



universität
wien

MASTERARBEIT / MASTER'S THESIS

Titel der Masterarbeit / Title of the Master's Thesis

Electron-Phonon Interactions Using Wannier-Fourier Interpolation

verfasst von / submitted by

Manuel Engel, BSc

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

Master of Science (MSc)

Wien, 2017 / Vienna, 2017

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:

Masterstudium Physik UG2002

Betreut von / Supervisor:

Univ.-Prof. Dipl.-Ing. Dr. Georg Kresse

Contents

1. Introduction	4
2. Density-Functional Theory	6
2.1. The Born-Oppenheimer Approximation	6
2.2. The Hohenberg-Kohn Theorems	7
2.3. The Kohn-Sham Equations	8
3. Electron Dynamics in a Periodic Potential	11
3.1. Bloch Orbitals	11
3.2. Electronic Band Structure	14
4. The Projector Augmented-Wave Method	17
4.1. The Transformation Operator	18
4.2. Operators	21
4.3. Total Energy and Hamiltonian	22
5. Lattice Dynamics	25
5.1. Properties of the Force-Constant Matrix	26
5.2. Dynamical Matrix and Vibrational Spectrum	27
5.3. Phonons	29
6. Band-Gap Renormalization	34
6.1. Fan-Migdal Term	38
6.2. Debye-Waller Term	42
7. Wannier Functions	44
7.1. Projection onto Trial Orbitals	45
7.2. Wannier-Fourier Interpolation	47
7.2.1. Interpolation of Electronic Band Structure	47
7.2.2. Interpolation of Electron-Phonon Matrix Elements	49

8. Implementation Details	52
8.1. General Remarks	52
8.2. Electron-Phonon Interaction	54
8.3. Program Outline	57
9. Results and Discussion	58
9.1. VASP Setup	58
9.2. Wannier Functions	59
9.3. Electronic Band Structure and Phonons	64
9.4. Electron-Phonon Interaction	66
10. Conclusion	69
A. Abstract (English)	74
B. Abstract (German)	75

Acknowledgments

It is my sincere desire to express my utmost gratitude to everyone who encouraged, supported and guided me throughout this great endeavor I call my thesis. First and foremost, I want to thank my supervisor, Georg Kresse, from the bottom of my heart for enabling this project, showing patience in the face of slow progress and providing help with his broad spectrum of expertise. I am also immeasurably thankful to Martijn Marsman, who calmly and expertly answered any and all of the many questions I confronted him with, as he guided me through the abyssal depths of the VASP source code. I consider myself very happy and fortunate to have met these two great individuals. This thesis would never have been possible without them.

Especially heartfelt thanks goes to my loving soul mate and soon-to-be wife, Beate Reichl, who encouraged me every single day and gave me the occasionally needed push towards productivity. In addition, I want to thank my supportive family and all of my friends and colleagues for putting up with me and staying by my side.

Lastly, I highly acknowledge open-source developers for the time and effort they invest in producing freely available software. In particular, I want to thank all people involved in the development of gnuplot, VisIt, Blender and the Tex Live distribution for providing these excellent tools.

1. Introduction

With computational materials physics being one of the most important and fastest growing scientific disciplines today, the theoretical developments in this area brought forth a multitude of different techniques and models enabling ab-initio simulations of condensed matter on modern computer hardware. Many widely used methods, however, lack the description of one of the most fundamental and important aspects of matter: electron-phonon interaction. To showcase their unquestionable importance, electron-phonon interactions were found to play key roles in explaining a wide variety of phenomena, including the temperature dependence of electrical conductivity [1, 2], superconductivity [3], the Kohn effect [4] and optical absorption via indirect band gap transitions [5]. Paramount, with regard to this thesis' topic, is the influence of electron-phonon interactions on the electronic band structure obtained from ab-initio simulations of materials.

It should thus not come as a surprise that the interaction between electrons and phonons has been a pivotal topic of theoretical and experimental research since the advent of physics of condensed matter. However, only in recent years have electron-phonon interactions been included in ab-initio software packages as a result of new developments in computational materials physics. This delay can mainly be attributed to the difficulty of achieving an accurate, yet efficient description of these interactions. Methods such as density-functional perturbation theory (DFPT) [6] or path-integral Monte Carlo simulations [7, 8] are in principle capable of accurately calculating the requested quantities but are computationally demanding in most cases. This is partly due to requiring an incredibly dense sampling of the first Brillouin zone, with respect to the electron or phonon crystal momenta, to achieve acceptable results. In other instances, such as very accurate post-density-functional-theory calculations, including dynamical-mean-field theory [9], the Bethe-Salpeter [10] and many-body *GW* approaches [11], the effects due to electron-phonon coupling are sometimes neglected. Although they mostly tend to contribute small corrections, recent findings indicate that for carbon-based systems, electron-phonon interactions significantly influence the electronic band structure, even at zero temperature [12, 13].

In 2007, Giustino, Cohen and Louie introduced a method utilizing the spatial localiza-

tion of generalized Wannier functions to efficiently interpolate electron-phonon matrix elements starting from a coarsely sampled grid to basically arbitrary points in the first Brillouin zone [14]. The interpolation technique consists primarily of cheap matrix-matrix multiplications and a generalized Fourier transform of the pre-calculated data, resulting in excellent computational performance. Potential and scope of its practical application seem promising [15].

The present thesis seeks to implement electron-phonon interactions into the Vienna Ab-initio Simulation Package (VASP) [16–19] based on the aforementioned Wannier-Fourier-interpolation technique. VASP makes intensive use of the projector augmented-wave (PAW) method [20, 21], so the physical quantities are to be derived in context of the PAW framework and are based on the Allen-Heine-Cardona (AHC) theory [22, 23]. The method of choice for evaluating derivatives arising from lattice vibrations is finite differences, which is both simple to implement and universally applicable. This allows for calculating the initial quantities directly in the Wannier basis utilizing moderately large super cells. As a prerequisite to achieving this goal, a force-constant-based approach to calculating phonon frequencies is implemented into VASP, as well.

To convince ourselves that the implementation operates as intended, the phonon-induced renormalization of the direct band gap of diamond is calculated along with verifiable smaller parts of the calculation, such as the phonon spectrum, the interpolated electronic band structure and certain spatial properties of the used Wannier functions. The primary concern of this thesis is not generating accurate physical results, but rather laying the ground work for an extensible and flexible framework allowing electron-phonon calculations to be carried out in VASP. That being said, numerical verification is still mandatory but deviations from recently published results are to be expected due to limitations in the present case.

Following this brief introduction, the most important aspects of the theoretical background are laid out in sections 2–5. In section 6, the derivation of the phonon-induced band-gap renormalization up to second order in atomic displacements is carried out, based on the AHC theory. A very brief overview of Wannier functions as well as the aforementioned Wannier-Fourier-interpolation technique are presented in section 7. Thereafter, section 8 provides insight into implementation details and arising nuances, including the justification and explanation of certain design choices. Finally, the implementation is put to test and the obtained results are presented and discussed in section 9, followed by a conclusion in section 10.

2. Density-Functional Theory

Computational models to study the electronic structure of matter are of great importance to the development of new technology as well as for our understanding of the complex many-body interactions found in condensed matter. Among the most successful and widely used models is density-functional theory (DFT), which is found at the heart of many simulation software packages, including VASP. Although VASP allows for more sophisticated methods to be utilized, the more traditional DFT approach still offers advantages in certain situations. Most notably, it is exceptionally fast compared to other methods in the ever-growing class of ab-initio-simulation models and its low computational cost is appealing.

In its original form, DFT was mainly developed by Walter Kohn [24, 25] as a method to calculate ground-state properties as functionals of the electron density, hence the name. Over the years, it has been greatly extended and further developed to describe a multitude of different phenomena, including spin polarization, temperature dependence, relativistic contributions, molecular dynamics and other time-dependent processes [26, 27]. Despite its huge success, the method is not a be-all and end-all solution. Strongly correlated systems, van der Waals forces and large biomolecules, for example, are notoriously hard to describe within the DFT framework. Naturally, these issues are areas of ongoing research to extend DFT even further. Nevertheless, due to its simplicity, flexibility and computational efficiency, it is still in widespread use today.

This section focuses on the fundamental aspects of Hohenberg-Kohn-Sham DFT and provides a very compact insight into its theoretical concepts.

2.1. The Born-Oppenheimer Approximation

When dealing with any kind of microscopic structure, ideally, one would like to use the full many-body wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}, \mathbf{R}_1, \dots, \mathbf{R}_{N_n})$, containing all physical information. It depends on the position coordinates $\mathbf{r}_i$ and $\mathbf{R}_j$ of the N_e electrons and N_n nuclei of the system, respectively.

Since the nuclei are vastly more massive than the electrons, however, their average

movement speed is comparatively slow. If we are only interested in the electronic degrees of freedom, it is therefore often reasonable to assume that each nucleus is completely static, which is known as the Born-Oppenheimer approximation [28]. In this case, the wave function of the system is simplified to the many-body electronic wave function

$$\Psi \equiv \Psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) \quad (2.1)$$

and the potential due to the atomic nuclei is now to be understood as an external potential for the electronic system.

In the context of electronic structure, all possible wave functions of the system are solutions to the non-relativistic, time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi, \quad (2.2)$$

with E being the corresponding energy. The electronic Hamiltonian $\hat{H}$ is given in position space as

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N_e} \Delta_i - \sum_{i=1}^{N_e} \sum_{j=1}^{N_n} \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i=1}^{N_e-1} \sum_{j=i+1}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2.3)$$

where Z_j is the atomic number of atom j . If not explicitly stated otherwise, Hartree atomic units are used throughout this thesis.

2.2. The Hohenberg-Kohn Theorems

Under the assumption that the ground state, i.e. the state with minimum Energy E_0 , is unique, equation (2.2) could be used to obtain the ground-state wave function Ψ_0 by applying the variational principle to minimize the energy for a given external potential. Any physical observable, represented by an operator $\hat{O}$, could then simply be evaluated in the ground state by taking the expectation value

$$\langle \hat{O} \rangle = \frac{\langle \Psi_0 | \hat{O} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}. \quad (2.4)$$

The obvious caveat with this approach is the sheer complexity of the many-electron wave function, rendering it completely unusable for any practical purposes, even in cases involving only few electrons.

Density-functional theory circumvents this issue by making use of the Hohenberg-Kohn

(HK) theorems [24]:

- (i) The external potential is a unique functional of the electron density $n(\mathbf{r})$ and so is, by extension, also the Hamiltonian. Thus, the electronic ground state must be a unique functional of the electron density as well.
- (ii) The ground-state density can be obtained using the variational principle by minimizing the total energy functional $E[n(\mathbf{r})]$.

In other words, the electron density of the ground state has to carry the same amount of information as the corresponding many-body electronic wave function Ψ_0 , while only being a three-dimensional quantity. In addition, the second HK theorem hints at a straight-forward computational scheme to arrive at the ground-state density.

Since the ground-state wave function Ψ_0 is, in principle, a functional of the electron density, we learn from equation (2.4) that the ground-state expectation value of any operator can also be written as an implicit functional of the electron density. Specifically, the energy functional, as the expectation value of the Hamiltonian, can be written as

$$E[n(\mathbf{r})] = \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + F[n(\mathbf{r})] , \quad (2.5)$$

where the functional

$$F[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{\text{ee}}[n(\mathbf{r})] \quad (2.6)$$

contains the kinetic energy $T[n(\mathbf{r})]$ as well as the energy $E_{\text{ee}}[n(\mathbf{r})]$ associated with all electron-electron interactions. Remarkably, $F[n(\mathbf{r})]$ does not depend on the external potential V_{ext} and is thus considered to be a universal functional, i.e. it is the same for any arbitrarily complicated system. Minimization of the total energy in equation (2.5) yields the exact ground-state electron density and with it, any observable is implicitly known for the ground state. Unfortunately, an explicit form of the functional $F[n(\mathbf{r})]$ has not been found. If it were known, equation (2.5) would provide an exact and quite general solution to the Schrödinger equation (2.2). Without it, however, implementations of DFT have to rely on good approximations for $E_{\text{ee}}[n(\mathbf{r})]$.

2.3. The Kohn-Sham Equations

A practical way of further simplifying the energy functional was introduced by Kohn and Sham [25] by calculating the kinetic energy only for a reference system of non-interacting particles, yet with identical density $n(\mathbf{r})$. In this system, the kinetic energy T_s can be

written as a sum over single-particle contributions:

$$T_s = -\frac{1}{2} \sum_{i=1}^{N_e} \int d^3r \Psi_i^*(\mathbf{r}) \Delta \Psi_i(\mathbf{r}) \quad (2.7)$$

where each $|\Psi_i\rangle$ is a one-electron state, called a Kohn-Sham (KS) orbital. Since the electron density of the reference system is the same as in the real one, it too can be expressed using KS orbitals:

$$n(\mathbf{r}) = \sum_{i=1}^{N_e} |\Psi_i(\mathbf{r})|^2. \quad (2.8)$$

Using the kinetic energy of the non-interacting system from equation (2.7), we can rewrite the unknown density functional from equation (2.6) as

$$F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})], \quad (2.9)$$

where the Hartree energy E_H is the classical contribution to electron-electron interactions:

$$E_H[n(\mathbf{r})] = \frac{1}{2} \iint d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}. \quad (2.10)$$

The term $E_{xc}[n(\mathbf{r})]$, known as the exchange-correlation energy, is defined by equation (2.9) and contains purely quantum-mechanical effects as well as all necessary corrections to the total energy.

At this point, we employ the variational principle to the total energy in equation (2.5) to arrive at the Euler-Lagrange equations [29]:

$$\delta E[n(\mathbf{r})] = \int d^3r \delta \tilde{n}(\mathbf{r}) \left[v_{\text{eff}}(\mathbf{r}) + \frac{\delta}{\delta \tilde{n}(\mathbf{r})} T_s[\tilde{n}(\mathbf{r})] \Big|_{\tilde{n}(\mathbf{r})=n(\mathbf{r})} - \varepsilon \right] = 0, \quad (2.11)$$

where the Lagrangian multiplier ε insures particle-number conservation and the effective external potential v_{eff} is given as

$$v_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} + v_{xc}(\mathbf{r}), \quad (2.12)$$

with

$$v_{xc}(\mathbf{r}) = \frac{\delta}{\delta \tilde{n}(\mathbf{r})} E_{xc}[\tilde{n}(\mathbf{r})] \Big|_{\tilde{n}(\mathbf{r})=n(\mathbf{r})} \quad (2.13)$$

being the local exchange-correlation potential. Equation (2.11) describes the independent movement of particles in an effective potential and thus the individual KS orbitals

have to satisfy the one-particle Schrödinger equation

$$\left(-\frac{1}{2}\Delta + v_{\text{eff}}(\mathbf{r})\right) \Psi_i(\mathbf{r}) = \varepsilon_i \Psi_i(\mathbf{r}) . \quad (2.14)$$

In principal, these self-consistent, so-called Kohn-Sham equations could now be solved iteratively to find the ground-state density. After an initial guess for the density, the solutions $\Psi_i(\mathbf{r})$ could be plugged into equation (2.8) to arrive at a more accurate estimate for the correct ground-state density. This process could be repeated until the desired accuracy was reached. Unfortunately, the functional form of the exchange-correlation energy, defined by equation (2.9), is not known and a suitable approximation has to be found in practice.

Finally, the sum over all KS eigenvalues reads

$$\begin{aligned} \sum_i \varepsilon_i &= T_s[n(\mathbf{r})] + \int d^3r v_{\text{eff}}(\mathbf{r})n(\mathbf{r}) \\ &= T_s[n(\mathbf{r})] + \iint d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \\ &\quad + \int d^3r v_{\text{xc}}(\mathbf{r})n(\mathbf{r}) + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) . \end{aligned} \quad (2.15)$$

This, when compared to the full-interaction HK energy functional in equation (2.5), provides an expression for the total energy in the KS formulation:

$$E = \sum_{i=1}^{N_e} \varepsilon_i + E_{\text{xc}}[n(\mathbf{r})] - \frac{1}{2} \iint d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} . \quad (2.16)$$

With this alternative expression for the total energy, the explicit computation of T_s can be avoided, since the KS eigenvalues are already known from solving equation (2.14).

For practical applications, the major challenge is to find good approximations for E_{xc} that strike a good balance between accuracy and computational performance. Prominent examples include the local-density approximation (LDA)[26] as well as the generalized-gradient approximation (GGA)[30], which will not be discussed further. It is important to mention that the KS orbitals and eigenvalues do not carry any physical meaning, with the exception that the KS eigenvalue of the highest occupied orbital equals the ionization energy relative to the vacuum. Finally, there is still some freedom in choosing a basis set for the KS orbitals, which gives rise to many computational methods dealing with the representation of the single-particle wave functions which can lead to useful approximations and optimizations.

3. Electron Dynamics in a Periodic Potential

The Kohn-Sham approach to density functional theory is a good example of how a complex system of interacting electrons can be decomposed into single-particle contributions. Such a decomposition represents a huge reduction in complexity. However, a macroscopic chunk of solid-state matter still contains a vast amount of electrons. Fortunately, most solids exhibit translational symmetry and can be modeled as a Bravais lattice, consisting of identical unit cells each made up of a small number of atoms. This means that the electrostatic potential V_{ext} , created by the ions of the crystal, is periodic as well:

$$V_{\text{ext}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r} + \hat{\mathbf{R}}) , \quad (3.1)$$

where $\hat{\mathbf{R}}$ is an arbitrary linear combination of lattice vectors.

In order to provide a natural representation of the electronic wave functions in these systems, Felix Bloch introduced a special class of functions to serve that purpose. More specifically, the Bloch theorem states that the full set of eigenfunctions of any lattice-periodic single-particle Hamiltonian can be written in the form of these so-called Bloch orbitals [1, 31]. In the context of DFT, they are particularly useful as a way of representing the KS orbitals obtained from equation (2.14). In that case, the potential V_{ext} is simply replaced by the effective potential v_{eff} .

3.1. Bloch Orbitals

Mathematically, a Bloch orbital consists of two parts, a cell-periodic function $u_{n\mathbf{k}}(\mathbf{r})$ with the property

$$u_{n\mathbf{k}}(\mathbf{r} + \hat{\mathbf{R}}) = u_{n\mathbf{k}}(\mathbf{r}) \quad (3.2)$$

and a phase $e^{i\mathbf{k}\cdot\mathbf{r}}$. The quantum numbers n and $\mathbf{k}$ are referred to as band index and Bloch vector, respectively. A general Bloch orbital then takes the form

$$\Psi_{n\mathbf{k}}(\mathbf{r}) \equiv e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) . \quad (3.3)$$

As solutions to a single-particle Schrödinger-like equation

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}\right)\Psi_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}}\Psi_{n\mathbf{k}} , \quad (3.4)$$

featuring the lattice-periodic potential V_{ext} , the Bloch orbitals have associated eigenvalues $\varepsilon_{n\mathbf{k}}$. For real potentials, the single-particle Hamiltonian on the left-hand side of equation (3.4) is obviously Hermitian and the eigenvalue spectrum is real. The band index n is used to label the discrete set of solutions obtained for a fixed Bloch vector $\mathbf{k}$, usually in ascending order with respect to the eigenvalues.

In order to learn more about the Bloch vector, let us write the cell-periodic part as a Fourier series of plane waves [32]:

$$u_{n\mathbf{k}}(\mathbf{r}) \equiv \sum_{\hat{\mathbf{G}}'} c_{n,\mathbf{k}-\hat{\mathbf{G}}'} e^{-i\hat{\mathbf{G}}' \cdot \mathbf{r}} , \quad (3.5)$$

where the sum extends over all reciprocal-lattice vectors $\hat{\mathbf{G}}'$. Then, it is easily demonstrated that Bloch orbitals are invariant under shifts along arbitrary reciprocal-lattice vectors $\hat{\mathbf{G}}$ with respect to the Bloch vector:

$$\begin{aligned} \Psi_{n\mathbf{k}+\hat{\mathbf{G}}}(\mathbf{r}) &= e^{i(\mathbf{k}+\hat{\mathbf{G}}) \cdot \mathbf{r}} \sum_{\hat{\mathbf{G}}'} c_{n,\mathbf{k}+\hat{\mathbf{G}}-\hat{\mathbf{G}}'} e^{-i\hat{\mathbf{G}}' \cdot \mathbf{r}} \\ &= e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\hat{\mathbf{G}}'} c_{n,\mathbf{k}+\hat{\mathbf{G}}-\hat{\mathbf{G}}'} e^{-i(\hat{\mathbf{G}}'-\hat{\mathbf{G}}) \cdot \mathbf{r}} \\ &= e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\hat{\mathbf{G}}''} c_{n,\mathbf{k}-\hat{\mathbf{G}}''} e^{-i\hat{\mathbf{G}}'' \cdot \mathbf{r}} \\ &= \Psi_{n\mathbf{k}}(\mathbf{r}) . \end{aligned} \quad (3.6)$$

Consequently, it is natural to think of the Bloch vector as an element of reciprocal space. It is also immediately apparent that any periodic image of the Bloch orbital in real space may only differ by a complex phase factor at most:

$$u_{n\mathbf{k}}(\mathbf{r} + \hat{\mathbf{R}}) = u_{n\mathbf{k}}(\mathbf{r}) \quad \Leftrightarrow \quad \Psi_{n\mathbf{k}}(\mathbf{r} + \hat{\mathbf{R}}) = \Psi_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k} \cdot \hat{\mathbf{R}}} . \quad (3.7)$$

From equation (3.6), we learn that the domain of any Bloch orbital in reciprocal space can be restricted to the first Brillouin zone without loss of generality. Considering a solid of infinite extent, the set of allowed Bloch vectors forms a continuum inside the first Brillouin zone.

Using Dirac notation, we can work with the more abstract Bloch state vector $|\Psi_{n\mathbf{k}}\rangle$

whose projection onto the continuous position orthonormal basis $|\mathbf{r}\rangle$ yields the corresponding wave function:

$$\int d^3r |\mathbf{r}\rangle\langle\mathbf{r}| = \mathbb{1} \quad \Rightarrow \quad |\Psi_{n\mathbf{k}}\rangle = \int d^3r |\mathbf{r}\rangle \langle\mathbf{r}|\Psi_{n\mathbf{k}}\rangle = \int d^3r \Psi_{n\mathbf{k}}(\mathbf{r}) |\mathbf{r}\rangle . \quad (3.8)$$

In order to find a suitable normalization convention as well as an orthogonality constraint, we evaluate the scalar product

$$\langle\Psi_{m\mathbf{k}'}|\Psi_{n\mathbf{k}}\rangle = \int_{\mathbb{R}^3} d^3r u_{m\mathbf{k}'}^*(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{r}\cdot(\mathbf{k}-\mathbf{k}')} . \quad (3.9)$$

The integration can now be performed separately for each unit cell of volume V_{UC} compliant with the periodicity of the underlying lattice. The total integral is then retrieved by summing over all lattice vectors $\hat{\mathbf{R}}$ corresponding to that unit cell:

$$\begin{aligned} \langle\Psi_{m\mathbf{k}'}|\Psi_{n\mathbf{k}}\rangle &= \sum_{\hat{\mathbf{R}}} \int_{\text{UC}} d^3r u_{m\mathbf{k}'}^*(\mathbf{r} + \hat{\mathbf{R}}) u_{n\mathbf{k}}(\mathbf{r} + \hat{\mathbf{R}}) e^{i(\mathbf{r}+\hat{\mathbf{R}})\cdot(\mathbf{k}-\mathbf{k}')} \\ &= \int_{\text{UC}} d^3r u_{m\mathbf{k}'}^*(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{r}\cdot(\mathbf{k}-\mathbf{k}')} \underbrace{\sum_{\hat{\mathbf{R}}} e^{i\hat{\mathbf{R}}\cdot(\mathbf{k}-\mathbf{k}')}}_{\frac{(2\pi)^3}{V_{\text{UC}}} \delta^{(3)}(\mathbf{k}-\mathbf{k}')} . \end{aligned} \quad (3.10)$$

Finally, it becomes clear that by choosing

$$\int_{\text{UC}} d^3r u_{m\mathbf{k}}^*(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) = \delta_{mn} , \quad (3.11)$$

the Bloch states are properly normalized with respect to the first Brillouin zone and orthogonal to each other:

$$\langle\Psi_{m\mathbf{k}'}|\Psi_{n\mathbf{k}}\rangle = \Omega \delta_{mn} \delta^{(3)}(\mathbf{k} - \mathbf{k}') , \quad (3.12)$$

where $\Omega \equiv \frac{(2\pi)^3}{V_{\text{UC}}}$ is defined as the reciprocal-space volume of the first Brillouin zone. As such, they also form a complete orthonormal basis obeying the completeness relation

$$\sum_n \int_{\text{BZ}} \frac{d^3k}{\Omega} |\Psi_{n\mathbf{k}}\rangle\langle\Psi_{n\mathbf{k}}| = \mathbb{1} , \quad (3.13)$$

where the integral runs over the entire first Brillouin zone.

