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X-ray Absorption Spectroscopy Studies Using the Projector
Augmented-Wave Method

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Zusammenfassung

Bei Experimenten zur Röntgenabsorptionsspektroskopie (englisch X-ray absorption spectroscopy (XAS)) wird ein Elektron der inneren Schale in die Leitungsbänder angeregt. Aufgrund des lokalisierten Potenzials, das durch das Loch erzeugt wird, ist die XAS ein element- und schalenspezifisches Instrument zur Untersuchung der lokalen Umgebung von Atomen. Mit den Fortschritten bei den Synchrotron- und Freie-Elektronen-Laseranlagen hat sich die XAS zu einer wichtigen Technik in Bereichen wie Katalyse, Koordinationschemie und Metallurgie entwickelt. Die Interpretation der immer feiner aufgelösten experimentellen Spektren erfordert den Einsatz der fortgeschrittenen Berechnungswerkzeuge der theoretischen Spektroskopie, da die Valenz- und Leitungsbänder stark vom Kern-Loch-Potenzial beeinflusst werden: Die Energien der Valenz- und Leitungsbandelektronen ändern sich, und das angeregte Elektron und das lokalisierte Kernloch bilden einen gebundenen Zustand, ein Kern-Exziton, das einen neuen Zustand unterhalb der Leitungsbandkante bildet. Diese Veränderungen spiegeln sich in den XAS-Spektren wider.

Zur Untersuchung von Kern-Exziton-Effekten in XAS-Spektren haben sich zwei Techniken etabliert. Bei dem auf der Vielteilchen-Theorie basierenden Ansatz der Bethe-Salpeter-Gleichung (englisch Bethe-Salpeter equation (BSE)) wird der gebundene Zustand durch eine Integralgleichung beschrieben, die mit numerischen Methoden gelöst wird. In der auf der Dichtefunktionaltheorie basierenden Näherung des Endzustandes (englisch final-state approximation (FSA)) wird der Röntgenabsorptionsprozess durch das Entfernen eines Kernelektrons aus einem Atom in einer Superzelle modelliert. Anschließend werden die exzitonischen Effekte auf die Bandstruktur durch die Änderungen in den Valenz- und Leitungsbändern aufgrund dieses zusätzlichen Kernlochs bestimmt.

In dieser Arbeit implementieren wir die BSE für Kernspektroskopien in das Vienna Ab-initio Simulation Package (VASP). Anschließend verwenden wir die BSE und die FSA, um Spektren von Referenzmaterialien und einwandigen Kohlenstoff-Nanoröhrchen zu berechnen. Der erste Teil dieser Arbeit beschreibt die theoretischen Grundlagen und die Implementierung der BSE, während im zweiten Teil die Ergebnisse präsentiert werden. Unsere Ergebnisse für Referenzmaterialien zeigen eine hervorragende Übereinstimmung der BSE mit Experimenten und Ergebnissen früherer Arbeiten, und wir zeigen, wie die FSA verbessert werden kann, so dass eine Genauigkeit nahe der BSE erreicht wird.

Anschließend zeigen wir die Ergebnisse für halbleitende einwandige Kohlenstoff-Nanoröhren. Um die Spektren zu interpretieren, mussten die Experimentatoren auf einen Ansatz zurückgreifen, der auf der Zustandsdichte im Grundzustand basiert. Während dieser Ansatz die Ergebnisse qualitativ erklären konnte, fehlte es noch an einem detaillierten Verständnis. Wir

werden die BSE und die FSA benutzen, um die experimentellen Ergebnisse zu reproduzieren und im Detail zu erklären, wie Kern-Exziton-Effekte die Spektren beeinflussen. Unsere Ergebnisse an Referenzmaterialien und unser detailliertes Verständnis der XAS-Spektren von Kohlenstoff-Nanoröhren werden die Bedeutung der theoretischen Spektroskopie in der XAS unterstreichen.

Abstract

In X-ray absorption spectroscopy (XAS) experiments, an inner-shell electron is excited into the conduction bands. Due to the localized nature of the potential created by the hole XAS is a highly element- and shell-specific tool for probing the local environment of target atoms. With advancements in synchrotron and free-electron laser facilities, XAS has become a principal technique in fields such as catalysis, coordination chemistry, and metallurgy. Interpreting the increasingly finely resolved experimental spectra requires to use the advanced computational tools offered by theoretical spectroscopy since the valence and conduction bands are strongly affected by the core-hole potential: the electronic valence and conduction band energies change and the excited electron and localized core hole form a bound state, a core exciton, which manifests as a new state below the conduction band edge. These changes are reflected in the XAS spectra.

Two techniques have emerged to investigate core-exciton effects in XAS spectra. In the many-body perturbation theory based Bethe-Salpeter equation (BSE) approach the bound state is described in terms of an integral equation which is solved computationally. In the density-functional theory based final-state approximation (FSA) the X-ray absorption process is modeled by removing a core electron from an atom in a supercell. Then, the excitonic effects on the band structure are simulated by the changes in the valence and conduction bands due to this additional core hole.

In this thesis we implement the BSE for core spectroscopies in the Vienna Ab-initio Simulation Package (VASP). We then use the BSE and the FSA to obtain spectra of reference materials and single walled carbon nanotubes. The first part of this thesis details the theoretical foundation and implementation of the BSE, while in the second the results are presented. Our results for reference materials show excellent agreement of the BSE with experiments and results of prior studies, and we demonstrate how the FSA can be improved so that near-BSE accuracy can be achieved.

We then show the results for semiconducting single walled carbon nanotubes. To interpret the spectra the experimental community had to resort to an approach based on the ground state density of states. While this approach could explain the results qualitatively, a detailed understanding was still missing. We will use BSE and the FSA to reproduce the experimental results and to explain in detail how core exciton effects influence the spectra. Our results on reference materials and our detailed understanding of XAS spectra of carbon nanotubes will underscore the importance of theoretical spectroscopy in XAS.

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Introduction

Spectroscopy, or the study of how light interacts with matter, is one of the principle research areas of modern day physics and has become an indispensable tool to answer fundamental and application oriented questions. Two driving forces contributed to establish spectroscopy as one of the principle research techniques. On the experimental side, the discovery of new experimental techniques and their development led to small and large scale research facilities with ever improving spectral brilliance, coherence, and stability. On the theoretical side, the challenge to understand the experimental spectra has led to the development of a research program called *theoretical spectroscopy* which aims to predict and understand spectra by the aid of computer simulations. The aim of this thesis is to use methods of theoretical spectroscopy in order to contribute to a particular sub field of spectroscopy, namely, *X-ray absorption spectroscopy* (XAS). In the following, we will first give a short overview of XAS and then highlight the necessity of theoretical spectroscopy techniques in understanding XAS results. Finally, we define the scope of this thesis.

Overview of X-ray absorption spectroscopy

In XAS a sample is irradiated with X-rays which ejects an electron from one of the inner shells of an atom and promotes it into the conduction bands. This process is sketched in panel (a) of Fig. 1 where a K shell electron is excited into the conduction bands. The valence bands are indicated by a gray shaded area. The quantity of interest is the frequency dependent absorption coefficient $\mu(\omega)$ which is a probe of the band structure of the unoccupied bands. To determine $\mu(\omega)$ the sample of a certain thickness d is irradiated with an initial intensity I_0 . The absorption coefficient is then calculated from the transmitted intensity $I(\omega)$ using Beer's law: $\mu(\omega) = \log(I(\omega)/I_0)/d$. An XAS spectrum covering a wide range of frequencies is given in panel (b) of Fig. 1. In the absorption spectrum, several distinct peaks can be observed which are called *edges*. The energy at the onset of each edge corresponds to the energy needed to excite an electron from one of the particular shells of a particular atom. The edges are correspondingly called K, L, M edges, etc. The usefulness of XAS comes from the large separation in frequency between separate edges of different atoms and shells which in turn makes XAS element and shell specific. If we zoom in one of those edges we see a structure as in panel (c) of Fig. 1. The spectrum consists of a rising pre-edge, a main edge, and the post-edge region. In addition to the main edge, a series of smaller peaks can be seen with varying amplitudes and widths, where we call the secondary peaks the *fine structure*. The region of the edge spectrum that includes the pre-edge, main edge, and up to around 20 eV in the post edge are called X-ray absorption near edge structure (XANES) or near edge

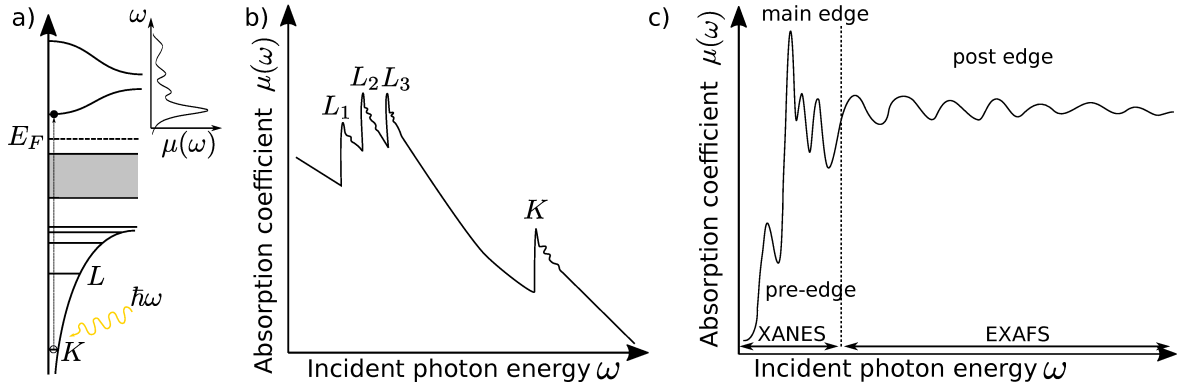


Figure 1: Overview of X-ray absorption spectroscopy (XAS). The individual panels are explained in the text.

X-ray absorption fine structure (NEXAFS). The oscillatory region above this energy range is called extended X-ray absorption fine structure (EXAFS). Some authors combine the fine structure seen in XANES and EXAFS into a single term that includes both energy ranges: X-ray absorption fine structure (XAFS) [142]. In this thesis, we are only concerned with the energy range 10-20 eV above the main edge, that is, we discuss only the fine structure seen in XANES results.

We will now summarize the basic principles of synchrotron and free electron laser (FEL) facilities where XAS spectra are routinely collected. Apart from these large-scale facilities, efforts have been made to build small-scale laboratory ("table-top") XAS setups that produce results on par with results from larger facilities [209, 100]. In synchrotrons the electrons are injected into a storage ring which uses magnets to keep the electrons on a circular trajectory. At points where the electron trajectory is bend synchrotron radiation is emitted and then fed into beamlines where the actual measurements take place. The figure of merit of synchrotron radiation sources is the brilliance which is defined as the number of photons per second radiated into a beam with a solid angle given in mrad^2 , a source area given in mm^2 , and a bandwidth determined by the spread in frequency around the central frequency. The brilliance is therefore given by the ratio [8]

$$B = \frac{\text{Photons } s^{-1}}{(\text{mrad})^2 (\text{mm source area})^2 0.1\% \text{ Bandwidth}}. \quad (1)$$

Current (third) generation facilities such as the European Synchrotron Research Facility (ESRF) in Grenoble (in its 2018 configuration), the National Synchrotron Light Source II in Brookhaven, or SPring8 in Japan reach average brilliances of about 10^{20} . Fourth generation synchrotrons [157] such as the extremely brilliant source (EBS) extension of the ESRF (EBS-ESRF) will reach values of 10^{22} [140].

In FELs facilities electrons are accelerated and injected into an undulator which consists of an array of (permanent or electromagnetic) magnets that create a sinusoidal magnetic field. In this field the electrons oscillate and produce a LASER field due to self-amplified spontaneous emission [8]. The current FEL flagship is the European X-ray free electron laser (X-FEL) which reaches average brilliances of up to 10^{22} and pulse durations of 100 femtoseconds [1].

Fourth-generation synchrotrons and the European X-FEL offer unparalleled capabilities for exploring matter at atomic and femtosecond scales. Their extreme brilliance, coherence, and ultrafast pulse duration enable researchers to capture real-time processes, such as chemical reactions and phase transitions, and to probe the structure and dynamics of complex systems with unprecedented detail. These advanced facilities allow for non-destructive imaging of biomolecules without crystallization, the study of matter under extreme pressures and temperatures, and insights into quantum phenomena and electronic interactions.

Theoretical spectroscopy and its role in XAS

Theoretical spectroscopy encompasses all computational methods used to describe the interaction of light with matter. To appreciate its relevance for X-ray absorption spectroscopy (XAS), it is essential to understand the XAS process, illustrated in Fig. 1(a), in detail.

Before light interacts with a material, we must first determine whether the material is capable of absorbing radiation, and in which frequency ranges this absorption occurs. To achieve this, a comprehensive understanding of the material’s ground-state properties is necessary, particularly its band structure and energy gaps. In principle, one could solve the Schrödinger equation for a multi-electron system to obtain the band structure. However, as materials and related questions grow more complex a computationally more affordable approach is necessary. The most widely used method to determine the ground-state band structure is Kohn-Sham density functional theory (DFT) [65, 81], which provides a computationally efficient way to calculate the ground-state properties *ab initio*, meaning without external fitting parameters.

While DFT enables efficient determination of the ground-state band structure, it introduces a number of approximations that can affect the accuracy of the band gaps and other features. To improve upon this, we must account for the fact that when an electron moves through a many-body system, it interacts with the surrounding electrons and drags a cloud of them along. This interaction prevents us from treating the electron as an isolated particle. Instead, we must consider the electron as a *quasiparticle*, which is a superposition of the bare electron and the electrons in the surrounding electron cloud. The electron is said to be *dressed* by the interactions within the many-body system, resulting in a quasiparticle with an energy different from that of the bare electron. Theoretical and computational methods that describe the properties of quasiparticles are referred to as many-body perturbation theory. This approach leads to improved values for band gaps and band structures.

Finally, we simulate X-ray absorption by promoting an inner-shell electron to the conduction bands, leaving behind a hole with a positive charge. This hole creates a *strong, immobile, and highly localized* potential known as the core-hole potential, which profoundly affects the material’s electronic structure. The core-hole potential, localized in real space, perturbs bands throughout the entire Brillouin zone, leading to dramatic changes in the band structure which lead to a partial screening of the core-hole potential. Furthermore, the electron and hole form a new quasiparticle which is a bound state of an electron and a hole and called an *exciton*. The excitons produced in X-ray excitations are commonly referred to as *core excitons*. These core excitons have a significant impact on the absorption spectra, as they manifest as new states below the conduction band onset. The energy difference between the excitonic state and the absorption band onset is the binding energy of the exciton. Due to the strength of the core-hole potential the core excitons are highly localized around the core hole and possess

large binding energies, typically on the order of 0.1–1.0 eV. This binding energy is often substantially larger than the binding energy of excitons created in visible-light excitations. The combination of these effects — band structure changes and formation of excitonic states — has a large influence on the XAS spectra.

Theoretical foundations for describing these processes have evolved from many-body research conducted in the 1960s. Kohn-Sham density functional theory [65, 81] enabled efficient *ab initio* calculation of ground-state properties, while Green’s function techniques applied to the many-body problem [104, 4, 61] allowed for the determination of spectroscopic quantities such as the many-body spectral function and the response function. The integration of these two frameworks resulted in the Bethe-Salpeter equation (BSE) approach [125], which is the state-of-the-art *ab initio* framework for calculating spectra including excitonic effects.

Another framework that is used to calculate XAS spectra is the final-state approximation (FSA) [13]. In this approach the many-body effects induced by the core-hole potential are simulated by introducing a core hole in a supercell. The band structure is then calculated using Kohn-Sham DFT, where the additional core-hole potential is included when determining the ground state. The band structure renormalizes which leads to band structure changes that mimics the many-body core-hole effects. In addition, this approach leads to the formation of excitonic states and is thus a viable alternative to determine XAS spectra.

Although the sketch of the XAS process of Fig. 1(a) is seemingly quite simple, a detailed analysis reveals its complexity. A comprehensive understanding of XAS spectra can only be achieved by using methods of theoretical spectroscopy. However, the true power of theoretical spectroscopy lies beyond accurately reproducing the XAS spectra. The methods of theoretical spectroscopy also allow us to discuss exciton wavefunctions, to identify which conduction band states are relevant in forming the exciton, and to adjust the strength of the core hole charge at will. This will allow us to not only to correctly reproduce, but also to understand the XAS spectra.

Scope and outline of this thesis

In this thesis, we implement the BSE methodology for core excitons into the Vienna Ab-initio Simulation Package (VASP) [84] and use it to calculate XAS spectra of reference materials and single-walled carbon nanotubes (SWCNTs). In conjunction with the BSE results we employ the final-state approximation which was implemented previously [75].

VASP is a plane-wave-based code that employs the projector augmented-wave (PAW) methodology [21, 85] to efficiently account for the rapid oscillations of wave functions near the core states. The BSE approach for optical excitations was previously implemented in VASP by Sander *et al.* [149]. In Part I of this thesis, we extend this implementation to include excitations from core to conduction band states.

The theoretical framework needed for the implementation is summarized in chapter 1 to 6. Chapters 1 and 2 focus on the methods required to determine the ground-state properties: DFT and the PAW method, respectively. In chapter 3, we discuss many-body perturbation theory, derive the BSE, and explain how it is transformed into an eigenvalue problem. In chapter 5 we evaluate the matrix elements used in the BSE eigenvalue equation within the PAW method. We also describe how to modify the resulting expression for core-to-conduction band

transitions. In chapter 4 we summarize the theory of linear response and derive an expression of the macroscopic dielectric function that allows to calculate XAS spectra including excitonic effects. Finally, chapter 6 presents an introduction to the FSA, including its theoretical basis and a discussion of the effects of basis set choice and self-interaction errors inherent in DFT.

The implementation is validated in chapter 7 of Part II. We test the implementation by calculating spectra of well-studied materials such as diamond, graphite, hexagonal boron nitride (h-BN), and lithium halides, for which experimental spectra and reference results from other authors are available. Within the framework of many-body perturbation theory, the interaction between quasiparticles is represented as a matrix in momentum space. For diamond and h-BN, we explore whether this interaction can be simplified using a model that retains only the diagonal matrix elements. Furthermore, we demonstrate improvements to the final-state approximation, bringing its spectra on par with those obtained using the BSE approach.

Following the successful validation of the BSE implementation for core excitations, we apply the methodology to larger systems, specifically semiconducting single-walled carbon nanotubes (SWCNTs) [148]. Electron-energy loss spectroscopy (EELS) studies on isolated SWCNTs by Senga *et al.* [153] have shown that each SWCNT can be distinguished by its particular fine structure above the absorption edge. To interpret these results, Senga *et al.* employed a ground-state approach that was also used in earlier studies [83, 20]. In their approach, the unoccupied density of states (DOS) for a given SWCNT was superimposed onto the experimental spectrum, aligning the first van Hove singularity (VHS) in the DOS with the first experimental peak. While this method allowed to assign the fine-structure peaks to the VHSs, misalignments still persisted. In chapter 8 of Part II, we provide a detailed explanation of how excitonic effects are responsible for this misalignment. The thesis is summarized and concluded in Part III.

Part I

Theory and implementation

Chapter 1

Density functional theory

In this chapter, we provide an overview of density functional theory (DFT), the method employed in this thesis to compute materials properties *ab-initio*, that is, from first principles. To understand the need for DFT, consider a system of N mutually interacting electrons moving within the potential of the atomic nuclei. Determining the properties of such a system requires solving the time-independent Schrödinger equation, given here in atomic units:

$$\left(-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{iI} \frac{1}{|\mathbf{r}_i - \mathbf{R}_I|} \right) \Psi(\mathbf{R}_I, \mathbf{r}_1, \dots, \mathbf{r}_N) = E \Psi(\mathbf{R}_I, \mathbf{r}_1, \dots, \mathbf{r}_N). \quad (1.1)$$

In this thesis, atomic units are used throughout. In the equation above, we have applied the Born-Oppenheimer approximation [26], which assumes that the electronic subsystem reacts instantaneously to the movements of the nuclei. This approximation decouples the electronic and ionic degrees of freedom, with the positions of the nuclei $\{\mathbf{R}_I\}$ entering as parameters into the Schrödinger equation. Furthermore, in the Born-Oppenheimer approximation, the electrostatic interaction of the nuclei is a constant and can be neglected for the determination of $\Psi(\mathbf{R}_I, \mathbf{r}_1, \dots, \mathbf{r}_N)$. The first term represents the kinetic energy of the electrons, the second term represents the pairwise electrostatic interaction of the electrons, and the third term represents the electrostatic interaction of the electrons with the nuclei.

By solving the Schrödinger equation, we obtain the many-body wavefunction $|\Psi\rangle$. According to the principles of quantum mechanics, this wavefunction contains all the information about the system. From it, we can calculate the expectation values of observables, $\langle \hat{O} \rangle = \langle \Psi | \hat{O} | \Psi \rangle$. In particular, if we found the ground state wavefunction $|\Psi_0\rangle$ we obtain the ground state energy $E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$.

However, in most cases, solving the many-body problem exactly is not feasible. To estimate the many-body ground state energy, we use the Rayleigh-Ritz variational principle. This principle states that the ground state energy can be approximated by minimizing over the space of trial wavefunctions $|\tilde{\Psi}\rangle$:

$$E_0 \leq \min_{\tilde{\Psi}} \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle, \quad (1.2)$$

under the constraint $\langle \tilde{\Psi} | \tilde{\Psi} \rangle = 1$. In practice, this minimization is performed by choosing a set of trial wavefunctions that depend on adjustable parameters. These parameters are then varied until a minimum $\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle$ is reached. For small systems such as molecules, approaches exist that determine the ground state properties by directly approximating the many-body wavefunction by a set of trial wavefunctions $|\tilde{\Psi}\rangle$ [172].

However, for large systems, methods that attempt to approximate the wavefunctions $|\Psi\rangle$ are destined to fail. This failure is due to the multidimensional nature of the many-body wavefunction $|\Psi\rangle$. For a system of N electrons, the number of parameters M needed to achieve a desired accuracy scales exponentially as $M = p^{3N}$, where p is the number of parameters per degree of freedom. For systems containing around 100 electrons, even with very modest accuracy requirements, M reaches values on the order of 10^{100} . Consequently, approximating the ground state energy using the Rayleigh-Ritz principle would require minimizing over 10^{100} parameters. Walter Kohn termed this bottleneck the “exponential wall” [80].

The basic idea behind DFT is to reformulate the many-body problem in terms of the electron density $n(\mathbf{r})$ which is a computationally much less demanding quantity. While in quantum mechanics all the information is contained in the many-body wavefunction $|\Psi\rangle$, in DFT, it is contained in $n(\mathbf{r})$.

The following sections provide a brief overview of DFT. First, we review Thomas-Fermi theory, which is the conceptual predecessor to DFT. Subsequently, we examine the Hohenberg-Kohn theorems, which provide a formal justification for a description in terms of $n(\mathbf{r})$. We then present a summary of the Kohn-Sham scheme which offers a method for self-consistently determining $n(\mathbf{r})$, the single-particle orbitals φ_i , and the energies ε_i . Finally, we show how DFT is used in practice.

1.1 Roots of DFT: Thomas-Fermi theory

Thomas-Fermi theory [179, 39, 101] was introduced shortly after the publications by Schrödinger and was the first attempt at formulating the many-body problem in terms of the electron density. In the Thomas-Fermi model, the electrons move in the potential of an atom with charge Z . The charge Z is assumed to be so large that the electrons can be treated semiclassically [87], implying a connection between the local density $n(\mathbf{r})$ and the kinetic energy of the electrons at that point [101, 87]:

$$\frac{1}{2}k_F(\mathbf{r}) = \frac{1}{2}(3\pi^2 n(\mathbf{r}))^{2/3}. \quad (1.3)$$

From this, we can approximate the mean kinetic energy of the electrons [101], or simply kinetic energy, as

$$T_{TF}[n(\mathbf{r})] = C \int n(\mathbf{r})^{5/2} d\mathbf{r}, \quad (1.4)$$

where C is a constant. To obtain an energy functional for the ground state energy we take the expectation value of the Hamiltonian from Eq. (1.1). The first term gives the expectation value of the kinetic energy, which we approximate by the Thomas-Fermi kinetic energy.

$$T = -\frac{\hbar^2}{2m} \sum_i^N \langle \Psi | \nabla_i^2 | \Psi \rangle \sim T_{TF} = C \int n(\mathbf{r})^{5/2} d\mathbf{r}. \quad (1.5)$$

The expectation value of the electron-electron interaction $\hat{V}_{ee}$, or simply electron-electron interaction, is given by

$$\begin{aligned}
V_{ee} &= \frac{1}{2} \sum_{i < j} \langle \Psi | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi \rangle = \frac{1}{2} \sum_{i < j} \int \frac{\Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_1 \dots d\mathbf{r}_N \\
&= \frac{1}{2} \sum_{i < j} \int \frac{\Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)}{|\mathbf{r} - \mathbf{r}'|} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{r} d\mathbf{r}' \\
&= \frac{1}{2} \sum_{i < j} \int \frac{\Psi^*(\mathbf{r}_1, \dots, \mathbf{r}, \mathbf{r}' \dots \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}, \mathbf{r}' \dots \mathbf{r}_N)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{r} d\mathbf{r}' \\
&= \int \frac{n_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}',
\end{aligned} \tag{1.6}$$

where we have introduced the two-particle (spinless) density matrix [129],

$$n_2(\mathbf{r}, \mathbf{r}') = \frac{N(N-1)}{2} \int |\Psi^*(\mathbf{r}_1, \dots, \mathbf{r}, \mathbf{r}' \dots \mathbf{r}_N)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_N. \tag{1.7}$$

The two-particle density matrix can be further decomposed by introducing the exchange-correlation hole n_{xc} , which is defined by

$$n_2(\mathbf{r}, \mathbf{r}') = \frac{1}{2} (n(\mathbf{r})n(\mathbf{r}') + n(\mathbf{r})n_{xc}(\mathbf{r}, \mathbf{r}')), \tag{1.8}$$

where the factor $\frac{1}{2}$ is introduced to avoid double-counting. This decomposition of the two-particle density matrix has a clear physical interpretation: the first term describes the classical electrostatic repulsion while the second term describes quantum mechanical effects such as exchange and correlation. The latter term will prove important in the following sections. Using this decomposition of $n_2(\mathbf{r})$, the electron-electron interaction reads

$$V_{ee} = \int \frac{n_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \int \frac{n(\mathbf{r})n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{1.9}$$

In the Thomas-Fermi model, exchange-correlation effects are neglected [129], so that we obtain the classical electron-electron repulsion, or Hartree energy, for the final expression of the electron-electron interaction,

$$V_H = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{1.10}$$

Finally, we calculate the expectation value of the ion-electron interaction, which is termed the external potential $\hat{V}_{\text{ext}}$. We first introduce the notation $v_{\text{ext}}(\mathbf{r}_i) = \sum_I 1/|\mathbf{r}_i - \mathbf{R}_I|$. Note that in the Born-Oppenheimer approximation, the positions of the ions are parameters. We then obtain for the expectation value of the external potential

$$\begin{aligned}
V_{\text{ext}} &= \sum_i \langle \Psi | v_{\text{ext}}(\mathbf{r}_i) | \Psi \rangle = \sum_i \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) v_{\text{ext}}(\mathbf{r}_i) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N \\
&= \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}.
\end{aligned} \tag{1.11}$$

When we sum these different energy terms we obtain the total energy functional in Thomas-Fermi theory written as a functional of the electron density, namely

$$E_{\text{TF}}[n(\mathbf{r})] = T + V_{ee} + V_{\text{ext}} = C \int n(\mathbf{r})^{5/2} d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}. \quad (1.12)$$

To find the density that yields the ground-state energy E_0 , i.e., the ground-state density $n_0(\mathbf{r})$, we cannot apply the Rayleigh-Ritz variational principle directly since the energy functional is expressed in terms of the density. Instead, we assume that a minimization principle exists for the energy functional $E_{\text{TF}}[n(\mathbf{r})]$ [129]. This means that the ground-state density is found by seeking the density that minimizes the energy E , or, in other words, the density for which $\delta E_{\text{TF}}[n(\mathbf{r})]/\delta n(\mathbf{r})$ vanishes. The constraint that the electron density integrates to N is incorporated using a Lagrange multiplier μ .

