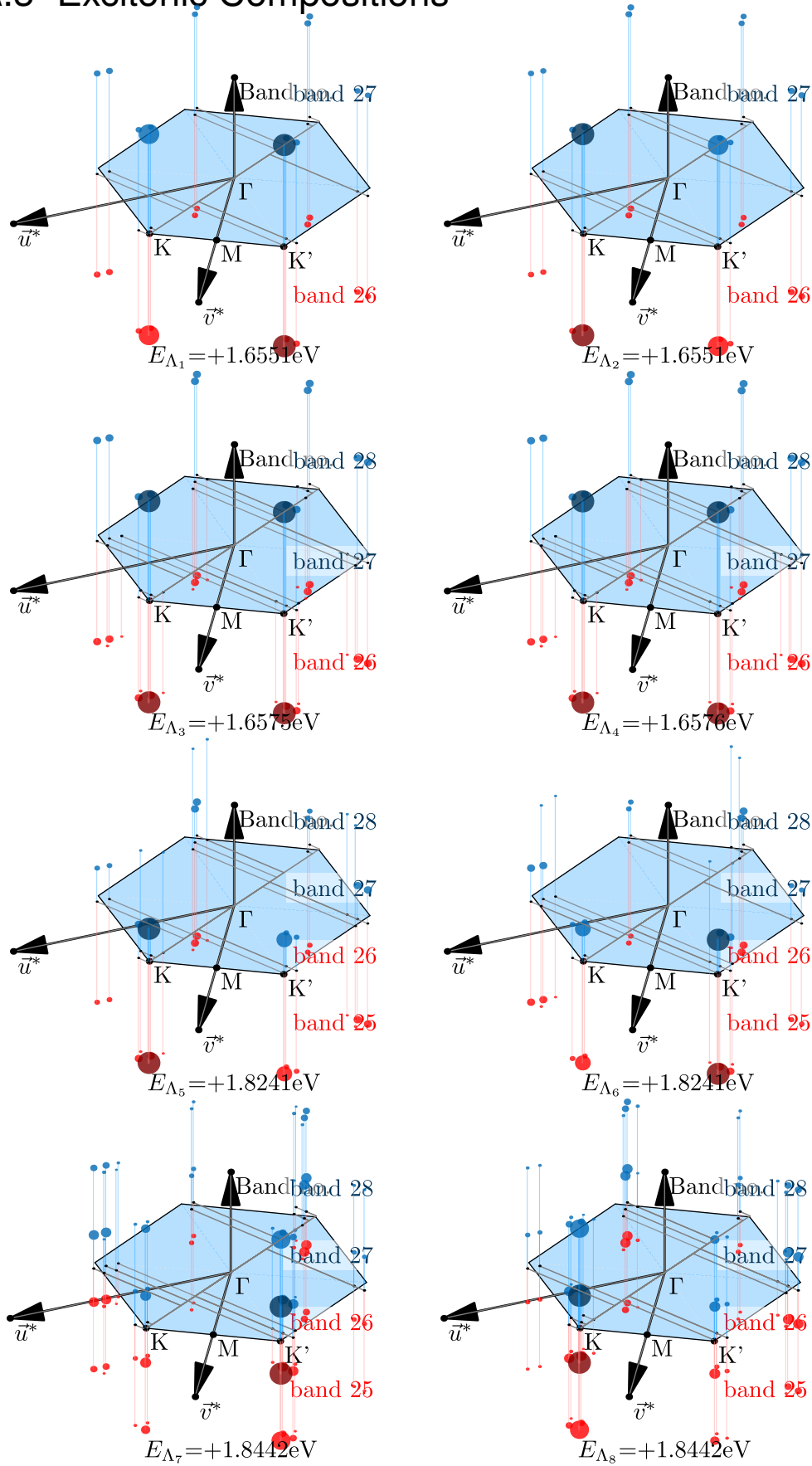


Figure A.29.: MoSe₂ ML: contributions to excitons 1-8 - The reader is referred to sec. 5.8.1 for a detailed explanation on how the data is visualized.