Another important property of Bloch orbitals is their phase freedom. Just like other

quantum states, they exhibit invariance under global phase shifts:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) \rightarrow \Psi_{n\mathbf{k}}(\mathbf{r})e^{i\varphi} \quad \text{for } \varphi \in [0, 2\pi[, \quad (3.14)$$

a fact which is tightly bound to the nature of wave functions in general. However, Bloch orbitals additionally feature invariance with respect to local phase shifts:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) \rightarrow \Psi_{n\mathbf{k}}(\mathbf{r})e^{i\varphi(\mathbf{k})} , \quad (3.15)$$

where $\varphi(\mathbf{k})$ is an arbitrary, not necessarily continuous, real function of the Bloch vector.

It is important to stress that the Bloch vector is not proportional to the true electron momentum. This fact becomes clear when applying the momentum operator $\hat{\mathbf{P}}$ to an arbitrary Bloch orbital:

$$\hat{\mathbf{P}}\Psi_{n\mathbf{k}}(\mathbf{r}) = -i\nabla(u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}) = \mathbf{k}\Psi_{n\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}}\nabla u_{n\mathbf{k}}(\mathbf{r}) . \quad (3.16)$$

Obviously, $|\Psi_{n\mathbf{k}}\rangle$ is not a momentum eigenstate and $\mathbf{k}$ cannot be a conserved quantity. For free electrons, the conservation of their wave vector is related to the continuous translational invariance of the equations of motions. In the case of lattice electrons, however, the underlying translational symmetry is of discrete nature and the corresponding Bloch vector is thus only conserved up to addition of a reciprocal lattice vector [32].

In the end, a system consisting of horrendously many independent electrons can be described fully by wave functions inside the first Brillouin zone. From a practical perspective, the continuum of Bloch vectors can be sampled quite efficiently on a finite grid of so-called k-points. Any Brillouin-zone integral involving Bloch vectors can then be written as a weighted sum over the k-point mesh. Additionally, the maximum number of involved functions can be capped by a relatively low bound with regard to the band index. This allows for efficient yet accurate treatment of non-interacting many-electron systems. Combined with the Kohn-Sham approach to DFT, this lays the very foundation of many electronic-structure calculations for solids.

3.2. Electronic Band Structure

For a fixed band index, the continuous dispersion curve $\varepsilon_n(\mathbf{k}) \equiv \varepsilon_{n\mathbf{k}}$ is referred to as an energy band, describing the energy of a single electron moving with Bloch vector $\mathbf{k}$ in the periodic potential. From equations (3.4) and (3.6), it immediately follows that each energy band $\varepsilon_{n\mathbf{k}}$ has the same periodicity in reciprocal space as the corresponding Bloch

orbital:

$$\varepsilon_{n\mathbf{k}+\hat{\mathbf{G}}} = \varepsilon_{n\mathbf{k}} . \quad (3.17)$$

Furthermore, if the potential V_{ext} is real, each band exhibits inversion symmetry in reciprocal space:

$$\varepsilon_n(-\mathbf{k}) = \varepsilon_n(\mathbf{k}) . \quad (3.18)$$

This fact follows directly from complex conjugation of equation (3.4) and the fact that the eigenvalues are real.

The full set of energy bands is called the electronic band structure and provides valuable information about many properties of condensed matter. Prime factors for determining these properties are the location of the Fermi level relative to the band structure as well as the existence and magnitude of band gaps. Firstly, the Fermi level $E_F(T)$ at temperature T is synonymous with the chemical potential of the electrons. At finite temperature, states at the Fermi level have an exact 50% probability of being occupied. For the ground state, the Fermi level coincides with the Fermi energy $E_F \equiv E_F(0)$. In this case, all electronic states with energies below the Fermi energy are fully occupied according to the Pauli principle, while all states above it are empty.

Secondly, materials feature so-called band gaps, regions of energy in which electron states cannot exist. In order for an electron to jump across such a gap, a finite amount of energy is either emitted or absorbed, depending on the initial and final states. This process is of significant importance to the optical properties of solids, since the width of the band gap can often times lie in the energy range of infrared photons or even visible light.

Additionally, the band gap can be used to roughly classify solids based on its effect on electrical conductivity. If the Fermi level is located within the band gap, the energy bands forming its upper and lower bounds are referred to as the conduction and valence band, respectively. Electrons in the valence manifold are usually tightly bound and contribute very little to electrical conductivity, whereas electrons moving in or above the conduction band contribute significantly, hence the name. Now, if the width of the band gap is large, the possibility for individual electrons to occupy states in the conduction manifold is low and the solid is considered an insulator. If, however, the Fermi level does not coincide with a band gap, the distinction between valence and conduction bands is not meaningful. Electrons can move easily into higher unoccupied states and the solid is considered a metal. Finally, there is also the case of semiconductors, whose band gap is either very small or the transition from the valence to the conduction band extrema is indirect. In the later case, for an electron transition to happen, there still needs to be an

exchange of crystal momentum, e.g. by exchanging a phonon. Ultimately, the electrical conductivity of a semiconductor is neither low nor high and can change significantly based on external influences, for example, by doping or a change in temperature.

It is important to understand that, while the electronic band structure is a continuous function of $\mathbf{k}$, the same is in general not true for the associated Bloch orbitals. This is partially due to the already discussed local phase freedom present in each Bloch orbital. Much more complicated discontinuities may arise whenever two or more electronic bands become degenerate in a region inside the first Brillouin zone. Such is often the case at high-symmetry points or along high-symmetry lines, governed by the underlying crystal structure. The degenerate Bloch orbitals may mix and transform into each other according to a unitary rotation in the spanned subspace. It might therefore be very challenging to find a smooth gauge in $\mathbf{k}$ for any given Bloch manifold.

4. The Projector Augmented-Wave Method

One of the major challenges of DFT lies in the accurate and efficient description of electron-ion interactions. A multitude of different techniques exist that range all the way from computationally inexpensive pseudopotential methods to very accurate plane-wave based approaches. The method of relevance for this thesis is the projector augmented-wave (PAW) method as it finds extensive use within VASP and other ab-initio software packages. Developed by P. E. Blöchl in 1994, the method can be understood as a generalization of pseudopotential approaches [21, 33] and full-potential linearized-augmented-plane-wave methods [34] in that it retains the formal simplicity of the former while achieving the same level of accuracy as the latter. As such, it represents a good compromise between speed and accuracy. It has been shown extensively that the PAW method is effective in describing a broad spectrum of different materials, including notoriously troublesome first-row and transition-metal elements [35]. This section follows Blöchl's original work [20] and presents the points most relevant to this thesis.

The main difficulty involved in the accurate treatment of the aforementioned elements stems from the region close to the nucleus. The valence wave functions, in particular, are rapidly oscillating in the core region due to the necessity of them being orthogonal to the core states, whereas in the bonding region, they tend to be very smooth. Therefore, a rather dense grid or, equivalently, a large number of Fourier components would be required to describe the wave functions. This would inhibit the computational performance severely and, as a consequence, electron-core interactions are often neglected. Instead, it is beneficial to treat the two regions independently, mitigating the drawbacks arising from these discrepancies. The PAW method accomplishes this by employing a dual-basis approach. In the bonding region, the wave function can be expanded into plane waves, while close to the cores, the basis is augmented by local ion-centered basis functions which are usually represented on a radial logarithmic grid. As long as the two representations can be treated independently, this method proves to be very efficient.

At the heart of the PAW method lies a linear transformation $\hat{T}$ connecting the physically relevant all-electron (AE) single-particle Kohn-Sham wave functions $|\Psi_n\rangle$ with a

new set of computationally convenient pseudo (PS) wave functions $|\tilde{\Psi}_n\rangle$, defined by

$$|\Psi_n\rangle = \hat{\mathcal{T}} |\tilde{\Psi}_n\rangle . \quad (4.1)$$

In this section, band index, Bloch vector and possibly spin index are contained in a composite quantum number n for the sake of simplicity.

Using the aforementioned transformation, equation (3.4) is rewritten in terms of the PS wave functions as

$$\hat{\mathcal{T}}^\dagger \hat{H} \hat{\mathcal{T}} |\tilde{\Psi}_n\rangle = \epsilon_n \hat{\mathcal{T}}^\dagger \hat{\mathcal{T}} |\tilde{\Psi}_n\rangle , \quad (4.2)$$

where $\hat{H}$ is the corresponding single-particle Hamiltonian. By absorbing the transformation operators, this can be written more compactly as

$$\tilde{H} |\tilde{\Psi}_n\rangle = \epsilon_n \tilde{S} |\tilde{\Psi}_n\rangle , \quad (4.3)$$

where we defined

$$\tilde{H} \equiv \hat{\mathcal{T}}^\dagger \hat{H} \hat{\mathcal{T}} , \quad (4.4)$$

$$\tilde{S} \equiv \hat{\mathcal{T}}^\dagger \hat{\mathcal{T}} . \quad (4.5)$$

$\tilde{H}$ and $\tilde{S}$ are referred to as the PAW Hamiltonian and the PAW overlap operator, respectively. It is easily verifiable that both are Hermitian.

Equation (4.3) takes the form of a generalized eigenvalue problem that can be solved iteratively to find the ground state energies and corresponding PS wave functions. The latter are now to be considered the variational quantities of the system and expectation values of diverse operators can be built without the need for the AE wave functions. In order to write down such an expectation value, though, the exact nature of the transformation operator needs to be known first.

4.1. The Transformation Operator

The PS wave functions are chosen such that they are smooth everywhere, including the critical core region, and differ from the AE wave functions only within a spherical atom-centered augmentation region. Therefore, the transformation can be written in terms of atom-centered contributions as

$$\hat{\mathcal{T}} = \mathbb{1} + \sum_a \hat{\mathcal{T}}_a , \quad (4.6)$$

where $\hat{\mathcal{T}}_a$ only acts within the augmentation region Ω_a of atom a . The exact form of $\hat{\mathcal{T}}$ can be determined by expanding the PS wave functions into a complete set of so-called pseudo partial waves $|\tilde{\phi}_{ai}\rangle$ inside any augmentation sphere:

$$|\tilde{\Psi}_n\rangle = \sum_i c_{nai} |\tilde{\phi}_{ai}\rangle \quad \text{within } \Omega_a, \quad (4.7)$$

with yet undetermined coefficients c_{nai} . The composite index i contains angular momentum quantum numbers as well as a label for additional partial waves inside the same augmentation region with identical angular momentum. A corresponding set of all-electron partial waves can then simply be obtained by transforming the PS partial waves accordingly:

$$|\phi_{ai}\rangle = (\mathbb{1} + \hat{\mathcal{T}}_a) |\tilde{\phi}_{ai}\rangle \quad \Leftrightarrow \quad \hat{\mathcal{T}}_a |\tilde{\phi}_{ai}\rangle = |\phi_{ai}\rangle - |\tilde{\phi}_{ai}\rangle. \quad (4.8)$$

From equation (4.8), it is clear that PS and AE partial waves have to coincide outside the augmentation region and their choice ultimately defines the transformation. Since $|\phi_{ai}\rangle = \hat{\mathcal{T}} |\tilde{\phi}_{ai}\rangle$, it follows from equation (4.1) that the expansion coefficients c_{nai} corresponding to the PS partial waves must be the same for an expansion in the AE picture:

$$|\Psi_n\rangle = \sum_i c_{nai} |\phi_{ai}\rangle \quad \text{within } \Omega_a. \quad (4.9)$$

Using equations (4.7) and (4.9), the AE wave function can be written as

$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle - \sum_{ai} c_{nai} |\tilde{\phi}_{ai}\rangle + \sum_{ai} c_{nai} |\phi_{ai}\rangle. \quad (4.10)$$

Furthermore, to determine the expansion coefficients, they can be expressed as a scalar product

$$c_{nai} = \langle \tilde{p}_{ai} | \tilde{\Psi}_n \rangle, \quad (4.11)$$

introducing a new set of fixed functions $|\tilde{p}_{ai}\rangle$, called projector functions. This is possible because $\hat{\mathcal{T}}$ was chosen to be a linear operator. For the expansion of the PS wave function in one particular augmentation region to equal the PS wave function itself, the projector functions must satisfy the completeness relation

$$\sum_i |\tilde{\phi}_{ai}\rangle \langle \tilde{p}_{ai}| = \mathbb{1} \quad \Rightarrow \quad \langle \tilde{p}_{ai} | \tilde{\phi}_{aj} \rangle = \delta_{ij} \quad \text{within } \Omega_a. \quad (4.12)$$

Finally, equation (4.10) can be expressed using the newly introduced projector functions as

$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_{ai} \left(|\phi_{ai}\rangle - |\tilde{\phi}_{ai}\rangle \right) \langle \tilde{p}_{ai} | \tilde{\Psi}_n \rangle , \quad (4.13)$$

which fully defines the PAW transformation

$$\hat{\mathcal{T}} = \mathbb{1} + \sum_{ai} \left(|\phi_{ai}\rangle - |\tilde{\phi}_{ai}\rangle \right) \langle \tilde{p}_{ai} | , \quad (4.14)$$

given $|\phi_{ai}\rangle$, $|\tilde{\phi}_{ai}\rangle$ and $|\tilde{p}_{ai}\rangle$.

Equation (4.13) can be seen as a decomposition of the AE valence wave function into three distinct parts: A PS term $|\tilde{\Psi}_n\rangle$, an AE partial term $|\Psi_n^1\rangle \equiv \sum_{ai} |\phi_{ai}\rangle \langle \tilde{p}_{ai} | \tilde{\Psi}_n \rangle$ and a PS partial term $|\tilde{\Psi}_n^1\rangle \equiv -\sum_{ai} |\tilde{\phi}_{ai}\rangle \langle \tilde{p}_{ai} | \tilde{\Psi}_n \rangle$. Figure 4.1 illustrates the concept of this decomposition schematically. Importantly, this way of decomposing a PAW quantity

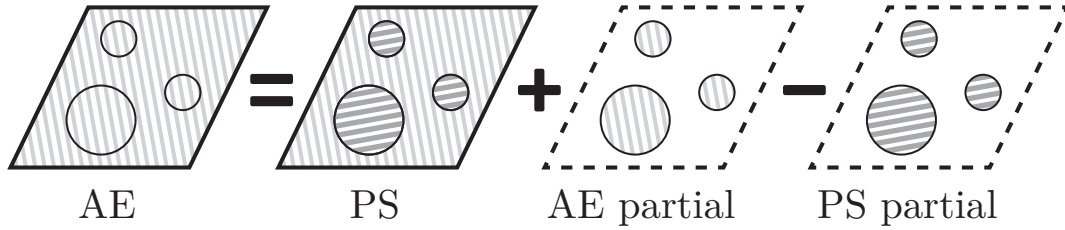


Figure 4.1.: Schematic representation of the decomposition of an AE quantity into a PS, an AE-partial and a PS-partial contribution. Each box represents a unit cell of the lattice, while the area inside the circles represents augmentation regions.

works similarly for the charge density, the kinetic energy, the Hamiltonian and virtually all other expectation values.

Returning to equation (4.13), the dual-basis aspect of the PAW method really comes to shine. The representation of each wave function can be chosen such that it best fits its respective domain. $|\phi_{ai}\rangle$, $|\tilde{\phi}_{ai}\rangle$ and $|\tilde{p}_{ai}\rangle$ are atom-centered localized functions. However, while the AE and PS partial waves are defined on radial logarithmic grids centered around each atom, the projector functions as well as the PS wave function can be expressed in a plane wave basis. Hence, the AE partial waves can be obtained by solving the radial portion of the Schrödinger equation of the isolated atom. The corresponding PS partial waves have to coincide with their AE counterparts outside the augmentation regions but can otherwise be chosen computationally convenient. As already mentioned, the PS wave functions are obtained as self-consistent solutions to

the generalized KS equations. Finally, for each PS partial wave, there is a projector function, obeying the orthogonality constraint in equation (4.12). It is important to note that these three quantities are system-independent and can be pre-calculated for each element of the periodic table.

4.2. Operators

As was already hinted at in equation (4.3), it is mandatory to express all quantities of interest in terms of the PS wave functions. This also means that the representation of operators has to change accordingly. For any arbitrary operator $\hat{A}$, its expectation value can be written as

$$\langle \hat{A} \rangle = \sum_n f_n \langle \Psi_n | \hat{A} | \Psi_n \rangle , \quad (4.15)$$

with f_n being the occupancy of the state $|\Psi_n\rangle$. After transformation to the PAW representation according to equation (4.1), the expectation value can be obtained within the PAW formulation as

$$\langle \hat{A} \rangle = \sum_n f_n \langle \tilde{\Psi}_n | \tilde{A} | \tilde{\Psi}_n \rangle , \quad (4.16)$$

where we have absorbed the transformation operators into the newly defined PAW operator

$$\tilde{A} \equiv \hat{\mathcal{T}}^\dagger \hat{A} \hat{\mathcal{T}} . \quad (4.17)$$

In general, finding a computationally convenient expression for $\tilde{A}$ is a non-trivial task and greatly depends on the nature of the operator in question. This thesis limits itself to the presentation of quasi-local operators. Although non-local operators are of interest, it is just beyond the scope of this thesis to describe them. Furthermore, for the sake of simplicity, the contributions due to electronic core states have been omitted. In general, however, they need to be included in order to obtain the exact observables.

For any quasi-local operator, a simple expansion of the projection operators in equation (4.17) according to equation (4.14) is sufficient to arrive at a useful expression:

$$\tilde{A} = \hat{A} + \sum_{aij} |\tilde{p}_{ai}\rangle \left(\langle \phi_{ai} | \hat{A} | \phi_{aj} \rangle - \langle \tilde{\phi}_{ai} | \hat{A} | \tilde{\phi}_{aj} \rangle \right) \langle \tilde{p}_{aj} | , \quad (4.18)$$

where many terms have been canceled due to the restrictions imposed on the partial waves inside and outside the augmentation regions. Most notably, there are no cross-terms between quantities represented on the radial logarithmic grids, i.e. $|\phi_{ai}\rangle$ and $|\tilde{\phi}_{ai}\rangle$, and quantities expressed in plane waves, i.e. $|\tilde{\Psi}_n\rangle$ and $|\tilde{p}_{ai}\rangle$. This allows for the PAW

method to be implemented very efficiently.

Let us, as an example, find the PAW representation of the electron density $n(\mathbf{r})$, which plays a pivotal role in DFT. It is obtained as the expectation value of the real-space projection operator $|\mathbf{r}\rangle\langle\mathbf{r}|$ as instructed by equation (4.18):

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}) , \quad (4.19)$$

where

$$\tilde{n}(\mathbf{r}) \equiv \sum_n f_n \langle \tilde{\Psi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Psi}_n \rangle , \quad (4.20)$$

$$n^1(\mathbf{r}) \equiv \sum_a n_a^1(\mathbf{r}) \equiv \sum_{aij} \langle \phi_{ai} | \mathbf{r} \rangle n_{aij} \langle \mathbf{r} | \phi_{aj} \rangle , \quad (4.21)$$

$$\tilde{n}^1(\mathbf{r}) \equiv \sum_a \tilde{n}_a^1(\mathbf{r}) \equiv \sum_{aij} \langle \tilde{\phi}_{ai} | \mathbf{r} \rangle n_{aij} \langle \mathbf{r} | \tilde{\phi}_{aj} \rangle \quad (4.22)$$

and

$$n_{aij} \equiv \sum_n f_n \langle \tilde{\Psi}_n | \tilde{p}_{ai} \rangle \langle \tilde{p}_{aj} | \tilde{\Psi}_n \rangle . \quad (4.23)$$

As mentioned before, this representation of the electron density is following the same pattern as depicted in figure 4.1. The smooth PS density $\tilde{n}(\mathbf{r})$ is a sum of plane waves on a regular grid, while the AE and PS partial expansions are products of radial functions and spherical harmonics.

4.3. Total Energy and Hamiltonian

Analogous to previous considerations, it is possible to write the total energy in a form similar to equation (4.19):

$$E[n(\mathbf{r})] = \tilde{E}[\tilde{n}(\mathbf{r})] + E^1[n^1(\mathbf{r})] - \tilde{E}^1[\tilde{n}^1(\mathbf{r})] . \quad (4.24)$$

Unfortunately, equation (4.18) cannot be applied directly to the total energy functional, since it involves non-local contributions, for instance from electrostatic interactions. To accommodate for this, atom-centered compensation charge densities $\hat{n}_a(\mathbf{r})$ are added to the PS as well as to each PS partial electron density. If we denote the point charge density of nucleus a by n_a^Z , the compensation charge densities can be constructed such that $n_a^1 + n_a^Z - \tilde{n}_a^1 - \hat{n}_a$ has vanishing multi-pole moments. This way, the localized atom-centered charge densities have no electrostatic interactions with charges outside

the corresponding augmentation regions. Finally, let us define $\hat{n} \equiv \sum_a \hat{n}_a$ as a compact notation to make the following equations more readable. The individual contributions to the total energy can then be written as

$$\begin{aligned} \tilde{E}[\tilde{n}(\mathbf{r})] &\equiv \sum_n f_n \langle \tilde{\Psi}_n | -\frac{1}{2}\Delta | \tilde{\Psi}_n \rangle + E_{\text{xc}}[\tilde{n}(\mathbf{r}) + \hat{n}(\mathbf{r})] \\ &\quad + E_{\text{H}}[\tilde{n}(\mathbf{r}) + \hat{n}(\mathbf{r})] + \int d^3r \bar{v}(\mathbf{r})(\tilde{n}(\mathbf{r}) + \hat{n}(\mathbf{r})) , \end{aligned} \quad (4.25)$$

$$\begin{aligned} E^1[n^1(\mathbf{r})] &\equiv \sum_a \left(\sum_{ij} n_{aij} \langle \phi_{ai} | -\frac{1}{2}\Delta | \phi_{aj} \rangle + E_{\text{xc}}[n_a^1(\mathbf{r})] \right. \\ &\quad \left. + E_{\text{H}}[n_a^1(\mathbf{r}) + n_a^Z(\mathbf{r})] \right) , \end{aligned} \quad (4.26)$$

$$\begin{aligned} \tilde{E}^1[\tilde{n}^1(\mathbf{r})] &\equiv \sum_a \left(\sum_{ij} n_{aij} \langle \tilde{\phi}_{ai} | -\frac{1}{2}\Delta | \tilde{\phi}_{aj} \rangle + E_{\text{xc}}[\tilde{n}_a^1(\mathbf{r}) + \hat{n}_a(\mathbf{r})] \right. \\ &\quad \left. + E_{\text{H}}[\tilde{n}_a^1(\mathbf{r}) + \hat{n}_a(\mathbf{r})] + \int d^3r \bar{v}(\mathbf{r})(\tilde{n}_a^1(\mathbf{r}) + \hat{n}_a(\mathbf{r})) \right) . \end{aligned} \quad (4.27)$$

The potential $\bar{v}(\mathbf{r})$ is zero outside the augmentation regions and can be chosen arbitrarily inside. Since $\tilde{n}(\mathbf{r})$ and $\tilde{n}_a^1(\mathbf{r})$ have to coincide each augmentation region, the effect of $\bar{v}(\mathbf{r})$ on the total energy is exactly zero, unless the partial-wave basis is incomplete. In practice, this is always the case and $\bar{v}(\mathbf{r})$ can be used to minimize truncation errors.