Applying the rules of the calculus of variations [129] results in

$$\frac{5}{3}n(\mathbf{r})^{3/2} + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{ext}}(\mathbf{r}) - \mu = 0, \quad (1.13)$$

which is then rearranged to

$$n_0(\mathbf{r}) = \frac{3}{5} \left(\mu - \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{ext}}(\mathbf{r}) \right)^{2/3}. \quad (1.14)$$

This equation gives us the ground-state density $n_0(\mathbf{r})$ in Thomas-Fermi theory as a functional of the external potential. While this equation is deceptively simple, one must point out the deficiencies of the Thomas-Fermi method. First, the approximation used to derive the kinetic energy functional, Eq. 1.4, is rather crude as all variations on the gradients of the density are neglected. Second, all exchange-correlation effects are neglected. Lastly, it can be shown that molecules do not bind in Thomas-Fermi theory [178].

However, Thomas-Fermi theory has one remarkable feature: albeit approximate, it furnishes a one-to-one correspondence between the external potential due to the nuclei and the ground state electron density. This feature prompted Walter Kohn to investigate whether an exact correspondence between the ground-state density and the external potential could be found [80]. The answer to this question is given by the Hohenberg-Kohn theorems presented in the next section.

1.2 Hohenberg-Kohn theorems

In the previous section, it was shown how Thomas-Fermi theory provides an approximate relationship between the ground state electron density $n_0(\mathbf{r})$ and the external potential $v_{\text{ext}}(\mathbf{r})$. We now want to find an exact correspondence between $n_0(\mathbf{r})$ and $v_{\text{ext}}(\mathbf{r})$. It is obvious that $v_{\text{ext}}(\mathbf{r})$, together with the number of electrons N , uniquely determines the electron density, since given $v_{\text{ext}}(\mathbf{r})$ and N , one can in principle solve the many-body Schrödinger equation, Eq. (1.1), which in turn determines the many-body wave function $|\Psi\rangle$ and thus $n(\mathbf{r})$.

To achieve a bijective, or one-to-one relationship, it is necessary to show the inverse, namely, that $v_{\text{ext}}(\mathbf{r})$ is determined by $n_0(\mathbf{r})$. This is achieved by the first theorem of Hohenberg and Kohn [65]:

The external potential $v_{\text{ext}}(\mathbf{r})$ is a unique functional of the ground state electron density $n_0(\mathbf{r})$.

This, in turn, implies that the complete many-body problem can be formulated in terms of $n_0(\mathbf{r})$: $n_0(\mathbf{r})$ determines v_{ext} and N , which fixes the many-body Hamiltonian and hence $|\Psi\rangle$. In particular, the energy and its terms can be rewritten as functionals of the electron density:

$$E[n(\mathbf{r})] = \underbrace{\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle}_{=F_{\text{HK}}} + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \quad (1.15)$$

where we have introduced the universal functional F_{HK} which is independent of the external potential, that is, the specific arrangement of the nuclei.

When formulating the many-body problem in terms of the wavefunction, we can use the Rayleigh-Ritz minimization principle. The question arises whether such a minimization principle exists for the energy functional $E[n(\mathbf{r})]$. This minimization principle appropriate for the density is provided by the second theorem of Hohenberg and Kohn [65]:

$$E[n_0(\mathbf{r})] \leq E[\tilde{n}(\mathbf{r})] \text{ for any trial density } \tilde{n}(\mathbf{r}) \text{ with } \tilde{n}(\mathbf{r}) \geq 0 \text{ and } \int \tilde{n}(\mathbf{r}) d\mathbf{r} = N.$$

In particular, this theorem states that the ground state energy $E_0[n_0(\mathbf{r})]$ is the minimum of the energy functional $E[n(\mathbf{r})]$, achieved when $n(\mathbf{r}) = n_0(\mathbf{r})$. The second theorem allows for the determination of the ground state energy by variationally minimizing the energy functional with respect to the electron density, rather than the many-body wavefunction, which significantly reduces the computational complexity.

To summarize these two theorems, all quantities of a many-electron system can be formulated as functionals of the electron density, and the ground state density uniquely determines the ground state energy. These theorems provide the conceptual justification for describing the many-body problem in terms of the electron density. This reduction in dimensionality makes DFT particularly powerful for studying large systems such as solids, surfaces, and large molecules. Consequently, since the publication of the seminal papers by Hohenberg and Kohn DFT has advanced to become the leading method in computational materials science.

Levy-Lieb constrained search procedure

In the previous discussion, it was implicitly assumed that the density $n(\mathbf{r})$ is physical, i.e. that it is associated with an antisymmetric many-body wavefunction derived from an external potential v_{ext} . If the electron density satisfies this criterion, it is said to be v -representable. However, it has been shown that not all densities that appear "reasonable" can be associated with an antisymmetric wavefunction corresponding to some external potential v_{ext} [92]. To overcome this limitation, Levy [91] and Lieb [94] reformulated the formalism of DFT so that only densities resulting from any antisymmetric wavefunction are required. These wavefunctions are then called N -representable. Although in practice it is rarely necessary to distinguish between v -representable and N -representable, the procedure of Levy and Lieb offers a new perspective on the Hohenberg-Kohn theorems.

In the originally formulated Hohenberg-Kohn theorems, the ground state energy is obtained by minimizing the energy functional given in Eq. (1.15). The Levy-Lieb formulation refines this approach by splitting the minimization into two steps. First, consider a set of wavefunctions

Ψ_n that integrate to a given density $n(\mathbf{r})$. Following Levy [92], we define a universal functional $F[n(\mathbf{r})]$ as:

$$F[n(\mathbf{r})] = \min_{\Psi_n} \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle, \quad (1.16)$$

where the minimization is performed over all wavefunctions Ψ_n that yield the density $n(\mathbf{r})$. This approach removes the constraint that densities must be v -representable and can handle degenerate states more effectively, since only one particular Ψ_n is chosen in the minimization process. To obtain the ground state energy, we then minimize over all possible densities:

$$E[n] = \min_n \left[F[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right]. \quad (1.17)$$

It can also be shown [92] that in the previous minimization procedure the ground state density $n_0(\mathbf{r})$ gives the ground state energy E_0 :

$$E_0[n_0] = F[n_0] + \int v_{\text{ext}}(\mathbf{r}) n_0(\mathbf{r}) d\mathbf{r}. \quad (1.18)$$

1.3 Kohn-Sham equations

While the Hohenberg-Kohn theorems have established that the many-body problem can be formulated in terms of the electron density, a practical procedure is needed to determine the ground-state density $n_0(\mathbf{r})$ and hence the ground-state energy E_0 . We now turn to the Kohn-Sham (KS) formulation of DFT, which provides a practical scheme for calculating $n_0(\mathbf{r})$ and also yields single-particle ground-state energies and orbitals. In this KS formulation, the interacting electron system is mapped onto a system of non-interacting electrons moving in an effective Kohn-Sham potential v_{KS} [81].

To derive KS equations, we first consider the energy functional for a non-interacting system of electrons, which reads

$$E_s[n(\mathbf{r})] = T_s[n(\mathbf{r})] + V_{\text{ext}}[n(\mathbf{r})], \quad (1.19)$$

where $T_s[n(\mathbf{r})]$ represents the single-particle, or non-interacting, kinetic energy. By minimizing this functional with respect to the density, subject to the constraint $\int n d\mathbf{r} = N$, we obtain the Euler equation

$$\mu = v_{\text{ext}}(\mathbf{r}) + \frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})}, \quad (1.20)$$

where μ is the chemical potential.

Next, we rewrite the energy functional for the interacting system [129],

$$E[n(\mathbf{r})] = T[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] + V_{\text{ext}}[n(\mathbf{r})], \quad (1.21)$$

$$= T_s[n(\mathbf{r})] + V_{\text{H}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})] + V_{\text{ext}}[n(\mathbf{r})], \quad (1.22)$$

$$\text{where } E_{\text{xc}}[n(\mathbf{r})] = T[n(\mathbf{r})] - T_s[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] - V_{\text{H}}[n(\mathbf{r})]. \quad (1.23)$$

Here, $E_{\text{xc}}[n(\mathbf{r})]$ is the exchange-correlation energy, which accounts for the non-classical part of the electron-electron interaction, including Pauli exchange effects and many-body correlation effects.

The Euler equation for this rewritten energy functional becomes

$$\mu = v_{\text{KS}}(\mathbf{r}) + \frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})}, \quad (1.24)$$

where the Kohn-Sham potential v_{KS} is given by

$$v_{\text{KS}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \quad (1.25)$$

The term $\delta E_{\text{xc}}[n(\mathbf{r})]/\delta n(\mathbf{r})$ defines the exchange-correlation potential $v_{\text{xc}}(\mathbf{r})[n(\mathbf{r})]$. With this definition, the Euler equation in Eq. (1.24) adopts a form that mirrors the Euler equation for a non-interacting system. This similarity implies that to find a density $n(\mathbf{r})$ that satisfies the above Euler equation, we can equivalently solve a set of N single-particle Schrödinger-like equations, known as the KS equations, which read

$$\left[-\frac{1}{2} \nabla_i^2 + v_{\text{KS}}(\mathbf{r})[n(\mathbf{r})] \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), \quad (1.26)$$

where $\varphi_i(\mathbf{r})$ are the KS orbitals and ε_i are the corresponding KS one-electron energies. The density that obeys Eq. (1.24) is obtained from the Kohn-Sham orbitals via

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2. \quad (1.27)$$

These equations need to be solved self-consistently. This process involves starting with an initial guess for $n(\mathbf{r})$, computing the Kohn-Sham potential $v_{\text{KS}}(\mathbf{r})$ from this density, and then solving the Kohn-Sham equations to update the density. The procedure is repeated until the results converge.

The sum of KS energies gives

$$\sum_i \varepsilon_i = \langle i | -\frac{1}{2} \nabla_i^2 | i \rangle + \int \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int v_{\text{xc}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}. \quad (1.28)$$

To recover the total energy given in Eq. (1.22) from the sum of KS energies we must subtract the Hartree energy as it counted twice in the result above, compare Eq. (1.10). Additionally, since $E_{\text{xc}} \neq \int v_{\text{xc}}[n]n(\mathbf{r})d\mathbf{r}$ we also need to subtract the third term and add E_{xc} so that

$$E = \sum_i \varepsilon_i - \frac{1}{2} \int \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - \int v_{\text{xc}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{\text{xc}}[n(\mathbf{r})]. \quad (1.29)$$

The primary challenge in the original many-body formulation was the exponential growth in computational resources needed to describe many-body interactions via wavefunctions. The Kohn-Sham DFT approach solves this issue in two ways. First, all quantities are expressed as functionals of the density, which is computationally less demanding. Additionally, it simplifies the problem to a system of N non-interacting particles moving in an effective potential. However, the main challenge remains to accurately approximate the unknown exchange-correlation energy $E_{\text{xc}}[n]$ and the related potential v_{xc} . This transforms the problem from one of computational complexity to the challenge of developing accurate and numerically tractable approximations for v_{xc} .

We now turn to the two common approximations for v_{xc} that are also used throughout this thesis.

Perdew-Burke Ernzerhof exchange-correlation functional

Historically, the first exchange-correlation functional was the local density approximation (LDA). In the LDA, the exchange correlation energy is obtained by assuming at each point $\mathbf{r}$ an exchange-correlation energy density $\epsilon_{xc}[n(\mathbf{r})]$ of a homogeneous electron gas with density $n(\mathbf{r})$. The total exchange-correlation energy is then obtained by integrating all local contributions,

$$E_{xc}^{\text{LDA}} = \int \epsilon_{xc}[n(\mathbf{r})]n(\mathbf{r})d\mathbf{r}. \quad (1.30)$$

This form of the exchange-correlation energy is suitable for a system with a slowly varying electron density. To improve on LDA, we need to incorporate the dependence on density gradients $|\nabla n|$ into the formulation of the exchange correlation energy. This is done with the so-called generalized gradient approximations (GGA)

$$E_{xc}^{\text{GGA}} = \int f_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))d\mathbf{r}, \quad (1.31)$$

where f_{xc} is a parameterized function of n and ∇n . In physics, the most widely used GGA functional is the Perdew-Burke Ernzerhof (PBE) functional [131], which is also used in this thesis. For PBE, the exchange correlation energy is approximated by writing it as a sum $E_{xc} = E_x + E_c$ where

$$E_x = \int n(\mathbf{r})\epsilon_x^{\text{unif}}[n(\mathbf{r})]F_x(s)d\mathbf{r}, \quad (1.32)$$

$$E_c = \int n(\mathbf{r}) [\epsilon_c^{\text{unif}}(r_s, \zeta) + H(r_s, \zeta, t)] d\mathbf{r}. \quad (1.33)$$

Here, s and t are dimensionless parameters that are functions of the density gradient $|\nabla n|$, r_s is the Wigner-Seitz radius, and ζ is the spin polarization factor. The enhancement functions $F_x(s)$ and $H(r_s, \zeta, t)$ are constructed so that the exchange and correlation energies obey certain physical constraints [131].

Hybrid functionals

In 1993, Becke [15] introduced a new class of functionals known as hybrid functionals E_{xc}^{hyb} . In this approach, a fraction α of the exact Fock exchange E_x^{Fock} is added to the exchange correlation energy. The general form of a hybrid functional is given by

$$E_{xc}^{\text{hyb}} = \alpha E_x^{\text{Fock}} + (1 - \alpha)E_x^{\text{GGA}} + E_c^{\text{GGA}}, \quad (1.34)$$

where E_x^{GGA} and E_c^{GGA} are the exchange and correlation energies, respectively, obtained by a particular flavor of the GGA exchange-correlation potential. This approach combines the strengths of both Hartree-Fock theory and DFT, since exchange is treated exactly in Hartree-Fock theory, while DFT provides computationally inexpensive approximations for the correlation energy. See Ref. [16] for an overview of the available hybrid functionals. In this work we use the PBE0 [132, 38, 5] scheme, where E_x^{PBE} and E_c^{PBE} from PBE are used and where the parameter α is fixed by a particular constraint. In Ref. [132], the parameter was set to $\alpha = 1/4$, resulting in the standard form of the PBE0 hybrid functional, which is

$$E_{xc}^{\text{PBE0}} = \frac{1}{4}E_x^{\text{Fock}} + \frac{3}{4}E_x^{\text{PBE}} + E_c^{\text{PBE}}. \quad (1.35)$$

In this thesis, we will use the PBE0 hybrid functional also using PBE correlation and exchange. However, instead of using the conventional value of $\alpha = 1/4$, we adopt an alternative method to determine the parameter α . The details of this approach will be provided in Sec. 8.2 below.

1.4 DFT in practice

We have now introduced the general formalism of KS DFT. Let us briefly summarize how DFT is performed in practice. Obtaining the physical quantities of interest involves self-consistently solving the KS equations using a specific functional for the exchange-correlation energy. This procedure provides the total energy of the system, the KS orbitals φ_i , and the KS eigenvalues ϵ_i . In the next step we must define a basis set. In this thesis, we use plane waves and employ the VASP code [85, 84] for our calculations.

For periodic solids, we can utilize Bloch's theorem, which states that each KS orbital can be expressed as

$$\varphi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (1.36)$$

where n denotes the band index and $\mathbf{k}$ is the wave vector within the first Brillouin zone. The function $u_{n\mathbf{k}}(\mathbf{r})$ is the cell-periodic part of the wavefunction, that is

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}). \quad (1.37)$$

We then expand $u_{n\mathbf{k}}(\mathbf{r})$ in terms of plane waves. The expression for the KS orbitals in reciprocal space is then given by

$$\varphi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{G}}^{G_{\text{cut}}} C_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (1.38)$$

where $\mathbf{G}$ are the reciprocal lattice vectors, V the crystal volume, and the sum is restricted to plane waves with energies below a chosen cutoff kinetic energy $\frac{1}{2}(\mathbf{G} + \mathbf{k})^2 < \frac{1}{2}G_{\text{cut}}^2$. Thus, the KS orbitals are represented by the plane wave coefficients $C_{n\mathbf{k}}(\mathbf{G})$.

A difficulty arises when describing the rapidly oscillating core states near the nuclei. Accurately representing these short-wavelength oscillations would require a very large number of plane waves. To overcome this issue, we employ pseudopotential theory, which replaces the potential created by the core electrons with an effective pseudopotential that smoothens out these rapid oscillations. This approach simplifies the calculations by removing the need to explicitly solve the KS equations for the core states. In VASP, this methodology is implemented within the projector-augmented wave (PAW) method, which will be discussed in the next chapter.

Chapter 2

Projector augmented-wave method

2.1 Introduction

In the previous chapter, we saw that in plane-wave codes the Kohn-Sham (KS) orbitals

$$\varphi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{G}}^{G_{\text{cut}}} C_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (2.1)$$

oscillate rapidly near the nuclei and that a large cutoff energy $\frac{\hbar^2}{2m_e} |\mathbf{G}_{\text{cut}}|^2$ is needed to represent the core states accurately. To overcome this problem, pseudopotential methods have been devised that replace the singular Coulomb potential with a smooth potential that reproduces the scattering properties within a certain radius, in particular the phase shift and the logarithmic derivative. This procedure leads to non-local pseudopotentials, such as those used in the orthogonalized plane wave (OPW) method [63], and additional auxiliary functions, which are for example introduced in the ultrasoft pseudopotentials method [188].

An alternative approach is taken by augmented wave methods, such as the linearized augmented plane wave (LAPW) method [102]. These methods divide space into atom-centered and interstitial regions. In the interstitial region, plane waves are used to expand the wavefunction, while in the atom-centered regions a different basis set is used. For example, in the LAPW method, the basis functions in the atom-centered regions are given as atomic radial functions multiplied by spherical harmonics, while in the interstitial region the wavefunction is expanded in plane waves.

The projector-augmented wave (PAW) method [21] combines aspects of both pseudopotential and augmented wave methods. Similar to the augmented-wave approach, PAW divides space into atom-centered and interstitial regions. In the interstitial region, plane waves are the basis set, while in the atom-centered regions, plane waves and auxiliary functions derived from pseudopotential theory are used. In this way, the advantages of both methods are combined to achieve computational efficiency and accuracy.

In this chapter we summarize the PAW method [21]. First, we outline the basics of the PAW method. Next, we discuss the treatment of core states within PAW. Finally, we describe

the concept of augmentation charges, which are essential for evaluating the Bethe-Salpeter equation within the PAW formalism.

2.2 Formalism

We first briefly summarize how to derive the transformation of all-electron (AE) to smooth, or pseudo (PS), quantities. In the PAW method the system is divided into atom-centered spheres Ω_a and an interstitial region Ω_I . We search a transformation T that transforms from the smooth PS quantities to the AE quantities such that the AE Kohn-Sham wavefunction $|\varphi_{n\mathbf{k}}\rangle$ is obtained from the PS wavefunction $|\tilde{\varphi}_{n\mathbf{k}}\rangle$ by

$$|\varphi_{n\mathbf{k}}\rangle = T|\tilde{\varphi}_{n\mathbf{k}}\rangle. \quad (2.2)$$

Since we have divided the system into atom-centered contributions and an intersititial region T has the form

$$T = 1 + \sum_a T_a, \quad (2.3)$$

where the operators T_a act only within the atomic spheres. Having defined how the operator T acts on wavefunctions we can evaluate Eq. (2.2) as

$$|\varphi_{n\mathbf{k}}\rangle = T|\tilde{\varphi}_{n\mathbf{k}}\rangle = |\tilde{\varphi}_{n\mathbf{k}}\rangle + \underbrace{\sum_a T_a}_{\text{within each } \Omega_a} |\tilde{\varphi}_{n\mathbf{k}}\rangle. \quad (2.4)$$

To evaluate $T_a|\tilde{\varphi}_{n\mathbf{k}}\rangle$, PS partial waves $|\tilde{\phi}_i^1\rangle$ are first introduced. The PS partial waves are used to expand the PS orbitals within each sphere Ω_a :

$$|\tilde{\varphi}_{n\mathbf{k}}^1\rangle = \sum_i c_i |\tilde{\phi}_i^1\rangle \quad \text{in } \Omega_a, \quad (2.5)$$

$$|\tilde{\varphi}_{n\mathbf{k}}\rangle = |\tilde{\varphi}_{n\mathbf{k}}^1\rangle \quad \text{in } \Omega_I, \quad (2.6)$$

where the superscript 1 denotes that the pseudo wavefunction is expanded inside the atomic spheres Ω_a . In the context of PAW, quantities defined within the spheres are referred to as on-site. At this stage we also introduce AE partial waves $|\phi_i\rangle$, which are used to expand the AE orbitals inside the PAW spheres:

$$|\varphi_{n\mathbf{k}}^1\rangle = \sum_i c_i |\phi_i^1\rangle \quad \text{in } \Omega_a, \quad (2.7)$$

$$|\varphi_{n\mathbf{k}}\rangle = |\varphi_{n\mathbf{k}}^1\rangle \quad \text{in } \Omega_I, \quad (2.8)$$

The AE and PS partial waves are constructed such that they are equal outside the PAW spheres. In Eqs. (2.5) and (2.7) the same expansion coefficients c_i are used which follows from the properties of the transformation operator T :

$$|\varphi_{n\mathbf{k}}^1\rangle = T|\tilde{\varphi}_{n\mathbf{k}}^1\rangle = \sum_i c_i T|\tilde{\phi}_i^1\rangle = \sum_i c_i |\phi_i\rangle. \quad (2.9)$$

In the next step, the action of T upon the PS partial waves within each Ω_a is evaluated. As T transform from PS to AE quantities the AE partial waves $|\phi_i\rangle$ are obtained:

$$|\phi_i\rangle = T|\tilde{\phi}_i\rangle = (1 + T_a)|\tilde{\phi}_i\rangle, \quad (2.10)$$

which also implies $T_a|\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle$. This result is inserted into Eq. (2.4):

$$|\varphi_{n\mathbf{k}}\rangle = |\tilde{\varphi}_{n\mathbf{k}}\rangle + \sum_a T_a |\tilde{\varphi}_{n\mathbf{k}}\rangle, \quad (2.11)$$

$$= |\tilde{\varphi}_{n\mathbf{k}}\rangle + \sum_a \underbrace{\sum_i c_i T_a |\tilde{\phi}_i\rangle}_{\text{within each } \Omega_a}, \quad (2.12)$$

$$= |\tilde{\varphi}_{n\mathbf{k}}\rangle + \sum_a \underbrace{\sum_i c_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)}_{\text{within each } \Omega_a}, \quad (2.13)$$

$$= |\tilde{\varphi}_{n\mathbf{k}}\rangle + \sum_a |\varphi_{n\mathbf{k}}^1\rangle - |\tilde{\varphi}_{n\mathbf{k}}^1\rangle. \quad (2.14)$$

The last of these expressions exhibits the principle of the PAW method: the AE wavefunction is obtained by adding to the PS wavefunction defined in the whole cell volume (first term) the AE partial waves inside the atomic spheres (second term) and subtracting the PS partial waves inside the atomic spheres (third term). From now on we will suppress the sum over atomic spheres.