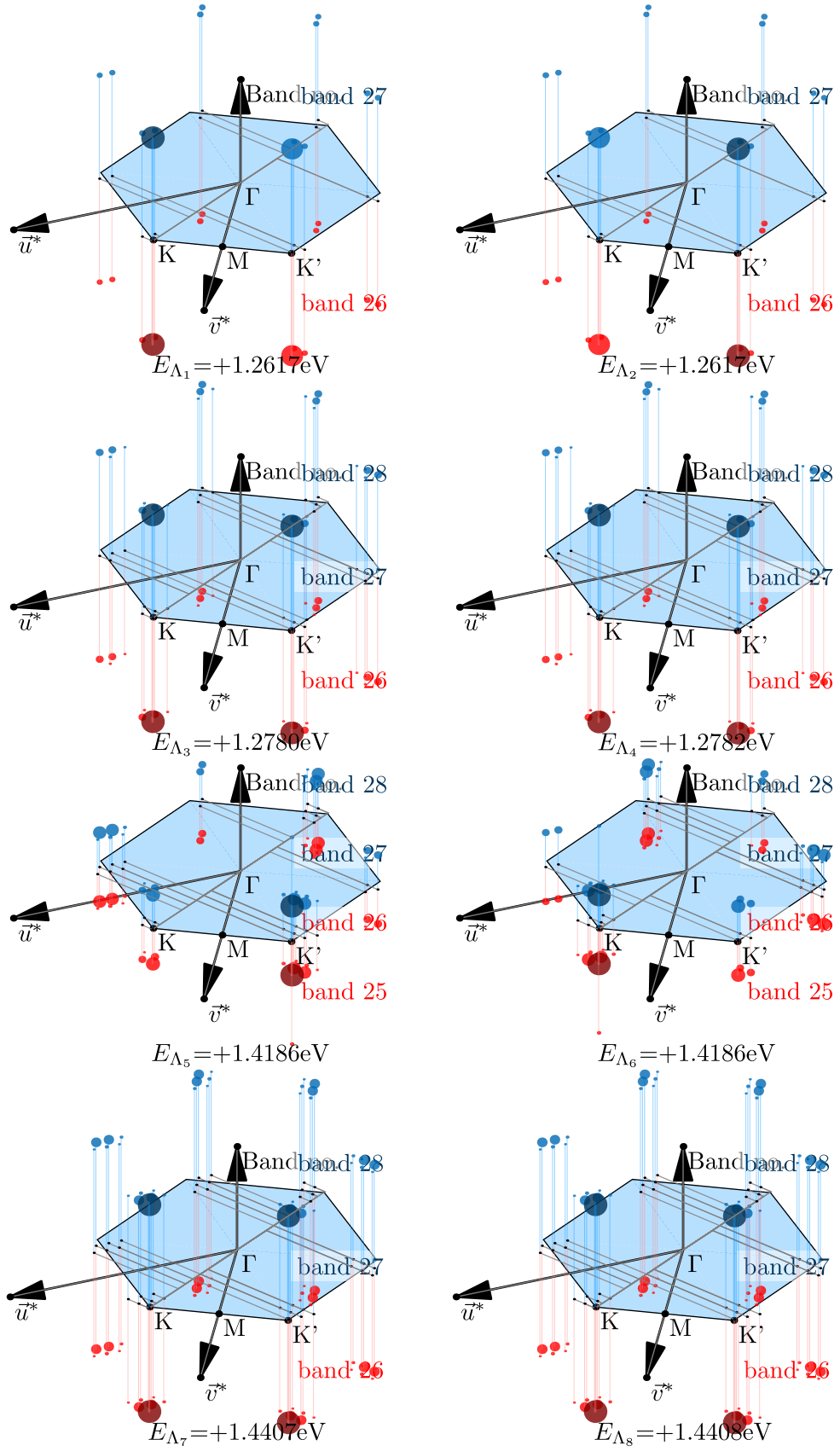


Figure A.30.: MoTe₂ ML: contributions to excitons 1-8

A.4 Files

Listing A.31: MoX₂ ML: POSCAR generation file - Variables a , c , z represent lattice constants, factor x scales the unit cell while keeping z constant.

```

1  #!/bin/sh
2
3  a=$1
4  c=$2
5  z=$3
6  x=$4
7
8  zd=$(echo "scale=16;_c*_0.75-_c*_z" | bc)
9
10 ascale=$(echo "scale=16;_x*_a" | bc)
11 cscale=$(echo "scale=16;_c*_x" | bc)
12
13 ahalf=$(echo "scale=16;_ascale/_2" | bc)
14 asqrt3h=$(echo "scale=16;_ascale*_0.86602540378444" | bc)
15
16 z14=$(echo "scale=16;_cscale*_0.25" | bc) # lower z position of atom type 1
17 z34=$(echo "scale=16;_cscale*_0.75" | bc) # upper z position of atom type 1
18
19 z1=$(echo "scale=16;_z14-_zd" | bc)
20 z2=$(echo "scale=16;_z14+_zd" | bc)
21 z3=$(echo "scale=16;_z34-_zd" | bc)
22 z4=$(echo "scale=16;_z34+_zd" | bc)
23
24 x1323=$(echo "scale=16;_ahalf*_0.3333333333333333+_ahalf*_0.6666666666666667" | bc)
25 y1323=$(echo "scale=16;_asqrt3h*_0.3333333333333333+_asqrt3h*_0.6666666666666667" | bc)
26 x2313=$(echo "scale=16;_ahalf*_0.6666666666666667+_ahalf*_0.3333333333333333" | bc)
27 y2313=$(echo "scale=16;_asqrt3h*_0.6666666666666667+_asqrt3h*_0.3333333333333333" | bc)
28
29 cat >POSCAR <<!
30 comment
31 1.0 # factor
32 $ahalf -$asqrt3h 0.0 # a1 x y z
33 $ahalf $asqrt3h 0.0 # a2 x y z
34 0.0 0.0 25.0 # a3 x y z
35 1 2 # number of atoms
36 cart # positions
37 $x1323 $y1323 $z14 # atom type 1
38 $x2313 $y2313 $z1 # atom type 2
39 $x2313 $y2313 $z2 # atom type 2
40 !