The total energy can be used to construct the PAW Hamiltonian $\tilde{H}$ as the functional derivative $\delta E[\tilde{n}(\mathbf{r}), n^1(\mathbf{r}), \tilde{n}^1(\mathbf{r})]/\delta \tilde{n}(\mathbf{r})$ with respect to the PS electron density. Since deemed too extensive for the scope of this thesis, a detailed derivation of the PAW Hamiltonian can be found in reference [20]. Ultimately, the PAW Hamiltonian takes the form

$$\tilde{H} = -\frac{1}{2}\Delta + \tilde{v}_{\text{eff}}[\tilde{n}(\mathbf{r}) + \hat{n}(\mathbf{r})] + \sum_{aij} |\tilde{p}_{ai}\rangle D_{aij} \langle \tilde{p}_{aj}| , \quad (4.28)$$

where we have defined

$$D_{aij} \equiv \langle \phi_{ai} | -\frac{1}{2}\Delta + v_{\text{eff}}^1[n_a^1(\mathbf{r})] | \phi_{aj} \rangle - \langle \tilde{\phi}_{ai} | -\frac{1}{2}\Delta + \tilde{v}_{\text{eff}}^1[\tilde{n}_a^1(\mathbf{r}) + \hat{n}_a(\mathbf{r})] | \tilde{\phi}_{aj} \rangle . \quad (4.29)$$

Just as with the electron density, the effective potential v_{eff} has been decomposed into

$$v_{\text{eff}}(\mathbf{r}) = \tilde{v}_{\text{eff}}(\mathbf{r}) + v_{\text{eff}}^1(\mathbf{r}) - \tilde{v}_{\text{eff}}^1(\mathbf{r}) . \quad (4.30)$$

Both PS potentials contain the compensation charge densities which deal with the Hamiltonian's non-local parts.

Finally, we can easily find a closed expression for the PAW overlap operator defined in equation (4.5). In the case of regular AE wave functions, $\tilde{S}$ is just the identity operator:

$$\langle \Psi_m | \hat{S} | \Psi_n \rangle = \langle \Psi_m | \Psi_n \rangle = \delta_{mn} \quad \Rightarrow \quad \hat{S} = \mathbb{1} . \quad (4.31)$$

Therefore, by virtue of equation (4.18), the overlap operator is found to be

$$\tilde{S} = \mathbb{1} + \sum_{aij} |\tilde{p}_{ai}\rangle \left(\langle \phi_{ai} | \phi_{aj} \rangle - \langle \tilde{\phi}_{ai} | \tilde{\phi}_{aj} \rangle \right) \langle \tilde{p}_{aj} | . \quad (4.32)$$

It is important to mention that the otherwise non-orthogonal PS wave functions $|\tilde{\Psi}_n\rangle$ obey the following orthogonality constraint involving the PAW overlap operator:

$$\langle \tilde{\Psi}_m | \tilde{S} | \tilde{\Psi}_n \rangle = \delta_{mn} . \quad (4.33)$$

Furthermore, by using the completeness relation for Bloch orbitals, equation (3.13), followed by a transformation to the PAW representation, a completeness relation involving the PS wave functions is discovered:

$$\sum_n |\tilde{\Psi}_n\rangle \langle \tilde{\Psi}_n| \tilde{S} = \sum_n \tilde{S} |\tilde{\Psi}_n\rangle \langle \tilde{\Psi}_n| = \mathbb{1} . \quad (4.34)$$

5. Lattice Dynamics

For a given infinite lattice, the equilibrium positions of the individual atoms can be written as

$$\mathbf{R}_{l\kappa} = \mathbf{R}_l + \boldsymbol{\tau}_\kappa , \quad (5.1)$$

where $\mathbf{R}_l$ is the origin of a particular primitive cell labeled by l , containing N_p basis atoms. $\boldsymbol{\tau}_\kappa$ is the position vector of basis atom κ within that cell relative to the cell origin. A specific atom of the lattice can therefore be uniquely identified by the index pair $(l\kappa)$. In case of lattice dynamics, these atoms deviate from their equilibrium positions by a certain amount as a function of time. Their instantaneous positions can simply be expressed as

$$\mathbf{r}_{l\kappa}(t) = \mathbf{R}_{l\kappa} + \mathbf{u}_{l\kappa}(t) , \quad (5.2)$$

where $\mathbf{u}_{l\kappa}(t)$ is the time-dependent displacement vector of atom $(l\kappa)$. It is sensible to assume that the magnitude of any atomic displacement is negligibly small compared to the lattice constant, allowing the potential energy Φ to be expanded in a Taylor series with respect to the displacement vectors:

$$\Phi = \Phi_0 + \sum_{l\kappa\alpha} \Phi_{l\kappa\alpha} u_{l\kappa\alpha} + \frac{1}{2} \sum_{l\kappa\alpha, l'\kappa'\beta} \Phi_{l\kappa\alpha, l'\kappa'\beta} u_{l\kappa\alpha} u_{l'\kappa'\beta} + \dots , \quad (5.3)$$

where α and β are Cartesian indices. The expansion coefficients are expressed using the first and second derivatives of the potential energy as

$$\Phi_{l\kappa\alpha} = \left. \frac{\partial \Phi}{\partial u_{l\kappa\alpha}} \right|_0 \quad (5.4)$$

and

$$\Phi_{l\kappa\alpha, l'\kappa'\beta} = \left. \frac{\partial^2 \Phi}{\partial u_{l\kappa\alpha} \partial u_{l'\kappa'\beta}} \right|_0 . \quad (5.5)$$

The first term in the Taylor expansion in equation (5.5), namely Φ_0 , is merely the time-independent potential energy in equilibrium. The second order quantity $\Phi_{l\kappa\alpha, l'\kappa'\beta}$ is known as the Hessian matrix or matrix of inter-atomic force constants, *force-constant*

matrix for short. Regarding notation, the evaluation of the derivatives at 0 is to be understood as an evaluation at the equilibrium positions.

At this point, it is beneficial to introduce the harmonic approximation, i.e. the series in equation (5.3) is truncated after the second order term. In other words, the potential is locally approximated by a parabola. Furthermore, it is easily shown that the first-order term in (5.3) has to vanish by considering its physical meaning. The first derivate of the potential energy is related to the effective force

$$\mathbf{F}_{l\kappa} = -\nabla_{l\kappa}\Phi \quad (5.6)$$

acting on an atom due to the influence of the potential. However, since the derivative is evaluated at the equilibrium positions, the resulting force must be zero. As such, the only remaining term that contributes due to atomic displacements is the second-order term.

5.1. Properties of the Force-Constant Matrix

From a practical standpoint, $\Phi_{l\kappa\alpha,l'\kappa'\beta}$ is just a generalization of the scalar force constant appearing in Hook's law for a system with many harmonic oscillators. A particular atom κ can be thought of as being connected to all other atoms of the lattice by elastic springs. The net force on that atom due to a displacement $\mathbf{u}_{l'\kappa'}$ is then calculated using the force constants as

$$F_{\kappa\alpha} = \sum_{l'\kappa'\beta} \Phi_{l\kappa\alpha,l'\kappa'\beta} u_{l'\kappa'\beta} . \quad (5.7)$$

From equation (5.5), some important symmetry-related properties can already be deduced. Firstly, the force-constant matrix is invariant under discrete spatial translations along integer multiples of the primitive lattice vectors:

$$\mathbf{R}_{l'} - \mathbf{R}_l = \mathbf{R}_{l''} - \mathbf{R}_0 \quad \Rightarrow \quad \Phi_{l\kappa\alpha,l'\kappa'\beta} = \Phi_{0\kappa\alpha,l''\kappa'\beta} . \quad (5.8)$$

In other words, for any pair of atoms $(l\kappa)$ and $(l'\kappa')$, the corresponding force-constant matrix $\Phi_{l\kappa\alpha,l'\kappa'\beta}$ can alternatively be obtained by limiting one of the atoms to a reference primitive cell $l = 0$ and shifting the lattice to compensate. This fact follows directly from the translational invariance of the potential V which, in equilibrium, has to be a periodic function with the periodicity of the primitive lattice:

$$V(\mathbf{R}) = V(\mathbf{R} + \hat{\mathbf{R}}) , \quad (5.9)$$

where $\hat{\mathbf{R}}$ can be any linear combination of primitive lattice vectors with integer coefficients.

Another very important property can be derived from the fact that the potential is periodic. The action of swapping two distinct unit cells in equilibrium must not influence the potential energy and by extension

$$\Phi_{l\kappa\alpha,l'\kappa'\beta} = \Phi_{l'\kappa'\beta,l\kappa\alpha} \quad (5.10)$$

must hold true. Thus, the matrix of inter-atomic force constants is real by definition and symmetric due to equation (5.10).

5.2. Dynamical Matrix and Vibrational Spectrum

Starting from equation (5.7), the equation of motion is trivially found to be

$$m_\kappa \ddot{u}_{l\kappa\alpha} = \sum_{l'\kappa'\beta} \Phi_{l\kappa\alpha,l'\kappa'\beta} u_{l'\kappa'\beta} , \quad (5.11)$$

with m_κ being the mass of atom κ . Not surprisingly, equation (5.11) takes the form of a wave equation for a system of coupled harmonic oscillators. To decouple it, the solutions can be written as plane waves:

$$u_{l\kappa\alpha} = \frac{1}{\sqrt{m_\kappa}} \text{Re} \left(a(\mathbf{q}) e_{\kappa\alpha}(\mathbf{q}) e^{i(\mathbf{q} \cdot \mathbf{R}_{l\kappa} - \omega(\mathbf{q})t)} \right) , \quad (5.12)$$

where $\mathbf{q}$ is the wave vector, $\omega(\mathbf{q})$ is the angular frequency and, finally, $a(\mathbf{q})$ and $e_{\kappa\alpha}(\mathbf{q})$ are the independent and atom-specific part of the wave amplitude, respectively. Reinsertion of equation (5.12) into the equation of motion yields a dispersion relation for the angular frequencies:

$$\omega^2(\mathbf{q}) e_{\kappa\alpha}(\mathbf{q}) = \sum_{\kappa'\beta} D_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) e_{\kappa'\beta}(\mathbf{q}) , \quad (5.13)$$

with $D_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$, known as the dynamical matrix, defined as the Fourier transform of the force-constant matrix:

$$D_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{l'} e^{i\mathbf{q} \cdot (\mathbf{R}_{l'\kappa'} - \mathbf{R}_{0\kappa})} \Phi_{0\kappa\alpha,l'\kappa'\beta} . \quad (5.14)$$

Equation (5.13) takes the form of a simple eigenvalue equation of order $3N_p$ for a continuous set of wave vectors $\mathbf{q}$. The eigenvectors are chosen to be orthonormal and are grouped together as column vectors of the unitary matrix $\hat{e}_{\mu\nu}(\mathbf{q})$. Similarly, the cor-

responding squared angular frequencies can be arranged as the individual elements of the diagonal matrix $\hat{\omega}_{\mu\nu}(\mathbf{q})$. In case of the eigenvector matrix, the first index μ can be considered as a composite index containing both κ and α , whereas the second index ν is referred to as the branch index, labeling the $3N_p$ different solutions of equation (5.13). Using this convention, the eigenvalue equation can be recast in matrix form as

$$\hat{e}(\mathbf{q})\hat{\omega}(\mathbf{q})\hat{e}^\dagger(\mathbf{q}) = D(\mathbf{q}) . \quad (5.15)$$

Since the force-constant matrix is real and symmetric, it follows from equation (5.14) that the dynamical matrix must be Hermitian. Therefore, the eigenvalues $\omega_\nu^2(\mathbf{q})$ are real and the eigenvectors can be chosen to form an orthonormal basis set. Furthermore, the spectrum exhibits certain symmetry-related properties which prove to be of great practical importance.

Firstly, the spectrum is periodic in reciprocal space with the periodicity of the reciprocal lattice:

$$\omega_\nu^2(\mathbf{q}) = \omega_\nu^2(\mathbf{q} + \hat{\mathbf{G}}) , \quad (5.16)$$

where $\hat{\mathbf{G}}$ can be an arbitrary linear combination of reciprocal lattice vectors with integer coefficients. This property follows directly from the fact that the dynamical matrix can be written as a Fourier series as shown in equation (5.14). More specifically, by shifting the wave vector, the dynamical matrix changes only up to a phase factor for each component:

$$D_{\kappa\alpha,\kappa'\beta}(\mathbf{q} + \hat{\mathbf{G}}) = D_{\kappa\alpha,\kappa'\beta}(\mathbf{q})e^{i\hat{\mathbf{G}}\cdot(\boldsymbol{\tau}_{\kappa'} - \boldsymbol{\tau}_\kappa)} . \quad (5.17)$$

It is important to note that the additional phase factor only depends on the relative positions of the atoms in the basis since any inter-cell vector $\mathbf{R}_l' - \mathbf{R}_l$ satisfies $\hat{\mathbf{G}} \cdot (\mathbf{R}_l' - \mathbf{R}_l) = 2\pi n$, $n \in \mathbb{Z}$. Now, the phase can be absorbed into the eigenvectors without changing the eigenvalues:

$$\hat{e}_{\kappa\alpha,\nu} \rightarrow \hat{e}_{\kappa\alpha,\nu} e^{i\hat{\mathbf{G}}\cdot\boldsymbol{\tau}_\kappa} \quad \Leftrightarrow \quad \hat{e}_{\kappa\alpha,\nu}^* \rightarrow \hat{e}_{\kappa\alpha,\nu}^* e^{-i\hat{\mathbf{G}}\cdot\boldsymbol{\tau}_\kappa} . \quad (5.18)$$

The dynamical matrix is still Hermitian and the eigenvectors can again be chosen to form an orthonormal basis. As such, a decomposition exists which takes the same form as in equation (5.15) and produces the same vibrational spectrum.

Secondly, the squared eigenvalues exhibit inversion symmetry:

$$\omega_\nu^2(\mathbf{q}) = \omega_\nu^2(-\mathbf{q}) , \quad (5.19)$$

which is even easier to verify as changing the sign in the exponent of equation (5.14) only leads to a complex conjugated dynamical matrix, leaving the real eigenvalues invariant.

From equation (5.16), we learn that the domain of the physically relevant wave vectors can be restricted to a small area of the reciprocal space. In most cases, the first Brillouin zone is a sensible choice for that area due to its inherently high symmetry and it is always guaranteed to contain all relevant vectors. Additionally, after consideration of equation (5.19), the area of relevant wave vectors can be further reduced to only an octant of the first Brillouin zone, often referred to as its irreducible wedge.

5.3. Phonons

The treatment of lattice dynamics presented so far is purely classical and is sufficient to obtain the vibrational spectrum. However, many physical processes, e.g. scattering of vibrational states with electrons, can more naturally be described using a quantum-mechanical formulation of lattice dynamics. In strong analogy to the electromagnetic field, where the excitations are bosons known as photons, the concept of an elastic lattice field can be introduced, giving rise to yet another bosonic excitation, the so-called phonon. The major difference is that, while the former is a fundamental field capable of producing real particles, the latter is merely a mathematical construct for an emergent phenomenon due to the complex dynamics of the lattice. A phonon is therefore often referred to as a quasi particle or collective excitation, distinguishing it from real, physically manifest particles like the photon. Nevertheless, it is very helpful to view the phonon as a particle, as many of the processes involving it can be understood more easily using concepts like momentum transfer, which requires a property inherent to particles. Following this brief introduction, the classical theory is quantized using canonical quantization, a very intuitive technique borrowed from quantum field theory. As in previous sections, Hartree atomic units are used.

To begin with, the dynamical lattice of individual atoms shall now be considered to be a discretized free real vector field, which is referred to as the elastic field. The displacement $\mathbf{u}_{l\kappa}$ of a particular atom relative to its equilibrium position can be viewed as the field's amplitude. It is straightforward to write down the classical Lagrangian of the vibrational system in terms of the fields and their first derivatives:

$$L^{\text{ph}}(\{\mathbf{u}_{l\kappa}\}, \{\dot{\mathbf{u}}_{l\kappa}\}) = \sum_{l\kappa} \frac{1}{2} m_{\kappa} \dot{\mathbf{u}}_{l\kappa}^2 - \Phi(\{\mathbf{u}_{l\kappa}\}) . \quad (5.20)$$

The next step involves a Legendre transformation to arrive at the classical Hamiltonian

$$H^{\text{ph}}(\{\mathbf{u}_{l\kappa}\}, \{\boldsymbol{\pi}_{l\kappa}\}) = \sum_{l\kappa} \frac{\boldsymbol{\pi}_{l\kappa}^2}{2m_\kappa} + \Phi(\{\mathbf{u}_{l\kappa}\}) , \quad (5.21)$$

having introduced the canonical momentum

$$\pi_{l\kappa\alpha} = \frac{\partial L^{\text{ph}}}{\partial \dot{u}_{l\kappa\alpha}} = m_\kappa \dot{u}_{l\kappa\alpha} . \quad (5.22)$$

In order to understand the state and energy spectra of the free theory, it is beneficial to perform quantization in the Schrödinger picture. In this context, the dynamic variables $\mathbf{u}_{l\kappa}$ and $\boldsymbol{\pi}_{l\kappa}$ are replaced by the respective quantum field operators $\hat{\boldsymbol{\varphi}}_{l\kappa}$ and $\hat{\boldsymbol{\pi}}_{l\kappa}$ at equal time. Both of which have to satisfy the canonical commutation relations

$$\begin{aligned} [\hat{\varphi}_{l\kappa\alpha}, \hat{\pi}_{l'\kappa'\beta}] &= i\delta_{ll'}\delta_{\kappa\kappa'}\delta_{\alpha\beta} , \\ [\hat{\varphi}_{l\kappa\alpha}, \hat{\varphi}_{l'\kappa'\beta}] &= 0 , \\ [\hat{\pi}_{l\kappa\alpha}, \hat{\pi}_{l'\kappa'\beta}] &= 0 . \end{aligned} \quad (5.23)$$

At this point, we would like to perform a Fourier transform on $\hat{\boldsymbol{\varphi}}_{l\kappa}$ and $\hat{\boldsymbol{\pi}}_{l\kappa}$ to express the field operators in momentum space. Since both are discretized in real space, however, a Fourier series is used instead to map the discrete quantum fields to the reciprocal space of the lattice:

$$\hat{\boldsymbol{\varphi}}_\kappa(\mathbf{q}) = \frac{1}{\sqrt{\Omega}} \sum_l \hat{\boldsymbol{\varphi}}_{l\kappa} e^{-i\mathbf{q}\cdot\mathbf{R}_{l\kappa}} \quad \Leftrightarrow \quad \hat{\boldsymbol{\varphi}}_{l\kappa} = \frac{1}{\sqrt{\Omega}} \int_\Omega d^3q \hat{\boldsymbol{\varphi}}_\kappa(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_{l\kappa}} , \quad (5.24)$$

$$\hat{\boldsymbol{\pi}}_\kappa(\mathbf{q}) = \frac{1}{\sqrt{\Omega}} \sum_l \hat{\boldsymbol{\pi}}_{l\kappa} e^{i\mathbf{q}\cdot\mathbf{R}_{l\kappa}} \quad \Leftrightarrow \quad \hat{\boldsymbol{\pi}}_{l\kappa} = \frac{1}{\sqrt{\Omega}} \int_\Omega d^3q \hat{\boldsymbol{\pi}}_\kappa(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_{l\kappa}} , \quad (5.25)$$

with Ω being the volume of the first Brillouin zone. From the Fourier series appearing in equations (5.24) and (5.25), we can learn that both $\hat{\boldsymbol{\varphi}}_\kappa(\mathbf{q})$ and $\hat{\boldsymbol{\pi}}_\kappa(\mathbf{q})$ are periodic functions in reciprocal space and their physically relevant domain can again be limited to the first Brillouin zone:

$$\hat{\boldsymbol{\varphi}}_\kappa(\mathbf{q}) = \hat{\boldsymbol{\varphi}}_\kappa(\mathbf{q} + \hat{\mathbf{G}}) , \quad \hat{\boldsymbol{\pi}}_\kappa(\mathbf{q}) = \hat{\boldsymbol{\pi}}_\kappa(\mathbf{q} + \hat{\mathbf{G}}) . \quad (5.26)$$

Furthermore, since the lattice was assumed to be infinite in size, they represent continuous quantum fields in reciprocal space. This is equivalent to taking the thermodynamic limit, i.e. letting the number of atoms approach infinity. For a finite lattice, equations

(5.24) and (5.25) take the form of discrete Fourier transforms and the corresponding quantum fields in reciprocal space would also be discretized.

It may be of interest to note that

$$\hat{\varphi}_{\kappa}^{\dagger}(\mathbf{q}) = \hat{\varphi}_{\kappa}(-\mathbf{q}) , \quad \hat{\pi}_{\kappa}^{\dagger}(\mathbf{q}) = \hat{\pi}_{\kappa}(-\mathbf{q}) , \quad (5.27)$$

as well as the fact that the reciprocal space operators, too, obey canonical commutation relations

$$\begin{aligned} [\hat{\varphi}_{\kappa\alpha}(\mathbf{q}), \hat{\pi}_{\kappa'\beta}(\mathbf{q}')] &= i\delta_{\kappa\kappa'}\delta_{\alpha\beta}\delta^{(3)}(\mathbf{q}' - \mathbf{q}) , \\ [\hat{\varphi}_{\kappa\alpha}(\mathbf{q}), \hat{\varphi}_{\kappa'\beta}(\mathbf{q}')] &= 0 , \\ [\hat{\pi}_{\kappa\alpha}(\mathbf{q}), \hat{\pi}_{\kappa'\beta}(\mathbf{q}')] &= 0 . \end{aligned} \quad (5.28)$$

From the classical Hamiltonian in equation (5.21), it is now possible to construct a phonon Hamiltonian operator using the reciprocal space operators introduced in equations (5.24) and (5.25).

$$\begin{aligned} \hat{H}^{\text{ph}} &= \int_{\Omega} d^3q \sum_{\kappa\alpha} \frac{1}{2m_{\kappa}} \hat{\pi}_{\kappa\alpha}^{\dagger}(\mathbf{q}) \hat{\pi}_{\kappa\alpha}(\mathbf{q}) \\ &+ \int_{\Omega} d^3q \sum_{\kappa\alpha, \kappa'\beta} \frac{\sqrt{m_{\kappa}m_{\kappa'}}}{2} \hat{\varphi}_{\kappa\alpha}^{\dagger}(\mathbf{q}) D_{\kappa\alpha, \kappa'\beta}(\mathbf{q}) \hat{\varphi}_{\kappa'\beta}(\mathbf{q}) , \end{aligned} \quad (5.29)$$

where we used equation (5.14) for the last term. The Hamiltonian in equation (5.29) is truncated at second order since we are only interested in harmonic contributions.

Finally, we can define a set of phonon creation and annihilation operators, reminiscent of the ladder operators used to describe the spectrum of one quantum harmonic oscillator:

$$\hat{a}_{\nu}^{\dagger}(\mathbf{q}) = \sum_{\kappa\alpha} \frac{1}{\sqrt{2m_{\kappa}\omega_{\nu}(\mathbf{q})}} \left(m_{\kappa}\omega_{\nu}(\mathbf{q}) \hat{\varphi}_{\kappa\alpha}^{\dagger}(\mathbf{q}) - i\hat{\pi}_{\kappa\alpha}(\mathbf{q}) \right) \hat{e}_{\kappa\alpha, \nu}(\mathbf{q}) , \quad (5.30)$$

$$\hat{a}_{\nu}(\mathbf{q}) = \sum_{\kappa\alpha} \frac{1}{\sqrt{2m_{\kappa}\omega_{\nu}(\mathbf{q})}} \left(m_{\kappa}\omega_{\nu}(\mathbf{q}) \hat{\varphi}_{\kappa\alpha}(\mathbf{q}) + i\hat{\pi}_{\kappa\alpha}^{\dagger}(\mathbf{q}) \right) \hat{e}_{\kappa\alpha, \nu}^{\star}(\mathbf{q}) , \quad (5.31)$$

which obey the commutation relations

$$\begin{aligned} [\hat{a}_{\nu}(\mathbf{q}), \hat{a}_{\nu'}^{\dagger}(\mathbf{q}')] &= \delta_{\nu\nu'}\delta^{(3)}(\mathbf{q}' - \mathbf{q}) , \\ [\hat{a}_{\nu}(\mathbf{q}), \hat{a}_{\nu'}(\mathbf{q}')] &= 0 , \\ [\hat{a}_{\nu}^{\dagger}(\mathbf{q}), \hat{a}_{\nu'}^{\dagger}(\mathbf{q}')] &= 0 . \end{aligned} \quad (5.32)$$

On the one hand, the creation operator $\hat{a}_\nu^\dagger(\mathbf{q})$, when acting on the ground state $|0\rangle$, creates a single-particle state $|1_\nu^{\text{ph}}(\mathbf{q})\rangle$ containing one so-called phonon with branch index ν and wave vector $\mathbf{q}$. By consecutive application of $\hat{a}_\nu^\dagger(\mathbf{q})$, it is possible to construct arbitrary multi-particle phonon states. The space spanned by all these states is called Fock space and consists of a direct sum of multi-particle Hilbert spaces.