To evaluate the expectation value of some operator A in the PAW method one needs to derive T explicitly. As the transformation T has to be linear the coefficients c_i are linear functionals of $|\tilde{\varphi}\rangle$,

$$c_i = \langle p_i | \tilde{\varphi}_{n\mathbf{k}} \rangle, \quad (2.15)$$

where we have introduced the projector functions $|p_i\rangle$. The projectors are dual to the PS partial waves,

$$c_i = \langle p_i | \tilde{\varphi}_{n\mathbf{k}} \rangle = \sum_j c_j \langle p_i | \tilde{\phi}_j \rangle, \quad (2.16)$$

$$\rightarrow \langle p_i | \tilde{\phi}_j \rangle = \delta_{ij}. \quad (2.17)$$

From the fact that the projectors are dual to the partial waves follows the completeness relation

$$\sum_i |p_i\rangle \langle \tilde{\phi}_i| = \mathbb{1}. \quad (2.18)$$

Inserting the explicit form of the coefficients, Eq. (2.15), into Eq. (2.13) gives

$$|\varphi_{n\mathbf{k}}\rangle = |\tilde{\varphi}_{n\mathbf{k}}\rangle + \sum_i (|\phi_i^1\rangle - |\tilde{\phi}_i^1\rangle) \langle p_i | \tilde{\varphi}_{n\mathbf{k}} \rangle. \quad (2.19)$$

Thus, we arrive at the final result which is the transformation T between PS and AE quantities:

$$T = 1 + \sum_i (|\phi_i^1\rangle - |\tilde{\phi}_i^1\rangle) \langle p_i|. \quad (2.20)$$

The expectation value of an operator $\hat{A}$ is then evaluated as

$$\langle \hat{A} \rangle = \sum_n f_n \langle \varphi_n | A | \varphi_n \rangle = \sum_n f_n \langle \tilde{\varphi}_n | \tilde{A} | \tilde{\varphi}_n \rangle, \quad (2.21)$$

where the sum runs over all bands and f_n are the Fermi occupation factors. Transforming the operator A gives

$$\tilde{A} = T^\dagger A T = [1 + \sum_{i,a} |p_i\rangle (\langle \phi_i^1| - \langle \tilde{\phi}_i^1|) A [1 + \sum_{j,b} (|\phi_j^1\rangle - |\tilde{\phi}_j^1\rangle) \langle p_j|], \quad (2.22)$$

$$= A + \sum_{ij,ab} \left[|p_i\rangle (\langle \phi_i^1| - \langle \tilde{\phi}_i^1|) \right]^a A \left[(|\phi_j^1\rangle - |\tilde{\phi}_j^1\rangle) \langle p_j| \right]^b \quad (2.23)$$

$$+ \sum_{i,a} |p_i\rangle (\langle \phi_i^1| - \langle \tilde{\phi}_i^1|) A + \sum_{i,a} A (|\phi_i^1\rangle - |\tilde{\phi}_i^1\rangle) \langle p_i|. \quad (2.24)$$

The indices a, b have been reintroduced to make it clear that the sums run over individual PAW spheres. In principle, this results in cross terms between different PAW spheres $a \neq b$, as can be seen from the second line. To simplify this expression we use that $|\tilde{\phi}_i\rangle = |\phi_i\rangle$ outside the augmentation regions. This implies that the cross terms $a \neq b$ between separate PAW spheres vanish and only the sum over individual PAW spheres a remains. Then, the completeness relation, Eq. (2.18), is inserted to the right and left of the operator A in the last line:

$$T^\dagger A T = A + \sum_{ij,a} |p_i\rangle (\langle \phi_i^1| - \langle \tilde{\phi}_i^1|) A (|\phi_j^1\rangle - |\tilde{\phi}_j^1\rangle) \langle p_j| \quad (2.25)$$

$$+ \sum_{ij,a} |p_i\rangle (\langle \phi_i^1| - \langle \tilde{\phi}_i^1|) A |\tilde{\phi}_j\rangle \langle p_j| + \sum_{ij,a} |p_j\rangle \langle \tilde{\phi}_j| A (|\phi_i^1\rangle - |\tilde{\phi}_i^1\rangle) \langle p_i|. \quad (2.26)$$

Expanding and canceling terms gives the final result

$$\tilde{A} = T^\dagger A T = A + \sum_{ij} |p_i\rangle (\langle \phi_i| A | \phi_j\rangle - \langle \tilde{\phi}_i| A | \tilde{\phi}_j\rangle) \langle p_j|. \quad (2.27)$$

From now on the sum over PAW spheres is again implied and the index a is omitted.

To summarize, we have obtained a linear transformation T that allows us to transform PS quantities into AE quantities. In the process, we had to introduce three auxiliary quantities:

i) The AE partial waves $|\phi_i^1\rangle$. These partial waves are solutions of the radial Schroedinger equation for a specific reference energy ϵ_i , where in the case of VASP one reference energy coincides with the eigenenergy of a valence state. The AE partial waves are written as a product of a radial function and spherical harmonics:

$$\langle \mathbf{r} | \phi_i^1 \rangle = \frac{1}{r} u_{\epsilon_i, l_i}(r) Y_{l_i m_i}(\theta, \phi), \quad (2.28)$$

where l_i, m_i are the orbital and magnetic quantum numbers of state i .

ii) The PS partial waves $|\tilde{\phi}_i^1\rangle$,

$$\langle \mathbf{r} | \tilde{\phi}_i^1 \rangle = \frac{1}{r} \tilde{u}_{\epsilon_i, l_i}(r) Y_{l_i m_i}(\theta, \phi), \quad (2.29)$$

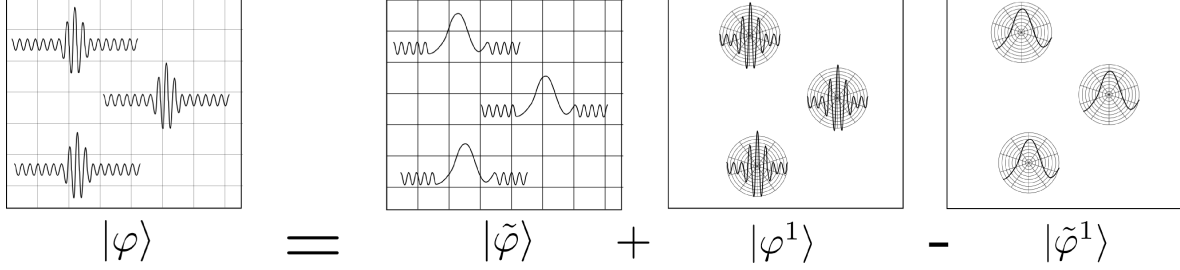


Figure 2.1: A sketch of how the PAW method works. The all-electron orbital $|\varphi\rangle$ is obtained by removing from the pseudo orbital $|\tilde{\varphi}\rangle$ the pseudo on-site terms $|\tilde{\varphi}^1\rangle$ and then adding the all-electron on-site terms $|\varphi^1\rangle$. The pseudo orbital is defined on a regular plane wave grid, while the on-site terms are defined on radial support grids.

where each PS partial wave $|\tilde{\phi}_i^1\rangle$ coincides with the corresponding AE partial wave $|\phi_i^1\rangle$ beyond a certain cutoff radius. In VASP the radial part of the PS partial wave is pseudized inside the augmentation region by writing it as a sum of two spherical Bessel function [84].

iii) Finally we introduced the projector functions $|p_i\rangle$. To each PS partial wave $|\tilde{\phi}_i^1\rangle$ corresponds one projector function $|p_i\rangle$ which is entirely localized within the atomic sphere Ω_a and for which $\langle p_i|\tilde{\phi}_j^1\rangle = \delta_{ij}$ holds. The projector functions probe the local character of the PS wavefunction within the atomic spheres [22].

All auxiliary quantities are defined within the atomic spheres and are expanded on radial grids. The total AE and PS wavefunctions $|\varphi_{n\mathbf{k}}\rangle$ and $|\tilde{\varphi}_{n\mathbf{k}}\rangle$ on the other hand are defined on regular grids spanning the volume of the cell. We can therefore visualize the principle of the PAW method as in Fig. 2.1.

In the next step, an expansion of the electron density $n(\mathbf{r}) = \sum_n f_n \langle \varphi_n | \mathbf{r} \rangle \langle \mathbf{r} | \varphi_n \rangle$ is needed. The expectation value of the charge density operator $|\mathbf{r}\rangle \langle \mathbf{r}|$ is evaluated by using Eq. (2.27) which results in

$$n(\mathbf{r}) = \sum_n f_n \langle \tilde{\varphi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\varphi}_n \rangle \quad (2.30)$$

$$+ \sum_{n,(i,j)} f_n \langle \tilde{\varphi}_n | p_i \rangle \langle p_j | \tilde{\varphi}_n \rangle \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle \quad (2.31)$$

$$- \sum_{n,(i,j)} f_n \langle \tilde{\varphi}_n | p_i \rangle \langle p_j | \tilde{\varphi}_n \rangle \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle. \quad (2.32)$$

The first line represents the PS charge-density which is the sum over PS charge densities and is evaluated in the entire cell. The second and third lines represent the on-site AE and PS charge densities respectively, and are evaluated in the atomic regions. We furthermore introduce the occupancies ρ_{ij} :

$$\rho_{ij} = \sum_n f_n \langle \tilde{\varphi}_n | p_i \rangle \langle p_j | \tilde{\varphi}_n \rangle \quad (2.33)$$

so that the total charge density is finally written as

$$n(\mathbf{r}) = \sum_n f_n \langle \tilde{\varphi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\varphi}_n \rangle + \sum_{(i,j)} \rho_{ij} \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle - \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle, \quad (2.34)$$

$$= \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}). \quad (2.35)$$

2.3 Frozen-core approximation

In this work we make the frozen-core approximation [21], where it is assumed that the core states do not extend beyond the cutoff radius of the atomic spheres and remain unchanged during electronic minimization. Consequently, all previous band sums include only the valence states. The AE core orbital $|\varphi_c\rangle$ is then obtained by applying the transformation T to the PS core orbital $|\tilde{\varphi}_c\rangle$:

$$|\varphi_c\rangle = T|\tilde{\varphi}_c\rangle = |\tilde{\varphi}_c\rangle + |\phi_c\rangle - |\tilde{\phi}_c\rangle. \quad (2.36)$$

Unlike the valence states, the coefficients for the core states are unity, since no projector functions need to be defined for core states. Here $|\tilde{\varphi}_c\rangle$ is the PS core state which is identical to the AE core state $|\phi_c\rangle$ outside the augmentation region. Since we assume that all quantities are completely localized inside the atomic spheres, we can further simplify this expression by assuming that $|\tilde{\varphi}_c\rangle = |\tilde{\phi}_c\rangle$, which leads to $|\varphi_c\rangle = |\phi_c\rangle$. The core states are thus determined by solving the radial Schrödinger equation for the isolated atom and are expressed as radial functions times spherical harmonics, see Eq. (2.29). In VASP the core states are precalculated in a preprocessing step where the boundary condition is imposed that the core orbitals are zero at the radius of the atomic sphere [21, 85].

2.4 Augmentation charges

Motivation

In this section, we introduce the concept of augmentation charges, which are crucial when implementing methods of many-body perturbation theory for X-ray spectra within the PAW methodology. Augmentation charges are motivated by the need for an accurate treatment of long-range electrostatic effects. We here provide a pedagogical introduction to augmentation charges.

When determining quantities such as the exchange energy or the matrix elements of the Bethe-Salpeter equation below, we encounter four-orbital integrals. For example, the exchange term of two orbitals is (see e.g. Eq. 15 of [127]):

$$K_{abba} = \frac{1}{2} \int \frac{\varphi_a^*(\mathbf{r}) \varphi_b(\mathbf{r}) \varphi_b^*(\mathbf{r}') \varphi_a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'. \quad (2.37)$$

Within PAW the two-orbital expressions $\varphi_a^*(\mathbf{r}) \varphi_b(\mathbf{r})$ is decomposed into the PS charge density and the on-site terms:

$$\varphi_a^*(\mathbf{r}) \varphi_b(\mathbf{r}) = n_{ab}(\mathbf{r}) = \tilde{n}_{ab}(\mathbf{r}) + n_{ab}^1(\mathbf{r}) - \tilde{n}_{ab}^1(\mathbf{r}). \quad (2.38)$$

Integrals of the above form involve now products of charge densities $n_{ab}(\mathbf{r}) n_{cd}(\mathbf{r}')$, where the indices in the expression for the second charge density are arbitrary. We look for a

decomposition of the term $n_{ab}(\mathbf{r})n_{cd}(\mathbf{r}')$ into PS terms evaluated on the regular grid and on-site terms evaluated on a radial grid. Expressing each charge density as the sum of the PS and on-site terms via Eq. (2.38) and expansion gives:

$$n_{ab}n_{cd} = \tilde{n}_{ab}\tilde{n}_{cd} + 2[n_{ab}^1 - \tilde{n}_{ab}^1]\tilde{n}_{cd} + [n_{ab}^1 - \tilde{n}_{ab}^1][n_{cd}^1 - \tilde{n}_{cd}^1], \quad (2.39)$$

where the position dependency is suppressed for convenience and where the symmetry of the Coulomb integral with respect to the exchange $\mathbf{r} \leftrightarrow \mathbf{r}'$ results in a factor of 2. The first term of equation. (2.39) is evaluated on the regular grid, while the third term is evaluated on the radial grid. The second term, however, contains cross terms between the two types of grids. To simplify the calculation, we introduce the augmentation charges $\hat{n}$. They are added to the total and on-site PS charge densities:

$$\begin{aligned} \tilde{n} &\rightarrow \tilde{n} + \hat{n}, \\ \tilde{n}^1 &\rightarrow \tilde{n}^1 + \hat{n}^1, \end{aligned}$$

and constructed such that $\tilde{n}^1 + \hat{n}$ has the same moments as the AE on-site charge density n^1 [21, 85]:

$$\int_{\Omega_r} (n^1 - \tilde{n}^1 - \hat{n})|\mathbf{r} - \mathbf{R}|^l Y_{l,m}^*(\widehat{\mathbf{r} - \mathbf{R}}) d^3r = 0, \quad (2.40)$$

where the atomic sphere is centered at $\mathbf{R}$, $Y_{l,m}(\widehat{\mathbf{r} - \mathbf{R}})$ are the (l, m) -spherical harmonics, and the integration is performed over the whole atomic sphere Ω_r . Below, we will detail how the augmentation charges are constructed.

When the PS on-site charge density $\tilde{n}^1$ is augmented, the Coulomb integrals involving the expression $[n_{ab}^1 - (\tilde{n}_{ab}^1 + \hat{n}^1)]$ have zero contributions outside the atomic spheres, since the multipoles vanish by construction. Since the charge density $[n_{ab}^1 - (\tilde{n}_{ab}^1 + \hat{n}^1)]$ has contributions only inside the atomic spheres and does not interact with charges in the interstitial region, $\tilde{n}_{cd}$ in the expression $[n_{ab}^1 - (\tilde{n}_{ab}^1 + \hat{n}^1)]\tilde{n}_{cd}$ can be replaced by its on-site approximation $\tilde{n}_{cd}^1$. This simplifies the above expression to

$$n_{ab}n_{cd} = (\tilde{n}_{ab} + \hat{n}_{ab})(\tilde{n}_{cd} + \hat{n}_{cd}) + n_{ab}^1n_{cd}^1 - (\tilde{n}_{ab}^1 + \hat{n}_{ab}^1)(\tilde{n}_{cd}^1 + \hat{n}_{cd}^1). \quad (2.41)$$

By introducing the augmentation charges, the product of charge densities is decomposed into a term evaluated on the regular grid (first term) and terms evaluated on the radial grid (second and third terms).

Constructing the augmentation charges

To construct the augmentation charges, we start with the defining equation for the augmentation charge density:

$$\int_{\Omega_r} (n^1 - \tilde{n}^1 - \hat{n})|\mathbf{r} - \mathbf{R}|^l Y_{l,m}^*(\widehat{\mathbf{r} - \mathbf{R}}) d^3r = 0. \quad (2.42)$$

First, we introduce the quantity $Q_{ij}(\mathbf{r})$ which represents the difference between the on-site AE and PS charge densities:

$$Q_{ij}(\mathbf{r}) = \varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r}) - \tilde{\varphi}_i^*(\mathbf{r})\tilde{\varphi}_j(\mathbf{r}). \quad (2.43)$$

Using the occupancies ρ_{ij} , Eq. (2.33), and $Q_{ij}(\mathbf{r})$, the charge density difference $n^1 - \tilde{n}^1$ can be expressed as:

$$n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}) = \sum_{ij} \rho_{ij} Q_{ij}(\mathbf{r}). \quad (2.44)$$

To determine the augmentation charge, we need to calculate the $\{l, m\}$ -moments of $Q_{ij}(\mathbf{r})$:

$$q_{ij}^{l,m} = \int_{\Omega_r} Q_{ij}(\mathbf{r}) r^l Y_{l,m}^*(\theta, \phi) d^3r. \quad (2.45)$$

Here, i is a compound index representing the reference energy ϵ_i and the orbital and magnetic quantum numbers l_i, m_i . We write the on-site AE and PS partial waves as products of radial functions and spherical harmonics, see Eqs. (2.28) and (2.29), so that $Q_{ij}(\mathbf{r})$ separates into radial and angular components:

$$Q_{ij}(\mathbf{r}) = \frac{1}{r^2} (u_{\epsilon_i, l_i}^*(r) u_{\epsilon_j, l_j}(r) - \tilde{u}_{\epsilon_i, l_i}^*(r) \tilde{u}_{\epsilon_j, l_j}(r)) Y_{l_i m_i}(\theta, \phi) Y_{l_j m_j}(\theta, \phi). \quad (2.46)$$

Substituting Eq. (2.46) into Eq. (2.45) separates the integral into radial and angular parts:

$$\begin{aligned} q_{ij}^{l,m} &= \int_0^{r_c} (u_{\epsilon_i, l_i}^*(r) u_{\epsilon_j, l_j}(r) - \tilde{u}_{\epsilon_i, l_i}^*(r) \tilde{u}_{\epsilon_j, l_j}(r)) r^l dr \\ &\times \int Y_{l_i m_i}(\theta, \phi) Y_{l_j m_j}(\theta, \phi) Y_{l, m}^*(\theta, \phi) d\phi d\cos\theta. \end{aligned} \quad (2.47)$$

The result of the angular integral involving three spherical harmonics are called the Gaunt coefficients which impose the usual selection rules for addition angular momentum:

$$m = m_i + m_j, \quad (2.48)$$

$$l = |l_i - l_j|, |l_i - l_j| + 2, \dots, |l_i + l_j|. \quad (2.49)$$

After evaluating the radial and angular integrals, we obtain the moments $q_{ij}^{l,m}$. We then write the augmentation charge $\hat{n}$ as:

$$\hat{n}(\mathbf{r}) = \sum_{ij, l, m} \rho_{ij} q_{ij}^{l,m} Y_{l, m}(\theta, \phi). \quad (2.50)$$

The on-site density matrix ρ_{ij} is formulated in terms of the angular momentum variables l_i, m_i, l_j, m_j . However, the augmentation charge that will be added to the grid is expressed in terms of the total angular momentum variables l, m . To make this basis change we sum the term $\rho_{ij} q_{ij}^{l,m}$ over all l_i, m_i, l_j, m_j variables:

$$\rho_{l, m} q_{ij}^{l, m} = \sum_{l_i, m_i, l_j, m_j} \rho_{l_i, m_i, l_j, m_j} q_{ij}^{l_i, m_i, l_j, m_j}. \quad (2.51)$$

With this change of basis, the augmentation charges $\hat{Q}_{ij}^{l,m}$ evaluate to

$$\hat{n}(\mathbf{r}) = \sum_{ij,l,m} \rho_{lm} \hat{Q}_{ij}^{l,m} = \sum_{ij,l,m} \rho_{lm} q_{ij}^{l,m} Y_{lm}(\theta, \phi). \quad (2.52)$$

This augmentation charge is then added to the PS charge density grid on the real space grid. This real space grid is not the same as the plane wave grid that is used to represent the PS wavefunctions $\tilde{\varphi}_{n\mathbf{k}}(\mathbf{r})$ and an interpolation technique is used to interpolate between these two grids [85]. Since we have restored the moments of the quantity Q the procedure above is called moment-restoration. In VASP, moment restoration is controlled by the parameter **LMAXFOCK** which determines up to which total angular momentum l the moments of Q are restored, that is, the value of l in Eq. (2.52).

For post-DFT methods it can be beneficial to restore not only the moments, but also the shape of the rapidly varying quantity Q . This process is accordingly called shape restoration. To restore the shape of the quantity Q we add to the right hand side of Eq. (2.52) for each total angular momentum l shape-restoring radial functions $\Delta g_l(r)$:

$$\hat{n} = \sum_{\substack{lm \\ i,j}} \rho_{lm} \left[q_{ij}^{lm} Y_{lm}(\theta, \phi) + c_{ij}^l \Delta g_l(r) Y_{lm}(\theta, \phi) \right], \quad (2.53)$$

where the shape-restoring functions are written as a sum of two spherical Bessel-functions,

$$\Delta g_l(r) = \sum_{\beta=1}^2 \alpha_{\beta}^l j_l(q_{\beta}^l r). \quad (2.54)$$

The details on how to determine the coefficients c , α , and q can be found in Refs. [85, 59, 184]. Note that the augmentation charge density including shape restoration, Eq. (2.53), is the augmentation charge that will be added to the PS charge density defined on the regular grid spanning the cell volume, that is, $\tilde{n} \rightarrow \tilde{n} + \hat{n}$.

In VASP, the parameters that control shape restoration are **NMAXFOCKAE** and **LMAXFOCKAE**. **NMAXFOCKAE** determines the cutoff energy **ENCUT** up to which the shape of Q is accurately restored. A setting of **NMAXFOCKAE**=1 or **NMAXFOCKAE**=2 means that shape restoration is accurate up to a cutoff of 150 eV or 400 eV, respectively. **LMAXFOCKAE** again specifies the total angular momentum quantum number l up to which shape restoration is performed, that is, the l in the second term of (2.53). Since the largest total angular momentum l is determined by $|l_i + l_j|$, a rule of thumb is to set **LMAXFOCKAE** to twice the angular momentum number of the partial wave with the largest l . For example, for a system with p and d elements, **LMAXFOCKAE**=6. Since in this thesis we consider elements with at most p electrons, the default values **LMAXFOCK**=4 and **LMAXFOCKAE**=4 have been used. The cutoff for shape restoration was set to 150 eV with **NMAXFOCKAE**=1.

Chapter 3

Many-body perturbation theory

In the first chapter, we introduced DFT which reformulates the many-body problem in terms of the electron density $n(\mathbf{r})$. DFT has become one of the leading methods in computational materials science for determining the ground-state properties of molecules, liquids, and solids. However, since DFT is inherently a ground-state theory, it is limited when describing excited states. This limitation is particularly relevant for X-ray absorption spectroscopy (XAS), where an excited state is generated when an electron is removed from an inner shell and promoted to a conduction band.

To overcome this limitation, we extend DFT by combining it with methods from many-body perturbation theory (MBPT), in particular Green's function techniques. At this point, we introduce the fundamental concept of MBPT which is that of the *quasiparticle*. Let us first consider the simple case of excited states in a non-interacting electron gas. The eigenstates of the Hamiltonian of free particles are plane waves that are classified by their momenta $\mathbf{k}$ and that fill up the Fermi sphere up to the Fermi momentum $\mathbf{k}_F$. To create an excited state of the non-interacting system, we add a particle with momentum $\mathbf{k} > \mathbf{k}_F$ above the Fermi surface. Alternatively, we can remove a state below the Fermi surface which is equivalent to adding a hole having momentum $-\mathbf{k}$ with $|\mathbf{k}| < \mathbf{k}_F$.

Now let us consider the case of interacting particles. In principle, the quantum mechanical problem of a gas of interacting particles has to be solved. The idea behind quasiparticles is to instead map the simple description of excited states in the non-interacting case to the interacting system. This is done by first creating an excited state of the non-interacting system by adding additional particles, as described above. Then, we turn on the interaction infinitely slowly (*adiabatically*). As the interaction is slowly turned on, the energy levels of the non-interacting system slowly and continuously evolve into the corresponding states of the interacting system. In turn, the particles that we have added above or below the Fermi surface in the non-interacting system continuously evolve into additional particles of the interacting system with a momentum above or below the Fermi surface. These states that adiabatically evolved from the states in the non-interacting system are the *quasiparticles*. Since more complicated excited states of the many-body system can be constructed from these quasiparticles, they are also called *elementary excitations*.

As we slowly turn on the interaction, we slowly build up the individual states of the interacting

system from linear combinations of the states of the non-interacting system. This is also true for the particles we have added above or below the Fermi surface. Figuratively speaking, the excited particle in the interacting system is no longer a simple, isolated particle, but is always interacting with a surrounding cloud of particles and drags this cloud along with it as it moves through the system. This has several consequences. First, the interaction of the excited particle with the surrounding electron cloud changes (*renormalizes*) its energy. The initial *bare* particle becomes *dressed* by the many-body interactions, resulting in a new energy called the *quasiparticle energy*. Second, the quasiparticle, being a superposition of many states, can decay into other states due to interactions, resulting in a finite quasiparticle *lifetime*. Since the probability of scattering is proportional to the available phase space, the lifetime is only significant for quasiparticles close to the Fermi surface. Therefore, only quasiparticles close to the Fermi surface are well defined. Finally, the cloud of particles surrounding the bare particle shields its charge from other charges. Due to the many body interactions, the strong Coulomb interaction is thus replaced by a weaker, effective interaction called the *screened interaction* that accounts for the complicated many-body polarization effects. In summary, in the formalism of MBPT the system of strongly interacting particles is replaced with a description in terms of weakly interacting quasiparticles.

The principal tool of MBPT that allows to calculate quasiparticle properties is the Green's function. In Sec. 3.2 the main concepts of MBPT are explained by using the Green's function of non-interacting particles. In order to discuss interacting particles, we must introduce the concept of the self-energy and Dyson's equation, which we will cover in Sec. 3.3. In Sec. 3.4 we discuss the screened interaction in general and the model for the screened interaction that was employed throughout this thesis. Next, we will demonstrate how to approximate the self-energy and solve Dyson's equation to obtain quasiparticle energies in Sec. 3.5.

In X-ray spectroscopies, the electron excited from the core shell interacts with the resulting hole, forming a quasiparticle known as an exciton. Excitons are two-particle excitations of the many-body system, requiring us to move beyond the single-particle Green's function and consider two-particle Green's functions. To account for the interaction between electrons and holes, we use the Dyson equation of two-particle excitations, the Bethe-Salpeter equation (BSE), which we will introduce in Sec. 3.6. We will derive the BSE and demonstrate how it can be reformulated as an eigenvalue problem.

3.1 Preliminaries

We summarize here the essential ingredients needed for MBPT, namely, second quantization and the interaction picture. We also summarize the Fourier transform conventions used throughout this chapter.

Second Quantization

The many-body wave function $|\Psi\rangle$ has to obey the correct symmetry properties with respect to interchange of particles. These symmetry requirements are summarized by

$$\Psi(\dots, \mathbf{r}_i, \mathbf{r}_j, \dots) = \pm \Psi(\dots, \mathbf{r}_j, \mathbf{r}_i, \dots), \quad (3.1)$$

where the upper (lower) sign is valid for Bosons (Fermions). We need a formalism which describes a system of a large number of interacting particles in an economical manner and

in which these symmetry properties are reflected. This is the language of *second quantization*. First, we introduce the creation and annihilation operators $a_k^\dagger, a_k$ which create or destroy a state with momentum k . Fermions (Bosons) obey the following (anti-) commutation rules:

$$\{a_k, a_{k'}^\dagger\} = a_k, a_{k'}^\dagger + a_{k'}^\dagger a_k = \delta_{k,k'}, \quad (3.2)$$

$$[a_k, a_{k'}^\dagger] = a_k, a_{k'}^\dagger - a_{k'}^\dagger a_k = \delta_{k,k'}, \quad (3.3)$$

$$\{a_k^\dagger, a_{k'}^\dagger\} = [a_k^\dagger, a_{k'}^\dagger] = 0, \quad (3.4)$$

$$\{a_k, a_{k'}\} = [a_k, a_{k'}] = 0. \quad (3.5)$$

Using these operators and a complete set of state $\psi_k^*(\mathbf{r})$ we further define *field operators* $\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}(\mathbf{r})$ that create or destroy a particle at position $\mathbf{r}$:

$$\hat{\psi}^\dagger(\mathbf{r}) = \sum_k \psi_k^*(\mathbf{r}) a_k^\dagger, \quad (3.6)$$

$$\hat{\psi}(\mathbf{r}) = \sum_k \psi_k(\mathbf{r}) a_k. \quad (3.7)$$

These field operators obey the same (anti-) commutation rules:

$$\{\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')\} = [\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}'), \quad (3.8)$$

$$\{\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')\} = [\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')] = 0, \quad (3.9)$$

$$\{\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')\} = [\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')] = 0. \quad (3.10)$$

In terms of these field operators the Hamiltonian can then be rewritten in the following form:

$$\hat{H} = \int d^3x \hat{\psi}^\dagger(\mathbf{r}) h(\mathbf{r}) \hat{\psi}(\mathbf{r}) + \frac{1}{2} \int d^3x d^3x' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}), \quad (3.11)$$

where the first term accounts for the single particle part of the Hamiltonian, that is, the kinetic energy and the potential energy due to the external field,

$$h(\mathbf{r}) = -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) \quad (3.12)$$

while the second part accounts for the electron-electron interaction

$$v(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (3.13)$$

Furthermore we can express the density operator in field operators:

$$\hat{n}(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}). \quad (3.14)$$

Interaction picture

Later in this chapter we will have to evaluate a time-dependent expectation values of an operator $\langle \hat{A}(t) \rangle$, where the states $|\psi\rangle$ are eigenstates of a Hamiltonian that can be decomposed into a non-interacting and interacting parts: $H = H_0 + H_{\text{int}}$. We first summarize the Schroedinger and Heisenberg pictures before we introduce the interaction picture which will be used later on.