```

Listing A.32: ReS₂ bulk: POSCAR generation file - Argument 1 defines the unit cell volume.

```

1  #!/bin/sh
2  # a and c are exchanged, b and c lie in the x/y plane
3
4  volume=$1
5
6  a=6.417
7  b=6.510
8  c=6.461
9
10 a=$(echo "scale=16;_a" | bc)
11 b=$(echo "scale=16;_b" | bc)
12 c=$(echo "scale=16;_c" | bc)
13
14 alpha=121.10
15 beta=88.38
16 gamma=106.47
17
18 pi=3.141592653589793
19
20 # http://afloplib.org/CrystalDatabase/triclinic_lattice.html
21
22 alphas=$(echo "scale=16;_(_alpha/_360.0)_*_2.0*_pi" | bc) # radians
23 betas=$(echo "scale=16;_(_beta/_360.0)_*_2.0*_pi" | bc) # radians
24 gammas=$(echo "scale=16;_(_gamma/_360.0)_*_2.0*_pi" | bc) # radians
25
26 ux=$c

```

```

27 uy=0.0
28 uz=0.0
29
30 vx=$(echo "scale=16;u$b_u*uc_u($alphar)" | bc -l)
31 vy=$(echo "scale=16;u$b_u*uc_u($alphar)" | bc -l)
32 vz=0.0
33
34 wx=$(echo "scale=16;u$a_u*uc_u($betar)" | bc -l)
35 wy=$(echo "scale=16;u$a_u*(uc_u($gammar)-uc_u($betar)-uc_u($alphar)-u/us_u($alphar)-u" | bc -l)
36 wz=$(echo "scale=16;usqrt(u$a*$a_u-u$wx*$wx_u-u$wy*$wy_u)" | bc -l)
37
38 e1c=0.4925 # Re1
39 e1b=0.0564 # Re1
40 e1a=0.2477 # Re1
41 e2c=0.5026 # Re2
42 e2b=0.5112 # Re2
43 e2a=0.2974 # Re2
44 e3c=0.2174 # S1
45 e3b=0.2498 # S1
46 e3a=0.3676 # S1
47 e4c=0.2769 # S2
48 e4b=0.7705 # S2
49 e4a=0.3819 # S2
50 e5c=0.7562 # S3
51 e5b=0.2729 # S3
52 e5a=0.1178 # S3
53 e6c=0.6975 # S4
54 e6b=0.7526 # S4
55 e6a=0.1169 # S4
56
57 cat >POSCAR <<!
58 comment
59 -$volume #
60 $ux $uy $uz # a1 x y z
61 $vx $vy $vz # a2 x y z
62 $wx $wy $wz # a3 x y z
63 4 8 # number of atoms
64 cart # positions
65 $(echo "scale=16;u(u$e1a*$ux_u+u$e1b*$vx_u+u$e1c*$wx_u)" | bc) $(echo "scale=16;u(u$e1a*$uy_u+u$e1b*$vy_u
+u$e1c*$wy_u)" | bc) $(echo "scale=16;u(u$e1a*$uz_u+u$e1b*$vz_u+u$e1c*$wz_u)" | bc) # Re1
66 $(echo "scale=16;u(u$e2a*$ux_u+u$e2b*$vx_u+u$e2c*$wx_u)" | bc) $(echo "scale=16;u(u$e2a*$uy_u+u$e2b*$vy_u
+u$e2c*$wy_u)" | bc) $(echo "scale=16;u(u$e2a*$uz_u+u$e2b*$vz_u+u$e2c*$wz_u)" | bc) # Re2