For simplicity's sake, let us temporarily group together branch index and wave vector into a composite index i . A general multi-particle state can then be written as a list of all its single particle contributions with proper normalization:

$$|\{n_i^{\text{ph}}\}\rangle \equiv \frac{1}{\sqrt{n_1^{\text{ph}}! n_2^{\text{ph}}! \dots}} |n_1^{\text{ph}}, n_2^{\text{ph}}, \dots\rangle, \quad (5.33)$$

where n_i^{ph} is the occupation number of the state denoted by i . Using this definition, the action of the creation operator can be formulated in the following way:

$$\hat{a}_i^\dagger |0\rangle = |1_i^{\text{ph}}\rangle, \quad (5.34)$$

$$\hat{a}_i^\dagger |n_1^{\text{ph}}, \dots, n_i^{\text{ph}}, \dots\rangle = \sqrt{n_i^{\text{ph}} + 1} |n_1^{\text{ph}}, \dots, n_i^{\text{ph}} + 1, \dots\rangle. \quad (5.35)$$

The annihilation operator $\hat{a}_\nu(\mathbf{q})$, on the other hand, removes a single phonon, characterized by the index i , from multi-particle states and annihilates the ground state:

$$\hat{a}_i |0\rangle = 0, \quad (5.36)$$

$$\hat{a}_i |n_1^{\text{ph}}, \dots, n_i^{\text{ph}}, \dots\rangle = \sqrt{n_i^{\text{ph}}} |n_1^{\text{ph}}, \dots, n_i^{\text{ph}} - 1, \dots\rangle. \quad (5.37)$$

From equation (5.32), we learn that phonons follow Bose statistics, since the creation and annihilation operators obey commutation relations, whereas in the fermionic case, they would obey anti-commutation relations. Therefore, there is generally no restriction on the number of phonons occupying the same state, i.e. $n_\nu^{\text{ph}}(\mathbf{q}) \in \mathbb{N}$. Looking at equations (5.35) and (5.37), we can see that the operator $\hat{N}_\nu(\mathbf{q}) \equiv \hat{a}_\nu^\dagger(\mathbf{q})\hat{a}_\nu(\mathbf{q})$ can be identified as the occupation-number operator:

$$\hat{N}_i |n_1^{\text{ph}}, \dots, n_i^{\text{ph}}, \dots\rangle = n_i^{\text{ph}} |n_1^{\text{ph}}, \dots, n_i^{\text{ph}}, \dots\rangle. \quad (5.38)$$

By inverting equations (5.30) and (5.31), it is possible to express the reciprocal-space

fields in terms of the creation and annihilation operators:

$$\hat{\varphi}_{\kappa\alpha}(\mathbf{q}) = \sum_{\nu} \sqrt{\frac{1}{2m_{\kappa}\omega_{\nu}(\mathbf{q})}} \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) \left(\hat{a}_{\nu}(\mathbf{q}) + \hat{a}_{\nu}^{\dagger}(-\mathbf{q}) \right) , \quad (5.39)$$

$$\hat{\pi}_{\kappa\alpha}(\mathbf{q}) = i \sum_{\nu} \sqrt{\frac{m_{\kappa}\omega_{\nu}(\mathbf{q})}{2}} \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) \left(\hat{a}_{\nu}^{\dagger}(-\mathbf{q}) - \hat{a}_{\nu}(\mathbf{q}) \right) . \quad (5.40)$$

At this point, the phonon Hamiltonian in equation (5.29) can be rewritten using the aforementioned relations for the reciprocal-space fields, equations (5.39) and (5.40), as

$$\hat{H}^{\text{ph}} = \int_{\Omega} d^3q \sum_{\nu} \frac{1}{2} \omega_{\nu}(\mathbf{q}) \left(\hat{a}_{\nu}^{\dagger}(\mathbf{q}) \hat{a}_{\nu}(\mathbf{q}) + \hat{a}_{\nu}(\mathbf{q}) \hat{a}_{\nu}^{\dagger}(\mathbf{q}) \right) . \quad (5.41)$$

The first thing to notice is that the ground state contribution from the Hamiltonian is divergent. This can easily be seen by using the non-zero commutator relation from (5.32) to rewrite the Hamiltonian as

$$\hat{H}^{\text{ph}} = \underbrace{\int_{\Omega} d^3q \sum_{\nu} \omega_{\nu}(\mathbf{q}) \hat{N}_{\nu}(\mathbf{q})}_{\hat{H}_{\text{N}}^{\text{ph}}} + \underbrace{\int_{\Omega} d^3q \sum_{\nu} \frac{1}{2} \omega_{\nu}(\mathbf{q}) \delta^{(3)}(\mathbf{0})}_{\hat{H}_{\text{0}}^{\text{ph}}} . \quad (5.42)$$

This is to be expected since the elastic field is comprised of infinitely many harmonic oscillators, each having a ground state energy $\frac{1}{2}\omega_{\nu}(\mathbf{q})$. The true ground state energy of the elastic field, however, cannot be infinite and, therefore, it is reasonable to only look at energy differences and ignore the ground state contribution $\hat{H}_{\text{0}}^{\text{ph}}$. A mathematically sound way of achieving this goal is by normal ordering, i.e. rewriting products of creation and annihilation operators such that creation operators are always to the left of annihilation operators. The physically relevant normal-ordered Hamiltonian $\hat{H}_{\text{N}}^{\text{ph}}$ can now be used to retrieve the phonon spectrum.

It is easy to see that the multi-particle states created by $\hat{a}_{\nu}^{\dagger}(\mathbf{q})$ are eigenstates of the Hamiltonian due to the use of the occupation-number operator in equation (5.42). The Hamiltonian is now fully decoupled and looks like a sum over infinitely many harmonic oscillators. As such, each phonon is assigned an energy $E_{\nu}^{\text{ph}}(\mathbf{q}) = \omega_{\nu}(\mathbf{q})$ and a so-called quasi momentum $\mathbf{p}^{\text{ph}}(\mathbf{q}) = \mathbf{q}$. This term reminds of the fact that phonons are not real particles, but rather collective excitations of the crystal lattice. Each momentum exchange in scattering processes involving other particles, e.g. electrons, neutrons and photons, is ultimately carried by the crystal itself.

6. Band-Gap Renormalization

The interaction between electrons and phonons plays an important role in any solid at finite temperature. However, even for $T = 0$, the solid experiences zero-point vibrations of the lattice ions, which may interact with the electronic states. For semiconductors and isolators, electron-phonon coupling leads to a renormalization of the band gap, which determines many of the material's optical and electrical properties. In the following, an expression for the shift of the KS eigenvalues up to second order is derived, closely following reference [22].

Let $E_{n\mathbf{k}}(T)$ be the single particle energy for an electron with band index n and Bloch vector $\mathbf{k}$, including electron-phonon interactions at temperature T . This energy can be expanded into a Taylor series:

$$E_{n\mathbf{k}}(T) = \varepsilon_{n\mathbf{k}} + \sum_{l\kappa\alpha} \left. \frac{\partial \varepsilon_{n\mathbf{k}}}{\partial u_{l\kappa\alpha}} \right|_0 \langle u_{l\kappa\alpha} \rangle_T + \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \left. \frac{\partial^2 \varepsilon_{n\mathbf{k}}}{\partial u_{l\kappa\alpha} \partial u_{l'\kappa'\beta}} \right|_0 \langle u_{l\kappa\alpha} u_{l'\kappa'\beta} \rangle_T + \dots, \quad (6.1)$$

where $\varepsilon_{n\mathbf{k}}$ are the KS eigenvalues obtained by DFT. The notation $\langle \mathbf{u} \rangle_T$ is to be understood as a thermal expectation value at temperature T . The evaluation of the derivatives at 0 indicates evaluation at the equilibrium positions. It has already been discussed in section 5 that the first-order term in such an expansion needs to vanish due to crystal symmetries. In the harmonic approximation, this only leaves the second-order term as the correction to the KS eigenvalues:

$$\Delta \varepsilon_{n\mathbf{k}} \equiv \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}} \langle u_{l\kappa\alpha} u_{l'\kappa'\beta} \rangle_T, \quad (6.2)$$

introducing the shorthand notation $\partial_{l\kappa\alpha} \equiv \frac{\partial}{\partial u_{l\kappa\alpha}}$. It is worth noting that in this thesis, we adopt the convention that each derivative only acts on the first object to its right in order to avoid excessive use of parentheses.

We continue the derivation by inspecting the term containing the temperature dependence. In the language of second quantization, the ionic displacements $\mathbf{u}_{l\kappa}$ are described

as discretized quantum field operators $\hat{\varphi}_{l\kappa}$. Using equations (5.24) and (5.39), it is therefore possible to express the displacements using creation and annihilation operators:

$$\begin{aligned} \langle u_{l\kappa\alpha} u_{l'\kappa'\beta} \rangle_T &= \frac{1}{\Omega} \iint_{\text{BZ}} d^3q d^3q' \sum_{\nu\nu'} \frac{e^{i\mathbf{q}\cdot\mathbf{R}_{l\kappa}} e^{i\mathbf{q}'\cdot\mathbf{R}_{l'\kappa'}}}{2\sqrt{m_\kappa m_{\kappa'} \omega_\nu(\mathbf{q}) \omega_{\nu'}(\mathbf{q}')}} \\ &\times \left\langle \left(\hat{a}_\nu(\mathbf{q}) + \hat{a}_\nu^\dagger(-\mathbf{q}) \right) \left(\hat{a}_{\nu'}(\mathbf{q}') + \hat{a}_{\nu'}^\dagger(-\mathbf{q}') \right) \right\rangle_T \\ &\times \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) \hat{e}_{\kappa'\beta,\nu'}(\mathbf{q}') . \end{aligned} \quad (6.3)$$

The thermal expectation value can now be calculated simply by letting the operators act on an average multi-particle state $|T\rangle$ with temperature T :

$$\begin{aligned} &\left\langle \left(\hat{a}_\nu(\mathbf{q}) + \hat{a}_\nu^\dagger(-\mathbf{q}) \right) \left(\hat{a}_{\nu'}(\mathbf{q}') + \hat{a}_{\nu'}^\dagger(-\mathbf{q}') \right) \right\rangle_T = \\ &= \left\langle T \left| \hat{a}_\nu(\mathbf{q}) \hat{a}_{\nu'}^\dagger(-\mathbf{q}') + \hat{a}_\nu^\dagger(-\mathbf{q}) \hat{a}_{\nu'}(\mathbf{q}') \right| T \right\rangle \\ &\quad + \underbrace{\left\langle T \left| \hat{a}_\nu(\mathbf{q}) \hat{a}_{\nu'}(\mathbf{q}') + \hat{a}_\nu^\dagger(-\mathbf{q}) \hat{a}_{\nu'}^\dagger(-\mathbf{q}') \right| T \right\rangle}_{=0} \\ &= \delta_{\nu\nu'} \delta^{(3)}(\mathbf{q} + \mathbf{q}') \left\langle T \left| 2\hat{N}_\nu(\mathbf{q}) + 1 \right| T \right\rangle \\ &= \delta_{\nu\nu'} \delta^{(3)}(\mathbf{q} + \mathbf{q}') (2n_\nu(\mathbf{q}, T) + 1) , \end{aligned} \quad (6.4)$$

where we used the first commutation relation in (5.32) and the fact that multi-particle states belonging to different subspaces of the phonon Fock space form an orthonormal basis. In particular, if the particle numbers differ, the corresponding subspaces are always orthogonal to each other. The occupation number $n_\nu(\mathbf{q}, T)$ is then simply the number of particles according to Bose-Einstein statistics for a given temperature:

$$n_\nu(\mathbf{q}, T) = \frac{1}{e^{\frac{\omega_\nu(\mathbf{q})}{k_B T}} - 1} . \quad (6.5)$$

The final expression for the thermal expectation value takes the form

$$\begin{aligned} \langle u_{l\kappa\alpha} u_{l'\kappa'\beta} \rangle_T &= \int_{\text{BZ}} \frac{d^3q}{\Omega} \sum_{\nu} \frac{e^{i\mathbf{q}\cdot(\mathbf{R}_{l\kappa} - \mathbf{R}_{l'\kappa'})}}{2\omega_\nu(\mathbf{q}) \sqrt{m_\kappa m_{\kappa'}}} (2n_\nu(\mathbf{q}) + 1) \\ &\times \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) \hat{e}_{\kappa'\beta,\nu}^*(\mathbf{q}) . \end{aligned} \quad (6.6)$$

In order to proceed, an expression for the second derivatives of the KS eigenvalues needs to be found within the PAW framework. Since the PAW Hamiltonian is known, the initial steps are straightforward. We start by taking the first derivative of the generalized

KS equation, (4.3), with respect to the atomic displacement $u_{l\kappa\alpha}$:

$$\partial_{l\kappa\alpha} \left(\tilde{H} |\tilde{\Psi}_{n\mathbf{k}}\rangle - \varepsilon_{n\mathbf{k}} \tilde{S} |\tilde{\Psi}_{n\mathbf{k}}\rangle \right) = 0 . \quad (6.7)$$

Continuing, we apply the chain rule and are able to isolate the term containing the first derivative of the KS eigenvalues:

$$\begin{aligned} \partial_{l\kappa\alpha} \varepsilon_{n\mathbf{k}} \tilde{S} |\tilde{\Psi}_{n\mathbf{k}}\rangle &= \left(\partial_{l\kappa\alpha} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l\kappa\alpha} \tilde{S} \right) |\tilde{\Psi}_{n\mathbf{k}}\rangle \\ &+ \left(\tilde{H} - \varepsilon_{n\mathbf{k}} \tilde{S} \right) |\partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}}\rangle . \end{aligned} \quad (6.8)$$

After multiplying with $\langle \tilde{\Psi}_{n\mathbf{k}} |$ from the left, equation (6.8) is greatly simplified by using the orthogonality constraint for the pseudo wave functions, equation (4.33), as well as the Hermitian conjugate of the generalized KS equation (4.3):

$$\begin{aligned} \partial_{l\kappa\alpha} \varepsilon_{n\mathbf{k}} \underbrace{\langle \tilde{\Psi}_{n\mathbf{k}} | \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle}_{=1} &= \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l\kappa\alpha} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l\kappa\alpha} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \\ &+ \underbrace{\langle \tilde{\Psi}_{n\mathbf{k}} | \tilde{H} - \varepsilon_{n\mathbf{k}} \tilde{S} | \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} \rangle}_{=0} . \end{aligned} \quad (6.9)$$

This leads to a special case of the Hellmann-Feynman theorem for the PAW method:

$$\partial_{l\kappa\alpha} \varepsilon_{n\mathbf{k}} = \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l\kappa\alpha} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l\kappa\alpha} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle . \quad (6.10)$$

Further differentiation of equation (6.10) with respect to another atomic displacement yields

$$\begin{aligned} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}} &= \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \\ &+ \langle \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \\ &+ \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta} \tilde{S} | \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} \rangle \\ &- \partial_{l\kappa\alpha} \varepsilon_{n\mathbf{k}} \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle . \end{aligned} \quad (6.11)$$

It is reasonable to separate all terms containing second derivatives in this expression from the ones containing only first derivatives. To this end, we define the Fan-Migdal (FM) self energy

$$\Delta \varepsilon_{n\mathbf{k}}^{\text{FM}} \equiv \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}}^{\text{FM}} \langle u_{l\kappa\alpha} u_{l'\kappa'\beta} \rangle_T \quad (6.12)$$

to contain all contributions due to factorizable single derivatives:

$$\begin{aligned} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}}^{\text{FM}} &= \langle \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \\ &+ \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta} \tilde{S} | \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} \rangle \\ &- \partial_{l\kappa\alpha} \varepsilon_{n\mathbf{k}} \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle . \end{aligned} \quad (6.13)$$

Conversely, the Debye-Waller (DW) self energy

$$\Delta \varepsilon_{n\mathbf{k}}^{\text{DW}} \equiv \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}}^{\text{DW}} \langle u_{l\kappa\alpha} u_{l'\kappa'\beta} \rangle_T \quad (6.14)$$

contains the remaining contribution

$$\partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}}^{\text{DW}} = \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle . \quad (6.15)$$

The total energy shift due to electron-phonon coupling up to second order is then simply

$$\Delta \varepsilon_{n\mathbf{k}} = \Delta \varepsilon_{n\mathbf{k}}^{\text{FM}} + \Delta \varepsilon_{n\mathbf{k}}^{\text{DW}} . \quad (6.16)$$

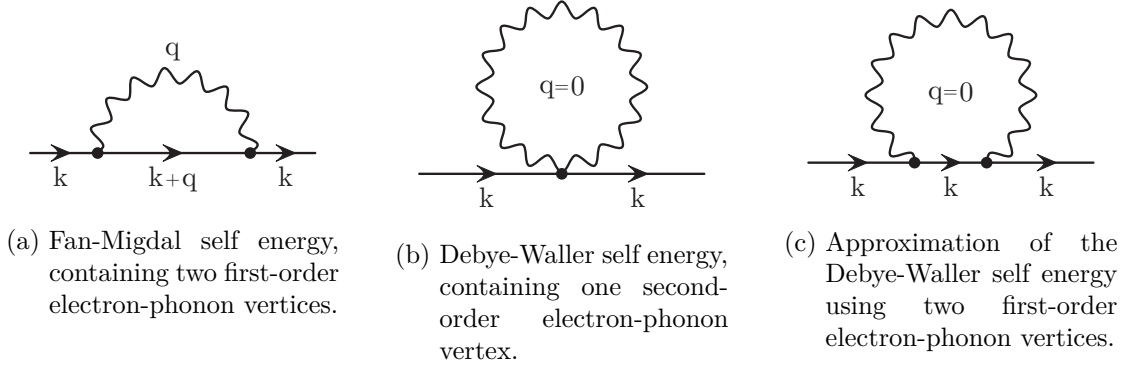


Figure 6.1.: Lowest-order phonon-induced self-energy diagrams for a crystal electron with Bloch vector $\mathbf{k}$ and an intermediary phonon with wave vector $\mathbf{q}$.

Physically, the split into two distinct contributions can be understood in terms of Goldstone diagrams [36]. Without going into too much detail, the lowest-order corrections to the energy stem from two processes. Their diagrams are associated with the FM and DW self energies and are depicted in figures 6.1(a) and 6.1(b), respectively. As can be seen, the former diagram features two first-order electron-phonon vertices, while the latter features only one of second order. The order of each vertex is directly linked to the order of the differential operators appearing in their mathematical representation. A

possible approximation of the DW contribution in terms of first-order vertices is hinted at in figure 6.1(c) but is discussed later on. First, we aim to provide an expression for the FM self energy.

6.1. Fan-Migdal Term

To begin with, the derivative of the eigenvalues in the last term of the right-hand side of equation (6.13) is given by equation (6.10) and can just be substituted back in. Furthermore, it is possible to rewrite $|\partial_{l\kappa\alpha}\tilde{\Psi}_{n\mathbf{k}}\rangle$ in terms of the unperturbed states $|\tilde{\Psi}_{n\mathbf{k}}\rangle$ by multiplying equation (6.8) with $\langle\tilde{\Psi}_{m\mathbf{k}}|$ from the left, where $m \neq n$:

$$\begin{aligned} \partial_{l\kappa\alpha}\varepsilon_{n\mathbf{k}} \underbrace{\langle\tilde{\Psi}_{m\mathbf{k}}|\tilde{S}|\tilde{\Psi}_{n\mathbf{k}}\rangle}_{=0} &= \langle\tilde{\Psi}_{m\mathbf{k}}|\partial_{l\kappa\alpha}\tilde{H} - \varepsilon_{n\mathbf{k}}\partial_{l\kappa\alpha}\tilde{S}|\tilde{\Psi}_{n\mathbf{k}}\rangle \\ &+ \underbrace{\langle\tilde{\Psi}_{m\mathbf{k}}|\tilde{H}}_{=\langle\tilde{\Psi}_{m\mathbf{k}}|\varepsilon_{m\mathbf{k}}\tilde{S}} - \varepsilon_{n\mathbf{k}}\tilde{S}|\partial_{l\kappa\alpha}\tilde{\Psi}_{n\mathbf{k}}\rangle . \end{aligned} \quad (6.17)$$

Rearranging the terms yields

$$\langle\tilde{\Psi}_{m\mathbf{k}}|\tilde{S}|\partial_{l\kappa\alpha}\tilde{\Psi}_{n\mathbf{k}}\rangle = \frac{\langle\tilde{\Psi}_{m\mathbf{k}}|\partial_{l\kappa\alpha}\tilde{H} - \varepsilon_{n\mathbf{k}}\partial_{l\kappa\alpha}\tilde{S}|\tilde{\Psi}_{n\mathbf{k}}\rangle}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}}} . \quad (6.18)$$

This provides a way of expressing $|\partial_{l\kappa\alpha}\tilde{\Psi}_{n\mathbf{k}}\rangle$, using the PAW completeness relation from equation (4.34):

$$\begin{aligned} |\partial_{l\kappa\alpha}\tilde{\Psi}_{n\mathbf{k}}\rangle &= \int_{\text{BZ}} \frac{d^3k'}{\Omega} \sum_{m \neq n} \frac{|\tilde{\Psi}_{m\mathbf{k}'}\rangle \langle\tilde{\Psi}_{m\mathbf{k}'}|\partial_{l\kappa\alpha}\tilde{H} - \varepsilon_{n\mathbf{k}}\partial_{l\kappa\alpha}\tilde{S}|\tilde{\Psi}_{n\mathbf{k}}\rangle}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}'}} \\ &+ |\tilde{\Psi}_{n\mathbf{k}}\rangle \langle\tilde{\Psi}_{n\mathbf{k}}|\tilde{S}|\partial_{l\kappa\alpha}\tilde{\Psi}_{n\mathbf{k}}\rangle , \end{aligned} \quad (6.19)$$

where the last term originates from the contribution $m = n$ and is required to include the entire Hilbert space. It is important to remember that, while the Bloch vector $\mathbf{k}$ was omitted in section 4 for simplicity's sake, it is necessary to include it in the current context. In order to find an explicit expression for $\langle\tilde{\Psi}_{n\mathbf{k}}|\tilde{S}|\partial_{l\kappa\alpha}\tilde{\Psi}_{n\mathbf{k}}\rangle$ in terms of the unperturbed states, we apply the derivative $\partial_{l\kappa\alpha}$ to the PAW orthogonality constraint found in equation (4.33):

$$\partial_{l\kappa\alpha} \left(\underbrace{\langle\tilde{\Psi}_{n\mathbf{k}}|\tilde{S}|\tilde{\Psi}_{n\mathbf{k}}\rangle}_{=1} \right) = \langle\partial_{l\kappa\alpha}\tilde{\Psi}_{n\mathbf{k}}|\tilde{S}|\tilde{\Psi}_{n\mathbf{k}}\rangle + \langle\tilde{\Psi}_{n\mathbf{k}}|\partial_{l\kappa\alpha}\tilde{S}|\tilde{\Psi}_{n\mathbf{k}}\rangle + \langle\tilde{\Psi}_{n\mathbf{k}}|\tilde{S}|\partial_{l\kappa\alpha}\tilde{\Psi}_{n\mathbf{k}}\rangle \quad (6.20)$$

$$\Leftrightarrow \langle \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} | \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle + \langle \tilde{\Psi}_{n\mathbf{k}} | \tilde{S} | \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} \rangle = - \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l\kappa\alpha} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle . \quad (6.21)$$

We know that the matrix element $\langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l\kappa\alpha} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle$ needs to be real since the enclosed operator is Hermitian. Without loss of generality, we can assume that $\langle \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} | \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle$ is real as well and therefore

$$\langle \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} | \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle = \langle \tilde{\Psi}_{n\mathbf{k}} | \tilde{S} | \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} \rangle . \quad (6.22)$$

Substituting this identity back into equation (6.21) and multiplying with the state vector $|\tilde{\Psi}_{n\mathbf{k}}\rangle$, we arrive at the expression

$$|\tilde{\Psi}_{n\mathbf{k}}\rangle \langle \tilde{\Psi}_{n\mathbf{k}} | \tilde{S} | \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} \rangle = -\frac{1}{2} |\tilde{\Psi}_{n\mathbf{k}}\rangle \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l\kappa\alpha} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle , \quad (6.23)$$

which can be used in equation (6.19) to finally obtain

$$\begin{aligned} |\partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}}\rangle &= \int_{\text{BZ}} \frac{d^3 k'}{\Omega} \sum_{m \neq n} \frac{|\tilde{\Psi}_{m\mathbf{k}'}\rangle \langle \tilde{\Psi}_{m\mathbf{k}'} | \partial_{l\kappa\alpha} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l\kappa\alpha} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}}\rangle}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}'}} \\ &\quad - \frac{1}{2} |\tilde{\Psi}_{n\mathbf{k}}\rangle \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l\kappa\alpha} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle . \end{aligned} \quad (6.24)$$

Strictly speaking, this expression is not well-defined in the case of degenerate electronic bands. The problem becomes immediately apparent when inspecting the energy denominator $\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}'}$, since it becomes zero for two degenerate bands m and n at $\mathbf{k}' = \mathbf{k}$. Later on, in equation (6.30), this limitation is somewhat lifted by introducing an infinitesimal imaginary shift in the denominator.