Consider an operator A in the Schroedinger representation which we indicate by a subscript S. In this representation the operator is time independent while the state is time dependent:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)_S\rangle = \hat{H} |\psi(t)_S\rangle, \quad (3.15)$$

which implies the time evolution of a state in the Schrödinger picture given as

$$|\psi(t)_S\rangle = e^{-i\hat{H}t} |\psi(0)_S\rangle. \quad (3.16)$$

In the Heisenberg representation (subscript H) on the other hand the states are time-independent while the operators acquire a time-dependency according to

$$\hat{A}(t)_H = e^{+i\hat{H}t/\hbar} \hat{A}_S e^{-i\hat{H}t/\hbar}, \quad (3.17)$$

$$\hat{A}(t)_H^\dagger = e^{+i\hat{H}t/\hbar} \hat{A}_S^\dagger e^{-i\hat{H}t/\hbar}, \quad (3.18)$$

where the equation of motion of an operator in the Heisenberg representation is

$$i\hbar \frac{\partial}{\partial t} \hat{A}(t)_H = [\hat{A}(t)_H, \hat{H}]. \quad (3.19)$$

Let us turn to the interaction picture. Consider a Hamiltonian $\hat{H}$ which can be decomposed into non-interacting and interacting components,

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}, \quad (3.20)$$

where the solution of $\hat{H}_0$ is known. Then, we factor the time-dependence on $\hat{H}_0$ out of the state in the Schrödinger picture:

$$|\psi_I(t)\rangle = e^{i\hat{H}_0 t} |\psi(t)_S\rangle. \quad (3.21)$$

From this transformation following equations can be derived [42] which constitute the defining equations of the interaction representation:

$$i \frac{\partial}{\partial t} |\psi_I(t)\rangle = \hat{H}_{\text{int}}(t) |\psi_I(t)\rangle, \quad (3.22)$$

$$i \frac{\partial}{\partial t} \hat{O}_I(t) = [\hat{O}_I(t), \hat{H}_0]. \quad (3.23)$$

We see that the time dependence of the states is governed by $\hat{H}_{\text{int}}(t)$, while the operators in the interaction representation have the same form as the operators in the Heisenberg picture

for a non-interacting system. Using the interaction picture the expectation value $\langle A(t) \rangle$ will have the form

$$\langle \psi | \hat{A}_0(t) e^{-i \int H_{\text{int}} dt} | \psi \rangle. \quad (3.24)$$

In the interaction picture, the operator in $\hat{A}_0(t)$ is the operator in the Heisenberg representation, where its time dependency is given by the non-interacting part H_0 of the Hamiltonian. This form of the expectation value will be useful when developing a perturbation theory of Green's functions.

Fourier transform conventions

The Fourier expansion and the Fourier coefficients of a lattice periodic function $f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$ satisfying Born-von Karman boundary conditions are given by

$$f(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{qG}} f_{\mathbf{G}}(\mathbf{q}) e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}, \quad (3.25)$$

$$f_{\mathbf{G}}(\mathbf{q}) = \int f(\mathbf{r}) e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}} d\mathbf{r}, \quad (3.26)$$

where the vectors $\mathbf{G}$ are reciprocal lattice vectors, the vectors $\mathbf{q}$ reciprocal vectors limited to the first Brillouin zone, and V is the crystal volume. By convention, a two-point function $f(\mathbf{r}, \mathbf{r}')$ is expanded as

$$f(\mathbf{r}, \mathbf{r}') = \frac{1}{V} \sum_{\mathbf{qG}, \mathbf{q'G'}} e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} f_{\mathbf{GG'}}(\mathbf{q}) e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}, \quad (3.27)$$

$$f_{\mathbf{GG'}}(\mathbf{q}) = \int e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}} f(\mathbf{r}, \mathbf{r}') e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}'} d\mathbf{r} d\mathbf{r}'. \quad (3.28)$$

Notation

To simplify expressions we introduce the following notation:

$$\begin{aligned} 1 &= \{\mathbf{r}_1, t_1\}, 2 = \{\mathbf{r}_2, t_2\}, \dots \\ 1^+ &= \{\mathbf{r}_1, t_1 + \delta\} \\ 1^- &= \{\mathbf{r}_1, t_1 - \delta\} \\ d1 &= d^3 r_1 dt_1, d(12) = d^3 r_1 dt_1 d^3 r_2 dt_2, \dots \\ \delta(1, 2) &= \delta(\mathbf{r}_1, \mathbf{r}_2) \delta(t_1 - t_2) \end{aligned}$$

3.2 Single particle Green's functions

We now introduce the time-ordered single-particle Green's function:

$$iG(2, 1) = \langle \Psi_0 | T [\hat{\psi}(2) \hat{\psi}^\dagger(1)] | \Psi_0 \rangle, \quad (3.29)$$

where $|\Psi_0\rangle$ is the N -particle ground state in the Heisenberg representation. The time-ordering operator T arranges operators in its argument so that time decreases from left to right, which can be written using Heavisides' step function as

$$T [\hat{\psi}(2) \hat{\psi}^\dagger(1)] = \hat{\psi}(2) \hat{\psi}^\dagger(1) \theta(t_2 - t_1) - \hat{\psi}^\dagger(1) \hat{\psi}(2) \theta(t_1 - t_2). \quad (3.30)$$

Let us first discuss the physical content of the Green's function. One way to interpret G is through its definition in terms of field operators. Let $t_2 > t_1$. When we act on the ground state with $\hat{\psi}^\dagger(1)$, we create an additional particle at position $\mathbf{r}_1$ and time t_1 , leading to a new state $|\dots, 1_+, \dots\rangle_{N+1}$. Next, we remove a particle from this state at position $\mathbf{r}_2$ and a later time $t_2 > t_1$, resulting in the state $|\dots, 1_+, \dots, 2_-\rangle_N$. The Green's function is then i times the overlap $\langle N | \dots, 1_+, \dots, 2_-\rangle_N$, or, in other words, the probability of finding a particle at $(\mathbf{r}_2, t_2)$ when a particle is added to the many-body system at $(\mathbf{r}_1, t_1)$. For $t_2 < t_1$ we interpret the Green's function as the probability to find a hole at position $\mathbf{r}_2$ and time t_2 after it was added at position $\mathbf{r}_1$ and time t_1 .

Equivalently, the Green's function can be interpreted as the propagator of a particle in a many-body system. To make this more explicit, let's consider the non-interacting Green's function G_0 . By substituting the free-particle Heisenberg operators,

$$\hat{\psi}^\dagger(1) = \sum_{\mathbf{k}} e^{-i(\mathbf{k} \cdot \mathbf{r}_1 - \epsilon(\mathbf{k})t_1)} a_{\mathbf{k}}^\dagger, \quad (3.31)$$

into Eq. (3.29), we obtain

$$iG(2, 1) = \langle \Psi_0 | T \left[\hat{\psi}(2) \hat{\psi}^\dagger(1) \right] | \Psi_0 \rangle = e^{i[\mathbf{k} \cdot (\mathbf{r}_2 - \mathbf{r}_1) - \epsilon(\mathbf{k})(t_2 - t_1)]} [(1 - f_{\mathbf{k}})\theta(t_2 - t_1) - f_{\mathbf{k}}\theta(t_1 - t_2)], \quad (3.32)$$

where $f_{\mathbf{k}}$ is the Fermi occupation factor. To simplify the analysis, let's set $t_1 = 0$ and $\mathbf{r}_1 = 0$. Performing the Fourier transform with respect to the variable $\mathbf{r}$, we find:

$$t > 0: \quad iG(\mathbf{k}, t) = +\theta(\mathbf{k} - \mathbf{k}_F) e^{+i\epsilon(\mathbf{k})t}, \quad (3.33)$$

$$t < 0: \quad iG(\mathbf{k}, t) = -\theta(\mathbf{k}_F - \mathbf{k}) e^{-i\epsilon(\mathbf{k})|t|}, \quad (3.34)$$

where $\mathbf{k}_F$ is the Fermi momentum. For $t > 0$, an additional particle is introduced into the system, propagating in an originally unoccupied state ($\mathbf{k} > \mathbf{k}_F$) with momentum $\mathbf{k}$ and energy $\epsilon(\mathbf{k})$. Conversely, for $t < 0$, the Green's function describes a hole propagating in an originally occupied state, with momentum $-\mathbf{k}$ and energy $-\epsilon(\mathbf{k})$ [107]. In other words, the electron propagates forward in time while the hole propagates backwards in time.

Finally, the poles of the Green's function correspond to the quasiparticle energies and quasiparticle lifetimes. This connection will become clearer when we introduce the Lehmann representation of the Green's function in the next section.

Lehmann representation

We now derive the Lehmann representation of the one-particle Green's function. In the course of the derivation we perform Fourier transforms on position and time variables, for this purpose we write position and time variables explicitly in this section. We start from the defining equation, Eq. (3.29),

$$\begin{aligned} iG(r_1, t_1; r_2, t_2) &= \langle \Psi_0 | \hat{\psi}(r_1, t_1) \hat{\psi}^\dagger(r_2, t_2) | \Psi_0 \rangle \theta(t_1 - t_2) \\ &\quad - \langle \Psi_0 | \hat{\psi}^\dagger(r_2, t_2) \hat{\psi}(r_1, t_1) | \Psi_0 \rangle \theta(t_2 - t_1) \end{aligned} \quad (3.35)$$

in which we insert complete sets of states of arbitrary particle number $|n\rangle$ as well as the explicit expressions for the Heisenberg operators, Eq. (3.18):

$$iG(r_1, t_1; r_2, t_2) = \sum_n [\langle \Psi_0 | e^{i\hat{H}t_1/\hbar} \hat{\psi}(r_1) e^{-i\hat{H}t_1/\hbar} | n \rangle \langle n | e^{i\hat{H}t_2/\hbar} \hat{\psi}^\dagger(r_2) e^{-i\hat{H}t_2/\hbar} | \Psi_0 \rangle \theta(t_1 - t_2) - \langle \Psi_0 | e^{i\hat{H}t_2/\hbar} \hat{\psi}^\dagger(r_2) e^{-i\hat{H}t_2/\hbar} | n \rangle \langle n | e^{-i\hat{H}t_1/\hbar} \hat{\psi}(r_1) e^{-i\hat{H}t_1/\hbar} | \Psi_0 \rangle \theta(t_2 - t_1)]. \quad (3.36)$$

We now note that in the first expression the field operator $\hat{\psi}^\dagger(r_2)$ acts on the right on the N particle ground state $|\Psi_0\rangle$ which now contains $N + 1$ particles. For the expression for $t_1 > t_2$ not to vanish the intermediate states $|n\rangle$ must contain $N + 1$ particles. An analogous argument holds for $t_1 < t_2$. The previous expression now becomes

$$iG(r_1, r_2, t_2 - t_1) = \sum_N [e^{-i(E_n(N+1) - E_0(N))(t_1 - t_2)/\hbar} \langle \Psi_0 | \hat{\psi}(r_1) | n \rangle \langle n | \hat{\psi}^\dagger(r_2) | \Psi_0 \rangle \theta(t_1 - t_2) - e^{i(E_n(N-1) - E_0(N))(t_1 - t_2)/\hbar} \langle \Psi_0 | \hat{\psi}^\dagger(r_2) | n \rangle \langle n | \hat{\psi}(r_1) | \Psi_0 \rangle \theta(t_2 - t_1)], \quad (3.37)$$

where we note that it depends only on time differences $t_1 - t_2$.

We now take a closer look at the expression $E_n(N + 1) - E_0(N)$. To this we add a zero, $0 = E_0(N + 1) - E_0(N + 1)$:

$$E_n(N + 1) - E_0(N) = [E_n(N + 1) - E_0(N + 1)] + [E_0(N + 1) - E_0(N)] = \epsilon_n(N + 1) + \mu, \quad (3.38)$$

which defines the excitation energies $\epsilon_n(N + 1)$ and the chemical potential μ of the $N + 1$ particle system [42]. Similarly, for $E_n(N - 1) - E_0(N)$, we write

$$E_n(N - 1) - E_0(N) = \epsilon_n(N - 1) - \mu', \quad (3.39)$$

where $\mu' = E_0(N) - E_0(N - 1)$. For large N , μ and μ' are equal, as in the thermodynamic limit $\mu(N + 1) = \mu(N) + \text{corrections of order } 1/N$ [42]. We can make the dependency of the annihilation and creation operators on position explicit by using the translation operator: $\hat{\psi}^\dagger(\mathbf{r}_1) = \exp(-i\hat{\mathbf{k}}\mathbf{r}_1)\hat{\psi}^\dagger(0)\exp(i\hat{\mathbf{k}}\mathbf{r}_1)$. Additionally, since the ground state is translationally invariant, we have $\hat{\mathbf{k}}|\Psi_0\rangle = 0$ [42]. This approach allows us to express the intermediate states as eigenstates of the momentum operator, $|n\rangle = |n\mathbf{k}\rangle$. Consequently, factors of the form $\exp(\pm i\mathbf{k}(\mathbf{r}_2 - \mathbf{r}_1))$ are introduced into Eq. 3.37.

Next, we Fourier transform Eq. 3.37 with respect to the time and position differences, $t_2 - t_1$ and $\mathbf{r}_2 - \mathbf{r}_1$, yielding the Lehmann representation of the Green's function given in momentum-frequency space:

$$G(\mathbf{k}, \omega) = \sum_{n\mathbf{k}} \frac{|\langle n\mathbf{k}(N + 1) | \hat{\psi}^\dagger(0) | \Psi_0 \rangle|^2}{\omega - (\epsilon_{n\mathbf{k}}(N + 1) + \mu) + i\delta} + \frac{|\langle n\mathbf{k}(N - 1) | \hat{\psi}(0) | \Psi_0 \rangle|^2}{\omega + (\epsilon_{n\mathbf{k}}(N - 1) - \mu) - i\delta}. \quad (3.40)$$

In this expression, we have introduced a small convergence factor δ . This is the Lehmann representation of the Green's function which is exact, as we have not introduced any approximations.

Looking at the denominators, we see that the Green's function is a meromorphic function of the complex variable ω , where its poles correspond to the many-body excitation energies. Depending on where the poles of the Green's function are located in the complex ω plane they correspond to quasiparticles with energy $\epsilon_{n\mathbf{k}}(N+1)$ or quasiholes with energy $\epsilon_{n\mathbf{k}}(N-1)$. We will refer to them as particles and holes for short, respectively. In other words, the Green's function encodes the quasiparticle spectrum of the system. The pole structure of the time-ordered Green's function is visualized in Fig. 3.1

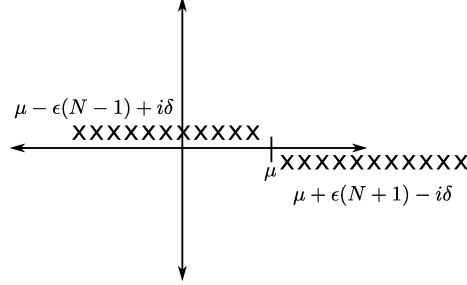


Figure 3.1: Positions of the poles of the time-ordered Green's function in the complex ω plane. The poles are marked with crosses and the chemical potential μ is indicated with a vertical bar. The poles with $\epsilon < \mu$ lying above the real axis correspond to excitations of $N - 1$ particle system, that is, to holes. The poles with $\epsilon > \mu$ lying below the real axis correspond to excitations of a $N + 1$ particle system, that is, to particles.

As an example to show how the quasiparticle energy and lifetime are connected to the poles of the Green's function consider the case where $t_1 > t_2$ and where the Green's function exhibits one single pole at $\omega = \epsilon_{n\mathbf{k}} - i\gamma$ in the fourth quadrant of the complex variable ω . In this case it can be shown [4, 42] that the Green's function evaluates to

$$iG(\mathbf{k}, t_2 - t_1) \sim +\theta(\mathbf{k} - \mathbf{k}_F) Z e^{(i\epsilon_{n\mathbf{k}} - \gamma)(t_1 - t_2)}, \quad (3.41)$$

$$iG_0(\mathbf{k}, t_2 - t_1) = +\theta(\mathbf{k} - \mathbf{k}_F) e^{+i\epsilon_{n\mathbf{k}}(t_1 - t_2)}, \quad (3.42)$$

where we have added the corresponding non-interacting Green's function for comparison. We see that the real part of the pole gives the quasiparticle energy, while the imaginary part gives the lifetime of the quasiparticle. The factor Z corresponds to the residue of the pole. The factor Z is also called the renormalization factor and is the amplitude of the quasiparticle.

Spectral function

Another fundamental quantity in MBPT that is closely related to the Green's function is the spectral function. The spectral function provides a direct connection between the theoretical description of quasiparticles and experimental observations, such as those from photoemission spectroscopy [50]. We first introduce the quantities

$$A(\mathbf{k}, \omega) = \sum_{n\mathbf{k}} |\langle n\mathbf{k}(N+1) | \hat{\psi}^\dagger(0) | \Psi_0 \rangle|^2 \delta(\omega - \epsilon_{\mathbf{k}}), \quad (3.43)$$

$$B(\mathbf{k}, \omega) = \sum_{n\mathbf{k}} |\langle n\mathbf{k}(N-1) | \hat{\psi}(0) | \Psi_0 \rangle|^2 \delta(\omega + \epsilon_{\mathbf{k}}). \quad (3.44)$$

With these quantities we can rewrite $G(\mathbf{k}, \omega)$ as an integral

$$G(\mathbf{k}, \omega) = \int_0^\infty \left[\frac{A(\mathbf{k}, \omega')}{\omega - (\omega' + \mu) + i\delta} + \frac{B(\mathbf{k}, \omega')}{\omega - (\omega' - \mu) - i\delta} \right] d\omega'. \quad (3.45)$$

The quantities A and B are real and positive quantities and are called the spectral functions. Each pole of the Green's function corresponds to one peak in the spectral function, with their positions corresponding to quasiparticle energies and their widths corresponding to the quasiparticle lifetimes. It can be shown [4] that the spectral function can be rewritten as

$$\frac{dN}{d\omega} = \sum_{\mathbf{k}} A(\mathbf{k}, \omega), \quad (3.46)$$

so that we can interpret the spectral function as a quasiparticle density of states. The relationship between the Green's function and the spectral functions A, B is given by [107, 4]

$$A(\mathbf{k}, \omega) = -\frac{1}{\pi} \text{Im}(G(\mathbf{k}, \omega)) \quad \omega > \mu, \quad (3.47)$$

$$B(\mathbf{k}, \omega) = \frac{1}{\pi} \text{Im}(G(\mathbf{k}, \omega)) \quad \omega < \mu. \quad (3.48)$$

3.3 Dyson's equation and the self-energy

In the previous section we introduced the single-particle Green's function and explored its physical interpretation, in particular how the Lehmann representation shows that the poles of the Green's function correspond to the quasiparticle energies and lifetimes. We have used non-interacting particles as examples to illustrate these concepts. However, to determine the quasiparticle energies of interacting particles, we must develop a method to evaluate the interacting Green's function, $G(\mathbf{k}, \omega)$. To achieve this, we introduce two fundamental concepts from MBPT: Dyson's equation and the self-energy Σ . Dyson's equation provides a framework for relating the interacting Green's function to the non-interacting one, while the self-energy contains the effects of a particle's interactions with the rest of the many-body system. These concepts can be approached in two different ways: a pictorial approach using Feynman diagrams, and an analytical approach using the equations of motion.

Dyson's equation and Σ from Feynman diagrams

We now briefly summarize the Feynman Diagram method used to determine interacting Green's functions. We start again from the definition of the Green's function:

$$iG(2, 1) = \langle \Psi_0 |_H T \left[\hat{\psi}(2)_H \hat{\psi}^\dagger(1)_H \right] | \Psi_0 \rangle_H. \quad (3.49)$$

Here, the field operators and the states are given in the Heisenberg picture. The central idea behind the Feynman diagram technique is to rewrite the Green's function into a form that is more suited for a perturbation theory approach. To expand the Green's function in powers of the interaction it will be necessary to change to the interaction picture. In order to do this we apply the principle of *adiabatic switching*, which allows us to connect the interacting to the non-interacting ground state. The following section closely follows the derivation in [3].

Using the principle of adiabatic switching on it can be shown that the desired transformation reads

$$|\psi_I(t)\rangle = U(t, -\infty)|\psi_H\rangle, \quad (3.50)$$

where the propagator $U(t, -t)$ is

$$U(t, -t) = T \exp \left\{ -i \int_{-t}^t \hat{H}_{int}(t') dt' \right\}, \quad (3.51)$$

and $\lim_{t \rightarrow -\infty} |\psi_H\rangle$ is the non-interacting ground state. Defining $U(t) = U(t, -\infty)$, we obtain the Green's function transformed into the interaction picture:

$$iG(2, 1) = \frac{\langle \Psi_0 |_H T \left[\hat{\psi}(2)_I \hat{\psi}^\dagger(1)_I U(+\infty) \right] | \Psi_0 \rangle_H}{\langle \Psi_0 |_H U(+\infty) | \Psi_0 \rangle_H}. \quad (3.52)$$

This will be our starting point for perturbation theory and Feynman diagrams. We emphasize again that in the interaction picture, the field operators obey the equations of motion of free particles. From now on all operators will be given in the interaction picture and we will omit the subscript “ I ”.

To arrive at a diagrammatic expansion of the Green's function we proceed in three steps. First we expand the propagator $U(\infty)$ into a series. In the next step we evaluate the resulting expectation values using Wick's theorem. Finally we interpret these expressions as diagrams and formulate the Feynman rules for position and momentum space.

Into the previous result, Eq. (3.52), we insert the propagator 3.51,

$$iG(2, 1) = \frac{\langle \Psi_0 |_H T \left[\hat{\psi}(2) \hat{\psi}^\dagger(1) \exp \left\{ -i \int_{-\infty}^{\infty} \hat{H}_{int}(t') dt' \right\} \right] | \Psi_0 \rangle_H}{\langle \Psi_0 |_H U(+\infty) | \Psi_0 \rangle_H}, \quad (3.53)$$

and expand the exponential:

$$\begin{aligned} iG(2, 1) &= \frac{1}{\langle \Psi_0 |_H U(+\infty) | \Psi_0 \rangle_H} \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n \\ &\times \langle \Psi_0 |_H T \left[\hat{\psi}(2) \hat{\psi}^\dagger(1) \hat{H}_{int}(t_1) \cdots \hat{H}_{int}(t_n) \right] | \Psi_0 \rangle_H \end{aligned} \quad (3.54)$$

We concentrate here for a moment on the expression

$$\langle \Psi_0 |_H T \left[\hat{\psi}(x) \hat{\psi}^\dagger(x') \hat{H}_{int}(t_1) \cdots \hat{H}_{int}(t_n) \right] | \Psi_0 \rangle_H. \quad (3.55)$$

The interaction Hamiltonian is given as an even product of destruction and annihilation field operators, see Eq. (3.11). Therefore, we have to evaluate terms of the form

$$\langle \Psi_0 |_H T \left[\hat{\psi}(x) \hat{\psi}^\dagger(x') \hat{\psi}(t_1) \cdots \hat{\psi}^\dagger(t_n) \right] | \Psi_0 \rangle_H \quad (3.56)$$

for which we use Wick's theorem [41] which states that the average over the ground state of a product of operators decomposes into a sum of all possible products of averages:

$$\begin{aligned} \langle \Psi_0 | T(\hat{A}\hat{B}\hat{C} \cdots \hat{X}\hat{Y}\hat{Z}) | \Psi_0 \rangle &= \langle \Psi_0 | T(\hat{A}\hat{B}) | \Psi_0 \rangle \langle \Psi_0 | T(\hat{C}\hat{D}) | \Psi_0 \rangle \cdots \langle \Psi_0 | T(\hat{Y}\hat{Z}) | \Psi_0 \rangle \\ &\pm \langle \Psi_0 | T(\hat{A}\hat{C}) | \Psi_0 \rangle \langle \Psi_0 | T(\hat{B}\hat{D}) | \Psi_0 \rangle \cdots \langle \Psi_0 | T(\hat{Y}\hat{Z}) | \Psi_0 \rangle \pm \cdots \end{aligned} \quad (3.57)$$

We now return to the series expansion of the Green's function, Eq. (3.54). As an example of how to develop the Feynman rules for a theory, we take as $\hat{H}_{int}(t)$ a two body interaction in second quantization

$$\hat{H}_{int}(t_1) = \frac{1}{2} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \hat{\psi}^\dagger(\mathbf{r}_1, t_1) \hat{\psi}^\dagger(\mathbf{r}_2, t_1) v(\mathbf{r}_1 - \mathbf{r}_2) \hat{\psi}(\mathbf{r}_2, t_1) \hat{\psi}(\mathbf{r}_1, t_1), \quad (3.58)$$

where we write the interaction as $v(1-2) = V(\mathbf{r}_1 - \mathbf{r}_2)\delta(t_1 - t_2)$ so that the interaction integral has the form $\int \hat{H}_{int}(t_1, t_2) dt_1 dt_2$. For the four dimensional integrals and interaction we introduce the notation $\int d^3\mathbf{r}_1 dt_1 = \int dx_1$.