67 $(echo "scale=16;u-$e1a*$ux_u-u$e1b*$vx_u+(1.0-$e1c)*$wx" | bc) $(echo "scale=16;u-$e1a*$uy_u-u$e1b*$
vy_u+(1.0-$e1c)*$wy" | bc) $(echo "scale=16;u-$e1a*$uz_u-u$e1b*$vz_u+(1.0-$e1c)*$wz" | bc) #
Re1
68 $(echo "scale=16;u-$e2a*$ux_u-u$e2b*$vx_u+(1.0-$e2c)*$wx" | bc) $(echo "scale=16;u-$e2a*$uy_u-u$e2b*$
vy_u+(1.0-$e2c)*$wy" | bc) $(echo "scale=16;u-$e2a*$uz_u-u$e2b*$vz_u+(1.0-$e2c)*$wz" | bc) #
Re2
69 $(echo "scale=16;u(u$e3a*$ux_u+u$e3b*$vx_u+u$e3c*$wx_u)" | bc) $(echo "scale=16;u(u$e3a*$uy_u+u$e3b*$vy_u
+u$e3c*$wy_u)" | bc) $(echo "scale=16;u(u$e3a*$uz_u+u$e3b*$vz_u+u$e3c*$wz_u)" | bc) # S1
70 $(echo "scale=16;u(u$e4a*$ux_u+u$e4b*$vx_u+u$e4c*$wx_u)" | bc) $(echo "scale=16;u(u$e4a*$uy_u+u$e4b*$vy_u
+u$e4c*$wy_u)" | bc) $(echo "scale=16;u(u$e4a*$uz_u+u$e4b*$vz_u+u$e4c*$wz_u)" | bc) # S2
71 $(echo "scale=16;u(u$e5a*$ux_u+u$e5b*$vx_u+u$e5c*$wx_u)" | bc) $(echo "scale=16;u(u$e5a*$uy_u+u$e5b*$vy_u
+u$e5c*$wy_u)" | bc) $(echo "scale=16;u(u$e5a*$uz_u+u$e5b*$vz_u+u$e5c*$wz_u)" | bc) # S3
72 $(echo "scale=16;u(u$e6a*$ux_u+u$e6b*$vx_u+u$e6c*$wx_u)" | bc) $(echo "scale=16;u(u$e6a*$uy_u+u$e6b*$vy_u
+u$e6c*$wy_u)" | bc) $(echo "scale=16;u(u$e6a*$uz_u+u$e6b*$vz_u+u$e6c*$wz_u)" | bc) # S4
73 $(echo "scale=16;u-$e3a*$ux_u-u$e3b*$vx_u+(1.0-$e3c)*$wx" | bc) $(echo "scale=16;u-$e3a*$uy_u-u$e3b*$
vy_u+(1.0-$e3c)*$wy" | bc) $(echo "scale=16;u-$e3a*$uz_u-u$e3b*$vz_u+(1.0-$e3c)*$wz" | bc) #
S1
74 $(echo "scale=16;u-$e4a*$ux_u-u$e4b*$vx_u+(1.0-$e4c)*$wx" | bc) $(echo "scale=16;u-$e4a*$uy_u-u$e4b*$
vy_u+(1.0-$e4c)*$wy" | bc) $(echo "scale=16;u-$e4a*$uz_u-u$e4b*$vz_u+(1.0-$e4c)*$wz" | bc) #
S2
75 $(echo "scale=16;u-$e5a*$ux_u-u$e5b*$vx_u+(1.0-$e5c)*$wx" | bc) $(echo "scale=16;u-$e5a*$uy_u-u$e5b*$
vy_u+(1.0-$e5c)*$wy" | bc) $(echo "scale=16;u-$e5a*$uz_u-u$e5b*$vz_u+(1.0-$e5c)*$wz" | bc) #
S3
76 $(echo "scale=16;u-$e6a*$ux_u-u$e6b*$vx_u+(1.0-$e6c)*$wx" | bc) $(echo "scale=16;u-$e6a*$uy_u-u$e6b*$
vy_u+(1.0-$e6c)*$wy" | bc) $(echo "scale=16;u-$e6a*$uz_u-u$e6b*$vz_u+(1.0-$e6c)*$wz" | bc) #
S4
77 !