Finally, all Cartesian derivatives are transformed to the phonon basis:

$$\partial_{l\kappa\alpha} = \sqrt{m_\kappa} \int_{\text{BZ}} \frac{d^3 q}{\Omega} \sum_\nu e^{-i\mathbf{q} \cdot \mathbf{R}_{l\kappa}} \hat{e}_{\kappa\alpha,\nu}^*(\mathbf{q}) \partial_{\mathbf{q}\nu} , \quad (6.25)$$

where $\partial_{\mathbf{q}\nu}$ denotes a derivative with respect to a phonon with wave vector $\mathbf{q}$ and branch index ν . At this point, it is very beneficial to define the matrix element

$$\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q}) \equiv \langle \tilde{\Psi}_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{\mathbf{q}\nu} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \quad (6.26)$$

as a shorthand notation for the involved matrix elements. This definition is sufficient, given that any product of the form $\langle \tilde{\Psi}_{m\mathbf{k}'} | \partial_{\mathbf{q}\nu} \tilde{H} | \tilde{\Psi}_{n\mathbf{k}} \rangle$ or $\langle \tilde{\Psi}_{m\mathbf{k}'} | \partial_{\mathbf{q}\nu} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle$ has to vanish if $\mathbf{k}'$ is not equivalent to $\mathbf{k} + \mathbf{q}$.

Equations (6.24)–(6.26) can now be used to rewrite the contribution to the FM self energy. For clarity, we start by inspecting only the first term on the right-hand side of

equation (6.13):

$$\begin{aligned}
 & \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta} \tilde{S} | \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} \rangle = \\
 & = \sum_{\nu_1 \nu_2} \int_{\text{BZ}} \frac{d^3 q}{\Omega} \sqrt{m_\kappa m_{\kappa'}} e^{i\mathbf{q} \cdot (\mathbf{R}_{l\kappa} - \mathbf{R}_{l'\kappa'})} \hat{e}_{\kappa\alpha, \nu_1}(\mathbf{q}) \hat{e}_{\kappa'\beta, \nu_2}^*(\mathbf{q}) \\
 & \times \left(\sum_{m \neq n} \frac{\tilde{g}_{mn, \nu_1}^*(\mathbf{k}, \mathbf{q}) \tilde{g}_{mn, \nu_2}(\mathbf{k}, \mathbf{q})}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}}} - \frac{1}{2} \tilde{g}_{nn, \nu_1}(\mathbf{k}, \mathbf{0}) \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{\mathbf{0}\nu_2} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \right), \quad (6.27)
 \end{aligned}$$

where the aforementioned condition on the Bloch and phonon momenta has been utilized. Now, we take advantage of the fact that the second term is very similar to the complex conjugate of the first one:

$$\langle \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle = \left(\langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta}^* \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta}^* \tilde{S} | \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} \rangle \right)^*. \quad (6.28)$$

From this observation, we can infer that their sum involves two times the real part of the quantity inside the parentheses in equation (6.27). Finally, the last term is transformed to the phonon basis in a completely analogous way by using equation (6.25). For this term, the condition on the Bloch and phonon momenta only allows for the case $\mathbf{q} = 0$.

Taking into account all previous considerations, the contribution to the FM self energy can be written more compactly as

$$\begin{aligned}
 \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}}^{\text{FM}} &= \sum_{\nu_1 \nu_2} \int_{\text{BZ}} \frac{d^3 q}{\Omega} \Xi_{n, \nu_1 \nu_2}(\mathbf{k}, \mathbf{q}) \\
 &\times \sqrt{m_\kappa m_{\kappa'}} e^{i\mathbf{q} \cdot (\mathbf{R}_{l\kappa} - \mathbf{R}_{l'\kappa'})} \hat{e}_{\kappa\alpha, \nu_1}(\mathbf{q}) \hat{e}_{\kappa'\beta, \nu_2}^*(\mathbf{q}), \quad (6.29)
 \end{aligned}$$

where we have defined

$$\begin{aligned}
 \Xi_{n, \nu_1 \nu_2}(\mathbf{k}, \mathbf{q}) &\equiv \sum_m 2 \operatorname{Re} \left[\frac{\tilde{g}_{mn, \nu_1}^*(\mathbf{k}, \mathbf{q}) \tilde{g}_{mn, \nu_2}(\mathbf{k}, \mathbf{q})}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + i\delta} \right] \\
 &- \tilde{g}_{nn, \nu_1}(\mathbf{k}, \mathbf{0}) \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{\mathbf{0}\nu_2} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \\
 &- \tilde{g}_{nn, \nu_2}(\mathbf{k}, \mathbf{0}) \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{\mathbf{0}\nu_1} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle. \quad (6.30)
 \end{aligned}$$

As mentioned earlier, the energy denominator $\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}}$ has been modified to include an infinitesimal imaginary shift $i\delta$. Assuming the numerator is purely real, taking the real part amounts to removing all contributions for which the denominator would usually vanish. This conveniently manages degeneracies and allows the sum over bands to formally include the case $m = n$.

The FM energy shift $\Delta\varepsilon_{n\mathbf{k}}^{\text{FM}}$ can now be calculated from equation (6.2) by inserting (6.6) and (6.29):

$$\begin{aligned} \Delta\varepsilon_{n\mathbf{k}}^{\text{FM}} &= \frac{1}{2} \iint_{\text{BZ}} \frac{d^3q}{\Omega} \frac{d^3q'}{\Omega} \sum_{\nu\nu_1\nu_2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \Xi_{n,\nu_1\nu_2}(\mathbf{k}, \mathbf{q}') \\ &\times \frac{2n_\nu(\mathbf{q}) + 1}{2\omega_\nu(\mathbf{q})} e^{i(\mathbf{q}+\mathbf{q}')\cdot(\mathbf{R}_{l\kappa}-\mathbf{R}_{l'\kappa'})} \\ &\times \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) \hat{e}_{\kappa'\beta,\nu}^*(\mathbf{q}) \hat{e}_{\kappa\alpha,\nu_1}(\mathbf{q}') \hat{e}_{\kappa'\beta,\nu_2}^*(\mathbf{q}') . \end{aligned} \quad (6.31)$$

Summing over all primitive cells l and l' results in

$$\sum_{ll'} e^{i(\mathbf{q}+\mathbf{q}')\cdot(\mathbf{R}_{l\kappa}-\mathbf{R}_{l'\kappa'})} = \Omega \delta^{(3)}(\mathbf{q} + \mathbf{q}') , \quad (6.32)$$

which ultimately gives

$$\begin{aligned} \Delta\varepsilon_{n\mathbf{k}}^{\text{FM}} &= \frac{1}{2} \int_{\text{BZ}} \frac{d^3q}{\Omega} \sum_{\nu\nu_1\nu_2} \frac{2n_\nu(\mathbf{q}) + 1}{2\omega_\nu(\mathbf{q})} \Xi_{n,\nu_1\nu_2}(\mathbf{k}, \mathbf{q}) \\ &\times \underbrace{\sum_{\kappa\alpha} \hat{e}_{\kappa\alpha,\nu}^*(\mathbf{q}) \hat{e}_{\kappa\alpha,\nu_1}(\mathbf{q})}_{\delta_{\nu\nu_1}} \underbrace{\sum_{\kappa'\beta} \hat{e}_{\kappa'\beta,\nu}(\mathbf{q}) \hat{e}_{\kappa'\beta,\nu_2}^*(\mathbf{q})}_{\delta_{\nu\nu_2}} \\ &= \frac{1}{2} \int_{\text{BZ}} \frac{d^3q}{\Omega} \sum_{\nu} \frac{2n_\nu(\mathbf{q}) + 1}{2\omega_\nu(\mathbf{q})} \Xi_{n,\nu\nu}(\mathbf{k}, \mathbf{q}) . \end{aligned} \quad (6.33)$$

In terms of the matrix elements defined in equation (6.26), the FM self energy can be written as

$$\begin{aligned} \Delta\varepsilon_{n\mathbf{k}}^{\text{FM}} &= \int_{\text{BZ}} \frac{d^3q}{\Omega} \sum_{\nu} \frac{2n_\nu(\mathbf{q}) + 1}{2\omega_\nu(\mathbf{q})} \\ &\times \text{Re} \left[\sum_m \frac{|\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q})|^2}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + i\delta} - \tilde{g}_{nn,\nu}(\mathbf{k}, \mathbf{0}) \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{\mathbf{0}\nu} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \right] . \end{aligned} \quad (6.34)$$

Finally, when we compare this result to the Goldstone diagram appearing in figure 6.1(a), we can infer that the matrix element $\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q})$ is associated with the first-order electron-phonon vertex for $\mathbf{q} \neq \mathbf{0}$. For Γ -point phonons, however, there is an additional correction due to the PAW orthogonality constraint. To this end, $\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q})$ can be regarded as a direct generalization of the electron-phonon matrix element $g_{mn,\nu}(\mathbf{k}, \mathbf{q})$ for the PAW method. A definition of $g_{mn,\nu}(\mathbf{k}, \mathbf{q})$ is given at the beginning of chapter 7.2.2. The above observation is reinforced by the fact that in the limiting case $\tilde{S} \leftarrow \mathbf{1}$,

the expression for the FM self-energy, equation (6.33), is identical to the one given in reference [15].

6.2. Debye-Waller Term

In this section, the DW self energy is recast in a form that contains first derivatives only. In order to find such an expression, we must first manipulate equation (6.15) such that it can be factorized. As mentioned earlier, this is equivalent to splitting up the second-order vertex appearing in the Goldstone diagram, figure 6.1(b), into two first-order vertices, whereby the intermediary phonon needs to have a wave vector $\mathbf{q} = \mathbf{0}$. This approximation is depicted in figure 6.1(c).

We start by writing down the acoustic sum rule

$$\sum_{l'\kappa'} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}} = \sum_{l'\kappa'} \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle = 0. \quad (6.35)$$

This is equivalent to shifting all atoms by an infinitesimal amount along the same direction β , in other words, a rigid translation of the lattice. Thus, the eigenvalue associated with this translational mode must vanish.

The next step involves taking the derivative of equation (6.35) with respect to additional independent atomic displacements $\partial_{l\kappa\alpha}$. Since equation (6.35) is closely related to the Hellmann-Feynman theorem shown in equation (6.10), the result can be inferred from equation (6.11):

$$\begin{aligned} \sum_{l'\kappa'} \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle &= \\ &= - \sum_{l'\kappa'} \left(\langle \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \right. \\ &\quad + \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{H} - \varepsilon_{n\mathbf{k}} \partial_{l'\kappa'\beta} \tilde{S} | \partial_{l\kappa\alpha} \tilde{\Psi}_{n\mathbf{k}} \rangle \\ &\quad \left. - \partial_{l\kappa\alpha} \varepsilon_{n\mathbf{k}} \langle \tilde{\Psi}_{n\mathbf{k}} | \partial_{l'\kappa'\beta} \tilde{S} | \tilde{\Psi}_{n\mathbf{k}} \rangle \right). \end{aligned} \quad (6.36)$$

When comparing this result to equations (6.13) and (6.15) we can see that

$$\sum_{l'\kappa'} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}}^{\text{DW}} = - \sum_{l'\kappa'} \partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}}^{\text{FM}}. \quad (6.37)$$

Unfortunately, this equivalence does not provide a way of calculating the quantity of interest, $\partial_{l\kappa\alpha} \partial_{l'\kappa'\beta} \varepsilon_{n\mathbf{k}}^{\text{DW}}$. Consequently, we need to focus on removing the sum over all atoms first. One way of achieving this goal is to employ the rigid-ion approximation,

introduced by Allen and Heine [22]. In this approximation, all summands with $(l\kappa) \neq (l'\kappa')$ on the left-hand side of equation (6.37) are neglected. This allows for writing the contribution to the DW self energy using the already calculated FM contribution from equation (6.29):

$$\begin{aligned} \partial_{l\kappa\alpha}\partial_{l\kappa\beta}\varepsilon_{n\mathbf{k}}^{\text{DW}} &= - \sum_{l'\kappa'} \partial_{l\kappa\alpha}\partial_{l'\kappa'\beta}\varepsilon_{n\mathbf{k}}^{\text{FM}} \\ &= - \sum_{\nu_1\nu_2} \sum_{l'\kappa'} \int_{\text{BZ}} \frac{d^3q}{\Omega} \Xi_{n,\nu_1\nu_2}(\mathbf{k}, \mathbf{q}) \\ &\quad \times \sqrt{m_\kappa m_{\kappa'}} e^{i\mathbf{q}\cdot(\mathbf{R}_{l\kappa}-\mathbf{R}_{l'\kappa'})} \hat{e}_{\kappa\alpha,\nu_1}(\mathbf{q}) \hat{e}_{\kappa'\beta,\nu_2}^*(\mathbf{q}) . \end{aligned} \quad (6.38)$$

Summing over all cells l' of the lattice yields

$$\sum_{l'} e^{i\mathbf{q}\cdot(\mathbf{R}_{l\kappa}-\mathbf{R}_{l'\kappa'})} = \Omega \delta^{(3)}(\mathbf{q}) , \quad (6.39)$$

which, combined with the fact that $\hat{e}_{\kappa\alpha,\nu}(\mathbf{0})$ is real, results in

$$\partial_{l\kappa\alpha}\partial_{l\kappa\beta}\varepsilon_{n\mathbf{k}}^{\text{DW}} = - \sum_{\nu_1\nu_2} \sum_{\kappa'} \Xi_{n,\nu_1\nu_2}(\mathbf{k}, \mathbf{0}) \sqrt{m_\kappa m_{\kappa'}} \hat{e}_{\kappa\alpha,\nu_1}(\mathbf{0}) \hat{e}_{\kappa'\beta,\nu_2}(\mathbf{0}) . \quad (6.40)$$

Inserting equations (6.6) and (6.40) into the expression for the DW self energy, equation (6.2), yields

$$\begin{aligned} \Delta\varepsilon_{n\mathbf{k}}^{\text{DW}} &= -\frac{1}{2} \int_{\text{BZ}} \frac{d^3q}{\Omega} \sum_{\nu\nu_1\nu_2} \sum_{\kappa\kappa'} \sum_{\alpha\beta} \Xi_{n,\nu_1\nu_2}(\mathbf{k}, \mathbf{0}) \frac{2n_\nu(\mathbf{q}) + 1}{2\omega_\nu(\mathbf{q})} \\ &\quad \times \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) \hat{e}_{\kappa'\beta,\nu}^*(\mathbf{q}) \hat{e}_{\kappa\alpha,\nu_1}(\mathbf{0}) \hat{e}_{\kappa'\beta,\nu_2}(\mathbf{0}) . \end{aligned} \quad (6.41)$$

7. Wannier Functions

Starting from a specific Bloch-manifold, it is possible to construct a set of orbitals which are well localized in real space, carry the same amount of information and span the same subspace [37]. This transformation can be written as a generalized Fourier transform,

$$|\mathcal{W}_{ml}\rangle = \int_{\text{BZ}} \frac{d^3k}{\Omega} e^{-i\mathbf{k}\cdot\boldsymbol{\xi}_{lm}} \sum_n |\Psi_{n\mathbf{k}}\rangle U_{nm,\mathbf{k}} , \quad (7.1)$$

where the localized orbitals $|\mathcal{W}_{ml}\rangle$ are referred to as Wannier functions [37]. The integration is carried out over the Brillouin zone with reciprocal-space volume $\Omega \equiv \frac{(2\pi)^3}{V_{\text{UC}}}$, corresponding to the Bloch orbitals' domain. The Wannier index m labels different Wannier functions inside the same unit cell l , whereas $\boldsymbol{\xi}_{lm}$ denotes their spatial locations. More specifically, m may also refer to functions with identical spatial location but different orbital character. In the most general case, this transformation also includes a unitary band-mixing matrix $U_{nm,\mathbf{k}}$ for each $\mathbf{k}$ -point, which is necessary in case of degeneracies to untangle the band structure. By inverting equation (7.1), it is possible to express a transformation back to the original Bloch manifold:

$$|\Psi_{n\mathbf{k}}\rangle = \sum_{ml} e^{i\mathbf{k}\cdot\boldsymbol{\xi}_{lm}} |\mathcal{W}_{ml}\rangle U_{mn,\mathbf{k}}^\dagger . \quad (7.2)$$

Considerable complexity is added due to the phase freedom naturally incorporated in Bloch states as shown in equation (3.15). This freedom transfers to the Wannier functions, resulting in a high level of non-uniqueness regarding their exact spatial form, position and spread. This arbitrariness is incorporated into the unitary matrix $U_{nm,\mathbf{k}}$. Different choices with regard to its exact form will, in general, lead to different sets of Wannier functions. Many criteria for localization exist, which also entails that their spatial location may potentially be an ambiguous quantity and has to be treated with care. In the present work, choosing a well defined localization criterion and minimizing the spatial spread is not of relevance. Instead, a simple projection-based approach is used to generate orthonormal Wannier functions.

7.1. Projection onto Trial Orbitals

The only restriction imposed on $U_{nm,\mathbf{k}}$ so far is its unitarity. However, as mentioned earlier, a major reason for why this matrix is part of the transformation is degeneracy. As discussed in section 3.2, the Bloch manifold may be discontinuous with respect to $\mathbf{k}$ within a degenerate subspace. By choosing the entries of $U_{nm,\mathbf{k}}$ accordingly, the Bloch states can be rotated in such a way that the resulting manifold is smooth in $\mathbf{k}$, giving rise to well-defined Wannier functions.

A simple method to achieve this goal is by projecting the initial Bloch wave functions onto a set of localized trial orbitals, which should remotely resemble the final form of the Wannier functions. A set of hydrogen-like atomic orbitals is sufficient for this purpose but other choices are possible as well. The following derivation leads to a practical scheme for obtaining the unitary matrices $U_{nm,\mathbf{k}}$ for each reciprocal-space vector $\mathbf{k}$ independently. For the sake of readability, the dependency on $\mathbf{k}$ is omitted.

Let $|\Psi_n\rangle$ be an initial wave function and $|g_n\rangle$ be a localized trial orbital. Then, a reference Wannier function $|\mathcal{W}_m\rangle$ can formally be calculated in a two step process as

$$|\mathcal{W}_m\rangle = \sum_n |\Psi_n^S\rangle \left(S^{-\frac{1}{2}}\right)_{nm} , \quad (7.3)$$

using the smooth non-orthogonal intermediary wave functions

$$|\Psi_n^S\rangle = \sum_m |\Psi_m\rangle A_{mn} , \quad (7.4)$$

where both matrices A_{mn} and S_{mn} are defined in terms of overlaps with the trial functions:

$$A_{mn} = \langle \Psi_m | g_n \rangle , \quad (7.5)$$

$$S_{mn} = \left(A^\dagger A\right)_{mn} . \quad (7.6)$$

This choice for the matrix S_{mn} enforces orthogonality of the resulting Wannier functions which can be seen in the following. At this point, it is important to note that the overlap matrix A_{mn} need not be square in the most general case. In other words, the respective dimensions of the Hilbert spaces underlying the Wannier and Bloch wave functions can differ. To accommodate for this fact, the overlap matrix can be decomposed using a singular-value decomposition:

$$A_{mn} = \sum_{ij} \bar{Z}_{mi} d_j \delta_{ij} Z_{jn}^\dagger , \quad (7.7)$$

where Z_{ij} and $\bar{Z}_{ij}$ are unitary matrices of potentially different dimensions and d_j are the so-called singular values of A_{mn} . Now, we substitute the overlap matrix from equation (7.7) back into equation (7.6) and, after only a few algebraic manipulations, the inverse square root of S_{mn} can be recovered:

$$\begin{aligned}
 S_{mn} &= \sum_{ijrs} Z_{mi} d_i \delta_{ij} \underbrace{\left(\bar{Z}^\dagger \bar{Z} \right)_{jr}}_{\delta_{jr}} d_s \delta_{rs} Z_{sn}^\dagger \\
 &= \sum_i Z_{mi} d_i^2 Z_{in}^\dagger \\
 \Leftrightarrow \left(S^{-\frac{1}{2}} \right)_{mn} &= \sum_i Z_{mi} \frac{1}{d_i} Z_{in}^\dagger .
 \end{aligned} \tag{7.8}$$

The last step in equation (7.8) uses some of the convenient properties of unitary matrices. If some of the singular values are zero, the inverse of the diagonal matrix $d_i \delta_{ij}$ is formally not well defined. In this case, the transformation may still be defined for a subspace spanned by the column vectors of Z_{ij} corresponding to the non-zero singular values. Finally, combining equations (7.3), (7.4), (7.7) and (7.8) yields the entire transformation:

$$\begin{aligned}
 |\mathcal{W}_m\rangle &= \sum_{ni} |\Psi_n\rangle A_{ni} \left(S^{-\frac{1}{2}} \right)_{im} \\
 &= \sum_{nijr} |\Psi_n\rangle \bar{Z}_{ni} d_j \delta_{ij} \underbrace{\left(Z^\dagger Z \right)_{jr}}_{\delta_{jr}} \frac{1}{d_r} Z_{rm}^\dagger \\
 &= \sum_{nij} |\Psi_n\rangle \bar{Z}_{ni} \delta_{ij} Z_{jm}^\dagger .
 \end{aligned} \tag{7.9}$$

When comparing this result to the Wannier transformation in equation (7.1), we see that $\left(\bar{Z} \delta Z^\dagger \right)_{nm}$ can be identified as the band-mixing matrix and thus

$$|\mathcal{W}_{ml}\rangle = \int_{\text{BZ}} \frac{d^3k}{\Omega} e^{-i\mathbf{k} \cdot \boldsymbol{\xi}_{lm}} \sum_{nij} |\Psi_{n\mathbf{k}}\rangle \bar{Z}_{ni,\mathbf{k}} \delta_{ij} Z_{jm,\mathbf{k}}^\dagger . \tag{7.10}$$

Henceforth, it is assumed that the Wannier functions exhibit the same translational symmetries as the underlying lattice, i.e. $\boldsymbol{\xi}_{lm}$ can be written as a sum of the cell position $\mathbf{R}_l$ and the relative position $\boldsymbol{\xi}_m$ of the Wannier function within that cell. Noticeably, in references [14] and [37], we find that the definition for a Wannier function $|W'_{ml}\rangle$ does

not involve their relative position ξ_m :

$$|W'_{ml}\rangle \equiv \int_{\text{BZ}} \frac{d^3k}{\Omega} e^{-i\mathbf{k}\cdot\mathbf{R}_l} |\Psi_{n\mathbf{k}}\rangle . \quad (7.11)$$

In order to bridge this formal gap, we need to make the following observation: It is possible to absorb the phase factor $e^{-i\mathbf{k}\cdot\boldsymbol{\xi}_m}$ appearing in equation (7.1) into the band-mixing matrix. In the case of the projection-based approach discussed here, this means that the phase factor is ultimately contained within the trial-orbitals $|g_n\rangle$. The reason for a deviating phase convention in this thesis is rooted in the way Wannier functions are implemented, which is discussed in section 8. Nonetheless, for all physically relevant purposes, any phase convention is suitable due to the phase freedom of Bloch orbitals.

7.2. Wannier-Fourier Interpolation

This section makes heavy use of the concepts and methods introduced in reference [14]. It aims to provide a method for interpolating matrix elements to arbitrary Bloch vectors using Wannier functions and finite differences.

In principle, it is possible to obtain an arbitrarily fine sampling of k-space by increasing the number of Bloch orbitals. However, attached to this approach comes considerable computational cost, since the KS equations need to be solved self-consistently for a far larger set of functions. Furthermore, a straight-forward interpolation approach using Bloch orbitals is often not applicable or very difficult. This is partly due to degeneracy and the local phase freedom of Bloch orbitals displayed in equation (3.15). A related problem arises when using large super-cells during simulation. In this case, the corresponding Brillouin zone is smaller and potentially distorted, compared to the Brillouin zone of the lattice's primitive cell. The electronic band structure is then folded back into the smaller Brillouin zone. To restore the information related to the primitive cell, it is often necessary to unfold the band structure. Wannier-Fourier interpolation circumvents both of these issues by utilizing a change of basis, combined with a Fourier sum in real space. Despite electron-phonon matrix elements being a pivotal concept in this thesis, it is instructive to first discuss the arguably simpler case of interpolating the electronic band structure.