With all this, expanding Eq. (3.54) to first order yields

$$\begin{aligned} iG(2, 1) &= \frac{1}{\langle \Psi_0 |_H U(+\infty) | \Psi_0 \rangle_H} \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \\ &\quad \frac{(-i)}{2} \langle \Psi_0 |_H T \left[\hat{\psi}(2) \hat{\psi}^\dagger(1) \hat{\psi}^\dagger(x_1) \hat{\psi}^\dagger(x_2) \hat{\psi}(x_2) \hat{\psi}(x_1) \right] | \Psi_0 \rangle_H V(x_1 - x_2). \end{aligned} \quad (3.59)$$

Now we apply Wick's theorem. The three creation and three annihilation operators can be contracted in 6 different ways. In general, a time ordered product of N creation and N annihilation operators can be contracted in $N!$ different ways. In our case these six combinations are

$$\begin{aligned} \langle \Psi_0 |_H T [\dots] | \Psi_0 \rangle_H &= G_0(2, 1) G_0(x_2, x_1) G_0(x_1, x_2) - G_0(2, 1) G_0(x_1, x_1) G_0(x_2, x_2) \\ &\quad + G_0(2, x_1) G_0(x_1, x_2) G_0(x_2, 1) - G_0(2, x_1) G_0(x_2, x_2) G_0(x_1, 1) \\ &\quad + G_0(2, x_2) G_0(x_2, x_1) G_0(x_1, 1) - G_0(2, x_2) G_0(x_1, x_1) G_0(x_2, 1), \end{aligned} \quad (3.60)$$

where we have used the free particle Green's function $G_0(x, x') = \langle T(\hat{\psi}(x) \hat{\psi}^\dagger(x')) \rangle$. We now represent this expression graphically with Feynman diagrams. The four dimensional points are represented on a x, t plane. The arguments of the Green's functions are connected by an arrow and the points appearing in the argument of the interaction are connected by a wavy line. Since the interaction is assumed to act instantaneously the points connected by the interaction have the same time argument.

We now divide all diagrams into connected and disconnected diagrams. Connected diagrams are diagrams where all points are connected to the external points by lines. We now state without proof the following theorem: the factor

$$\frac{1}{\langle \Psi_0 |_H U(+\infty) | \Psi_0 \rangle_H} \quad (3.61)$$

cancels all disconnected diagrams. Proofs can be found in all standard textbooks on MBPT [3, 107, 41]. This means that expanding the Green's function

$$iG(2, 1)_{\text{conn.}} = \langle \Psi_0 |_H T \left[\hat{\psi}(2) \hat{\psi}^\dagger(1) \exp \left\{ -i \int_{-\infty}^{\infty} \hat{H}_{int}(t') dt' \right\} \right] | \Psi_0 \rangle_H \quad (3.62)$$

into a perturbation series gives us all connected diagrams. Furthermore, we can simplify the expression by noting that permuting the n different interaction Hamiltonians $\hat{H}_{int}(t_1) \dots \hat{H}_{int}(t_m)$ gives identical diagrams where only the labels are swapped. We can therefore cancel the factor

$\frac{1}{n!}$ in the series expansion of Eq. (3.54) and consider only topologically different diagrams, that is, diagrams which cannot be obtained by swapping labels.

In summary, we have developed a series expansion of the Green's function in powers of the interaction where each term of the series can be represented as a Feynman diagram. The above procedure is summarized by the so-called Feynman rules, which help us to translate a given diagram into an expression involving Green's function. The Feynman diagram technique and the associated Feynman rules can be formulated in coordinate space - as above - or in momentum space for the Green's function $G(\mathbf{k}, \omega)$. The Feynman rules are listed in the standard textbooks of MBPT [107, 42, 4].

Using the Feynman diagram technique, it is possible to perform a partial summation of certain diagrams in the series expansion of the Green's function G . To achieve this, we introduce the self-energy Σ , which is defined as the sum of all connected diagrams that can be connected to the rest of the diagram by two non-interacting Green's function lines G_0 . If a self-energy diagram cannot be separated into distinct diagrams connected by G_0 lines, it is called an irreducible self-energy diagram and denoted by Σ_0 ; otherwise, it is called reducible.

Now consider a particular subset of diagrams summarized by an irreducible self-energy Σ_0 . Among all possible interactions represented as Feynman diagrams in the series expansion of G , the interacting Green's function G will contain a partial sum of all irreducible self-energy insertions Σ_0 connected by non-interacting Green's functions G_0 . This sum can be expressed as

$$G = G_0 + G_0 \Sigma_0 G_0 + G_0 \Sigma_0 G_0 \Sigma_0 G_0 + \dots \quad (3.63)$$

If we isolate the first non-interacting Green's function G_0 and the first self-energy insertion Σ_0 from this infinite series, then the rest of the diagram still represents the interacting Green's function G . Therefore, we can write

$$G = G_0 + G_0 \Sigma \underbrace{(G_0 + G_0 \Sigma_0 G_0 + \dots)}_{=G}, \quad (3.64)$$

which simplifies in momentum and coordinate space to

$$G(\mathbf{k}, \omega) = G_0(\mathbf{k}, \omega) + G_0(\mathbf{k}, \omega) \Sigma_0(\mathbf{k}, \omega) G(\mathbf{k}, \omega), \quad (3.65)$$

$$G(2, 1) = G_0(2, 1) + \int G_0(2, 2') \Sigma_0(2', 1') G(1', 1) d(1' 2'). \quad (3.66)$$

This result is known as Dyson's equation. Dyson's equation can also be expressed in the following equivalent forms:

$$G^{-1} = (G_0)^{-1} - \Sigma_0, \quad (3.67)$$

$$G = \frac{G_0}{1 - G_0 \Sigma_0}. \quad (3.68)$$

The usefulness of partially summing a subset of diagrams using Dyson's equation and the self-energy comes from the exponential scaling of the Wick contraction procedure. We have seen that a term containing $2N$ field operators leads to $N!$ Wick contractions, so Wick contraction scales exponentially. While evaluating the series expansion for $N = 1$ or $N = 2$ is trivial, it becomes cumbersome for larger values of N . Using the self-energy, we can partially sum an infinite series of diagrams, even though the diagrammatic expression of the self-energy itself is comparatively simple. Below we will see how we can interpret the self-energy.

Equation of motion approach

The self-energy can also be derived from the equations of motion of the Heisenberg operators $\hat{\psi}^\dagger(x), \hat{\psi}(x)$ [4, 118]. Consider the Hamiltonian in second quantization

$$H = \int \hat{\psi}^\dagger(\mathbf{r}, t) h(\mathbf{r}) \hat{\psi}(\mathbf{r}, t) d\mathbf{r} + H_{\text{int}}, \quad (3.69)$$

where $\hat{\psi}(\mathbf{r}, t)$ are the field operators in the Heisenberg representation and H_{int} is some yet unspecified interaction Hamiltonian. The Heisenberg equations of motion,

$$i \frac{\partial \hat{\psi}(\mathbf{r}, t)}{\partial t} = [\hat{\psi}(\mathbf{r}, t), H] \quad (3.70)$$

yield

$$i \frac{\partial \hat{\psi}(\mathbf{r}, t)}{\partial t} = h(\mathbf{r}, t) \hat{\psi}(\mathbf{r}, t) + [\hat{\psi}(\mathbf{r}, t), H_{\text{int}}]. \quad (3.71)$$

We next need the time derivative of the Green's function:

$$i \frac{\partial}{\partial t} G(\mathbf{r}, t; \mathbf{r}', t') = i \frac{\partial}{\partial t} \langle \Psi_0 | T [\hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t')] | \Psi_0 \rangle, \quad (3.72)$$

$$= \frac{\partial}{\partial t} (\hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \theta(t - t') - \hat{\psi}^\dagger(\mathbf{r}', t') \hat{\psi}(\mathbf{r}, t) \theta(t' - t)), \quad (3.73)$$

$$= \langle T [\frac{\partial \hat{\psi}(\mathbf{r}, t)}{\partial t} \hat{\psi}^\dagger(\mathbf{r}', t')] \rangle + \delta(\mathbf{r}' - \mathbf{r}) \delta(t' - t). \quad (3.74)$$

In the next step we multiply Eq. (3.71) separately from the right by $\hat{\psi}^\dagger(\mathbf{r}', t') \theta(t - t')$ and from the left by $\hat{\psi}^\dagger(\mathbf{r}, t) \theta(t' - t)$ and subtract the equations, which gives

$$\left(i \frac{\partial}{\partial t} + h(\mathbf{r}) \right) G(\mathbf{r}, t; \mathbf{r}', t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') - iT [\hat{\psi}(\mathbf{r}, t), H_{\text{int}}] \hat{\psi}^\dagger(\mathbf{r}', t'). \quad (3.75)$$

In the case of two-particle interactions the interaction Hamiltonian is given as

$$H_{\text{int}} = \frac{1}{2} \int \hat{\psi}^\dagger(1') \hat{\psi}^\dagger(2') v(1' - 2') \hat{\psi}(2') \hat{\psi}(1') d(1' 2'), \quad (3.76)$$

which gives for the commutator $[\hat{\psi}(1), H_{\text{int}}]$

$$[\hat{\psi}(1), H_{\text{int}}] = \int v(1 - 2') \hat{\psi}^\dagger(2') \hat{\psi}(2') \hat{\psi}(1) d2', \quad (3.77)$$

so that we obtain as a result the equations of motion for the Green's function

$$\left(i \frac{\partial}{\partial t} + h(1) \right) G(1, 2) + i \underbrace{\int v(1 - 2') T [\hat{\psi}^\dagger(2') \hat{\psi}(2') \hat{\psi}(1) \hat{\psi}^\dagger(1')] d(2')}_{=G_2(2', 1, 2^+, 2)} = \delta(1 - 2). \quad (3.78)$$

The time-ordered product of four field-operators is related to the two-particle Green's function which will be encountered below in the context of two-particle excitations and the Bethe-Salpeter equation. For now we proceed with rewriting this equation. By splitting the two

particle Green's function into free and bound parts, it can be shown [118] that the equation of motion can be rewritten in the form

$$\left(i\frac{\partial}{\partial t} + h(1)\right) G(1, 2) + \int \Sigma(1, 2) G(2, 1) d2 = -\delta(1 - 2), \quad (3.79)$$

where Σ is the self-energy. Or in other words, the self-energy incorporates all the complex two-particle interactions into a diagram which can be joined to the one-particle Green's function G . We can also derive Dyson's equation using Eq. (3.79). Using the definition of the inverse of the Green's function

$$\int G_0^{-1}(1, 3) G_0(3, 2) d3 = \delta(1, 2). \quad (3.80)$$

and the expression for the non-interacting Green's function

$$\left(i\frac{\partial}{\partial t} + h(1)\right) G_0(1, 2) = \delta(1, 2) \quad (3.81)$$

we can rewrite Eq. (3.79) in the form

$$G(1, 2) = G_0(1, 2) + \int G_0(1, 1') \Sigma(1', 2') G(2', 2) d(1' 2'), \quad (3.82)$$

which is again the Dyson equation that we derived in the previous section using Feynman diagrams.

Quasiparticle energies from the self-energy

To understand the relationship between the quasiparticle energies and the self-energy we consider the case of a homogeneous medium. In this case the Green's function depends only on space and time differences $\mathbf{r} - \mathbf{r}'$, $t - t'$ in which case Dyson's equation simplifies to [41]

$$G(\mathbf{k}, \omega) = \frac{1}{G_0^{-1}(\mathbf{k}, \omega) - \Sigma(\mathbf{k}, \omega) + i\delta}. \quad (3.83)$$

Using the relationship for the non-interacting Green's function

$$(\omega - \epsilon_{n\mathbf{k}}^0) G_0(\mathbf{k}, \omega) = 1 \quad (3.84)$$

we obtain

$$G(\mathbf{k}, \omega) = \frac{1}{\omega - (\epsilon_{n\mathbf{k}}^0 + \text{Re}(\Sigma(\mathbf{k}, \omega)) + i(\delta - \text{Im}(\Sigma(\mathbf{k}, \omega)))}. \quad (3.85)$$

In other words, the real part of the self-energy determines the change in energy of a particle due to the interactions of the particle with the rest of the many-body system. The energy of this particle is called the quasiparticle energy and below we will discuss how the quasiparticle energies are determined in practice. The imaginary part on the other hand changes the imaginary part of the quasiparticle pole which means that it determines the quasiparticle lifetime.

3.3.1 Note on the Hartree contribution to the self-energy

It is common in the literature to separate out the Hartree energy

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (3.86)$$

from the self-energy, add it to the single-particle operator $h(\mathbf{r})$, and refer to the remaining diagrams as the “self energy”. This separation can be understood by evaluating the first term of a series expansion of the self-energy in powers of the interaction [42], by decomposing the two-particle Green’s function into free and bound parts [118], or by deriving the Dyson equation using the functional derivative technique [170]. In either case, the Dyson equation is then modified to

$$\left(i \frac{\partial}{\partial t} + V_{\text{ext}}(\mathbf{r}_1) \right) G(1, 2) + \int \Sigma(1, 2) G(2, 1) d2 = -\delta(1 - 2), \quad (3.87)$$

$$\rightarrow \left(i \frac{\partial}{\partial t} + V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1) \right) G(1, 2) + \int \tilde{\Sigma}(1, 2) G(2, 1) d2 = -\delta(1 - 2), \quad (3.88)$$

where the self-energy without the Hartree contribution $\tilde{\Sigma}$ is occasionally called the mass operator M [62, 170, 118]. In the following we will indicate whether the self-energy includes the Hartree energy.

3.4 Screening

We have now introduced the self-energy, the fundamental concept in MBPT. The self-energy contains the effects of interactions between a particle and the many-body system, determining both the energy and lifetime of the resulting quasiparticle. By employing Dyson’s equation, we can partially sum over all particular subsets of irreducible self-energy diagrams.

To calculate the quasiparticle energies, we now require an approximation for Σ . The state-of-the-art approach is the GW approximation, as introduced in Hedin’s seminal work [62]. In the GW approximation, the self-energy is expressed as the product of the Green’s function G and the screened interaction W . The concept of the screened interaction will be introduced in this section.

Consider an electron gas in which we place a negative point charge at point $\mathbf{r}$. The point charge will repel the electrons next to it so that close to the point charge there is a depletion of electrons, that is, a positive charge distribution. This positive charge distribution will again attract electrons, which results in a negative charge distribution, and so on. An electron positioned at point $\mathbf{r}'$ far from the negative point charge will therefore feel not the bare interaction $V(\mathbf{r} - \mathbf{r}')$, but a reduced interaction which we call the screened, or effective, interaction $W(\mathbf{r} - \mathbf{r}')$. The ratio defines the dielectric function ϵ of the medium [42, 105],

$$W = \frac{V}{\epsilon}. \quad (3.89)$$

By using a model for the dielectric function ϵ we can account for the weakening of the Coulomb interaction in the many-body system. The particular model for screening that is used in this thesis is the random phase approximation (RPA) which was first introduced by Bohm

and Pines [23, 136, 24]. Within the RPA the many body screening effects are described in terms of a momentum and frequency dependent function $W(\mathbf{q}, \omega)$, where the momentum dependence accounts for the non-locality of W and the frequency dependence account for the time dependent polarization effects. While in this thesis we are mainly interested in the RPA as a model for the screened interaction we point out that the RPA formalism can be used to calculate response functions and correlation energies. However, these topics are beyond the scope of this thesis and we point the reader to the detailed review of Ren [144] and in the theses of Harl [59] and Riemelmoser [145].

RPA from Feynman diagrams

In this section we will derive the RPA screened interaction using the method of Feynman diagrams.

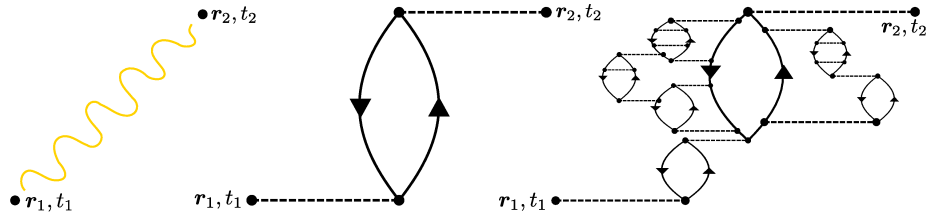


Figure 3.2: Sketch of how the screened interaction is represented as Feynman diagrams.

Let the interaction line corresponding to V represent a photon propagating through the many-body system. The photon polarizes the medium which we visualize by creating an electron-hole pair at position and time $\mathbf{r}_1$ and t_1 . This electron-hole pair then annihilates at a later time t_2 and position $\mathbf{r}_2$. This type of graph which can be joined by two external interaction lines is a simple example of a so-called polarization graph. In principle, more complex processes can occur, involving multiple electron-hole pairs between times t_1 and t_2 , as depicted in the right panel of Fig. 3.2.

To generalize this concept, we introduce the polarization $P(\mathbf{r}, \mathbf{r}', t, t')$, which represents the sum of all connected diagrams that can be linked to the rest of the diagram by two interaction lines V . If a diagram cannot be further decomposed into smaller polarization diagrams by cutting interaction lines, it is referred to as V -irreducible polarization $P_0(\mathbf{r}, \mathbf{r}', t, t')$. This is analogous to the self-energy insertions in the single particle Green's function. The polarization graph in the middle panel of Fig. 3.2 is an example of an irreducible polarization graph.

We can now define the effective or screened interaction W as a partial sum over all chosen irreducible polarization diagrams. Drawing an analogy to the Dyson equation for the single-particle Green's function, we obtain:

$$W = V + VP_0 \underbrace{(V + VP_0VP_0V + \dots)}_{=W} = V + VP_0W. \quad (3.90)$$

Writing this equation in terms of W ,

$$W = V(1 - VP_0)^{-1}, \quad (3.91)$$

and using $\epsilon = V/W$ leads to the dielectric function:

$$\epsilon = 1 - VP_0. \quad (3.92)$$

The RPA corresponds to the simplest choice of the irreducible polarization diagram where we approximate P_0 by the so-called pair-bubble diagram shown in the middle panel of Fig. 3.2. Or in other words, the RPA is the partial sum of all pair-bubble excitations in the system. Consequently, the dielectric function within the RPA framework is given by:

$$\epsilon^{\text{RPA}} = 1 - VP_{\text{pair bubble}}. \quad (3.93)$$

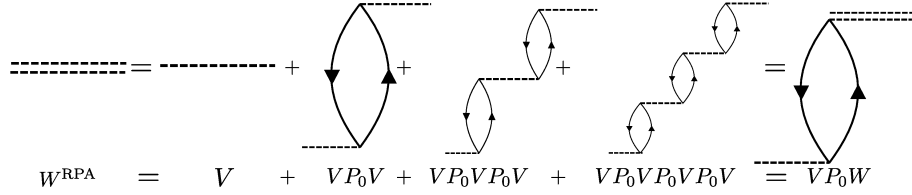


Figure 3.3: Feynman diagram analysis of the screened interaction approximated in the RPA. The screened interaction W^{RPA} is the partial sum of all pair bubble diagrams.

Evaluating the pair-bubble diagram using the Feynman rules gives $P_{\text{pair bubble}} = -2iG_0G_0$. The factor 2 due to spin degeneracy. We seek the expression that is used in practice, that is, the momentum and frequency dependent dielectric function $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$. For this we first transform Eq. (3.93) into momentum space:

$$\epsilon_{\mathbf{G},\mathbf{G}'}^{\text{RPA}}(\mathbf{q},\omega) = \delta_{\mathbf{G},\mathbf{G}'} - V_{\mathbf{G}}(\mathbf{q})P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega), \quad (3.94)$$

where we omit the "pair bubble" subscript to simplify notation and where the Coulomb kernel in momentum space is given as

$$V_{\mathbf{G}}(\mathbf{q}) = \frac{4\pi e^2}{|\mathbf{q} + \mathbf{G}|^2} \delta_{\mathbf{G},\mathbf{G}'}. \quad (3.95)$$

The momentum and frequency dependent polarizability $P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ is obtained from a Fourier transform,

$$P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \int e^{-i(\mathbf{G}+\mathbf{q})\mathbf{r}} P(\mathbf{r},\mathbf{r}',\omega) e^{i(\mathbf{G}'+\mathbf{q})\mathbf{r}'} d\mathbf{r} d\mathbf{r}'. \quad (3.96)$$

To evaluate P we use another form of the Green's function which is obtained by inserting into Eq. (3.29) the definition of the field operators, Eq. (3.6), where the φ_i are a complete set of states. Furthermore, we assume for simplicity a gapped system with occupied valence states i and unoccupied conduction band states a . Then the non-interacting Green's function reads

$$G_0(\mathbf{r},\mathbf{r}',t-t') = \sum_a \varphi_a(\mathbf{r})\varphi_a^*(\mathbf{r}')e^{-i\epsilon_a(t-t')}\theta(t-t') - \sum_i \varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')e^{-i\epsilon_i(t-t')}\theta(t'-t). \quad (3.97)$$

Multiplying out the expression $G_0(\mathbf{r},\mathbf{r}',t-t')G_0(\mathbf{r}',\mathbf{r},t'-t)$ gives

$$\begin{aligned} P(\mathbf{r},\mathbf{r}',t-t') &= -2iG_0(\mathbf{r},\mathbf{r}',t-t')G_0(\mathbf{r}',\mathbf{r},t'-t) \\ &= -2i \sum_{ia} \varphi_a(\mathbf{r})\varphi_a^*(\mathbf{r}')\varphi_i(\mathbf{r}')\varphi_i^*(\mathbf{r}) \\ &\quad \times \left[e^{-i(\epsilon_a-\epsilon_i)(t-t')}\theta(t-t') + e^{-i(\epsilon_a-\epsilon_i)(t'-t)}\theta(t'-t) \right]. \end{aligned} \quad (3.98)$$

In order to obtain the Fourier transform with respect to the variable $t - t'$ we use the integral representation of the Heaviside step function, see Eq. (7.43) of Ref. [42]:

$$\theta(\pm x) = \lim_{\delta \rightarrow 0} \mp \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega x}}{\omega \pm i\delta}. \quad (3.99)$$

Representing the Heaviside step function as an integral and inserting into Eq. (3.98) we find

$$P(\mathbf{r}, \mathbf{r}', \omega) = \sum_{ia} \varphi_a(\mathbf{r}) \varphi_a^*(\mathbf{r}') \varphi_i(\mathbf{r}') \varphi_i^*(\mathbf{r}) \left[\frac{1}{\omega - (\epsilon_a - \epsilon_i) + i\delta} - \frac{1}{\omega - (\epsilon_a - \epsilon_i) - i\delta} \right], \quad (3.100)$$

where the first and second term in the square brackets are called resonant and antiresonant part, respectively. The spatial Fourier transforms of Eq. (3.96) yields the desired result for the pair-bubble polarizability in momentum space

$$P_{\mathbf{G}, \mathbf{G}'}^0(\mathbf{q}, \omega) = \sum_{ai} \langle a | e^{i(\mathbf{G} + \mathbf{q})\mathbf{r}} | i \rangle \langle a | e^{-i(\mathbf{G}' + \mathbf{q})\mathbf{r}} | i \rangle \left[\frac{1}{\omega - (\epsilon_a - \epsilon_i) + i\delta} - \frac{1}{\omega - (\epsilon_a - \epsilon_i) - i\delta} \right]. \quad (3.101)$$

Inserting this result into the expression for the RPA dielectric function, Eq. (3.93), we obtain our final result which is the momentum and frequency dependent dielectric function in the random phase approximation:

$$\epsilon_{\mathbf{G}, \mathbf{G}'}^{\text{RPA}}(\mathbf{q}, \omega) = \delta_{\mathbf{G}, \mathbf{G}'} - V_{\mathbf{G}}(\mathbf{q}) \sum_{ai} \langle a | e^{i(\mathbf{G} + \mathbf{q})\mathbf{r}} | i \rangle \langle a | e^{-i(\mathbf{G}' + \mathbf{q})\mathbf{r}} | i \rangle \left[\frac{1}{\omega - (\epsilon_a - \epsilon_i) + i\delta} - \frac{1}{\omega - (\epsilon_a - \epsilon_i) - i\delta} \right]. \quad (3.102)$$

This result can also be derived using the method of the self-consistent field [6, 199]. Note that the dielectric function above corresponds to the longitudinal, or density-density, dielectric function, that is, the dielectric function that describes the density response due to an external charge density. From the equation above we obtain the screened interaction in momentum-frequency space

$$W_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega) = \frac{\epsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega)}{|\mathbf{G} + \mathbf{q}| |\mathbf{G}' + \mathbf{q}|}. \quad (3.103)$$

3.5 Hedin equations and quasiparticle energies

We have now introduced the principal quantities of many-body perturbation theory. The Green's function encapsulates all the information about single-particle excitations in a many-body system, where its complex poles give us the quasiparticle energies and lifetimes. The interactions between a particle and the many-body system are captured by the self-energy, which, through the Dyson equation, links the non-interacting and interacting Green's functions. Finally, we have introduced the concept of screening, where the dielectric function describes how the interaction between two particles is weakened by the many-body environment.

Now, we introduce the scheme that is used in practice to calculate quasiparticle energies. When introducing the self-energy we saw that the equations of motion of the single-particle Green's function

$$\left(i\frac{\partial}{\partial t_1} + \nabla_1^2\right) G(1, 2) = \delta(1 - 2) - \int V(1 - 2) G_2(2, 2, 1, 2) d2. \quad (3.104)$$

linked the single-particle Green's function G with the two-particle Green's function G_2 . If we wished to derive the equations of motion of the two-particle Green's function we would obtain an equation which links G_2 with the three particle Green's function G_3 . This way we obtain a hierarchy of Green's function where the equation of motion of G_n links G_n to G_{n+1} and lower orders of G [34].

Hedin [62] and Hedin and Lundquist [61] rewrote this hierarchy of equations into a set of five coupled equations, also called Hedin's equations. These five equations are written in terms of the physical quantities that describe the many-body system, such as the Green's function and the screened interaction. The Hedin equations read [105]

$$\Sigma(1, 2) = \int iG(1, 4)W(1^+, 3)\tilde{\Gamma}(4, 2; 3)d(34), \quad (3.105)$$

$$G(1, 2) = G_0(1, 2) + \int G_0(1, 3)\Sigma(3, 4)G(4, 2)d(34), \quad (3.106)$$

$$\tilde{\Gamma}(1, 2; 3) = \delta(1, 2)\delta(1, 3) + \frac{\delta\Sigma(1, 2)}{\delta V(3)}, \quad (3.107)$$

$$P(1, 2) = -i \int G(1, 3)G(4, 1)\tilde{\Gamma}(3, 4; 2)d(34), \quad (3.108)$$

$$W(1, 2) = V(1, 2) + \int V(1, 3)P(3, 4)W(4, 2)d(34), \quad (3.109)$$

where we have introduced the irreducible vertex $\tilde{\Gamma}$. These equations must be solved self-consistently. The process begins by making an initial approximation for the vertex. Using this approximation, the equations are solved iteratively, updating the vertex and other quantities at each step.