```

Listing A.33: extract_optics.sh script for VASP - This script extracts the dielectric function from vasprun.xml to the files REAL.in and IMAG.in

```

1 # extract image and real parts of dielectric function from vasprun.xml
2 awk 'BEGIN{i=1} /imag/,\
3      /\img/ \
4      {a[i]=$2 ; b[i]=$3 ; c[i]=$4 ; d[i]=$5 ; e[i]=$6 ; f[i]=$7 ; g[i]=$8 ; i=i+1} \

```

```

5      END{for (j=12;j<i-3;j++) print a[j],b[j],c[j],d[j],e[j],f[j],g[j]}' vasprun.xml > IMAG.in
6
7  awk 'BEGIN{i=1} /real/,\
8      /\real/ \
9      {a[i]=$2 ; b[i]=$3 ; c[i]=$4; d[i]=$5 ; e[i]=$6 ; f[i]=$7; g[i]=$8; i=i+1} \
10     END{for (j=12;j<i-3;j++) print a[j],b[j],c[j],d[j],e[j],f[j],g[j]}' vasprun.xml > REAL.in

```

Listing A.34: MoX₂ ML: wannier90.win band structure configuration

```

1  exclude_bands = 1-12,35-$nbands # exclude Mo 4s (=1), Mo 4p (=3), X 3s (=2*1), total low = 1+3+2 = 6,
   next 11 are wanted and (everything * 2)
2  num_wann = 22
3  mp_grid = 18 18 1
4  iprint = 5
5  num_iter = 1000
6
7  begin projections
8  Mo:d
9  $atom:p
10 end projections
11
12 bands_plot = true
13 bands_plot_format = xmgrace
14
15 kmesh = 64 64 1
16
17 begin kpoint_path
18 G 0.00000000 0.00000000 0.00000000 M 0.50000000 0.00000000 0.00000000
19 M 0.50000000 0.00000000 0.00000000 K 0.33333333 0.33333333 0.00000000
20 K 0.33333333 0.33333333 0.00000000 G 0.00000000 0.00000000 0.00000000
21 end kpoint_path

```

Listing A.35: ReS₂ ML: wannier90.win band structure configuration

```

1  exclude_bands = 1-48,137-$nbands
2  num_wann = 88
3  search_shells = 48 # 'cures error: Your cell might be very long, or you may have an irregular MP grid'
4  mp_grid = 12 12 1
5  iprint = 5
6  num_iter = 1000
7
8  begin projections
9  Re:d
10 S:p
11 end projections
12
13 bands_plot = true
14 bands_plot_format = xmgrace
15
16 kmesh = 64 64 1
17
18 begin kpoint_path
19 G 0.0000000000000000 0.0000000000000000 0.0 M1 0.0000000000000000 0.5000000000000000 0.0
20 M1 0.0000000000000000 0.5000000000000000 0.0 K1 0.3322490784946616 0.3254978874736156 0.0
21 K1 0.3322490784946616 0.3254978874736156 0.0 G 0.0000000000000000 0.0000000000000000 0.0
22 G 0.0000000000000000 0.0000000000000000 0.0 M2 0.5000000000000000 0.0000000000000000 0.0
23 M2 0.5000000000000000 0.0000000000000000 0.0 K2 0.6677509215053383 -0.3254978874736156 0.0
24 K2 0.6677509215053383 -0.3254978874736156 0.0 G 0.0000000000000000 0.0000000000000000 0.0
25 G 0.0000000000000000 0.0000000000000000 0.0 M3 0.5000000000000000 -0.5000000000000000 0.0
26 M3 0.5000000000000000 -0.5000000000000000 0.0 K3 0.3322490784946616 -0.6745021125263844 0.0
27 K3 0.3322490784946616 -0.6745021125263844 0.0 G 0.0000000000000000 0.0000000000000000 0.0
28 end kpoint_path

```

Listing A.36: VASP makefile

```

1  # Precompiler options
2  CPP_OPTIONS= -DHOST="LinuxIFC"\
3  -DMPICH2=DMPI -DMPICH2_BLOCK=8000\
4  -Duse_collective\
5  -DscLAPACK\
6  -DCACHE_SIZE=4000\
7  -Davoidallocc\
8  -Duse_bse_te\
9  -DVASP2WANNIER90v2\