7.2.1. Interpolation of Electronic Band Structure

To begin with, we aim to interpolate a Bloch-space matrix element $\langle\Psi_{m\mathbf{k}}|\hat{A}|\Psi_{n\mathbf{k}}\rangle$, involving a Hermitian lattice-periodic operator $\hat{A}$ onto a much finer k-point mesh. Using

equation (7.2), it is possible to express this matrix element in a basis spanned by Wannier functions:

$$\langle \Psi_{m\mathbf{k}} | \hat{A} | \Psi_{n\mathbf{k}} \rangle = \sum_{m'n'} \sum_{ll'} e^{i\mathbf{k} \cdot (\boldsymbol{\xi}_{l'n'} - \boldsymbol{\xi}_{lm'})} U_{mm',\mathbf{k}} \langle \mathcal{W}_{m'l} | \hat{A} | \mathcal{W}_{n'l'} \rangle U_{n'n,\mathbf{k}}^\dagger. \quad (7.12)$$

Due to the discrete translational invariance of the electronic Hamiltonian, it is possible to rewrite the Fourier sum using a reference primitive cell $l = 0$, following the same argumentation as in section 5.1:

$$\langle \Psi_{m\mathbf{k}} | \hat{A} | \Psi_{n\mathbf{k}} \rangle = \sum_{m'n'} U_{mm',\mathbf{k}} \left(\sum_l e^{i\mathbf{k} \cdot (\boldsymbol{\xi}_{ln'} - \boldsymbol{\xi}_{0m'})} \langle \mathcal{W}_{m'0} | \hat{A} | \mathcal{W}_{n'l} \rangle \right) U_{n'n,\mathbf{k}}^\dagger. \quad (7.13)$$

The Wannier-space matrix element $\langle \mathcal{W}_{ml} | \hat{A} | \mathcal{W}_{n'l'} \rangle$ can in turn easily be obtained from an initial Bloch manifold by inverting equation (7.13) or, alternatively, by using equation (7.1):

$$\langle \mathcal{W}_{ml} | \hat{A} | \mathcal{W}_{n'l'} \rangle = \int_{\text{BZ}} \frac{d^3k}{\Omega} e^{-i\mathbf{k} \cdot (\boldsymbol{\xi}_{l'n} - \boldsymbol{\xi}_{lm})} \sum_{m'n'} U_{mm',\mathbf{k}}^\dagger \langle \Psi_{m'\mathbf{k}} | \hat{A} | \Psi_{n'\mathbf{k}} \rangle U_{n'n,\mathbf{k}}. \quad (7.14)$$

Using equations (7.13) and (7.14), it is in principle possible to perform an interpolation onto arbitrary Bloch vectors by first transforming to the Wannier basis, then performing a Fourier sum over all unit cells and finally transforming back to a new Bloch basis. In practice, any integral, such as the one appearing in equation (7.14), would of course be represented as a discrete sum over finitely many $\mathbf{k}$ -points.

While the band-mixing matrices $U_{mn,\mathbf{k}}$ in equation (7.14) can easily be obtained, for example, by using the projection scheme detailed in section 7.1, they are in general unknown for arbitrary Bloch vectors. Fortunately, this scheme also works for the electronic Hamiltonian, whose eigenfunctions are Bloch orbitals. Using $\hat{H}$ in place of $\hat{A}$, we can therefore rewrite equation (7.13) as

$$\delta_{mn} \varepsilon_{n\mathbf{k}} = \sum_{m'n'} U_{mm',\mathbf{k}} \left(\sum_l e^{i\mathbf{k} \cdot (\boldsymbol{\xi}_{ln'} - \boldsymbol{\xi}_{0m'})} \langle \mathcal{W}_{m'0} | \hat{H} | \mathcal{W}_{n'l} \rangle \right) U_{n'n,\mathbf{k}}^\dagger. \quad (7.15)$$

This form is easily recognizable as the eigen decomposition of a Hermitian matrix. Consequently, the band-mixing matrix $U_{mn,\mathbf{k}}$ can be obtained by diagonalizing the term inside the parenthesis.

Equation (7.15) implicitly provides a working method for interpolating electronic band structure to arbitrary Bloch vectors when the Wannier-space Hamiltonian matrix is

known. This is especially useful since the interpolated k-point mesh need not be uniform in any way and its density can be adjusted locally. It is important to note that, in practice, only a relatively small number of Wannier functions need to be constructed as the matrix elements $\langle \mathcal{W}_{ml} | \hat{H} | \mathcal{W}_{n'l'} \rangle$ tend to decay rapidly with the distance $|\boldsymbol{\xi}_{l'n} - \boldsymbol{\xi}_{lm}|$ between Wannier functions. This last property is tremendously important for the success of this method and needs to be verified numerically before any actual calculation can be performed.

7.2.2. Interpolation of Electron-Phonon Matrix Elements

For the purpose of deriving and presenting the interpolation technique, let us define an electron-phonon matrix element as the probability amplitude

$$g_{mn,\nu}(\mathbf{k}, \mathbf{q}) \equiv \langle \Psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} \hat{H} | \Psi_{n\mathbf{k}} \rangle , \quad (7.16)$$

for an initial electronic state $|\Psi_{n\mathbf{k}}\rangle$ to scatter via a phonon with wave vector $\mathbf{q}$ and branch index ν into the final state $|\Psi_{m\mathbf{k}+\mathbf{q}}\rangle$ [14]. The notation $\partial_{\mathbf{q}\nu}$ describes a derivative with respect to a collective displacement of atoms due to the corresponding phonon. Essentially, it only acts on the external potential since the kinetic part of the electronic Hamiltonian commutes with this differential operator.

The matrix element $g_{mn,\nu}(\mathbf{k}, \mathbf{q})$ can be used to calculate many physically relevant properties, e.g. electron as well as phonon self-energy corrections, quasi-particle life times and contributions to temperature-dependent band structure [15]. However, it is important to mention that this definition does not generally suffice for use within the PAW framework. An appropriate expression compatible with the PAW method has been derived in section 6.

To begin with, the Bloch orbitals found in equation (7.16) are expressed in the Wannier basis using equation (7.2). In addition, the phonon derivative is rewritten in terms of localized single-atom displacements as

$$\partial_{\mathbf{q}\nu} = \sum_{l\kappa\alpha} \frac{1}{\sqrt{m_\kappa}} e^{i\mathbf{q}\cdot\mathbf{R}_{l\kappa}} \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) \partial_{l\kappa\alpha} , \quad (7.17)$$

where the shorthand notation $\partial_{l\kappa\alpha} \equiv \frac{\partial}{\partial u_{l\kappa\alpha}}$, introduced at the beginning of section 6, is used. To reiterate, $\mathbf{R}_{l\kappa}$ denotes the equilibrium position of atom κ in cell l , while $\mathbf{u}_{l\kappa}$ is its non-equilibrium displacement. Applying these two transformations to the electron-

phonon matrix element in equation (7.16) yields

$$g_{mn,\nu}(\mathbf{k}, \mathbf{q}) = \sum_{m'l'n'l'} \sum_{p\kappa\alpha} e^{-i(\mathbf{k}+\mathbf{q})\cdot\boldsymbol{\xi}_{lm'}} e^{i\mathbf{q}\cdot\mathbf{R}_{p\kappa}} e^{i\mathbf{k}\cdot\boldsymbol{\xi}_{l'n'}} \times U_{mm',\mathbf{k}+\mathbf{q}} \langle \mathcal{W}_{m'l} | \partial_{p\kappa\alpha} \hat{H} | \mathcal{W}_{n'l'} \rangle U_{n'n,\mathbf{k}}^\dagger \frac{1}{\sqrt{m_\kappa}} \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) . \quad (7.18)$$

Similar to previous considerations, it is once more possible to exploit translational invariance of the Wannier-space matrix element. We aim to restrict the derivative $\partial_{p\kappa\alpha}$ to one reference unit cell, $p = 0$. The reason for this is implementation related and is discussed in more detail in section 8. Consequently, the lattice needs to be shifted accordingly and the relation expressing translational invariance is found to be

$$\begin{aligned} \boldsymbol{\xi}_{lm} - \mathbf{R}_{p\kappa} &= \boldsymbol{\xi}_{l_1m} - \mathbf{R}_{0\kappa} \\ \boldsymbol{\xi}_{l'm} - \mathbf{R}_{p\kappa} &= \boldsymbol{\xi}_{l_2m} - \mathbf{R}_{0\kappa} \\ &\Leftrightarrow \\ \langle \mathcal{W}_{m'l} | \partial_{p\kappa\alpha} \hat{H} | \mathcal{W}_{n'l'} \rangle &= \langle \mathcal{W}_{m'l_1} | \partial_{0\kappa\alpha} \hat{H} | \mathcal{W}_{n'l_2} \rangle , \end{aligned} \quad (7.19)$$

and equation (7.18) can be rewritten as

$$g_{mn,\nu}(\mathbf{k}, \mathbf{q}) = \sum_{m'l'n'l'} \sum_{\kappa\alpha} e^{-i(\mathbf{k}+\mathbf{q})\cdot(\boldsymbol{\xi}_{lm'} - \mathbf{R}_{0\kappa})} e^{i\mathbf{k}\cdot(\boldsymbol{\xi}_{l'n'} - \mathbf{R}_{0\kappa})} \times U_{mm',\mathbf{k}+\mathbf{q}} \langle \mathcal{W}_{m'l} | \partial_{0\kappa\alpha} \hat{H} | \mathcal{W}_{n'l'} \rangle U_{n'n,\mathbf{k}}^\dagger \frac{1}{\sqrt{m_\kappa}} \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) . \quad (7.20)$$

This expression provides an interpolation scheme for the electron-phonon matrix element which is similar to equation (7.15). However, additional complexity is added by the phononic degrees of freedom. The matrix of vibrational eigenvectors $\hat{e}_{\kappa\alpha,\nu}(\mathbf{q})$ can be obtained by diagonalizing the dynamical matrix for a specific phonon wave vector $\mathbf{q}$. The exact procedure for accomplishing this is outlined in section 5.2. The band-mixing matrices $U_{mn,\mathbf{k}}$ cannot be obtained by explicit calculation for arbitrary Bloch vectors $\mathbf{k}$. Instead, they are easily obtained from equation (7.15) by diagonalizing the term inside the parentheses.

In order to calculate the Wannier-space matrix elements $\langle \mathcal{W}_{ml} | \partial_{0\kappa\alpha} \hat{H} | \mathcal{W}_{nl'} \rangle$, they could first be calculated in the Bloch picture, followed by a transformation to the Wannier representation. The transformational behavior is obtained by inverting equation

(7.18):

$$\begin{aligned} \langle \mathcal{W}_{ml} | \partial_{p\kappa\alpha} \hat{H} | \mathcal{W}_{nl'} \rangle &= \sum_{m'n'\nu} \iint \frac{d^3k}{\Omega} \frac{d^3q}{\Omega} e^{i(\mathbf{k}+\mathbf{q}) \cdot (\boldsymbol{\xi}_{lm} - \mathbf{R}_{p\kappa})} e^{-i\mathbf{k} \cdot (\boldsymbol{\xi}_{l'n} - \mathbf{R}_{p\kappa})} \\ &\times U_{mm', \mathbf{k}+\mathbf{q}}^\dagger g_{m'n', \nu}(\mathbf{k}, \mathbf{q}) U_{n'n, \mathbf{k}} \sqrt{m_\kappa} \hat{e}_{\kappa\alpha, \nu}^*(\mathbf{q}) . \end{aligned} \quad (7.21)$$

In practice, the idea is to sample the integrals appearing in equation (7.21) on a coarse grid, requiring only a small number of Bloch-space matrix elements to be calculated.

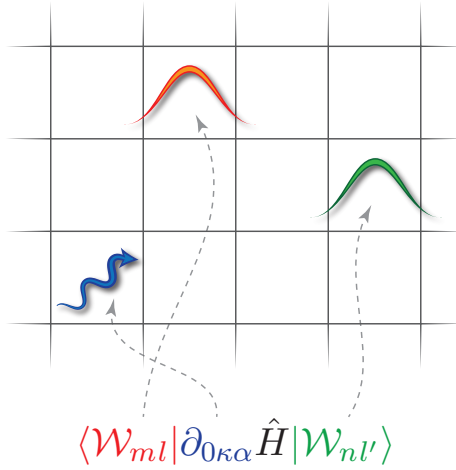


Figure 7.1.: Exemplified spatial arrangement of Wannier functions and phonon perturbation entering the electron-phonon matrix element $\langle \mathcal{W}_{ml} | \partial_{0\kappa\alpha} \hat{H} | \mathcal{W}_{nl'} \rangle$. Their spatial localization ensures that whenever two functions are occupying unit cells far enough apart, the matrix element vanishes.

In the scope of this thesis, the matrix elements $\langle \mathcal{W}_{ml} | \partial_{0\kappa\alpha} \hat{H} | \mathcal{W}_{nl'} \rangle$ are calculated directly in the Wannier basis using finite differences. In section 8, an adequate expression is given in equation (8.1). Additionally, figure 7.1 gives an idea of how the spatial arrangement of Wannier functions and phonon perturbation might look like for a specific matrix element in the super cell. The phonon perturbation is confined to the unit cell $p = 0$, while the Wannier functions may each occupy any cell. Whenever the distance between any two of these is large enough, the electron-phonon matrix element vanishes and an effective cut-off radius can be introduced. The usefulness of this method strictly depends on this assumption. As mentioned earlier, if the Wannier functions' overlap is small enough, the Wannier-space matrix elements are expected to decay rapidly with distance. Just as in the case of interpolating electronic band structure, the decay of

matrix elements with distance needs to be verified numerically for any given system in order for this method to be reliable.

8. Implementation Details

As part of this thesis, the Wannier-Fourier-interpolation method as well as the force-constant-based approach to calculating phonons presented in section 7.2 and 5.2, respectively, have both been implemented in VASP. In its current state, the former algorithm provides a way of interpolating electronic band structures using equation (7.15) as well as electron-phonon matrix elements of the same form as shown in equation (7.16). The interpolation method itself, however, is far more general and can be applied to matrix elements beyond the ones mentioned here. This section aims to provide some insight into the actual implementation of the theoretical framework and discusses the arising nuances.

8.1. General Remarks

To begin with, both algorithms are designed to utilize finite differences. Although other ways of evaluating the derivatives might be more sophisticated, this approach profits from generality and simplicity. It can be applied to a wide range of different exchange-correlation potentials, including e.g. hybrid functionals, independent of their exact form or the representation chosen for the wave functions. The numerical implementation is also straight forward since any matrix element of the form $\langle a | \frac{\partial}{\partial r_\alpha} V(\mathbf{r}) | b \rangle$ can be evaluated as

$$\left\langle a \left| \frac{\partial}{\partial r_\alpha} V(\mathbf{r}) \right| b \right\rangle = \frac{1}{2|\Delta_\alpha|} \left[\langle a | V(\mathbf{r} + \Delta_\alpha) | b \rangle - \langle a | V(\mathbf{r} - \Delta_\alpha) | b \rangle \right], \quad (8.1)$$

where Δ_α is a small displacement vector pointing in the Cartesian direction α . Using finite differences for calculating either phonons or electron-phonon coupling, however, always requires a large enough super cell. Since VASP employs periodic boundary condition for its real-space geometry, the super cell must be large enough so a small displacement of an ion has only a negligibly small effect on its periodic images.

Usually, VASP would choose appropriate spatial directions for individual displacements by symmetry considerations. This often leads to a reduction in the number of required displacements. In this particular case, the exact symmetry properties of the

electron-phonon matrix elements have not been studied, thus this behavior can not yet be taken into account. Disabling the symmetrization routine, however, leads to every atom in the super cell being displaced in all independent directions. Considering that every Wannier-space electron-phonon matrix element presented so far can be calculated using displacements in the primitive cell only, this is excessively redundant. Therefore, a new way of displacing only the atoms in the primitive cell in all possible independent directions has been implemented, representing a middle ground between the two former extremes.

For a sufficiently large super cell, the corresponding first Brillouin zone is comparatively small and often times the sampling thereof can effectively be reduced to just the Γ -point at the zone center. This neat trick opens up great possibilities for optimization. Firstly, all Bloch functions can now be chosen real, since the dependence on the Bloch vector $\mathbf{k}$ is restricted to Γ . The only remaining freedom for these functions is then just the choice of the sign. Secondly, any matrix element involving Bloch functions and Hermitian operators must be real, too. Lastly, the Wannier transformation in equation (7.14) loses the phase factor and is now just a unitary rotation of the Bloch manifold into a set of localized Wannier orbitals. It is important to note that this approximation is not generally applicable as, for example, metals might still require finer sampling of the small Brillouin zone. For the purposes of this thesis, however, sampling only the Γ -point is a reasonable first step.

There is one subtlety for the calculation of matrix elements involving derivatives of PAW operators in VASP. Recalling section 4, the expansion coefficients c_{nai} corresponding to the partial waves $|\phi_{ai}\rangle$ are calculated using the projector functions $|\tilde{p}_{ai}\rangle$ as

$$c_{nai} = \langle \tilde{p}_{ai} | \tilde{\Psi}_n \rangle . \quad (8.2)$$

In VASP, these coefficients are stored within the same structure holding the plane-wave coefficients of the PS wave function. In terms of the formalism, however, projector functions and partial waves are thought to be part of operators:

$$\tilde{O} = \hat{T}^\dagger \hat{O} \hat{T} , \quad \text{where} \quad \hat{T} = \mathbb{1} + \sum_{ai} \left(|\phi_{ai}\rangle - |\tilde{\phi}_{ai}\rangle \right) \langle \tilde{p}_{ai} | , \quad (8.3)$$

and $\tilde{O}$ is the PAW representation of an operator $\hat{O}$. Hence, when calculating matrix elements of the form $\langle \Psi_n | \partial_\alpha \tilde{O} | \Psi_n \rangle$, the derivative ∂_α has to affect the partial-wave coefficients without influencing the PS plane-wave coefficients. To avoid muddling with the preexisting code, the partial-wave coefficients c_{nai} stored in the initial wave-function

structure are recalculated during each displacement step. This is done by using equation (8.2) to project the initial PS wave functions onto the perturbed projector functions. The wave-function structure can then simply be passed to a subroutine that calculates the matrix elements.

As already mentioned in section 7, the present definition of Wannier functions entails an additional phase which depends on their relative position inside each cell. This choice has been made with the actual implementation in mind. The problem becomes apparent when implementing the Fourier sum of Wannier-space matrix elements involving periodic boundary conditions. Equation (7.15) helps to illustrate this issue in the case of interpolating electronic band structure:

$$\delta_{mn}\varepsilon_{n\mathbf{k}} = \sum_{m'n'} U_{mm',\mathbf{k}} \left(\sum_l e^{i\mathbf{k}\cdot(\xi_{ln'} - \xi_{0m'})} \langle \mathcal{W}_{m'0} | \hat{H} | \mathcal{W}_{n'l} \rangle \right) U_{n'n,\mathbf{k}}^\dagger. \quad (8.4)$$

The Wannier function $|\mathcal{W}_{m'0}\rangle$ is confined to the primitive cell $l' = 0$, while $|\mathcal{W}_{n'l}\rangle$ may be found anywhere in the entire super cell. In practice, the super cell features periodic boundary conditions and each Wannier function has multiple periodic images, each obtained by translation along a super-cell lattice vector. When implementing a minimum-image convention to determine which primitive cells to include in the Fourier sum, it is therefore particularly important to know which periodic image of $|\mathcal{W}_{n'l}\rangle$ is closest to $|\mathcal{W}_{m'0}\rangle$. In some edge cases, however, a particular periodic image of a cell might contain a Wannier function that is closest, while a different Wannier function inside the same cell might be closer in a different periodic image. From this point of view, it is easier to form a decision based on individual functions rather than on entire cells and thus the inclusion of the exact location is reasonable in the Wannier function phase factors. This way, the periodic images of $|\mathcal{W}_{n'l}\rangle$ to be included in the Fourier sum can be found simply by checking against their distance from $|\mathcal{W}_{m'0}\rangle$. Occasionally, some periodic images of a particular function might actually be equivalent. In this case, the Fourier factor is just the arithmetic mean value of all exponentials corresponding to these periodic images. This argument can be repeated in exactly the same way for the force-constant-based calculation of phonon frequencies as well as for the electron-phonon-interpolation technique outlined in section 7.2.2.

8.2. Electron-Phonon Interaction

Using the rigid-ion approximation, we learned how to rewrite the DW term in a way very similar to the FM term. This marvelous relationship is highlighted in equation (6.38).

Sums over large numbers of occupied and unoccupied Kohn-Sham states, such as the one found in equation (6.30), are notoriously slow to converge and should be avoided if possible. Therefore, it may be of interest to note that the DW contribution to the self-energy could be evaluated directly using finite differences and the rigid-ion approximation in the Wannier basis. While this would require a larger number of independent displacements in the super cell which would obviously scale far worse with system size, it would not involve a sum over unoccupied Kohn-Sham states. The DW contribution would simply be calculated by virtue of equation (6.15) for each Wannier function and then interpolated back to the Bloch basis. By itself, this alternative does not feature many benefits, but if a similarly simple way of calculating the FM term could be found using finite differences, the requirement of including large numbers of electronic bands could be dropped. The issue with the latter is that (6.11) features derivatives of states mixed with independent derivatives of operators. A direct calculation is out of the question due to the excessive computational cost and it is not a-priori clear which approximation would be a sensible choice to simplify such an expression. Further investigation might show whether such an alternative implementation would show significant numerical advantages.

In section 7.2.2, the exact form of the Wannier-space matrix element $\langle W_{ml} | \partial_{0\kappa\alpha} | W_{nl'} \rangle$ was chosen deliberately to restrict the phonon perturbation to just one primitive cell of the lattice. This allows finite differences to be applied efficiently and ensures good scaling with system size.

The algorithm for calculating the PAW electron-phonon matrix element $\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q})$ is outlined in algorithm 1 using pseudocode. The majority of the computation time is spent calculating the correct Fourier phases for each Wannier-space matrix element. After performing the Fourier sum to the primitive cell, the resulting matrices have much smaller dimensions. Consequently, the subsequent matrix-matrix multiplications are extremely cheap.

For the numerical evaluation of the Brillouin-zone integrals appearing in equations (6.33) and (6.41), a sampling algorithm has been implemented, specifically designed to sample arbitrary Brillouin zones in potentially non-regular ways. To provide an example of when this could be important, it is sometimes beneficial to perform sampling using Monte-Carlo algorithms or to include points in the Brillouin zone which are commensurable with a certain lattice. In the present case, the Wannier-Fourier interpolation performs a transformation from a super cell to one of its primitive cells. We know that using a primitive cell and N^3 k-points to calculate the electronic band structure, for example, is equivalent to using a super cell consisting of N^3 such primitive cells and only sampling the Γ -point. This fact is a direct consequence of the electronic band structure

Algorithm 1 Interpolation of electron-phonon matrix elements to the Bloch basis.