An approximation that is widely used and which is also used in this thesis is the GW approximation (GWA) introduced by Hedin [62]. In this approximation the second term of the irreducible vertex $\tilde{\Gamma}$ is neglected in all iterations. When the Hedin equation are iterated only once, we obtain the G_0W_0 , or 'single-shot', self-energy:

$$\Sigma^{(0)}(1, 2) = iG_0(1, 2)W_0(1, 2). \quad (3.110)$$

To derive the quasiparticle equations we start from the Dyson equation of the single-particle Green's function,

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = G_0(\mathbf{r}_1, \mathbf{r}_2; \omega) + \int G_0(\mathbf{r}_1, \mathbf{r}'_1; \omega)\Sigma(\mathbf{r}'_1, \mathbf{r}'_2; \omega)G(\mathbf{r}'_2, \mathbf{r}_2; \omega)d\mathbf{r}'_1d\mathbf{r}'_2. \quad (3.111)$$

Here, the self-energy is composed of the Hartree term and the G_0W_0 self-energy, see Sec. 3.3.1:

$$\Sigma = \Sigma_H + \Sigma^{(0)}. \quad (3.112)$$

For the non-interacting Green's function $G_0(\mathbf{r}_1, \mathbf{r}_2; \omega)$ we use the Fourier transform of Eq. (3.97). The complete set of states that is used to expand the Green's function is given by the eigenstates of the Hamiltonian $H = -\nabla^2/2 + V_{\text{ext}}$:

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r})\right)\varphi_i^0(\mathbf{r}) = \epsilon_i^0\varphi_i^0(\mathbf{r}). \quad (3.113)$$

In the next step, we introduce the operator $L_0 = \omega + \nabla_1^2/2 - V_{\text{ext}}(\mathbf{r}_1)$ for which

$$L_0 G_0(\mathbf{r}_1, \mathbf{r}'_1; \omega) = \delta(\mathbf{r}_1 - \mathbf{r}'_1). \quad (3.114)$$

holds [42]. Multiplying Eq. (3.111) from the left with L_0 gives

$$L_0 G(\mathbf{r}_1, \mathbf{r}_2; \omega) = \delta(\mathbf{r}_1, \mathbf{r}_2) + \int \Sigma(\mathbf{r}_1, \mathbf{r}'_2; \omega) G(\mathbf{r}'_2, \mathbf{r}_2; \omega) d\mathbf{r}'_2. \quad (3.115)$$

Inserting the expressions for L_0 and $G(\mathbf{r}_1, \mathbf{r}_2; \omega)$ results in

$$\begin{aligned} &\left(\omega + \frac{1}{2}\nabla_1^2 - V_{\text{ext}}(\mathbf{r}_1)\right) \sum_j \varphi_j(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \left(\frac{\theta(\epsilon_j - \mu)}{\omega - \epsilon_j + i\delta} + \frac{\theta(\mu - \epsilon_j)}{\omega - \epsilon_j - i\delta}\right) \\ &- \int \Sigma(\mathbf{r}_1, \mathbf{r}'_2; \omega) \sum_j \varphi_j(\mathbf{r}'_2) \varphi_j^*(\mathbf{r}_2) \left(\frac{\theta(\epsilon_j - \mu)}{\omega - \epsilon_j + i\delta} + \frac{\theta(\mu - \epsilon_j)}{\omega - \epsilon_j - i\delta}\right) \\ &= \delta(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (3.116)$$

In the final step we multiply by $\varphi_k(\mathbf{r}_2)$ and integrate over $d\mathbf{r}_2$ which gives after adding the Hartree energy to the one-body operators and rearranging

$$\left(-\frac{1}{2}\nabla_1^2 + V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1)\right) \varphi_k(\mathbf{r}_1) + \int \Sigma^{(0)}(\mathbf{r}_1, \mathbf{r}_2; \omega) \varphi_k(\mathbf{r}_2) d\mathbf{r}_2 = \epsilon_k^{\text{qp}}(\omega) \varphi_k(\mathbf{r}_1). \quad (3.117)$$

These are the quasiparticle equations. When one solves these equations, one obtains the quasiparticle energies $\epsilon_k^{\text{qp}}(\omega)$ and the quasiparticle wavefunctions φ_k . In this form, the self-energy $\Sigma^{(0)}$ acts as a non-local and frequency-dependent potential. Since the self-energy is generally non-Hermitian, the resulting eigenvalues are complex, with the real part corresponding to the quasiparticle energy and the imaginary part giving the quasiparticle lifetime [68].

The frequency dependence of the self-energy implies that the quasiparticle energies themselves are frequency dependent. When discussing the physical meaning of the Green's function, we saw that the quasiparticles correspond to poles of the Green's function G . For sufficiently long-lived quasiparticles this implies that the self-energy should also be evaluated at the quasiparticle energy ϵ_k^{qp} . Thus, the quasiparticle equation can be written

$$\left(-\frac{1}{2}\nabla_1^2 + V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1)\right) \varphi_k(\mathbf{r}_1) + \int \Sigma^{(0)}(\mathbf{r}_1, \mathbf{r}_2; \omega = \epsilon_k^{\text{qp}}) \varphi_k(\mathbf{r}_2) d\mathbf{r}_2 = \epsilon_k^{\text{qp}} \varphi_k(\mathbf{r}_1). \quad (3.118)$$

Next, we express the quasiparticle wave functions as a linear combination of Kohn-Sham (KS) orbitals obtained from a previous DFT calculation. Specifically, we write the quasiparticle wave function $\varphi_i(\mathbf{r})$ as

$$\varphi_i(\mathbf{r}) = \sum_{n\mathbf{k}} \alpha_{i,n\mathbf{k}} \varphi_{n\mathbf{k}}(\mathbf{r}), \quad (3.119)$$

where $\alpha_{i,n\mathbf{k}}$ are the expansion coefficients, and $\varphi_{n\mathbf{k}}(\mathbf{r})$ are the KS orbitals. At this point, we simplify the problem by neglecting the off-diagonal elements of the self-energy Σ , as is commonly done in quasiparticle calculations [68]. The quasiparticle energies ϵ_k^{qp} are then given by the solutions (or roots) of

$$\langle n\mathbf{k} | -\frac{1}{2}\nabla_1^2 + V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1) + \Sigma^{(0)}(\mathbf{r}_1, \mathbf{r}_2; \omega = \epsilon_k^{\text{qp}}) - \epsilon_k^{\text{qp}} | n\mathbf{k} \rangle = 0. \quad (3.120)$$

Viewing the term inside the brackets as a function $f(\epsilon_k^{\text{qp}})$ and using the Newton-Raphson method to find the root near the KS eigenvalues $\epsilon_{n\mathbf{k}}$ of the states $|n\mathbf{k}\rangle$,

$$\epsilon_k^{\text{qp}} = \epsilon_{n\mathbf{k}} - \frac{f(\epsilon_{n\mathbf{k}})}{f'(\epsilon_{n\mathbf{k}})}, \quad (3.121)$$

we obtain

$$\epsilon_k^{\text{qp}} = \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}} \langle n\mathbf{k} | -\frac{1}{2}\nabla_1^2 + V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1) + \Sigma^{(0)}(\mathbf{r}_1, \mathbf{r}_2; \omega = \epsilon_{n\mathbf{k}}) - \epsilon_{n\mathbf{k}} | n\mathbf{k} \rangle, \quad (3.122)$$

where we have re-obtained the normalization factor

$$Z_{n\mathbf{k}} = \left(\langle n\mathbf{k} | 1 - \frac{\partial \Sigma^{(0)}(\mathbf{r}_1, \mathbf{r}_2; \omega)}{\partial \omega} \Big|_{\omega=\epsilon_{n\mathbf{k}}} | n\mathbf{k} \rangle \right)^{-1}. \quad (3.123)$$

By inserting the expression for the G_0W_0 self-energy into the quasiparticle equation, we obtain the G_0W_0 quasiparticle energies, denoted as $\epsilon^{G_0W_0}$. It is important to note that in the single-shot G_0W_0 method only the eigenvalues are updated while the orbitals remain fixed at the level of the initial approximation, such as GGA.

3.6 Bethe-Salpeter Equation

The Green's function formalism that we have introduced so far primarily addresses single-particle excitations. However, for the X-ray spectroscopies investigated in this thesis, this single-particle framework is inadequate. In absorption experiments, both a (quasi-)particle and a (quasi-)hole are excited, and their interaction leads to bound states of an electron and a hole which are called excitons. These excitons strongly modify X-ray absorption spectra and they are the primary focus of this thesis. To accurately describe such two-particle excitations within the framework of MBPT, it is necessary to introduce the two-particle Green's function

$$G_2(1, 2, 3, 4) = \langle \Psi_0 | T \left[\hat{\psi}(1) \hat{\psi}(2) \hat{\psi}^\dagger(3) \hat{\psi}^\dagger(4) \right] | \Psi_0 \rangle. \quad (3.124)$$

Depending on the order of operators this expression can describe either the propagation of two particles, of two holes or one particle and one hole. We first separate from the two-particle Green's function the uncorrelated part GG part [170, 125] and define the two-particle correlation function

$$L(1, 2, 3, 4) = -G_2(1, 2, 3, 4) + G(1, 3)G(2, 4). \quad (3.125)$$

The two-particle correlation function describes how particle-hole pairs interact in a many-body system, taking into account exchange and correlation effects. We will now derive the Dyson equation for the two-particle correlation function L which is called the *Bethe-Salpeter equation* (BSE).

Derivation of the Bethe-Salpeter equation

One can derive the Bethe-Salpeter equation using the functional derivative approach introduced by Martin and Schwinger [104] and later by Kadanoff and Baym [104, 14]. Derivations of the BSE using this technique can be found in the review by Strinati [170] and in the book by Martin *et al.* [105]. We include here a shortened derivation for completeness. This derivation closely follows Ref. [170].

The idea of the functional derivative technique is to add a fictive and local potential $U(\mathbf{r}, t)$ to the Hamiltonian in second quantization,

$$\begin{aligned} \hat{H} = & \int d^3x \hat{\psi}^\dagger(\mathbf{r}) h(\mathbf{r}) \hat{\psi}(\mathbf{r}) + \frac{1}{2} \int d^3x d^3x' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') V(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}) \\ & + \underbrace{\int d^3x \hat{\psi}^\dagger(\mathbf{r}) U(\mathbf{r}, t) \hat{\psi}(\mathbf{r})}_{=H'(t)}, \end{aligned} \quad (3.126)$$

which serves merely as a tool to derive various quantities as functional derivatives with respect to this fictitious potential. At the end of the calculations the limit $U \rightarrow 0$ is performed. Using this fictitious potential we define the operator

$$S = T \left[\exp \left(-i \int_{-\infty}^{+\infty} H'_I(t) dt, \right) \right], \quad (3.127)$$

where $H'_I(t) = e^{iHt} H' e^{-iHt}$, using for the unperturbed Hamiltonian H the first two terms of Eq. (3.126). With this operator we can define the generalized Green's functions

$$iG(1, 2) = \frac{\langle \Psi_0 | T [S \hat{\psi}(1) \hat{\psi}^\dagger(2)] | \Psi_0 \rangle}{\langle \Psi_0 | T [S] | \Psi_0 \rangle}, \quad (3.128)$$

$$-G_2(1, 2, 3, 4) = \frac{\langle \Psi_0 | T [S \hat{\psi}(1) \hat{\psi}(2) \hat{\psi}^\dagger(3) \hat{\psi}^\dagger(4)] | \Psi_0 \rangle}{\langle \Psi_0 | T [S] | \Psi_0 \rangle}. \quad (3.129)$$

For the purpose of the derivation we write the fictitious potential as a non-local potential $U(1, 2)$ that depends on a pair of space and time variables. Then, the following identity can be derived [14, 170]

$$L(1, 2, 3, 4) = \frac{\delta G(1, 3)}{\delta U(2, 4)}. \quad (3.130)$$

To rewrite Eq. (3.130) we then use the identity [170]

$$\frac{\delta G(1, 3)}{\delta U(2, 4)} = - \int G(1, 1') \frac{\delta G^{-1}(1', 3')}{\delta U(2, 4)} G(3', 3) d1' d3' \quad (3.131)$$

and Dyson's equation

$$G^{-1} = G_0^{-1} - U - (V_H + \tilde{\Sigma}), \quad (3.132)$$

where in this case the Hartree term is separated from the self-energy. We then obtain

$$\begin{aligned} L(1, 2, 3, 4) = & - \int G(1, 1') G(3', 3) \\ & \times \frac{\delta}{\delta U(2, 4)} \left[G_0^{-1}(1', 3') - U(1', 3') - (V_H(1', 3') + \tilde{\Sigma}(1', 3')) \right] d1' d3'. \end{aligned} \quad (3.133)$$

To evaluate the first term in the square brackets we use the identity Eq. (3.131) and that the non-interacting Green's function obeys the relation

$$\left[\frac{\partial}{\partial t_1} - \nabla_1^2 + V_{\text{ext}}(1) \right] G_0(1, 2) = \delta(1, 2) \quad (3.134)$$

and is as such not a functional of the additional fictitious potential U . This means that the first term in the square brackets of Eq. (3.133) vanishes. The second term yields a product of delta functions so that we obtain

$$\begin{aligned} L(1, 2, 3, 4) &= \int G(1, 1') G(3', 3) \left[\delta(1' - 2) \delta(3' - 4) + \frac{\delta(V_H(1', 3') + \tilde{\Sigma}(1', 3'))}{\delta U(2, 4)} \right] d1' d3', \\ &= G(1, 2) G(4, 3) + \int G(1, 1') \frac{\delta(V_H(1', 3') + \tilde{\Sigma}(1', 3'))}{\delta U(2, 4)} G(3', 3) d(1' 3'). \end{aligned} \quad (3.135)$$

Using the chain rule

$$\frac{\delta(V_H(1', 3') + \tilde{\Sigma}(1', 3'))}{\delta U(2, 4)} = \int \frac{\delta(V_H(1', 3') + \tilde{\Sigma}(1', 3'))}{\delta G(2', 4')} \frac{\delta G(2', 4')}{\delta U(2, 4)} d2' d4' \quad (3.136)$$

and introducing the free polarization propagator $L_0(1, 2, 3, 4) = G(1, 2) G(4, 3)$ which describes the independent propagation of an electron-hole pair, we finally arrive at the Bethe-Salpeter equation, that is, the Dyson equation of the two-particle correlation function L ,

$$L(1, 2, 3, 4) = L_0(1, 2, 3, 4) + \int L_0(1, 1', 3, 3') I(1', 2', 3', 4') L(2', 2, 4', 4) d(1' 2' 3' 4'), \quad (3.137)$$

where we have introduced the interaction kernel

$$I(1, 2, 3, 4) = \frac{\delta(V_H(1, 3) + \tilde{\Sigma}(1, 3))}{\delta G(2, 4)}. \quad (3.138)$$

Evaluating the interaction kernel

To evaluate the interaction kernel we use for the self-energy the single-shot self-energy discussed in the previous section,

$$\Sigma(1, 3) = iG_0(1, 3)W_0(1, 3). \quad (3.139)$$

Additionally, we write the Hartree contribution to the self-energy as [170]

$$V_H(1, 3) = -i\delta(1, 3) \int V(1, 1') G(1', 1^+) d1', \quad (3.140)$$

so that the interaction kernel becomes

$$I(1, 2, 3, 4) = -i\delta(1, 3)\delta(4, 2)V(1, 2) + i\delta(1, 2)\delta(3, 4)W_0(1, 3) + iG_0(1, 3)\frac{\delta W_0(1, 3)}{\delta G_0(2, 4)}. \quad (3.141)$$

We further neglect the variation of the screened interaction, the last term in the equation above. This term describes the change in screening due to the interaction and is considered to be small [170]. This gives as an approximation of the irreducible interaction, which will be considered in this work:

$$I(1, 2, 3, 4) = -i\delta(1, 3)\delta(4, 2)V(1, 2) + i\delta(1, 2)\delta(3, 4)W_0(1, 3). \quad (3.142)$$

Rewriting the BSE as an eigenvalue equation

The following section is adapted from Sec. IIA of Ref. [184].

We have now derived the BSE. In order to evaluate the BSE computationally one usually chooses a basis and translates the BSE into an eigenvalue equation. At this point, we make the static approximation to the screened interaction $W(1, 2)$ [103]. In this approximation, the full frequency-dependent screened interaction is approximated by its static value: $W(1, 2) \approx W(\mathbf{r}_1, \mathbf{r}_2, \omega = 0)$. Using this approximation the interaction I is frequency-independent and equation (3.137) can be solved in frequency space for $L(\omega)$:

$$L(\omega)^{-1} = L_0(\omega)^{-1} - I. \quad (3.143)$$

Until now all equations involved quantities which are continuous functions of space. To cast Eq. (3.143) into a matrix form, one needs to introduce a basis. Since we consider neutral electron-hole excitations, a suitable basis are the products of occupied and unoccupied orbitals, called resonant and antiresonant two-orbital states

$$\begin{aligned} \Phi_K^r(\mathbf{r}, \mathbf{r}') &= \varphi_i(\mathbf{r})\varphi_a^*(\mathbf{r}') \\ \Phi_K^a(\mathbf{r}, \mathbf{r}') &= \varphi_a(\mathbf{r})\varphi_i^*(\mathbf{r}'), \end{aligned} \quad (3.144)$$

where the indices $i, j, \dots$ and $a, b, \dots$ enumerate occupied and unoccupied states, respectively. Here and in the following we use the notation $K = \{i, a\}$ and $J = \{j, b\}$. In general, one also needs to include $\mathbf{k}$ -point indices, $K = \{i\mathbf{k}, a\mathbf{k}\}$, $J = \{j\mathbf{k}', b\mathbf{k}'\}$, but for brevity we will suppress them in the following. It can be easily restored, by adding $\mathbf{k}$ to i and a , and $\mathbf{k}'$ to j and b .

To evaluate the matrix elements of L_0 we write it in the form

$$L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4; \omega) = \sum_{klmn} \varphi_k(\mathbf{r}_1)\varphi_l^*(\mathbf{r}_2)\varphi_m(\mathbf{r}_3)\varphi_n^*(\mathbf{r}_4)[L_0(\omega)]_{mn}^{kl}, \quad (3.145)$$

where the frequency dependent matrix elements of $L_0(\omega)$ are given by [42]

$$[L_0(\omega)]_{mn}^{kl} = \delta_{km}\delta_{ln} \left[\frac{\theta(m-\mu)\theta(\mu-n)}{\omega - (\omega_m - \omega_n) + i\delta} - \frac{\theta(\mu-m)\theta(n-\mu)}{\omega + (\omega_n - \omega_m) - i\delta} \right]. \quad (3.146)$$

The first and second terms in the equation above are termed resonant and antiresonant term, respectively. In the basis of resonant and antiresonant two-orbital states the matrix elements of L_0 evaluate to

$$(L_0(\omega)^{-1})_{KJ}^{(r,r)} = (\omega - (\epsilon_a - \epsilon_i))\delta_{ij}\delta_{ab}, \quad (3.147)$$

$$(L_0(\omega)^{-1})_{KJ}^{(a,a)} = (-\omega - (\epsilon_a - \epsilon_i))\delta_{ij}\delta_{ab}. \quad (3.148)$$

The resonant-resonant matrix elements of the irreducible interaction are then written

$$\mathcal{H}_{KJ}^{(r,r)} = \int d\mathbf{r}_1 \dots d\mathbf{r}_4 \Phi_K^{r*}(\mathbf{r}_2, \mathbf{r}_4) I(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \Phi_J^r(\mathbf{r}_3, \mathbf{r}_1), \quad (3.149)$$

the matrix elements $\mathcal{H}_{KJ}^{(r,a)}$ and $\mathcal{H}_{KJ}^{(a,a)}$ are obtained analogously. Using the more compact Dirac notation, we list here all anti-symmetrized two electron integrals corresponding to the

interaction I :

$$\mathcal{H}_{KJ}^{(r,r)} = \langle bi|V|ja\rangle - \langle bi|W|aj\rangle, \quad (3.150)$$

$$\mathcal{H}_{KJ}^{(r,a)} = \langle ja|V|bi\rangle - \langle ja|W|ib\rangle, \quad (3.151)$$

$$\mathcal{H}_{KJ}^{(a,r)} = \langle ji|V|ba\rangle - \langle ji|W|ab\rangle, \quad (3.152)$$

$$\mathcal{H}_{KJ}^{(a,a)} = \langle ba|V|ji\rangle - \langle ba|W|ij\rangle. \quad (3.153)$$

We have now arrived at a matrix representation of (3.143):

$$(L(\omega)^{-1})_{KJ} = \omega \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} - (\epsilon_a - \epsilon_i) \begin{pmatrix} \delta_{ij}\delta_{ab} & 0 \\ 0 & \delta_{ij}\delta_{ab} \end{pmatrix} - \begin{pmatrix} \mathcal{H}_{KJ}^{(r,r)} & \mathcal{H}_{KJ}^{(r,a)} \\ \mathcal{H}_{KJ}^{(r,a)*} & \mathcal{H}_{KJ}^{(r,r)*} \end{pmatrix}. \quad (3.154)$$

Elementary excitations are determined by the poles of $L(\omega)$, in other words, those frequencies Ω for which the right hand side of Eq. (3.154) is not invertible. This in turn means that the kernel of the matrix on the right hand side of Eq. (3.154) is non-trivial, using the shorthand notation

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} = (\epsilon_a - \epsilon_i) \begin{pmatrix} \delta_{ij}\delta_{ab} & 0 \\ 0 & \delta_{ij}\delta_{ab} \end{pmatrix} + \begin{pmatrix} \mathcal{H}_{KJ}^{(r,r)} & \mathcal{H}_{KJ}^{(r,a)} \\ \mathcal{H}_{KJ}^{(r,a)*} & \mathcal{H}_{KJ}^{(r,r)*} \end{pmatrix}, \quad (3.155)$$

this argument leads us to a generalized eigenvalue problem

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \Omega \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}. \quad (3.156)$$

For real-valued symmetric matrices A and B , methods exist to solve this generalized eigenvalue problem [169, 46]. For complex-valued matrices, one can take advantage of the time inversion symmetry of Bloch states and reorder the antiresonant states in the second row and column to transform B^* and A^* to B and A , respectively [149]. This way one can reduce the $2N$ non-Hermitian eigenvalue problem into two diagonalizations of Hermitian matrices of size N , where N is the number of particle-hole pairs [149].

In this work, we use the well-known Tamm-Dancoff approximation (TDA) [36, 175], which simplifies the Bethe-Salpeter Equation (BSE) by neglecting the off-diagonal matrices B, B^* . The physical meaning of the TDA is discussed below. We further use the analytical property that response functions derived from $L(\omega)$ are even functions of ω and the simplification that for Bloch states $A = A^*$ [149]. All of this reduces the preceding generalized eigenvalue problem in Eq. (3.156) to a simple eigenvalue equation for a Hermitian matrix A

$$AX = \Omega X. \quad (3.157)$$

The physical content of the TDA can be understood by Fourier-transforming the free polarization propagator $L_0(\omega)$, Eq. (3.145) [42]. The resonant term propagates forward in time, while the antiresonant term propagates backward in time. When the full BSE without TDA is solved, this results in electron-hole pairs that propagate both forward and backward in time. In particular, this implies that forward and backward propagating electron-hole pairs are coupled through the matrices B, B^* . When the matrix elements (3.151) are evaluated as diagrams this coupling manifests as diagrams where forward and backward propagating pairs are present

at the same time and scatter against each other or annihilate [149]. In the TDA, however, the antiresonant term is excluded, effectively decoupling the resonant and antiresonant components. Conceptually, the TDA therefore treats electron-hole pairs as propagating only forward in time, meaning that at any given moment, only a single electron-hole pair is present [42]. Furthermore, the TDA can be obtained by simply removing the antiresonant component from L_0 [42]. It is easy to see that repeating the steps above without the antiresonant term leads to an eigenvalue problem without the coupling matrices B, B^* .

An example where TDA fails was found by Grüning *et al.* [54]. Their study demonstrated that, when excitons hybridize with plasmons, it is essential to go beyond TDA, as in this case excitons propagate forward and backward in time.

3.6.1 Spectral representation of L

In the following we will compute the macroscopic dielectric function including excitonic effects for which we need the spectral representation of L . Using the eigenvalues Ω_λ and eigenvectors $|X_\lambda\rangle$ enumerated by the index λ the spectral representation of L is given by [46]

$$L(\omega) = \sum_{\lambda} |X_\lambda\rangle\langle X_\lambda| \left(\frac{1}{\Omega_\lambda - \omega} + \frac{1}{\Omega_\lambda + \omega} \right), \quad (3.158)$$

from which we obtain the corresponding K, J matrix elements:

$$[L(\omega)]_J^K = \sum_{\lambda} X_\lambda^{i,a} (X_\lambda^{j,b})^* \left(\frac{1}{\Omega_\lambda - \omega} + \frac{1}{\Omega_\lambda + \omega} \right). \quad (3.159)$$

Above, we have used that the eigenvectors are written in the transition basis:

$$|X_\lambda\rangle = X_\lambda^{i,a} |\Phi_{i,a}^r\rangle + X_\lambda^{i',a'} |\Phi_{i',a'}^r\rangle + \dots \quad (3.160)$$

We have now summarized the BSE formalism and its main ingredients: the matrix elements of the resonant-resonant matrix A , Eq. (3.149), and the eigenvalue problem that needs to be solved, Eq. (3.157). After having solved the eigenvalue problem we obtained the spectral representation of $L(\omega)$, Eq. (3.159).

Chapter 4

Ab-initio X-ray absorption spectroscopy from MBPT

In the first chapter, we introduced DFT, which, combined with the PAW methodology from the second chapter, serves as the foundation for calculating ground-state KS orbitals and energies. Building on this, the previous chapter detailed how quasiparticle energies can be calculated using MBPT. We specifically demonstrated how these energies are derived from the quasiparticle equations, with KS orbitals and energies serving as input, and the self-energy acting as a non-local potential to account for many-body correlation effects. Additionally, we introduced the BSE as the appropriate framework for describing the two-particle excitations generated during the X-ray absorption process. We derived the BSE, discussed the approximations used for the interaction kernel, and reformulated it as an eigenvalue equation.