```

```

10  Dlibbeef\
11  Duse_shmem\
12  Dtbdyn\
13  Dvasp6\
14  Dmemalign64\
15  Dshmem_rproj\
16  Dshmem_bcast_buffer\
17  Dfock_dblbuf
18
19  GITCOMMIT=$(shell git --no-pager describe --tags --abbrev=10)'
20  CPP_OPTIONS+=-DVASP_VERSION=$(GITCOMMIT)
21
22  CPPFLAGS+=-fcommon-free-w0$(FUFFIX)$(SUFFIX)$(CPP_OPTIONS)
23
24  FCFLAGS+=-mpif90-qopt-report5
25  FCLFLAGS+=-mpif90-mkl=sequential
26
27  FREEFLAGS+=-free-nameslowercase
28
29  FFLAGS+=-assume_byterecl-w-axCORE-AVX2,AVX
30  OFLAGS+=-O2
31  OFLAG_IN=$(OFLAG)
32  DEBUGFLAGS+=-O0
33
34  MKL_PATH=$(MKLR00T)/lib/intel64
35  BLASLIBS=
36  LAPACKLIBS=
37  BLACSLIBS=
38  SCALAPACKLIBS=/opt/intel/i15/scalapack-2.0.2-mpi-1.10.2-INTEL-15.0.3/libscalapack.a
39
40
41  OBJECTS+=fftwmpi.o,fftwmpi_map.o,fftw3dlib.o,fftw3d.o
42
43  INCS+=-I$(MKLR00T)/include/fftw
44
45  LLIBS+=$(SCALAPACK)$(LAPACK)$(BLAS)
46
47  LLIBS+=/fs/home/user/vasp_source/wannier90-2.1.0/libwannier.a
48  LLIBS+=-L/fs/home/mmars/src/vasp/libs/libbeef-0.1.1/lib-lbeef
49
50  OBJECTS_01+=fftw3d.o,fftwmpi.o,fftwmpi.o
51  OBJECTS_02+=fftw3dlib.o
52
53  #For what used to be vasp.5.lib
54  CPP_LIBS=$(CPP)
55  FC_LIBS=$(FC)
56  CC_LIBS=icc
57  CFLAGS_LIB=-O
58  FFLAGS_LIB=-O1
59  FREE_LIBS=$(FREE)
60
61  OBJECTS_LIB=linpack_double.o,getshmem.o
62
63  #For the parser library
64  CXX_PARS=icpc
65
66  LIBS+=parser
67  LLIBS+=-Lparser-ldc++
68
69  #Normally no need to change this
70  SRCDIR=../src
71  BINDIR=../bin
72
73  limit.o:
74  cc -Wall -O2 -vasp_source/vasp.5.4.4/src/limit.c

```

Listing A.37: Changes to VASPKIT linearoptics.f90

```

1  SUBROUTINE LINEAROPTICS
2  [..]
3      CHARACTER(LEN=12) :: IMAG_PART='IMAG.in', REAL_PART='REAL.in'
4      REAL(KIND=8) :: ABSORB(6), ABSORBRB(6), REFRACTIVE(6), ENERGYLOSSSPECTRUM(6), EXTINCTION(6), REFLECTIVITY
          (6), FREQ !rb
5      REAL(KIND=8) :: EN, EPSILON_REAL(6), EPSILON_IMAG(6)
6  [..]
7      OPEN(61, FILE='ABSORB'//DATSUFF, FORM='FORMATTED', STATUS='REPLACE', ACTION='WRITE')

```

```

8      WRITE(61,'(A100)')"#_energy_(eV)_____xx_____yy_____zz_____xy_____
      _yz_____zx"
9      OPEN(66,FILE='ABSORBRB'//DATSUFF,FORM='FORMATTED',STATUS='REPLACE',ACTION='WRITE')
10     WRITE(66,'(A100)')"#_energy_(eV)_____xx_____yy_____zz_____xy_____
      _yz_____zx" !rb
11  [...]
12     DO WHILE(IOSTAT==0)
13  [...]
14         EXTINCTION(J)=(SQRT(-EPSILON_REAL(J)+SQRT(EPSILON_IMAG(J)*EPSILON_IMAG(J)+EPSILON_REAL(J)*
      EPSILON_REAL(J))))/1.4142
15         ABSORBCOEFF(J)=2*FREQ*EXTINCTION(J)/CO !rb
16  [...]
17         END DO
18         WRITE(61,'(F8.3,6E16.4)')EN,(ABSORB(J),J=1,6)
19         WRITE(66,'(F8.3,6E16.4)')EN,(ABSORBRB(J),J=1,6) !rb
20  [...]
21     CLOSE(65)
22     CLOSE(66) !rb
23     200 RETURN
24 END SUBROUTINE