Require: $\mathbf{k}, \mathbf{q}, \langle W_{m'l} | \tilde{H} | W_{n'l'} \rangle, \langle W_{m'l} | \partial_{0\kappa\alpha} \tilde{H} | W_{n'l'} \rangle, \langle W_{m'l} | \partial_{0\kappa\alpha} \tilde{S} | W_{n'l'} \rangle$

$$H_{ll',m'n'}^I = \langle W_{m'l} | \tilde{H} | W_{n'l'} \rangle$$

$$H_{ll',m'n',\kappa\alpha}^P = \langle W_{m'l} | \partial_{0\kappa\alpha} \tilde{H} | W_{n'l'} \rangle$$

$$S_{ll',m'n',\kappa\alpha}^P = \langle W_{m'l} | \partial_{0\kappa\alpha} \tilde{S} | W_{n'l'} \rangle$$

$$H_{m'n',\kappa\alpha}^{\text{RED}} = 0$$

$$S_{m'n',\kappa\alpha}^{\text{RED}} = 0$$
for all $\kappa \in \text{atoms}$ **do**
 for $\alpha = 1$ **to** 3 **do**
 for all $(m', n') \in \text{Wannier functions in primitive cell}$ **do**
 for all $(l, l') \in \text{primitive cells}$ **do**
 $phase = \text{calculate Fourier phase for } (lm', l'n', \kappa)$
 $H_{m'n',\kappa\alpha}^{\text{RED}} = H_{m'n',\kappa\alpha}^{\text{RED}} + H_{ll',m'n',\kappa\alpha}^P * phase$
 $S_{m'n',\kappa\alpha}^{\text{RED}} = S_{m'n',\kappa\alpha}^{\text{RED}} + S_{ll',m'n',\kappa\alpha}^P * phase$
 end for
 end for
 end for
 for $\alpha = 1$ **to** 3 **do**
 $(U_{n'n,\mathbf{k}}, \varepsilon_{n\mathbf{k}}) = \text{diagonalize } H_{ll',m'n'}^I \text{ at } \mathbf{k} \text{ in primitive cell}$
 $(U_{m'm,\mathbf{k}+\mathbf{q}}, \varepsilon_{m\mathbf{k}+\mathbf{q}}) = \text{diagonalize } H_{ll',m'n'}^I \text{ at } \mathbf{k} + \mathbf{q} \text{ in primitive cell}$
 $U_{mm',\mathbf{k}+\mathbf{q}} = \text{conjugate transpose of } U_{m'm,\mathbf{k}+\mathbf{q}}^\dagger$
 for all $\nu \in \text{vibrational modes}$ **do**
 for all $\kappa \in \text{atoms}$ **do**
 for $\alpha = 1$ **to** 3 **do**
 for all $(m, n) \in \text{electronic bands}$ **do**
 for all $(m', n') \in \text{Wannier functions in primitive cell}$ **do**
 $\tilde{g}_{mn,\kappa\alpha}(\mathbf{k}, \mathbf{q}) = U_{mm',\mathbf{k}+\mathbf{q}} * H_{m'n',\kappa\alpha}^{\text{RED}} * U_{n'n,\mathbf{k}}^\dagger - U_{mm',\mathbf{k}+\mathbf{q}} * S_{m'n',\kappa\alpha}^{\text{RED}} * U_{n'n,\mathbf{k}}^\dagger * \varepsilon_{n\mathbf{k}}$
 end for
 end for
 end for
 end for
 end for
 end for
 $(\omega_\nu(\mathbf{q}), \hat{e}_{\kappa\alpha,\nu}(\mathbf{q})) = \text{calculate phonons at } \mathbf{q}$
 for all $\nu \in \text{vibrational modes}$ **do**
 for all $(m, n) \in \text{electronic bands}$ **do**
 for all $\kappa \in \text{atoms}$ **do**
 for $\alpha = 1$ **to** 3 **do**
 $\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q}) = \tilde{g}_{mn,\kappa\alpha}(\mathbf{k}, \mathbf{q}) * \hat{e}_{\kappa\alpha,\nu}(\mathbf{q}) / \sqrt{m_\kappa}$
 end for
 end for
 end for
 end for
 return $\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q})$

folding back into the much smaller Brillouin zone of the super cell compared to the primitive cell. As a consequence of this equivalence, after interpolating the electronic band structure to the Brillouin zone of the primitive cell, there exist certain k-points at which the result is exact. Using the reciprocal-space lattice vectors of the super cell's Brillouin zone to generate a uniform k-point mesh in the Brillouin zone of the primitive cell, ensures that these special points lie on high-symmetry lines. The same line of arguments holds true for the PAW electron-phonon matrix element.

When calculating the DW energy shift using equation (6.41), it is possible to perform the integration over the Brillouin zone independently of the calculation of the matrix elements contained in $\Xi_{n,\nu_1\nu_2}(\mathbf{k}, \mathbf{0})$. Furthermore, since the Wannier-Fourier-interpolation scheme is used to calculate the individual matrix elements, $\hat{e}_{\kappa\alpha,\nu_1}(\mathbf{0})$ and $\hat{e}_{\kappa'\beta,\nu_2}(\mathbf{0})$ cancel with the eigenvectors appearing in equation (7.20). This cancellation is exploited to reduce the computational cost even further.

8.3. Program Outline

In the beginning, VASP needs to determine the ground state for a given structure with super-cell geometry in equilibrium, e.g. by iteratively solving the Kohn-Sham equations, (2.14). After this initial electronic minimization, a set of Wannier functions is generated by using the projection-based technique outlined in section 7.1. In order for the transformation to work properly, a large number of electronic bands need to be included in the calculation. Additionally, the unperturbed Hamiltonian matrix $\langle \mathcal{W}_{ml} | \hat{H} | \mathcal{W}_{nl'} \rangle$ is calculated using the previously generated Wannier functions.

Then, an atom κ of a reference primitive cell is displaced by a small amount in one particular direction α and the electronic states are determined for this non-equilibrium structure. Together with a subsequent displacement in the opposite direction, the matrix elements $\langle \mathcal{W}_{ml} | \partial_{0\kappa\alpha} \tilde{H} | \mathcal{W}_{nl'} \rangle$ and $\langle \mathcal{W}_{ml} | \partial_{0\kappa\alpha} \tilde{S} | \mathcal{W}_{nl'} \rangle$ are calculated using equation (8.1). This process is repeated for all possible independent displacements inside the reference primitive cell and the results are stored for later use. There is no need to construct any more Wannier functions for the perturbed systems as none of the matrix elements relevant to this thesis feature perturbed states. However, this is not expected to be the case anymore when considering higher-order corrections. In this case, the program would need to recalculate Wannier functions during each displacement step. In a post-processing step, the stored matrix elements can be used for repeated interpolation to obtain, for example, the temperature-dependent band-gap renormalization.

9. Results and Discussion

In this section, the implementation of the Wannier-Fourier-interpolation algorithm is put to the test and the numerical results are presented and discussed. Carbon-based diamond has been chosen as an appropriate test system in the simulation. This is mainly due to the fact that diamond is very easily studied within DFT and a huge amount of scientific research and publications are available. Since carbon is a strong insulator in its diamond form, it exhibits a large band gap at which the influence of electron-phonon coupling on the electronic band structure can be analyzed.

For the purpose of validating the present algorithms, only the direct band gap is taken into account. The quantities of interest are the electronic band structure, the phonon spectrum as well as the renormalization of the band gap. In addition, it is possible to study electron-phonon matrix elements in isolation. These are important for the lifetimes of carriers and the formation of polarons or superconductors.

9.1. VASP Setup

All calculations were performed using PAW potentials with the generalized gradient approximation (GGA-PBE) [38, 39] in the Γ -only version of VASP. In this particular version, the first Brillouin zone is only sampled at the Γ -point, hence the name. Consequently, many otherwise complex-valued quantities are declared as real variables in the code. This ensures a significant performance boost but requires the use of a large super cell, which is a necessity of the present algorithms anyway.

The test system used to determine various quantities was chosen to be carbon-based diamond, as it is a well-understood and easy-to-study structure in the context of DFT. In addition, the effects related to electron-phonon interactions are expected to be comparably large in diamond. Its primitive cell generates a face-centered cubic Bravais lattice with a lattice constant of $a_{\text{CD}} = 3.543 \text{ \AA}$ and contains two carbon atoms. The chosen super cell consists of $4 \times 4 \times 4$ such primitive cells. Thus, the total number of atoms in the simulation is found to be 128. For the purpose of generating Wannier functions, four localized hydrogen-like trial orbitals have been set up for each atom. One of them

has atomic s-like character, while the other three are p-like orbitals. By setting the number of calculated electronic bands to 512, it is guaranteed that the involved Bloch states span the same subspace as all generated Wannier functions. This is convenient since the transformation between the two spaces is now truly unitary, simplifying testing purposes.

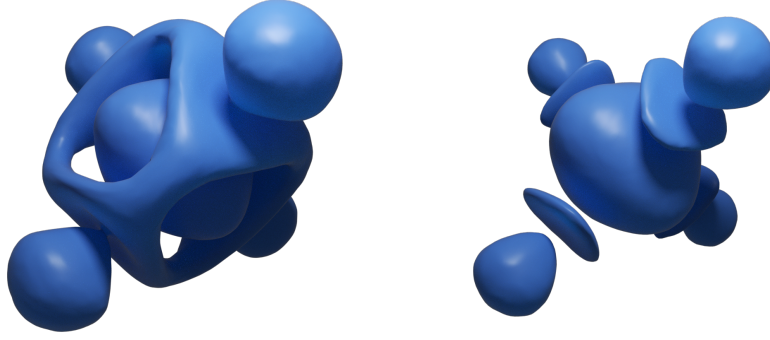
In order to qualitatively compare quantities dependent on reciprocal-space vectors, the exact same set of points is used for sampling all of them. This set of points is a continuous path running through the first Brillouin zone, whose individual segments are high-symmetry lines of the reciprocal lattice. In particular, the order in which high-symmetry points are traversed is $L-\Gamma-X-W-K-\Gamma$. This allows for comparable plots to be created, visualizing electronic band structure, phonon dispersion curves and similar quantities. For using any of the interpolation routines, the information regarding this Brillouin-zone path is supplied in a file which has the same structure as the KPOINTS file.

Spin-correlated effects are disabled since they are not yet supported by the implementation.

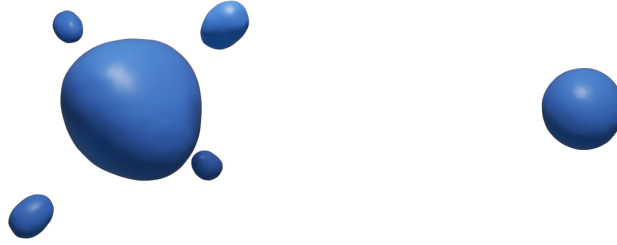
9.2. Wannier Functions

After a set of Wannier functions has been generated using the projection scheme outlined in section 7.1, the first property that needs to be verified is their spatial localization. Although a rigorous localization criterion has not been used in this thesis, it is possible to get an intuitive feeling for the form and spread of these functions by visualizing the electronic charge density. Luckily, VASP already provides a way of writing out partial charge densities for each separate band by setting the INCAR flags LPARD and LSEPB to true. To successfully use this method in the case of Wannier functions, it is necessary to also disable symmetrization by specifying $ISYM = -1$ in the INCAR file. Otherwise, VASP would symmetrize the final densities in the Wannier representation, yielding undesired results.

Figures 9.1 and 9.2 show isosurfaces of the charge densities corresponding to an s-like and a p-like Wannier function, respectively. Each isosurface was created using the program VisIt [40]. The resulting 3D models were then imported into Blender to remove noise, smoothen geometry and finally render an output image. The Wannier functions corresponding to the shown charge densities are centered on the same atom of the primitive cell. Due to symmetry considerations, there is no reason to believe that the shape of Wannier functions surrounding other atoms would look any different. Again, it



(a) Isosurface at $5.621 \times 10^{-3} e \text{ \AA}^{-3}$. (b) Isosurface at $11.24 \times 10^{-3} e \text{ \AA}^{-3}$.



(c) Isosurface at $28.11 \times 10^{-3} e \text{ \AA}^{-3}$. (d) Isosurface at $562.1 \times 10^{-3} e \text{ \AA}^{-3}$.

Figure 9.1.: Visualization of the partial charge density of an atom-centered s-like Wannier function in carbon-based diamond. Shown is an isosurface, generated for different levels of the charge density.

is important to note that the position of a Wannier function does not need to coincide with the location of an atom, in general.

As is to be expected for diamond, the charge density depicted in figure 9.1 shows tetrahedral symmetry. This is reminiscent of the fact that the atomic s and p-orbitals undergo hybridization when forming bonds in carbon-based diamond. The typical s and p-like characters of atomic orbitals can also be seen in figures 9.1(d) and 9.2(d), respectively, for large charge thresholds. There are, of course, two more p-like Wannier functions being used in the simulation, yet they are just rotated copies of the one depicted in figure 9.2.

Intuitively speaking, the shapes of these Wannier functions appear to be localized and

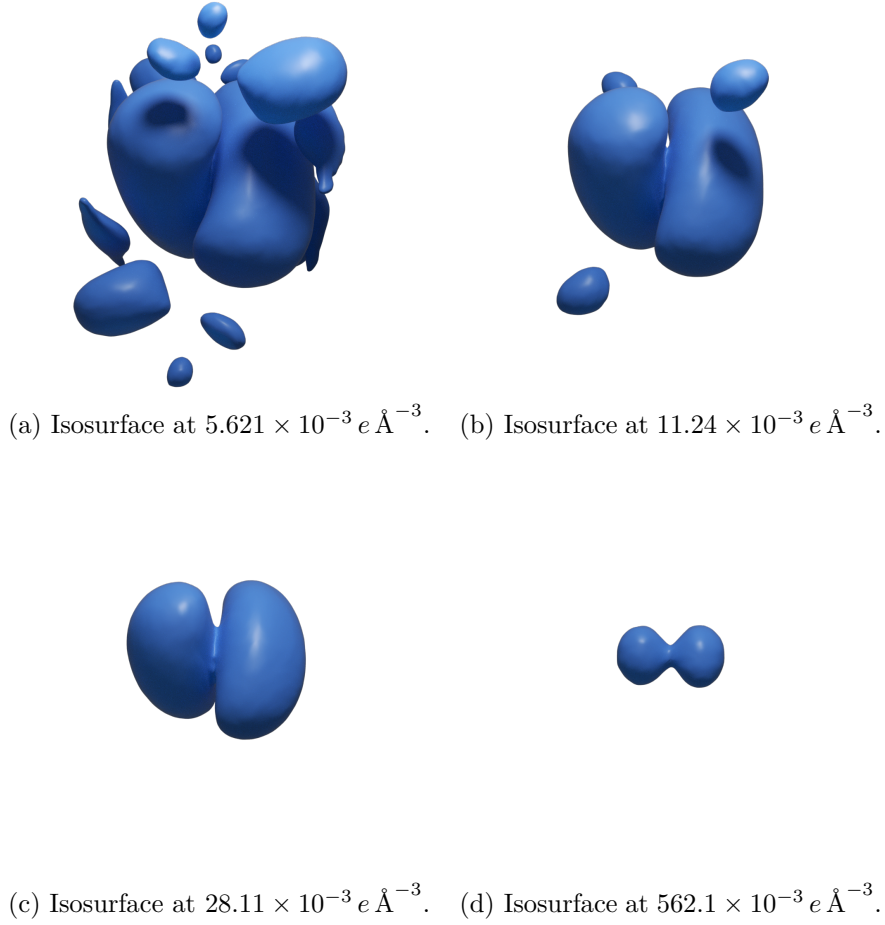


Figure 9.2.: Visualization of the partial charge density of an atom-centered p-like Wannier function in carbon-based diamond. Shown is an isosurface, generated for different levels of the charge density.

meaningful. However, in order for the interpolation schemes discussed in section 7.2 to function correctly, we need the involved matrix elements to decay rapidly with the distance between Wannier functions. Now, it is important to verify this prerequisite numerically. To accomplish this goal, each matrix element is studied as a function of the distance between a reference Wannier function located at ξ_{00} and all other Wannier functions of the super cell. The distance function takes into account the periodic boundary conditions of the super cell.

The real-space falloff of the Hamiltonian matrix $\langle \tilde{W}_{ml} | \tilde{H} | \tilde{W}_{n'l'} \rangle$ is presented in figure 9.3. Obviously, this matrix approaches zero for increasingly large distances, however, there is a peak at a distance of about $4 \text{ \AA}$ from the original Wannier function. This can

likely be attributed to the fact that the present Wannier functions are not maximally localized.

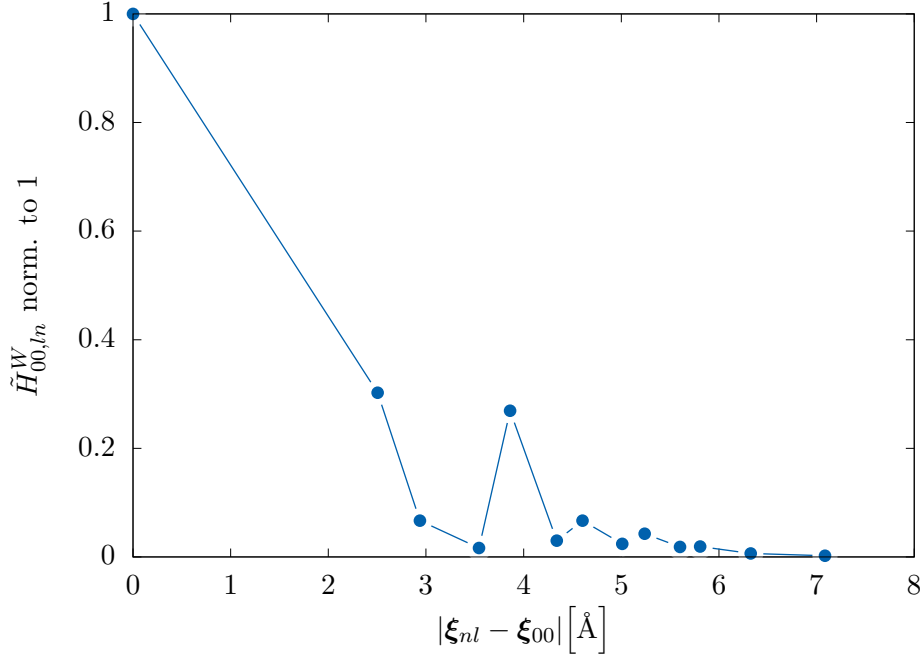


Figure 9.3.: Decay of the Wannier-space Hamiltonian matrix $\langle \tilde{W}_{ml} | \tilde{H} | \tilde{W}_{nl'} \rangle$ as a function of distance between the involved Wannier functions. Only the maximum absolute value $\tilde{H}_{lm,l'n}^W \equiv \max_{\xi_{lm}, \xi_{l'n}} |\langle \tilde{W}_{ml} | \tilde{H} | \tilde{W}_{nl'} \rangle|$ over all Wannier indices at each possible location is taken into account. One Wannier function is restricted to a specific site in the primitive cell while the other varies over the entire super cell. Each data set is normalized to 1.

The constituents of the PAW electron-phonon matrix element, i.e. $\langle \tilde{W}_{ml} | \partial_{p\kappa\alpha} \tilde{H} | \tilde{W}_{nl'} \rangle$ and $\langle \tilde{W}_{ml} | \partial_{p\kappa\alpha} \tilde{S} | \tilde{W}_{nl'} \rangle$, are treated similarly. Their spatial decay is presented in figure 9.4. Since these matrix elements depend on three independent cell indices l, l' and p , there are more ways of studying their dependence on distance. Following earlier considerations, the phonon perturbation is restricted to the reference primitive cell $p = 0$ without loss of generality. In panels (a) and (c) of figure 9.4, one of the Wannier functions varies across the entire super cell while the other is set to the same location as the phonon perturbation. Conversely, in panels (b) and (d), the Wannier functions are varied identically across the super cell. Due to symmetry, this is equivalent to varying only the location of the phonon perturbation but keeping the Wannier functions fixed.

While the matrix elements displayed in panels (b), (c) and (d) of figure 9.4 approach

zero very fast with increasing distance, the derivative of the Hamiltonian matrix shown in panel (a) appears to show oscillatory behavior. Again, it stands to reason that this is an artifact of the Wannier functions not being maximally localized. Fortunately, the matrix elements eventually become negligibly small.

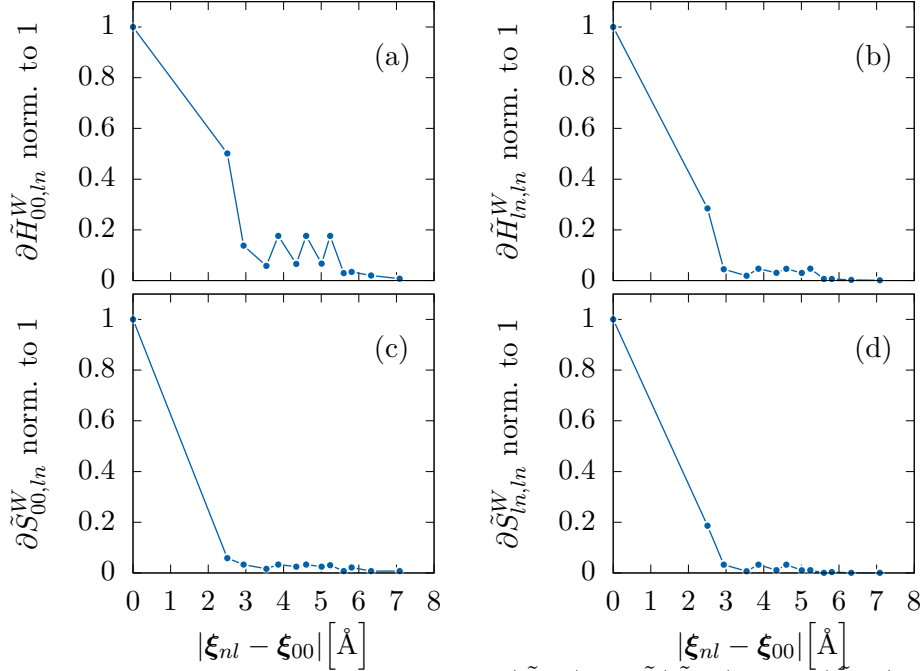


Figure 9.4.: Decay of the matrix elements $\langle \tilde{W}_{ml} | \partial_{00\alpha} \tilde{H} | \tilde{W}_{nl'} \rangle$ and $\langle \tilde{W}_{ml} | \partial_{00\alpha} \tilde{S} | \tilde{W}_{nl'} \rangle$ as functions of distance between the involved Wannier functions and the phonon perturbation. Only the maximum absolute values $\partial \tilde{H}_{lm,l'n}^W \equiv \max_{\xi_{lm}, \xi_{l'n}} |\langle \tilde{W}_{ml} | \partial_{00\alpha} \tilde{H} | \tilde{W}_{nl'} \rangle|$ and $\partial \tilde{S}_{lm,l'n}^W \equiv \max_{\xi_{lm}, \xi_{l'n}} |\langle \tilde{W}_{ml} | \partial_{00\alpha} \tilde{S} | \tilde{W}_{nl'} \rangle|$ over all Wannier and Cartesian indices at each possible location are taken into account. Each data set is normalized to 1. In panels (a) and (c), one Wannier function is varied across the entire super cell, while the remaining Wannier function and the phonon perturbation are kept fixed at the same site. In panels (b) and (d), both Wannier functions vary identically across the super cell, while keeping the phonon perturbation fixed. This is equivalent to fixing both Wannier functions and varying the phonon perturbation.

From a numerical standpoint, these real-space falloffs are sufficiently strong for the interpolation method to work correctly. However, compared to the results presented in reference [14], the spatial decay of the present Hamiltonian matrices evolves worse, which leads to a potentially larger effective cut-off radius. Thus, the use of maximally localized Wannier functions may be a desirable feature for future implementations but

is not needed for the current application.

9.3. Electronic Band Structure and Phonons

By virtue of equation (7.15), it is possible to interpolate the electronic band structure given on a coarse k-point grid to the primitive cell for arbitrary Bloch vectors. In the present simulation, the reciprocal space of the super cell is sampled only at the Γ -point, hence the obtained band structure is exact only at a very small number of k-points. At all remaining points, deviations are expected due to the Wannier functions spanning only an incomplete subspace. In other words, each electronic band exhibits small wiggles caused by the termination of the Wannier-space Fourier series.

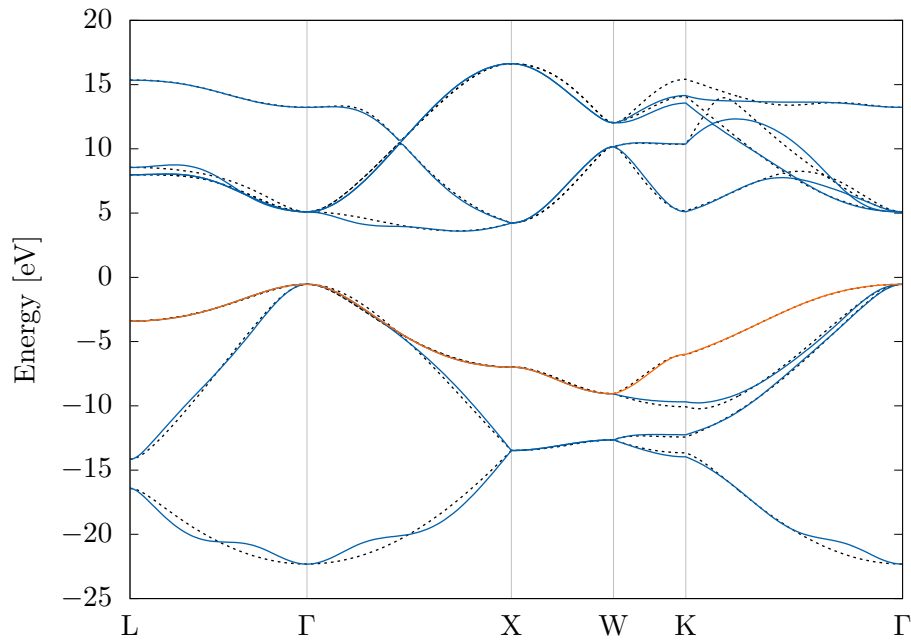


Figure 9.5.: Comparison between electronic band structures obtained by Wannier-Fourier interpolation (solid blue and orange lines) and by explicit calculation at each k-point using DFT (dashed black lines). Both methods calculate the first 8 electronic bands along the same high-symmetry path. Each data set is shifted such that the maxima of the shown valence bands coincide with zero.