In this chapter, we outline the theoretical framework for calculating the primary physical quantity of interest: the X-ray absorption spectra. These spectra are obtained from the imaginary part of the macroscopic dielectric constant, ϵ_M . We begin by deriving in the first three sections the expression for the macroscopic dielectric function using the theory of linear response. In Sec. 4.4, we link this theory to the MBPT results from the previous chapter by incorporating excitonic effects into the macroscopic dielectric function. Next, we address two technicalities. In Sec. 4.5, we discuss how the singularity in the Coulomb potential in momentum space is handled, and in Sec. 4.6, we examine the choice of gauge in the transition matrix elements. In Sec. 4.9, we detail the specific modifications required for transitions from the core to conduction states. Finally, in Sec. 4.10, we provide an overview of how BSE calculations are performed in practice.

4.1 Preliminaries

Before deriving ϵ_M , we need to address two points. First, we introduce the procedure to derive macroscopic quantities from microscopic quantities. Second, we will discuss the concept of gauge invariance in optical properties.

Deriving macroscopic from microscopic quantities

Let A be an external field acting upon the system,

$$A(\mathbf{r}) = \sum_{\mathbf{q}} A(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (4.1)$$

where $\mathbf{q}$ is a reciprocal vector in the first Brillouin zone. Then this external field will induce in the system a rapidly varying quantity

$$f(\mathbf{r}) = \sum_{\mathbf{G}, \mathbf{q}} f_{\mathbf{G}}(\mathbf{q}) e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}}, \quad (4.2)$$

where the $\mathbf{G}$ are the reciprocal lattice vectors. To arrive at the macroscopic average of $\bar{f}(\mathbf{r})$ we choose a point $\mathbf{r}$ in the crystal and average over a unit cell with volume V :

$$\bar{f}(\mathbf{r}) = \frac{1}{V} \int_V f(\mathbf{r} + \mathbf{R}) d\mathbf{R}. \quad (4.3)$$

Into this we insert Eq. (4.2) which gives

$$\bar{f}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{G}, \mathbf{q}} \int_V f_{\mathbf{G}}(\mathbf{q}) e^{i(\mathbf{q} + \mathbf{G}) \cdot (\mathbf{r} + \mathbf{R})} d\mathbf{R}. \quad (4.4)$$

Since the wavelength of the external field is assumed much larger than the size of the unit cell we can use $\exp(i\mathbf{R} \cdot \mathbf{q}) \approx 1$, hence

$$\bar{f}(\mathbf{r}) = \sum_{\mathbf{G}, \mathbf{q}} e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} f_{\mathbf{G}}(\mathbf{q}) \underbrace{\frac{1}{V} \int_V e^{i\mathbf{G} \cdot \mathbf{R}} d\mathbf{R}}_{\delta_{\mathbf{G}, 0}} \quad (4.5)$$

$$= \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} f_{\mathbf{G}=0}(\mathbf{q}). \quad (4.6)$$

Comparing Fourier coefficients we see that we get the $\mathbf{q}$ component of the averaged, macroscopic quantity $\bar{f}(\mathbf{r})$ from the $\mathbf{G} = 0, \mathbf{q}$ component of the microscopic quantity.

Gauge invariance of the optical response

The experimental spectra that serve as a reference in this thesis were obtained by considering both transverse and longitudinal external fields: in chapter 7 below, the experiments were all obtained using X-ray absorption spectroscopy, where light, that is, a transverse electromagnetic field impinges on the surface of the sample. In chapter 8 on the other hand we consider electron energy loss experiments, where the electron-hole pairs are excited by accelerated electrons which represent a longitudinal electromagnetic field.

In homogeneous systems one can show that a transverse field only induces a transverse current while a longitudinal field only induces a longitudinal current [200]. The response is then separated into transverse and longitudinal dielectric functions. In crystals this strict separation does not hold and longitudinal (transverse) fields can induce transverse (longitudinal) currents. However, for external fields for which the long-wavelength limit $\mathbf{q} \rightarrow 0$ holds Ambegaokar and

Kohn [9] have shown that the longitudinal dielectric function and transverse dielectric function are exactly equal. Or in other words, the optical response is gauge invariant. This limit is justified for all experiments considered in this thesis. In the XAS experiment of chapter 7 the wavelength of the impinging laser field is much larger than the unit cells of the considered materials. For the electron-energy loss experiment of chapter 8 we discuss in Sec. 8.2 that they are equivalent to the $\mathbf{q} \rightarrow 0$ results of the corresponding XAS spectra. As the $\mathbf{q} \rightarrow 0$ limit is justified in all cases considered we make use of the gauge invariance and discuss in this thesis only the longitudinal dielectric function.

4.2 Linear response theory and the dielectric function

We begin this section by the macroscopic Maxwell equations in cgs units:

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = 4\pi\rho_{\text{ext}}, \quad (4.7)$$

$$\nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{1}{c} \frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t}, \quad (4.8)$$

$$\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0, \quad (4.9)$$

$$\nabla \times \mathbf{H}(\mathbf{r}, t) = \frac{1}{c} \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} + \frac{4\pi}{c} \mathbf{J}_{\text{ext}}(\mathbf{r}, t), \quad (4.10)$$

where $\mathbf{E}(\mathbf{r}, t), \mathbf{B}(\mathbf{r}, t)$ are the macroscopic electric and magnetic fields and $\rho_{\text{ext}}, \mathbf{J}_{\text{ext}}$ are the external charge density and currents. $\mathbf{D}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$ are the electric displacement and the magnetic field strength, respectively, and are connect to the macroscopic electric and magnetic fields via the polarization $\mathbf{P}(\mathbf{r}, t)$ and the magnetization $\mathbf{M}(\mathbf{r}, t)$ by

$$\mathbf{D}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}, t) + 4\pi\mathbf{P}(\mathbf{r}, t), \quad (4.11)$$

$$\mathbf{H}(\mathbf{r}, t) = \mathbf{B}(\mathbf{r}, t) - 4\pi\mathbf{M}(\mathbf{r}, t). \quad (4.12)$$

In this thesis we consider non-magnetic materials and therefore discuss only the linear response with regards to external electric fields. To make the physical meaning entering the different terms in equation (4.11) clearer we rewrite it as

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{D}(\mathbf{r}, t) - 4\pi\mathbf{P}(\mathbf{r}, t). \quad (4.13)$$

Here $\mathbf{E}$ is the *total* electric field which appears in the usual form of the microscopic Maxwell equations in which only $\mathbf{E}$ and $\mathbf{B}$ enter. We now introduce the self-consistent field formalism, in which the total electric field is the sum of the external field $\mathbf{E}_{\text{ext}}$ and the field induced by it, $\mathbf{E}_{\text{ind}}$:

$$\mathbf{E}^{\text{ext}}(\mathbf{r}, t) + \mathbf{E}^{\text{ind}}(\mathbf{r}, t) = \mathbf{D}(\mathbf{r}, t) - 4\pi\mathbf{P}(\mathbf{r}, t). \quad (4.14)$$

Since the induced field is given by the polarization $\mathbf{P}$ we can identify the electric displacement $\mathbf{D}$ with the external field $\mathbf{E}_{\text{ext}}$. If this externally applied field is weak then we can relate the total field linearly with the external field:

$$\mathbf{D}(\mathbf{r}, t) = \mathbf{E}^{\text{ext}}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}, t) + 4\pi\mathbf{P}(\mathbf{r}, t) \quad (4.15)$$

$$= \int \epsilon(\mathbf{r}', \mathbf{r}, t - t') \mathbf{E}(\mathbf{r}', t') d^3r' dt', \quad (4.16)$$

where we have introduced the *dielectric tensor* ϵ and used time translation symmetry, so that the dielectric function only depends on time differences $t - t'$. In non-isotropic media the dielectric tensor relates the components of the external and total electric fields,

$$(E_{\text{ext}})_\alpha = \epsilon_{\alpha\beta} E_\beta. \quad (4.17)$$

To simplify the following formulas we suppress the indices α, β . Inverting the last equation gives us the linear response relationship between the external field and the total field:

$$\mathbf{E}(\mathbf{r}, t) = \int \epsilon^{-1}(\mathbf{r}', \mathbf{r}, t - t') \mathbf{E}^{\text{ext}}(\mathbf{r}', t') d^3 r' dt'. \quad (4.18)$$

Next, we insert the two-point Fourier transform of the dielectric function

$$\epsilon(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\mathbf{q}, \mathbf{G}, \mathbf{G}'} e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} \epsilon_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega) e^{-i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}'}, \quad (4.19)$$

into Eq. (4.16) and Fourier transform $\mathbf{E}_{\text{ext}}$ and $\mathbf{E}$ with respect to coordinate and time variables. We get

$$\mathbf{E}_{\mathbf{G}}^{\text{ext}}(\mathbf{q}, \omega) = \sum_{\mathbf{G}'} \epsilon_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega) \mathbf{E}_{\mathbf{G}'}(\mathbf{q}, \omega). \quad (4.20)$$

In other words, in reciprocal space the linear relationship between external field and electric field is a matrix equation, where the matrix establishing that connection is the *dielectric matrix* with components $\mathbf{G}, \mathbf{G}'$. Defining the inverse of the dielectric matrix as

$$\sum_{\mathbf{G}''} \epsilon_{\mathbf{G}, \mathbf{G}''}^{-1}(\mathbf{q}) \epsilon_{\mathbf{G}'', \mathbf{G}'}(\mathbf{q}) = \delta_{\mathbf{G}, \mathbf{G}'} \quad (4.21)$$

we can invert Eq. (4.20):

$$\mathbf{E}_{\mathbf{G}}(\mathbf{q}, \omega) = \sum_{\mathbf{G}'} \epsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega) \mathbf{E}_{\mathbf{G}'}^{\text{ext}}(\mathbf{q}, \omega). \quad (4.22)$$

Note, that in general the dielectric matrix is non-diagonal and that all elements of the matrix contribute to one particular element of its inverse. This mixing of all components of the dielectric matrix is termed the *local field effects*. As local field effects we understand the fluctuations on the microscopic scale induced by an external field.

4.3 Macroscopic dielectric constant

The macroscopic dielectric function ϵ_M relates the averaged external electric field $\bar{\mathbf{E}}_{\text{ext}}$ to the averaged total electric field $\bar{\mathbf{E}}$ via

$$\epsilon_M \bar{\mathbf{E}} = \bar{\mathbf{E}}^{\text{ext}}. \quad (4.23)$$

Averaging equation (4.22) according to Sec. 4.1 gives us the relationship

$$\bar{\mathbf{E}}(\mathbf{q}, \omega) = \epsilon_{\mathbf{G}=0, \mathbf{G}'=0}^{-1}(\mathbf{q}, \omega) \bar{\mathbf{E}}^{\text{ext}}(\mathbf{q}, \omega) \quad (4.24)$$

which connects the macroscopic external field to the total macroscopic field. Since the external field is assumed to be of long wavelength we then perform the $\mathbf{q} \rightarrow 0$ limit which leads to the definition of the macroscopic dielectric function [57, 125]:

$$\epsilon_M(\omega) = \lim_{\mathbf{q} \rightarrow 0} \left[\left(\epsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega) \right)_{\mathbf{G}=0, \mathbf{G}'=0} \right]^{-1}. \quad (4.25)$$

Here, the notation emphasizes the sequence of operations necessary to calculate the macroscopic dielectric function. First, we compute the dielectric matrix $\epsilon_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega)$ and take its inverse $\epsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega)$. From this inverse matrix, we extract the $\mathbf{G} = 0, \mathbf{G}' = 0$ component, known as the *head* of the matrix. The $\mathbf{G} \neq 0, \mathbf{G}' = 0$ and $\mathbf{G} = \mathbf{G}' \neq 0$ components are called *wings* and *body*, respectively. The head forms a 3×3 tensor. Finally, we invert this 3×3 tensor and perform the $\mathbf{q} \rightarrow 0$ limit.

4.4 Excitonic effects within linear response

To obtain the macroscopic dielectric function ϵ_M , we need to calculate the dielectric constant in reciprocal space, Eq. (4.25). To incorporate excitonic effects into linear response theory we need to derive a formula for ϵ_M and then link the linear response theory to the MBPT methods discussed in the previous chapter.

We now derive the longitudinal dielectric constant following the procedure presented in Ref. [59]. Here, we simplify the derivation by assuming a homogeneous electron gas which allows us to perform Fourier transforms to the variables $\mathbf{q}, \omega$. Starting point is the relationship that connects the total microscopic electric field with the external electric field, Eq. (4.22), which in the case of a homogeneous electron gas reads

$$\mathbf{E}(\mathbf{q}, \omega) = \epsilon^{-1}(\mathbf{q}, \omega) \mathbf{E}^{\text{ext}}(\mathbf{q}, \omega). \quad (4.26)$$

In the next step, the electric fields are replaced by densities using Poisson's equation

$$\nabla \mathbf{E}(\mathbf{q}, \omega) = i\mathbf{q} \mathbf{E}(\mathbf{q}, \omega) = 4\pi e^2 n(\mathbf{q}, \omega). \quad (4.27)$$

The external field is replaced by using $|\mathbf{E}|^{\text{ext}} = 4\pi e^2 n/|\mathbf{q}|i$. In the framework of the self-consistent field the microscopic electric field on the left-hand side of Eq. (4.26) is written as a sum of induced and external fields, $\mathbf{E} = \mathbf{E}^{\text{ind}} + \mathbf{E}^{\text{ext}}$, so that

$$[n^{\text{ext}}(\mathbf{q}, \omega) + n^{\text{ind}}(\mathbf{q}, \omega)] = \epsilon^{-1}(\mathbf{q}, \omega) n^{\text{ext}}(\mathbf{q}, \omega). \quad (4.28)$$

Rearranging and writing the external charge density in terms of the external potential v^{ext} using Poisson's equation $n = v|\mathbf{q}|^2/4\pi e^2$ gives

$$\frac{4\pi e^2}{|\mathbf{q}|^2} n^{\text{ind}}(\mathbf{q}, \omega) = [\epsilon^{-1}(\mathbf{q}, \omega) - 1] v^{\text{ext}}(\mathbf{q}, \omega). \quad (4.29)$$

Finally, the derivative with respect to the Fourier component of the external potential is evaluated, so that

$$\epsilon^{-1}(\mathbf{q}, \omega) = 1 + \frac{4\pi e^2}{|\mathbf{q}|^2} \frac{\partial n^{\text{ind}}(\mathbf{q}, \omega)}{\partial v^{\text{ext}}(\mathbf{q}, \omega)}. \quad (4.30)$$

By an analogous procedure we can also obtain the dielectric function in terms of the derivative of the induced field with respect to the total external potential,

$$\epsilon(\mathbf{q}, \omega) = 1 - \frac{4\pi e^2}{|\mathbf{q}|^2} \frac{\partial n^{\text{ind}}(\mathbf{q}, \omega)}{\partial v^{\text{tot}}(\mathbf{q}, \omega)}. \quad (4.31)$$

The derivatives of the induced charge density with respect to the external or total potential define the reducible (P) and irreducible ($\hat{P}$) polarizabilities, respectively:

$$\frac{\partial n^{\text{ind}}(\mathbf{q}, \omega)}{\partial v^{\text{ext}}(\mathbf{q}, \omega)} = P(\mathbf{q}, \omega), \quad (4.32)$$

$$\frac{\partial n^{\text{ind}}(\mathbf{q}, \omega)}{\partial v^{\text{tot}}(\mathbf{q}, \omega)} = \hat{P}(\mathbf{q}, \omega) \quad (4.33)$$

With these definitions the dielectric function and its inverse can be written

$$\epsilon(\mathbf{q}, \omega) = 1 - \frac{4\pi e^2}{|\mathbf{q}|^2} \hat{P}(\mathbf{q}, \omega), \quad (4.34)$$

$$\epsilon^{-1}(\mathbf{q}, \omega) = 1 + \frac{4\pi e^2}{|\mathbf{q}|^2} P(\mathbf{q}, \omega). \quad (4.35)$$

Connecting to MBPT

To connect the linear response theory above with the many-body formalism of the last chapter we consider the Green-Kubo relations [53, 86]

$$\delta \langle \hat{O}(t) \rangle = i \int_{t_0}^t \langle \Psi_0 | [H_H^{\text{per.}}(t'), \hat{O}_H(t)] | \Psi_0 \rangle dt'. \quad (4.36)$$

that connect the fluctuations of an operator $\hat{O}$ to the ground state expectation value of the perturbing Hamiltonian in the Heisenberg representation $H_H^{\text{per.}}$. Let the perturbing Hamiltonian represent an external charge with scalar potential $e\varphi^{\text{ext.}}(\mathbf{r}, t)$:

$$H_H^{\text{per.}}(t) = \int \hat{n}_H(\mathbf{r}, t) e\varphi(\mathbf{r}, t) dt. \quad (4.37)$$

We are interested in the density fluctuations $\delta \langle \hat{n}(\mathbf{q}, \omega) \rangle$. It can be shown [42] that the reducible polarizability that we introduced in the last section equals

$$P(\mathbf{q}, \omega) = \frac{\delta \langle \hat{n}(\mathbf{q}, \omega) \rangle}{\delta v^{\text{ext.}}(\mathbf{q}, \omega)} = D^R(\mathbf{q}, \omega), \quad (4.38)$$

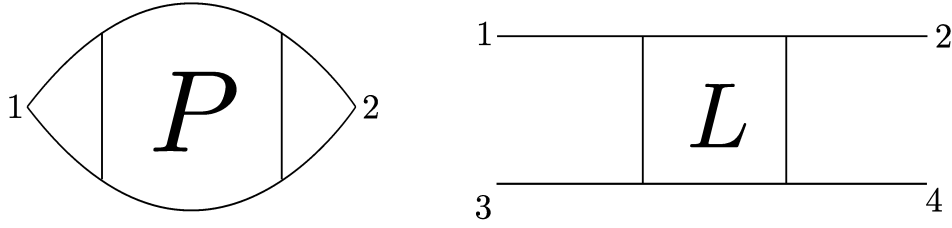
where $D^R(\mathbf{q}, \omega)$ is the Fourier transform of the retarded density-density correlation function

$$D^R(1, 2) = \theta(t_1 - t_2) \langle \Psi_0 | [\hat{n}_H(1), \hat{n}_H(2)] | \Psi_0 \rangle. \quad (4.39)$$

The retarded density-density correlation function is obtained from the time ordered density-density correlation function via [42]

$$\text{Re} D(\mathbf{q}, \omega) = \text{Re} D^R(\mathbf{q}, \omega), \quad (4.40)$$

$$-\text{sign}(\omega) \text{Im} D(\mathbf{q}, \omega) = \text{Im} D^R(\mathbf{q}, \omega). \quad (4.41)$$



$$P(1, 2) = \delta(1, 3)\delta(2, 4)L(1, 2, 3, 4) = L(1, 2, 1, 2)$$

Figure 4.1: Feynman diagrams of the irreducible polarization P (left) and the two particle correlation function L (left). The irreducible polarization P is obtained as a limiting case of the two-particle correlation function L .

This relationship between the reducible polarization and the density-density correlation function was shown above to hold for the simple case of a homogeneous system, but it can be shown [41] that this relationship holds in the general case so that

$$D^R(1, 2) = P^R(1, 2), \quad (4.42)$$

where P is the *reducible* polarizability that we introduced when we discussed the RPA in Sec. 3.4. In other words, the density-density response due to an external charge is equal to the retarded reducible polarizability. We note that the equation above implies that the retarded polarizability P^R has the same analytical properties of D^R . Additionally, the reducible polarizability can be viewed as a limit of the two-particle correlation function as shown in Fig. 4.1 so that we finally obtain

$$P^R(1, 2) = L^R(1, 2, 1^+, 2^+). \quad (4.43)$$

This means that if we want to include excitonic effects incorporated in L we proceed as follows. First, we compute the two-particle correlation function L using the BSE. From L we obtain the limiting case of the retarded two particle correlation function, $L^R(1, 2, 1^+, 2^+)$. Then, we insert $L^R(1, 2, 1^+, 2^+)$ for the reducible polarization P in the longitudinal dielectric function, Eq. (4.35). Finally, we invert ϵ^{-1} and obtain the macroscopic dielectric function according to Eq. (4.25).

The final expression for the dielectric matrix

We now derive the expression for the longitudinal dielectric matrix taking into account excitonic effects. First, we generalize Eq. (4.35) from the homogeneous to the inhomogeneous case and write it in momentum space as

$$\epsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega) = \delta_{\mathbf{G}, \mathbf{G}'} + V_{\mathbf{G}}(\mathbf{q})L_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega), \quad (4.44)$$

where, according to the discussion above, the two-particle correlation function $L_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega)$ was used for the total polarization. The function $L_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega)$ is obtained as the two-point Fourier transform of the real-space correlation function,

$$L_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega) = \int e^{-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} L(\mathbf{r}, \mathbf{r}', \omega) e^{i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}'} d\mathbf{r} d\mathbf{r}'. \quad (4.45)$$

According to Sec. 3.6, the two-particle correlation function depends only on one time difference, allowing us to perform the Fourier transform to the frequency variable ω . We proceed by using the four-point correlation function $L(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4; \omega)$, taking the limits $\mathbf{r}_3 \rightarrow \mathbf{r}_1$ and $\mathbf{r}_4 \rightarrow \mathbf{r}_2$ at the end. When formulating the BSE as an eigenvalue problem in Sec. 3.6 we saw that the free polarization operator $L_0(1, 2, 3, 4) = G_0(2, 1)G_0(4, 3)$ had the Lehmann representation

$$L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4; \omega) = \sum_{ij,ab} \varphi_i^*(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_a(\mathbf{r}_3) \varphi_b^*(\mathbf{r}_4) [L_0(\omega)]_J^L. \quad (4.46)$$

Since the product of four orbitals forms a complete basis, we generalize the above equation and write the four-point correlation function in the basis of transition pairs in the form

$$L(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4; \omega) = \sum_{ij,ab} \varphi_i^*(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_a(\mathbf{r}_3) \varphi_b^*(\mathbf{r}_4) [L(\omega)]_J^K, \quad (4.47)$$

where we introduce the notation $K = i, a$ and $J = j, b$, as in Sec. 3.6. By inserting the spectral representation for $[L(\omega)]_J^K$, Eq. (3.159), we obtain

$$L(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4; \omega) = \sum_{i,a,j,b;\lambda} \varphi_i^*(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_a(\mathbf{r}_3) \varphi_b^*(\mathbf{r}_4) \left(\frac{1}{\Omega_\lambda - \omega} + \frac{1}{\Omega_\lambda + \omega} \right) (X^{i,a}_\lambda)(X^{j,b}_\lambda)^*. \quad (4.48)$$

We now take the limits $\mathbf{r}_3 \rightarrow \mathbf{r}_1$, $\mathbf{r}_4 \rightarrow \mathbf{r}_2$, perform the two-point Fourier transform in Eq. (3.96), and insert the resulting expression into Eq. (4.44). We then obtain the longitudinal dielectric constant in momentum space:

$$\begin{aligned} \epsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega) &= \delta_{\mathbf{G}, \mathbf{G}'} + V_{\mathbf{G}}(\mathbf{q}) \sum_{\lambda} \left(\frac{1}{\Omega_\lambda - \omega} + \frac{1}{\Omega_\lambda + \omega} \right) \\ &\quad \times \sum_{i,a,j,b} \langle a | e^{i\mathbf{r} \cdot (\mathbf{q} + \mathbf{G})} | i \rangle \left(X_\lambda^{i,a} \right) \left[\langle b | e^{i\mathbf{r} \cdot (\mathbf{q} + \mathbf{G}')} | j \rangle \left(X_\lambda^{j,b} \right) \right]^* \end{aligned} \quad (4.49)$$

Above, we use the Dirac notation

$$\langle a | e^{-i\mathbf{r} \cdot (\mathbf{q} + \mathbf{G})} | i \rangle = \int \varphi_a^*(\mathbf{r}) e^{i\mathbf{r} \cdot (\mathbf{q} + \mathbf{G})} \varphi_i(\mathbf{r}) d\mathbf{r}. \quad (4.50)$$

For finite momentum transfers $\mathbf{q}$, the macroscopic dielectric function can be obtained directly from Eq. (4.49) by first extracting the head, that is, the $\mathbf{G} = \mathbf{G}' = 0$ component,

$$\epsilon_{0,0}^{-1}(\mathbf{q}, \omega) = 1 + V_0(\mathbf{q}) \sum_{\lambda} \left(\frac{1}{\Omega_\lambda - \omega} + \frac{1}{\Omega_\lambda + \omega} \right) \sum_{i,a} |\langle a\mathbf{k} + \mathbf{q} | e^{i\mathbf{r} \cdot \mathbf{q}} | i\mathbf{k} \rangle X_\lambda^{i,a}|^2 \quad (4.51)$$

and then inverting the resulting tensor. However, as discussed, we assume that the wavelength of the external field is sufficiently large so that we can perform the long-wavelength limit $\mathbf{q} \rightarrow 0$. In the following two sections we address two technicalities associated with this limit.

4.5 Long-range part of the Coulomb kernel

In the limit $\mathbf{q} \rightarrow 0$, the long-range behaviour of the Coulomb potential requires particular attention as

$$V_{\mathbf{G}}(\mathbf{q}) = \frac{4\pi e^2}{|\mathbf{q} + \mathbf{G}|^2} \quad (4.52)$$

diverges for $\mathbf{G} = 0$ as $\mathbf{q} \rightarrow 0$.