```

Bibliography

- [Ash+77] N. W. Ashcroft, N. D. Mermin, and R. Smoluchowski. *Solid State Physics*. Vol. 30. 1. AIP Publishing, 1977, pp. 61–65 (cit. on p. 23).
- [Bec15] Friedhelm Bechstedt. *Many-Body Approach to Electronic Excitations*. Springer Berlin Heidelberg, 2015 (cit. on pp. 2, 7–12, 14, 16, 18–20, 22, 23, 53).
- [Cap+07] Rodrigo B. Capaz, Catalin D. Spataru, Sohrab Ismail-Beigi, and Steven G. Louie. “Excitons in carbon nanotubes: Diameter and chirality trends”. In: *physica status solidi (b)* 244.11 (2007), pp. 4016–4020 (cit. on pp. 2, 36).
- [Cui+15] Qiannan Cui, Jiaqi He, Matthew Z. Bellus, et al. “Transient Absorption Measurements on Anisotropic Monolayer ReS₂”. In: *Small* 11.41 (2015), pp. 5565–5571 (cit. on pp. 2, 76, 80, 85).
- [Fuc+08] F. Fuchs, C. Rödl, A. Schleife, and F. Bechstedt. “Efficient O(N²) approach to solve the Bethe-Salpeter equation for excitonic bound states”. In: *Physical Review B* 78.8 (2008) (cit. on p. 23).
- [Geh+17] Mathias Gehlmann, Irene Aguilera, Gustav Bihlmayer, et al. “Direct Observation of the Band Gap Transition in Atomically Thin ReS₂”. In: *Nano Letters* 17.9 (2017), pp. 5187–5192 (cit. on pp. 71, 72).
- [GM12] Rudolf Gross and Achim Marx. *Festkörperphysik*. Oldenbourg Wissenschaftsverlag Verlag, 2012 (cit. on p. 13).
- [Har+17] Lewis S. Hart, James L. Webb, Sara Dale, et al. “Electronic bandstructure and van der Waals coupling of ReSe₂ revealed by high-resolution angle-resolved photoemission spectroscopy”. In: *Scientific Reports* 7.1 (2017) (cit. on p. 47).
- [Lem+15] Dominik Lembke, Simone Bertolazzi, and Andras Kis. “Single-Layer MoS₂ Electronics”. In: *Accounts of Chemical Research* 48.1 (2015), pp. 100–110 (cit. on p. 1).
- [Lia+13] Yufeng Liang, Shouting Huang, Ryan Soklaski, and Li Yang. “Quasiparticle band-edge energy and band offsets of monolayer of molybdenum and tungsten chalcogenides”. In: *Applied Physics Letters* 103.4 (2013), p. 042106 (cit. on pp. 40, 44, 57, 59, 61, 83).
- [Mak+12] Kin Fai Mak, Keliang He, Jie Shan, and Tony F. Heinz. “Control of valley polarization in monolayer MoS₂ by optical helicity”. In: *Nature Nanotechnology* 7.8 (2012), pp. 494–498 (cit. on pp. 46, 65).
- [Mav16] Juraj Mavracic. “Excitonic effects of novel 2D photocatalysts”. In: *Wien*, 2016 (cit. on pp. 50, 52).

- [Moo+16] Galan Moody, John Schaibley, and Xiaodong Xu. “Exciton dynamics in monolayer transition metal dichalcogenides”. In: *Journal of the Optical Society of America B* 33.7 (2016), p. C39 (cit. on pp. 1, 69, 84).
- [Mur+94] H. H. Murray, S. P. Kelty, R. R. Chianelli, and C. S. Day. “Structure of Rhenium Disulfide”. In: *Inorganic Chemistry* 33.19 (1994), pp. 4418–4420 (cit. on pp. 71, 84).
- [Net+09] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim. “The electronic properties of graphene”. In: *Reviews of Modern Physics* 81.1 (2009), pp. 109–162 (cit. on p. 1).
- [Ovc+16] Dmitry Ovchinnikov, Fernando Gargiulo, Adrien Allain, et al. “Disorder engineering and conductivity dome in ReS₂ with electrolyte gating”. In: *Nature Communications* 7 (2016), p. 12391 (cit. on pp. 79, 85).
- [Pal+15] Maurizia Palummo, Marco Bernardi, and Jeffrey C. Grossman. “Exciton Radiative Lifetimes in Two-Dimensional Transition Metal Dichalcogenides”. In: *Nano Letters* 15.5 (2015), pp. 2794–2800 (cit. on pp. 2, 22, 24–26, 29–31, 50, 63, 64, 68, 69, 83, 84).
- [Pee+11] H. Peelaers, B. Partoens, M. Giantomassi, et al. “Convergence of quasiparticle band structures of Si and Ge nanowires in the GW approximation and the validity of scissor shifts”. In: *Physical Review B* 83.4 (2011) (cit. on p. 50).
- [Pen+16] Haowei Peng, Zeng-Hui Yang, John P. Perdew, and Jianwei Sun. “Versatile van der Waals Density Functional Based on a Meta-Generalized Gradient Approximation”. In: *Physical Review X* 6.4 (2016) (cit. on p. 43).
- [Rah+17] Mohammad Rahman, Kenneth Davey, and Shi-Zhang Qiao. “Advent of 2D Rhenium Disulfide (ReS₂): Fundamentals to Applications”. In: *Advanced Functional Materials* 27.10 (2017), p. 1606129 (cit. on p. 2).
- [Rob+16] C. Robert, D. Lagarde, F. Cadiz, et al. “Exciton radiative lifetime in transition metal dichalcogenide monolayers”. In: *Physical Review B* 93.20 (2016) (cit. on p. 24).
- [RT15] Filip A. Rasmussen and Kristian S. Thygesen. “Computational 2D Materials Database: Electronic Structure of Transition-Metal Dichalcogenides and Oxides”. In: *The Journal of Physical Chemistry C* 119.23 (2015), pp. 13169–13183 (cit. on pp. 59, 65, 83, 84).
- [SC10] Wahyu Setyawan and Stefano Curtarolo. “High-throughput electronic band structure calculations: Challenges and tools”. In: *Computational Materials Science* 49.2 (2010), pp. 299–312 (cit. on p. 41).
- [Sun+16] Jianwei Sun, Richard C. Remsing, Yubo Zhang, et al. “Accurate first-principles structures and energies of diversely bonded systems from an efficient density functional”. In: *Nature Chemistry* 8.9 (2016), pp. 831–836 (cit. on p. 40).
- [Zho+15] Hong-Xia Zhong, Shiyuan Gao, Jun-Jie Shi, and Li Yang. “Quasiparticle band gaps, excitonic effects, and anisotropic optical properties of the monolayer distorted 1T diamond-chain structures ReS₂ and ReSe₂”. In: *Physical Review B* 92.11 (2015) (cit. on pp. 72–74, 76, 84).