In figure 9.5, the first 8 bands of the electronic band structure of diamond were calculated using two different methods: First, by solving the Kohn-Sham equations for many different Bloch states along a high-symmetry path in the first Brillouin zone of

the primitive cell. Second, by applying the Wannier-Fourier-interpolation scheme to the Wannier-space Hamiltonian matrix obtained from the super cell. The former method yields a suitable reference to which we can compare the results of the latter.

While the two methods produce very similar outputs overall, there are some noticeable deviations from the reference. Especially the bottom-most valence band exhibits strong oscillatory behavior. Additionally, between the high-symmetry points K and Γ , the highest calculated bands deviate by up to 2 eV. We believe that this is related to the fact that the highest bands do not necessarily have s or p-like character, so that the currently selected Wannier functions are insufficient to describe the top-most bands. It is assumed that for large enough super cells and an adequate number of bands and Wannier functions, these differences will eventually vanish. The use of maximally localized Wannier functions might provide an advantage here as well.

The phonon dispersion curves obtained from using equations (5.14) and (5.15) are shown in figure 9.6.

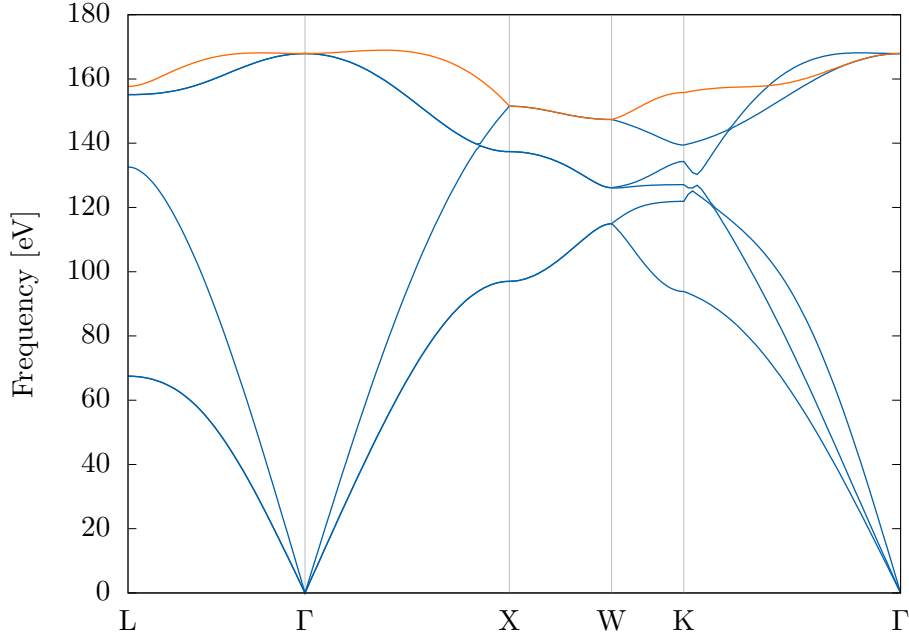


Figure 9.6.: Phonon frequencies obtained from super-cell force-constant calculations.

9.4. Electron-Phonon Interaction

The intermediary quantity $\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q})$, despite not being physically observable, holds valuable information about the coupling strength between electrons and phonons. It is therefore definitely worthwhile to investigate this quantity a bit further. Unfortunately, its high number of parameters renders it hard to grasp and visualize. Consequently, a representative set of values is generated by evaluating $\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q})$ only for a very special set of arguments.

The Bloch vector $\mathbf{k}$ of the initial electronic state is restricted to just the Γ -point, while the phonon wave vector $\mathbf{q}$ takes values along the already familiar high-symmetry path L- Γ -X-W-K- Γ . Both the initial and final electronic states are chosen to be on the top of the valence manifold. In figure 9.5, the corresponding bands are highlighted in orange. These choices were made to be consistent with reference [14], enabling a qualitative comparison.

It is of utmost importance to note that these bands are twofold degenerate along the high-symmetry directions L- Γ , Γ -X and X-W. Furthermore, most phonon branches feature similar degeneracies along the same directions and, therefore, unitary mixing between the affected bands and branches is to be expected. For the purpose of visualizing the PAW electron-phonon matrix element, however, we need to rid us of this nuisance. Let us define the set $D_m^{\text{el}} = \{m_1, m_2, \dots\}$ to contain all bands $m_1, m_2, \dots$, which are degenerate to band m . Then let us define the set D_ν^{ph} in exactly the same way for the phonon branches. Using this notation, it is possible to arrive at a mostly continuous matrix element

$$\bar{g}_{mn,\nu}(\mathbf{k}, \mathbf{q}) = \left[\sum_{m' \in D_m^{\text{el}}} \sum_{n' \in D_n^{\text{el}}} \sum_{\nu' \in D_\nu^{\text{ph}}} |\tilde{g}_{m'n',\nu'}(\mathbf{k}, \mathbf{q})|^2 \right]^{\frac{1}{2}}, \quad (9.1)$$

by averaging over all degenerate subspaces, which can now be plotted in an analogous way to figures 9.5 and 9.6.

Finally, after enforcing all restrictions to the initial and final states mentioned earlier, the resulting matrix element $\bar{g}_{44,\nu}(\mathbf{0}, \mathbf{q})$ is presented in figure 9.7. At certain high-symmetry points, especially at Γ , $\bar{g}_{mn,\nu}(\mathbf{k}, \mathbf{q})$ is discontinuous. This is a direct result of averaging degenerate bands and branches, since the higher symmetry at these points naturally results in higher levels of degeneracy. An average would therefore collapse more bands or branches into a single data point, giving rise to a discontinuity.

The black disks in figure 9.7 show the matrix element $g_{mn,\nu}(\mathbf{k}, \mathbf{q})$ found in reference

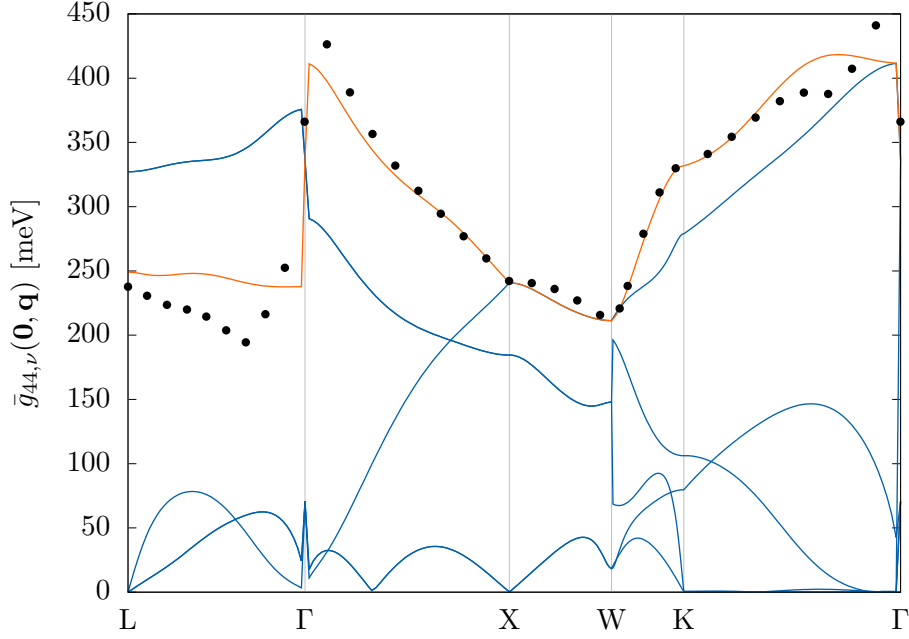


Figure 9.7.: Absolute value of the PAW electron-phonon matrix element, averaged over degenerate bands and branches. The initial state is fixed at the valence-band top at Γ , while the final state varies across the top valence band along the high symmetry path $L-\Gamma-X-W-K-\Gamma$ (orange line in figure 9.5). All phonon branches are shown in this graph. The orange line is highlighted for easier comparison with reference [14] (black disks) and corresponds to the highest phonon branch (orange line in figure 9.6).

[14] calculated by ab-initio DFPT simulations for certain phonon wave vectors. In order to compare these data points to the present case, the PAW electron-phonon matrix element corresponding to the highest phonon branch is highlighted in orange. First, it is important to note that Giustino et al. studied boron-doped diamond, which shows significant differences in the phonon spectrum compared to pristine diamond. A one-to-one correspondence is therefore not expected for the electron-phonon matrix element. Second, from equation (6.34), we know that for $\mathbf{q} = 0$ there exist additional PAW terms which, albeit small, are generally finite. This means that $\tilde{g}_{mn,\nu}(\mathbf{k}, \mathbf{q})$ can in general not be fully equivalent to $g_{mn,\nu}(\mathbf{k}, \mathbf{q})$, but this difference only manifests itself at the Γ -point. There, the averaged matrix element $\bar{g}_{44,\nu}(\mathbf{0}, \mathbf{0})$ takes on an already relatively meaningless value due to high degeneracy and discontinuity. It is therefore meaningful to exclude the Γ -point completely when comparing the two aforementioned quantities.

We can observe that both graphs appear to be very similar at first glance. Along the

lines X–W, W–K and, for the most part, also along Γ –X and K– Γ , the two data sets are very close. This makes sense since there is not much difference between the phonon dispersion curves of pristine and boron-doped diamond in these regions. In all other regions, the values differ significantly between the two materials, as is to be expected. The general trend, however, is still noticeably similar.

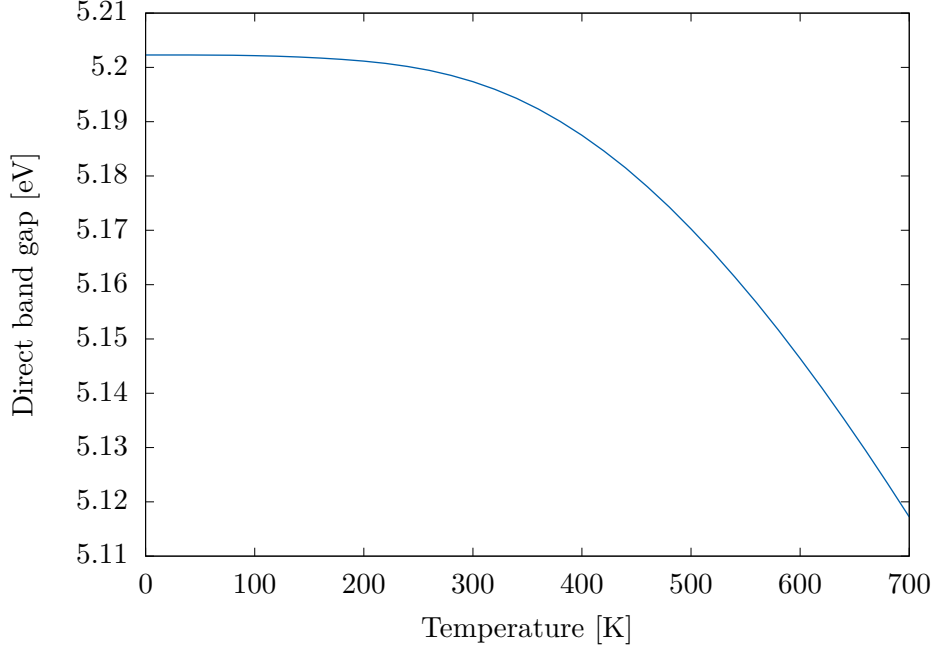


Figure 9.8.: Direct band gap of Diamond as a function of temperature.

Finally, the zero-point renormalization energy of the direct band gap of pristine diamond is calculated numerically using equations (6.16), (6.33) and (6.41) together with the Wannier-Fourier-interpolation scheme discussed in section 7.2.2. The integrals appearing in the FM and DW self-energy contributions were carried out over an equally-spaced k -point mesh consisting of $16 \times 16 \times 16$ points which extends over the entire first Brillouin zone. Energy shifts corresponding to equivalent degenerate bands need to be included and are therefore arithmetically averaged. The total energy shift between the top of the valence band and the bottom of the conduction band at Γ comes out to be approximately -441 meV. The negative sign indicates a narrowing of the direct band gap. Individually, the top and bottom of the gap experience shifts of approximately -297 meV and 0.145 meV, respectively. In comparison, Gonze et al. [41] obtained zero-point band-gap renormalization energies of the direct band gap of diamond of -436 meV and -439 meV using density-functional perturbation theory and the frozen-phonon ap-

proach, respectively. In both cases, the lattice constant was $3.55 \text{ \AA}$ and LDA was used to approximate the exchange-correlation energy.

Finally, the temperature dependence of the direct band gap is presented in figure 9.8 for a temperature range of 0 to 700 Kelvin.

It is reasonable to assume that with the inclusion of maximally localized Wannier functions as well as with a more complete set of basis functions, the final result will be much better converged. Having been able to achieve a reasonable result is nevertheless a strong indication that the present algorithm is working as intended and can be built upon.

10. Conclusion

In light of the numerical results presented in the previous section, we conclude that the implementation of the Wannier-Fourier-interpolation method as well as the force-constant-based approach to calculating phonons has been successful. Nonetheless, it is of utmost importance to conduct further and more intensive testing of the present algorithms to verify their correctness and determine their numerical accuracy.

In its current form, the Wannier-Fourier-interpolation method still lacks many desirable features and thus future development should improve upon the present framework by adding more functionality and flexibility. Prime examples of this are the inclusion of maximally localized Wannier functions, a generalization to polarized materials as well as adding more possibilities regarding the placement of Wannier functions. Additional interesting prospects are the inclusion of anharmonic effects and moving beyond AHC theory.

Bibliography

- ¹F. Bloch, „Über die quantenmechanik der elektronen in kristallgittern,“ *Zeitschrift für Physik* **52**, 555–600 (1929).
- ²R. L. Liboff, and G. K. Schenter, „Electron-phonon scattering contributions to metallic resistivity at 0 k,“ *Phys. Rev. B* **54**, 16591–16601 (1996).
- ³J. Bardeen, L. N. Cooper, and J. R. Schrieffer, „Theory of superconductivity,“ *Phys. Rev.* **108**, 1175–1204 (1957).
- ⁴W. Kohn, „Image of the fermi surface in the vibration spectrum of a metal,“ *Phys. Rev. Lett.* **2**, 393–394 (1959).
- ⁵J. I. Pankove, *Optical processes in semiconductors* (NY : Dover Publ, 1975).
- ⁶S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, „Phonons and related crystal properties from density-functional perturbation theory,“ *Rev. Mod. Phys.* **73**, 515–562 (2001).
- ⁷B. J. Berne, and D. Thirumalai, „On the simulation of quantum systems: path integral methods,“ *Annual Review of Physical Chemistry* **37**, 401–424 (1986).
- ⁸R. Ramírez, C. P. Herrero, and E. R. Hernández, „Path-integral molecular dynamics simulation of diamond,“ *Phys. Rev. B* **73**, 245202 (2006).
- ⁹A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, „Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions,“ *Rev. Mod. Phys.* **68**, 13–125 (1996).
- ¹⁰G. Onida, L. Reining, and A. Rubio, „Electronic excitations: density-functional versus many-body green’s-function approaches,“ *Rev. Mod. Phys.* **74**, 601–659 (2002).
- ¹¹W. G. Aulbur, L. Jönsson, and J. W. Wilkins, „Quasiparticle calculations in solids,“ in, Vol. 54, edited by H. Ehrenreich, and F. Spaepen, *Solid State Physics* (Academic Press, 2000), pp. 1–218.
- ¹²M. Cardona, and M. L. W. Thewalt, „Isotope effects on the optical spectra of semiconductors,“ *Rev. Mod. Phys.* **77**, 1173–1224 (2005).

- ¹³F. Giustino, S. G. Louie, and M. L. Cohen, „Electron-phonon renormalization of the direct band gap of diamond,“ *Phys. Rev. Lett.* **105**, 265501 (2010).
- ¹⁴F. Giustino, M. L. Cohen, and S. G. Louie, „Electron-phonon interaction using wannier functions,“ *Phys. Rev. B* **76**, 165108 (2007).
- ¹⁵F. Giustino, „Electron-phonon interactions from first principles,“ *Rev. Mod. Phys.* **89**, 015003 (2017).
- ¹⁶G. Kresse, and J. Hafner, „Ab initio molecular dynamics for liquid metals,“ *Phys. Rev. B* **47**, 558–561 (1993).
- ¹⁷G. Kresse, and J. Hafner, „Ab initio molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium,“ *Phys. Rev. B* **49**, 14251–14269 (1994).
- ¹⁸G. Kresse, and J. Furthmüller, „Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set,“ *Computational Materials Science* **6**, 15–50 (1996).
- ¹⁹G. Kresse, and J. Furthmüller, „Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set,“ *Phys. Rev. B* **54**, 11169–11186 (1996).
- ²⁰P. E. Blöchl, „Projector augmented-wave method,“ *Phys. Rev. B* **50**, 17953–17979 (1994).
- ²¹G. Kresse, and D. Joubert, „From ultrasoft pseudopotentials to the projector augmented-wave method,“ *Phys. Rev. B* **59**, 1758–1775 (1999).
- ²²P. B. Allen, and V. Heine, „Theory of the temperature dependence of electronic band structures,“ *Journal of Physics C: Solid State Physics* **9**, 2305 (1976).
- ²³P. B. Allen, and M. Cardona, „Theory of the temperature dependence of the direct gap of germanium,“ *Phys. Rev. B* **23**, 1495–1505 (1981).
- ²⁴P. Hohenberg, and W. Kohn, „Inhomogeneous electron gas,“ *Phys. Rev.* **136**, B864–B871 (1964).
- ²⁵W. Kohn, and L. J. Sham, „Self-consistent equations including exchange and correlation effects,“ *Phys. Rev.* **140**, A1133–A1138 (1965).
- ²⁶R. Parr, *Density-functional theory of atoms and molecules* (Oxford University Press Clarendon Press, New York Oxford England, 1989).
- ²⁷E. Engel, and R. Dreizler, *Density functional theory: an advanced course*, Theoretical and Mathematical Physics (Springer Berlin Heidelberg, 2011).

- ²⁸M. Born, and R. Oppenheimer, „Zur quantentheorie der molekeln,“ *Annalen der Physik* **389**, 457–484 (1927).
- ²⁹W. Kohn, „Nobel lecture: electronic structure of matter—wave functions and density functionals,“ *Rev. Mod. Phys.* **71**, 1253–1266 (1999).
- ³⁰J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, „Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation,“ *Phys. Rev. B* **46**, 6671–6687 (1992).
- ³¹N. W. Ashcroft, and N. D. Mermin, *Solid state physics* (Harcourt, 1976).
- ³²R. Gross, and A. Marx, *Festkörperphysik* (Oldenbourg Wissenschaftsverlag, 2012).
- ³³D. Vanderbilt, „Soft self-consistent pseudopotentials in a generalized eigenvalue formalism,“ *Phys. Rev. B* **41**, 7892–7895 (1990).
- ³⁴E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, „Full-potential self-consistent linearized-augmented-plane-wave method for calculating the electronic structure of molecules and surfaces: O₂ molecule,“ *Phys. Rev. B* **24**, 864–875 (1981).
- ³⁵T. Ono, M. Heide, N. Atodiresei, P. Baumeister, S. Tsukamoto, and S. Blügel, „Real-space electronic structure calculations with full-potential all-electron precision for transition metals,“ *Phys. Rev. B* **82**, 205115 (2010).
- ³⁶I. Lindgren, and J. Morrison, *Atomic many-body theory* (Springer Berlin Heidelberg, 1986).
- ³⁷N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, „Maximally localized wannier functions: theory and applications,“ *Rev. Mod. Phys.* **84**, 1419–1475 (2012).
- ³⁸J. P. Perdew, K. Burke, and M. Ernzerhof, „Generalized gradient approximation made simple,“ *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- ³⁹J. P. Perdew, K. Burke, and M. Ernzerhof, „Generalized gradient approximation made simple [phys. rev. lett. 77, 3865 (1996)],“ *Phys. Rev. Lett.* **78**, 1396–1396 (1997).
- ⁴⁰H. Childs, E. Brugger, B. Whitlock, J. Meredith, S. Ahern, D. Pugmire, K. Biagas, M. Miller, C. Harrison, G. H. Weber, H. Krishnan, T. Fogal, A. Sanderson, C. Garth, E. W. Bethel, D. Camp, O. Rübel, M. Durant, J. M. Favre, and P. Navrátil, „VisIt: An End-User Tool For Visualizing and Analyzing Very Large Data,“ in *High Performance Visualization—Enabling Extreme-Scale Scientific Insight* (Oct. 2012), pp. 357–372.

- ⁴¹G. Antonius, S. Poncé, E. Lantagne-Hurtubise, G. Auclair, X. Gonze, and M. Côté, „Dynamical and anharmonic effects on the electron-phonon coupling and the zero-point renormalization of the electronic structure,“ *Phys. Rev. B* **92**, 085137 (2015).

A. Abstract (English)

New techniques in computational materials physics allow for efficient calculations of electron-phonon interactions in ab-initio simulations of condensed matter. Specifically, a Wannier-Fourier-interpolation scheme has been developed, which is based on an alternative representation of electronic Bloch orbitals using Wannier functions. This technique utilizes the spatial localization of these functions combined with a real-space cut-off in order to perform an interpolation to arbitrary reciprocal lattice points via a generalized Fourier transform.

The aim of this thesis was to implement the aforementioned method into the Vienna Ab initio Simulation Package and provide a solid and flexible framework for further developments. Presently, the implementation is based on super-cell calculations utilizing finite differences and it is compatible with the projector augmented-wave method.

Incipient application of the interpolation scheme to diamond showed promising results, providing strong evidence that the present algorithms work as intended. In particular, the zero-point as well as temperature-dependent renormalization of the direct band gap have been calculated in the framework of the Allen-Heine-Cardona theory.

The current implementation, albeit potent, still lacks desirable features and is limited in functionality, which calls for further developments.

B. Abstract (German)

Neue Verfahren im Bereich der computergestützten Materialphysik ermöglichen eine effiziente Berechnung der Wechselwirkung zwischen Elektronen und Phononen in ab-initio Simulationen von Festkörpern. Im Speziellen ist ein Wannier-Fourier-Interpolations-Schema entwickelt worden, welches auf einer alternativen Representation der üblichen Bloch-Orbitale durch Wannier-Funktionen beruht. Diese Methode verwendet die räumliche Lokalisierung dieser Funktionen verbunden mit einem Cut-off-Radius im Ortsraum um eine Interpolation auf beliebige Punkte im reziproken Raum durch eine generalisierte Fourier-Transformation zu ermöglichen.

Das Ziel dieser wissenschaftlichen Arbeit war die zuvor genannte Methode in das Vienna Ab initio Simulation Package zu implementieren, sowie ein solides und flexibles Framework für weitere Entwicklungen bereitzustellen. Gegenwärtig stützt sich die Implementierung auf die Simulation von Superzellen, verwendet finite Differenzen und ist mit der projector-augmented-wave-Methode kompatibel.

Die Erstanwendung des Interpolations-Schemas auf Diamant zeigt vielversprechende Resultate, welche die Funktionstüchtigkeit der verwendeten Algorithmen untermauern. Insbesondere sind sowohl Nullpunkts- als auch temperaturabhängige Renormalisierung des direkten Bandübergangs im Rahmen der Allen-Heine-Cardona-Theorie berechnet worden.

Trotz ihrer Leistungsfähigkeit fehlt es der vorliegenden Implementierung an wünschenswerten Elementen und ihre Funktionalität ist eingeschränkt. Dies ist Grund genug um weitere Entwicklung anzustreben.