Websites

- [asy] *Asymptote - The Vector Graphics Language*. URL: <http://asymptote.sourceforge.net/> (visited on Apr. 29, 2018) (cit. on p. 39).
- [kit] *Postprocessing tool for VASP code*. URL: <http://vaspkit.sourceforge.net/> (visited on Apr. 29, 2018) (cit. on p. 53).
- [wan] *Maximally-Localised Wannier function*. URL: <http://www.wannier.org/> (visited on Apr. 29, 2018) (cit. on p. 51).

Abstract

2D materials exhibit interesting characteristics at a low production cost: for example, the superconductivity of graphene, the electro-optical properties of MoS_2 , or the directional dependence of the properties of ReS_2 . Many different factors and mechanisms influence the optical properties of these materials. A critical process for the light emission characteristics is the exciton radiative decay. The lifetime of this process has recently been computed for some isotropic 2D materials. In this thesis, simple formulas that describe the exciton lifetime for anisotropic 2D materials are derived from the theory. Furthermore, the calculation of these quantities is implemented into the VASP. To validate the development of this method, the isotropic structures MoS_2 , MoSe_2 , and MoTe_2 are investigated. The results conform well to experimental results. The method is then applied to the anisotropic material ReS_2 . The computed absorption spectrum conforms well to experimental results at room temperature; however, the calculated radiative exciton lifetime of 5.1ns is much larger than the experimental exciton lifetime of 40ps. This difference is most likely caused by non-radiative processes that are not considered in this thesis. Further experiments with ReS_2 and simulations with other materials would be helpful to better understand the exciton decay in such materials.

Zusammenfassung

2D-Materialien zeigen interessante Eigenschaften bei niedrigen Produktionskosten, wie zum Beispiel die Supraleitung von Graphen, die elektrooptischen Eigenschaften von MoS_2 oder die richtungsabhängigen Eigenschaften von ReS_2 . Die optischen Eigenschaften dieser Materialien werden von verschiedensten Faktoren und Prozessen beeinflusst. Ein Prozess, der die Lichtemissionseigenschaften maßgebend beeinflusst, ist der strahlende Exzitonen-Zerfallsprozess. Die Lebensdauer dieses Prozesses wurde kürzlich für einige isotrope 2D-Materialien berechnet. In dieser Arbeit werden Formeln, die diese Lebensdauer auch für anisotrope 2D-Materialien beschreiben, aus der Theorie abgeleitet. Weiterführend wird die Berechnung dieser Größen in dem VASP implementiert. Um die Methodenentwicklung zu verifizieren, werden zuerst die isotropen Strukturen MoS_2 , MoSe_2 und MoTe_2 untersucht. Die Resultate dieser Berechnungen stimmen gut mit experimentellen Ergebnissen überein. Das Verfahren wird dann auf das anisotrope Material ReS_2 angewandt. Das berechnete Absorptionsspektrum stimmt mit den experimentellen Ergebnissen bei Raumtemperatur gut überein. Die errechnete strahlende Exzitonen-Lebensdauer von 5,1ns ist jedoch viel größer als der experimentell bestimmte Wert von 40ps. Dieser Unterschied wird vermutlich durch nicht strahlende Prozesse verursacht, die in dieser Arbeit nicht berücksichtigt werden. Weitere Experimente mit ReS_2 und Simulationen mit anderen Materialien sind wünschenswert, um den Exzitonen-Zerfallsprozess in solchen Materialien besser zu verstehen.