To address this issue, we introduce two auxiliary quantities [125]. First, we introduce a modified (or amputated) Coulomb interaction $\bar{V}_{\mathbf{q}}(\mathbf{G})$, which is given by

$$\bar{V}_{\mathbf{G}}(\mathbf{q}) = \begin{cases} 0 & \text{if } \mathbf{G} = 0, \\ 4\pi e^2/|\mathbf{q} + \mathbf{G}|^2 & \text{otherwise.} \end{cases} \quad (4.53)$$

In other words, the $\mathbf{G} = 0$ component is removed from the modified Coulomb interaction $\bar{V}$. Using this auxiliary quantity, the total Coulomb potential can be decomposed as the sum of the amputated Coulomb kernel plus the $\mathbf{G} = 0$ component,

$$V_{\mathbf{G}}(\mathbf{q}) = \bar{V}_{\mathbf{G}}(\mathbf{q}) + V_0(\mathbf{q}). \quad (4.54)$$

With this decomposition, any Dyson equation for the irreducible polarization P with a kernel that involves the Coulomb potential can be split into two separate Dyson equations,

$$\bar{P} = P_0 + P_0 \bar{v} \bar{P}, \quad (4.55)$$

$$P = \bar{P} + \bar{P} v_0 P. \quad (4.56)$$

Here, Eq. (4.55) defines the proper polarizability $\bar{P}$ which contains the part of the polarization that does not include the diverging $\mathbf{G} = 0$ components. Additionally, we introduce an equation that connects the proper to the total polarization:

$$\bar{P} = P - P v_0 \bar{P}. \quad (4.57)$$

To calculate the macroscopic dielectric function from these relations, we divide Eq. (4.56) by $\bar{P}$ and extract the $\mathbf{G} = 0, \mathbf{G}' = 0$ component, so that

$$\frac{P_{0,0}(\mathbf{q}, \omega)}{\bar{P}_{0,0}(\mathbf{q}, \omega)} = 1 + V_0(\mathbf{q}) P_{0,0}(\mathbf{q}, \omega) = \epsilon_{0,0}^{-1}(\mathbf{q}, \omega) = [\epsilon_M(\mathbf{q}, \omega)]^{-1}. \quad (4.58)$$

We then divide Eq. (4.57) by P which together with Eq. (4.58) leads to

$$\epsilon_M(\mathbf{q}, \omega) = 1 - V_0(\mathbf{q}) \bar{P}_{0,0}(\mathbf{q}, \omega). \quad (4.59)$$

This expression is well-behaved in the optical limit since it can be shown that the polarization behaves as

$$\lim_{\mathbf{q} \rightarrow 0} \bar{P}(\mathbf{q}, \omega) \sim \mathbf{q}^2 \bar{P}(\omega), \quad (4.60)$$

which cancels the $\mathbf{q} \rightarrow 0$ singularity of the Coulomb kernel. Note that by using the proper polarizability $\bar{P}$ we directly obtain the macroscopic dielectric function without first inverting

ϵ . Note, however, that solving (4.57) requires implicitly an inversion. Using this procedure the macroscopic longitudinal dielectric function in momentum space reads

$$\epsilon_M(\mathbf{q}, \omega) = 1 - V_0(\mathbf{q}) \sum_{\lambda} \left(\frac{1}{\bar{\Omega}_{\lambda} - \omega} + \frac{1}{\bar{\Omega}_{\lambda} + \omega} \right) \left\{ \sum_{i,a} \lim_{\mathbf{q} \rightarrow 0} \langle a | e^{i\mathbf{r} \cdot \mathbf{q}} | i \rangle \bar{X}_{\lambda}^{i,a} \right\} \times \{\text{c.c.}\} \quad (4.61)$$

Here, we denote the eigenvalues and eigenvectors obtained from a modified BSE eigenvalue problem (Eq. (3.157)) with bars, as $\bar{\Omega}$ and $\bar{X}$. In this modified calculation, the $\mathbf{G} = 0$ component is set to zero when evaluating the Coulomb kernel matrix elements in Eq. (3.150).

4.6 Long-wavelength limit of the transitions matrix elements

What remains is to evaluate the $\mathbf{q} \rightarrow 0$ limit of the transition matrix elements:

$$\langle a | e^{i\mathbf{r} \cdot \mathbf{q}} | i \rangle = \int \varphi_a^*(\mathbf{r}) e^{i\mathbf{r} \cdot \mathbf{q}} \varphi_i(\mathbf{r}) d\mathbf{r}. \quad (4.62)$$

When calculating spectra of optical excitations, that is, excitations from the valence to the conduction band, the matrix elements

$$\langle a\mathbf{k}_a | e^{i\mathbf{r} \cdot \mathbf{q}} | i\mathbf{k}_i \rangle = \int_{\Omega} u_{a\mathbf{k}_i+\mathbf{q}}(\mathbf{r}) u_{i\mathbf{k}_i}(\mathbf{r}) d\mathbf{r} \quad (4.63)$$

are directly evaluated within the PAW method, where u denotes the cell-periodic part of the state φ , and where we have explicitly written the $\mathbf{k}$ -point indices. By employing momentum conservation as outlined in Sec. 5.1 below the exponential terms cancel out. Expanding $\tilde{u}_{a\mathbf{k}_i+\mathbf{q}}(\mathbf{r})$ into a series leads to the result:

$$\lim_{\mathbf{q} \rightarrow 0} \langle a | e^{i\mathbf{r} \cdot \mathbf{q}} | i \rangle = |\mathbf{q}| \left\langle \frac{\mathbf{q}}{|\mathbf{q}|} \beta_{a\mathbf{k}_i} | \tilde{u}_{i\mathbf{k}_i} \right\rangle. \quad (4.64)$$

See Sec. 5.1 for details. In this result, $\tilde{u}$ denotes the plane-wave component of the cell-periodic part, and β is a vector related to the first-order change of $|u_{i\mathbf{k}_i}\rangle$ with respect to $\mathbf{q}$. These matrix elements are termed the longitudinal matrix elements because they arise from a longitudinal external field $\propto e^{i\mathbf{q}\mathbf{r}}$. Importantly, the Coulomb singularity $1/q^2$ cancels with the square of the matrix elements which are $\propto q^2$.

We have now evaluated the long-wavelength limit. The longitudinal macroscopic dielectric function reads

$$\epsilon_M(\omega) = 1 - \frac{4\pi e^2}{V} \sum_{\lambda} \left(\frac{1}{\bar{\Omega}_{\lambda} - \omega} + \frac{1}{\bar{\Omega}_{\lambda} + \omega} \right) \left\{ \sum_{i,a} \left\langle \frac{\mathbf{q}}{|\mathbf{q}|} \beta_{a\mathbf{k}_i} | \tilde{u}_{i\mathbf{k}_i} \right\rangle \bar{X}_{\lambda}^{i,a} \right\} \times \{\text{c.c.}\}. \quad (4.65)$$

4.7 Spectra from the macroscopic dielectric function

Absorption spectra are derived from the imaginary part of the macroscopic dielectric function $\epsilon_M(\omega)$. To evaluate $\text{Im}(\epsilon_M(\omega))$ we need to examine the analytic properties of ϵ_M . In deriving ϵ_M , we transitioned from time-ordered to retarded quantities, as outlined in Sec. 4.4.

The frequency dependence of ϵ_M is contained within the round parentheses in Eq. (4.65). To ensure correct analytical properties of the retarded polarizability, we must include infinitesimal imaginary terms with the appropriate sign. Since the retarded density-density response function is analytic in the upper half of the complex frequency plane [4], the retarded total polarization, and therefore ϵ_M , are also analytic in this region. As a result, the poles of ϵ_M are positioned in the lower half of the complex frequency plane. This behavior is ensured by adjusting the frequency terms as follows:

$$\left(\frac{1}{\bar{\Omega}_\lambda - \omega - i\delta} + \frac{1}{\bar{\Omega}_\lambda + \omega + i\delta} \right), \quad (4.66)$$

where the addition of infinitesimal terms $-i\delta$ and $+i\delta$ shift the poles to the lower half-plane.

Using the identity [42]

$$\frac{1}{s \pm i\delta} = P \frac{1}{s} \mp \pi i \delta(s), \quad (4.67)$$

where P denotes the principal value, the imaginary part of the term in the parentheses, (4.66), becomes

$$\text{Im}(\dots) = \pi \left(\delta(\bar{\Omega}_\lambda - \omega) - \delta(\bar{\Omega}_\lambda + \omega) \right). \quad (4.68)$$

For positive frequencies, the imaginary part of the macroscopic dielectric function is then given by

$$\text{Im}[\epsilon_M(\omega)] = \frac{4\pi^2 e^2}{V} \sum_\lambda \left\{ \sum_{i,a} \left\langle \frac{\mathbf{q}}{|\mathbf{q}|} \beta_{a\mathbf{k}_i} | \tilde{u}_{i\mathbf{k}_i} \right\rangle \bar{X}_\lambda^{i,a} \right\} \{ \text{c.c.} \} \delta(\bar{\Omega}_\lambda - \omega). \quad (4.69)$$

Mathematically, the imaginary part of $\epsilon_M(\omega)$ corresponds to a Dirac delta function. However, in practice, it is approximated by a Lorentzian function. For example, calculating the imaginary part of the resonant term gives

$$\text{Im} \left(\frac{1}{\bar{\Omega}_\lambda - \omega - i\delta} \right) = \frac{\delta}{(\bar{\Omega}_\lambda - \omega)^2 + \delta^2}, \quad (4.70)$$

which is π times a Lorentzian function. Note that the parameter δ corresponds to *half* width at half maximum.

4.8 Wave functions from the BSE

In addition to the spectra, we can obtain the exciton wave function from the BSE formalism. Using the eigenvectors that result from solving the eigenvalue equation, Eq. (3.157), the exciton wave function associated with excitation λ is obtained by [105]

$$\Psi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{i,a} X_\lambda^{i,a} \varphi_a^*(\mathbf{r}_e) \varphi_i(\mathbf{r}_h), \quad (4.71)$$

which depends on the electron and hole coordinates $\mathbf{r}_e$ and $\mathbf{r}_h$, respectively. This state is a six-dimensional correlated state, as the position of the electron depends on the position of the

hole. In practice, the coordinate of the hole is kept fixed at some coordinate $\mathbf{R}_h$ so that the exciton wave function is written as a function of the coordinate of the electron only:

$$\Psi_\lambda(\mathbf{r}_e) = \sum_{i,a} X_\lambda^{i,a} \varphi_a(\mathbf{r}_e) \varphi_i^*(\mathbf{R}_h). \quad (4.72)$$

In particular, the charge density $n_\lambda(\mathbf{r}_e) = |\Psi_\lambda(\mathbf{r}_e)|^2$ gives the probability of finding the electron at position $\mathbf{r}_e$ when the hole is fixed at position $\mathbf{R}_h$.

4.9 Modifications for core excitations

We now show how the formula for the macroscopic dielectric function, Eq. (4.65), needs to be changed when the occupied states i denote core states. There are two modifications. The first concerns how the transition matrix elements are evaluated. In the case of optical excitations we use the longitudinal expression of the matrix elements, as explained in Sec. 4.6. In the case of excitations from core states, we presently use the so-called transverse expressions. To derive them we expand the exponential in

$$\langle a | e^{i\mathbf{r} \cdot \mathbf{q}} | i \rangle \quad (4.73)$$

as $\exp i\mathbf{r} \cdot \mathbf{q} \sim 1 + i\mathbf{r} \cdot \mathbf{q} + O(q^2)$ so that

$$\langle a | e^{i\mathbf{r} \cdot \mathbf{q}} | i \rangle \sim i\mathbf{q} \langle a | \mathbf{r} | i \rangle, \quad (4.74)$$

where it is assumed that $\langle a | i \rangle = 0$, that is, that core and conduction band state are orthogonal. To evaluate the expectation value of the position operator we consider the identity

$$\langle a | [H, \mathbf{r}] | i \rangle = (\epsilon_a - \epsilon_i) \langle a | \hat{\mathbf{r}} | i \rangle, \quad (4.75)$$

which is valid for any Hermitian Hamiltonian having as eigenstates $|a\rangle, |i\rangle$. Consider first a Hamiltonian that includes a local potential $V_{\text{loc.}}(\mathbf{r})$. In this case, the position operator commutes with the potential operator of the Hamiltonian and only the commutator with the kinetic energy $[p^2, \mathbf{r}]$ needs to be evaluated, which gives

$$\langle a | \hat{\mathbf{r}} | i \rangle = \frac{\langle a | \hat{\mathbf{p}} | i \rangle}{(\epsilon_a - \epsilon_i)}. \quad (4.76)$$

The situation is different in the case where the Hamiltonian contains a non-local potential. In this case we get

$$\langle a | \hat{\mathbf{r}} | i \rangle = \frac{\langle a | \mathbf{p} + [V_{\text{nl.}}, \mathbf{r}] | i \rangle}{(\epsilon_a - \epsilon_i)}, \quad (4.77)$$

where the commutator with the non-local part of the potential needs to be evaluated explicitly. These matrix elements are termed transversal as they can be understood as stemming from a transversal external field $\propto \mathbf{p}e^{i\mathbf{q} \cdot \mathbf{r}}$.

The present implementation of the BSE for core-excitation uses Eq. (4.76). Specifically, we evaluate the $\mathbf{q} \rightarrow 0$ limit of the transition matrix elements from a core state to a conduction band state as

$$\lim_{\mathbf{q} \rightarrow 0} \langle a | e^{i\mathbf{r} \cdot \mathbf{q}} | c \rangle = \mathbf{q} \frac{\langle a | \hat{\mathbf{p}} | c \rangle}{\epsilon_c - \epsilon_a}. \quad (4.78)$$

The ∇ -term is evaluated inside the PAW sphere between the exact all-electron partial waves of the core orbitals and the all-electron partial waves corresponding to the considered conduction band state $c\mathbf{k}$. As the PAW pseudopotentials are non-local Eq. (4.77) would be required in principle [12, 69]. However, it was shown that the momentum operator can give very accurate results within the PAW method, if the PAW potentials include projectors for large angular quantum numbers L [47]. Note that also in this case the Coulomb singularity $1/q^2$ is canceled by the square of the transition matrix elements $\propto q^2$.

The second modification concerns the treatment of the core state energies ϵ_c in the energy denominator of Eq. (4.78) and in the diagonal elements of the BSE matrix A , Eq. (3.155). Since the core states do not interact they are represented as flat bands in $\mathbf{k}$ -space. The required core eigenvalues ϵ_c are therefore assumed to be identical to the DFT core eigenvalues and identical for all $\mathbf{k}$ -points apart from a Bloch phase

$$|c\mathbf{k}\rangle = e^{i\mathbf{k}\mathbf{r}}|c\rangle. \quad (4.79)$$

VASP routinely calculates the DFT core eigenvalues by evaluating the expectation value of the frozen core orbitals in the self-consistent Kohn-Sham potential. Alternatively, one can specify the core eigenvalue as input using the parameter `CLE` in the `INCAR` file. However, results are largely independent of ϵ_c . Changing ϵ_c changes the onset of absorption and scales all intensities by roughly a constant value.

In principle, it would be possible to calculate absolute core-energies. Absolute core-energies are commonly calculated using the Δ -Self Consistent Field (Δ SCF) and related methods [11, 110] or recently the GW -approximation [187, 51]. However, these are not yet available within the frozen core PAW VASP implementation. Anyway, absolute core-energies and hence the onsets of absorption are not yet accurately predicted by standard DFT [171, 115] and even core-energies obtained from GW calculations are not expected to be accurate when vertex corrections are not included. Hence, in this thesis only the conduction band energies are GW -corrected, and we adjust the onset of the absorption spectrum to the experimental value.

These modification lead to the imaginary part of the macroscopic dielectric function as applied to core-excitations:

$$\text{Im}[\epsilon_M(\omega)] = \frac{4\pi^2 e^2}{V} \sum_{\lambda} \left\{ \sum_a \frac{\langle a|\hat{\mathbf{p}}|c\rangle}{\epsilon_c - \epsilon_a} \bar{X}_{\lambda}^{c,a} \right\} \times \{\text{c.c.}\} \delta(\bar{\Omega}_{\lambda} - \omega). \quad (4.80)$$

This is the final result. The X-ray absorption spectra that are obtained from the equation above are the primary quantities of interest of this thesis.

Justification of the long-wavelength limit for X-ray spectra

In this thesis we apply the long-wavelength, $\mathbf{q} \rightarrow 0$, limit. Corrections to this limit can be estimated from the quadrupole term

$$[\mathbf{q}\langle a|\mathbf{r}|i\rangle]^2, \quad (4.81)$$

which we have written as a scalar for simplicity. The energy range considered here is from 60 eV to 420 eV, so if we assume that variations of the system are of the order $1\text{\AA}$, then corrections to the long-wavelength limit (i.e. quadrupole transitions) are at most of order $(1\text{\AA}/30\text{\AA})^2 \approx 10^{-3}$. The limit $\mathbf{q} \rightarrow 0$ is justified for the systems investigated in this thesis.

4.10 BSE in practice

Let us summarize this chapter so far. We first introduced the macroscopic dielectric function and then derived an expression for the longitudinal macroscopic dielectric function in the long-wavelength limit. The excitonic effects are incorporated by choosing for the total retarded polarizability P the two-point limit of the total two-particle correlation function L . To evaluate the long-wavelength limit it was necessary to introduce an amputated Coulomb interaction $\bar{v}$ from which the $\mathbf{G} = 0$ term is removed. Using this amputated Coulomb interaction, the polarizability is determined by using the Dyson equation $\bar{P}^{-1} = P_0^{-1} - \bar{v}$. Note, that the $\mathbf{G} \neq 0$ elements are removed when P is evaluated from P_0 . Afterwards, the BSE matrix elements are evaluated. We then evaluated the long-wavelength limit of the transition matrix elements which reduced to the expectation value of the momentum operator. Finally, we obtained the absorption spectra from the imaginary part of the macroscopic dielectric function.

In this section we give an overview how BSE calculations are performed in practice with the code VASP.

DFT step

In the first step we calculate the ground state KS orbitals and energies using some flavor of the exchange-correlation potential. In the case of this thesis we use the PBE functional. Additionally, this step provides us with the derivatives of the orbitals that are needed for the transition matrix elements in the expression for the RPA, Eq. (3.102), and in the expression for the macroscopic dielectric matrix, Eq. (4.69). As the quasiparticle calculations require a large number of bands we adjust the corresponding value accordingly. A minimal example of a INCAR file appropriate for a simple system such as diamond or silicon reads

```
! Increase the number of bands manually.
NBANDS = 512
! Calculate the transition matrix elements.
LOPTICS = .TRUE.
```

G_0W_0 step

This step serves two purposes. First, we calculate the RPA dielectric function, Eq. (3.102). In the first iteration of Hedins equations, the screened interaction is built from the independent particle polarizability. We therefore use the ground state KS energies and orbitals when constructing the RPA dielectric function Eq. (3.102). The RPA dielectric function is inverted from which we obtain the screened interaction W_0 . Using the independent particle Green's function G_0 and the screened interaction W_0 , we then construct the self energy G_0W_0 . In the second step, we use this self-energy to calculate the quasiparticle energies according to Eq. (3.122). We stress that the orbitals are not updated in this step. Thus, the WAVECAR contains the GGA orbitals of the first step and the quasiparticle corrected eigenvalues. A minimal INCAR would be

```
NBANDS = 512
! Calculate W_0 and quasiparticle energies using the G_0W_0 self energy.
ALGO = EVGW0
NELGW = 1 NOMEGA_DUMP = 0
```

BSE step

Finally, we calculate the absorption spectra using the BSE formalism. In this step, the matrix elements of Eq. (3.150) are set up using the orbitals obtained in the first step (which are stored in the `WAVECAR` file of the G_0W_0 step) and the screened interaction W_0 obtained in the second step. The $\mathbf{G} = 0$ component is removed when evaluating the matrix elements of the Coulomb kernel. Since we have performed a G_0W_0 calculation in the preceding step the diagonal elements of the BSE matrix A , Eq. (3.155), contain the excitation energies in terms of the quasiparticle corrected energies, $(\epsilon_a^{\text{qp}} - \epsilon_i^{\text{qp}})$. In the case of core excitations only the conduction band energies are quasiparticle corrected so that the diagonal elements read $(\epsilon_a^{\text{qp}} - \epsilon_c)$. The transition matrix elements are evaluated according to Eq. (4.76) while in the case of core excitations Eq. (4.78) applies. Finally, the BSE matrix is diagonalized and the absorption spectrum computed from Eq. (4.69) in the case of optical excitations or Eq. (4.80) in the case of core excitations. A minimal `INCAR` reads

```

NBANDS = 512
! Use the BSE algorithm to solve the BSE eigenvalue equation.
ALGO = BSE
HARTREE = .TRUE. ! Include matrix elements of Coulomb kernel.
LADDER = .TRUE. ! Include matrix elements of screened interaction.
! BSE for optical excitations
NBANDSV = 4 ! Number of unoccpied (virtual) levels.
NBANDSO = 4 ! Number of occpied levels.
! BSE for core excitations.
ICORELEVEL = 2
NBANDSV = 4 ! Number of unoccpied (virtual) levels.
NBANDSO = 0 ! Number of occpied levels. Can be set to zero for core excitations.
CLNT = 1 ! Choose which atom species to excite.
CLN = 1 ! Principal quantum number of excited atom.
CLL = 1 ! Angular momentum number of excited atom (s,p,d,...).
CLZ = 1 ! Charge of core hole.
CLE = -280 ! Optional. Manual input of the core level energy  $\epsilon_c$  in eV.
CH_AMPLIFICATION = 1E6 ! Scaling factor of the transition matrix elements.
CSHIFT = 0.1 ! Broadening of the spectra.

```


Chapter 5

Implementing the BSE within PAW for X-ray spectra

In the preceding chapter we showed how the X-ray absorption spectra including excitonic effects are obtained from the imaginary part of the macroscopic dielectric function. This chapter provides further details on the implementation of the BSE within the PAW method. We follow a bottom-up approach: starting from the construction of the augmentation charges, we first describe how to obtain the BSE matrix elements within the PAW formalism. Then, we provide details regarding the transition matrix elements and the Coulomb kernel where we discuss both the $\mathbf{q} \rightarrow 0$ limit and the case $\mathbf{q} \neq 0$. Finally, we demonstrate how these components are combined to calculate the macroscopic dielectric function.

5.1 The BSE matrix elements within PAW

The following section is adapted from Sec. IIC of Ref. [184].

The first step in calculating the macroscopic dielectric function consists in evaluating the resonant-resonant BSE matrix elements within the PAW method. We will first show the expressions for the BSE matrix elements of Eq. (3.150) within the PAW and then show how the matrix elements are evaluated in a plane-wave basis.

Defining charge densities

$$n_{ab}(\mathbf{r}) = \varphi_a^*(\mathbf{r})\varphi_b(\mathbf{r}), \quad (5.1)$$

the two terms of the resonant-resonant matrix elements, Eq. (3.150), can be written as

$$\langle bi|V|ja\rangle = \int d\mathbf{r}d\mathbf{r}' n_{ia}(\mathbf{r})v(\mathbf{r}-\mathbf{r}')n_{jb}^*(\mathbf{r}'), \quad (5.2)$$

$$\langle bi|W|aj\rangle = \int d\mathbf{r}d\mathbf{r}' n_{ij}(\mathbf{r})W(\mathbf{r},\mathbf{r}')n_{ab}^*(\mathbf{r}'). \quad (5.3)$$

Following convention, we refer to the terms involving v and W as exchange and direct terms, respectively [125].

To calculate the matrix elements of Eqs. (5.2) and (5.13), we need to treat the long-range electrostatic interaction accurately within the PAW. This is achieved by introducing augmentation charges which have been discussed in Sec. 2.4. With this definition of the augmentation charge, we write the exact charge density as a sum of three terms, c.f. Eq. (17) of Ref. [127]:

$$n_{ab}(\mathbf{r}) = [\tilde{n}_{ab}(\mathbf{r}) + \hat{n}_{ab}(\mathbf{r})] + n_{ab}^1(\mathbf{r}) - [\tilde{n}_{ab}^1(\mathbf{r}) + \hat{n}_{ab}^1(\mathbf{r})]. \quad (5.4)$$

The first term is the plane-wave charge density plus the augmentation charge on the regular grid, the second term is the AE charge density, and the last term is the PS charge density plus PS augmentation charge on the radial grid.

By constructing the augmentation charges as in Sec. 2.4 the correct moments of the AE charge density are taken into account and restored. This leads to moment-restoration. Additionally, the exact all-electron charge density inside the PAW spheres can be reconstructed by adding so-called shape-restoring functions to the augmentation charges [162]. This process is accordingly called shape-restoration. Using moment as well as shape-restoration makes the PS charge density very similar to the AE charge density for low Fourier components. Typically both match up to a kinetic energy cutoff of 150-200 eV. With this in mind we make an important simplification and neglect the second line of (5.4):

$$n_{ab}(\mathbf{r}) \approx [\tilde{n}_{ab}(\mathbf{r}) + \hat{n}_{ab}(\mathbf{r})]. \quad (5.5)$$

This approximation is made consistently in the VASP code for the *GW*, RPA, and BSE implementations [162].

Using this approximation, we can write an explicit expression for the exchange and direct terms, respectively:

$$\begin{aligned} \langle bi|V|ja\rangle &= \int d\mathbf{r}d\mathbf{r}' [\tilde{n}_{ia}(\mathbf{r}) + \hat{n}_{ia}(\mathbf{r})] \\ &\quad \times v(\mathbf{r} - \mathbf{r}') [\tilde{n}_{jb}(\mathbf{r}') + \hat{n}_{jb}(\mathbf{r}')]^*, \end{aligned} \quad (5.6)$$

$$\begin{aligned} \langle bi|W|aj\rangle &= \int d\mathbf{r}d\mathbf{r}' [\tilde{n}_{ij}(\mathbf{r}) + \hat{n}_{ij}(\mathbf{r})] \\ &\quad \times W(\mathbf{r}, \mathbf{r}') [\tilde{n}_{ab}(\mathbf{r}') + \hat{n}_{ab}(\mathbf{r}')]^*. \end{aligned} \quad (5.7)$$

Modification for core states

If one of the occupied states i is a core state c , then there are three combinations of orbitals possible: $n_{cc'}$ (two core states), n_{ci} (a core state and a valence band state), or n_{ca} (a core state and a conduction band state). For a core state c inside a particular PAW sphere, this core state is confined entirely to the sphere and vanishes beyond this PAW sphere. It is then evident that the three charge densities mentioned above contribute only inside the PAW sphere in which the core state c is located.

We show here how this implies that the plane-wave contributions $\tilde{n}$ in Eqs. (5.6) and (5.7) vanish. We first use the formula for the expectation value of a local operator in the PAW

scheme for the real-space projection operator $|\mathbf{r}\rangle\langle\mathbf{r}|$, see Eq. (11) of Ref. [21]:

$$\begin{aligned}\langle\varphi_i|\mathbf{r}\rangle\langle\mathbf{r}|\varphi_b\rangle &= \langle\tilde{\varphi}_i|\mathbf{r}\rangle\langle\mathbf{r}|\tilde{\varphi}_b\rangle \\ &+ \sum_{nm} \langle\tilde{\varphi}_i|\tilde{p}_n\rangle\langle\tilde{p}_m|\tilde{\varphi}_b\rangle\langle\phi_n^1|\mathbf{r}\rangle\langle\mathbf{r}|\phi_m^1\rangle \\ &- \sum_{nm} \langle\tilde{\varphi}_i|\tilde{p}_n\rangle\langle\tilde{p}_m|\tilde{\varphi}_b\rangle\langle\tilde{\phi}_n^1|\mathbf{r}\rangle\langle\mathbf{r}|\tilde{\phi}_m^1\rangle.\end{aligned}\quad (5.8)$$

We now restrict the state i to a core state c , while the state b is a conduction band state. As argued above, the charge density $\langle\varphi_c|\mathbf{r}\rangle\langle\mathbf{r}|\varphi_b\rangle$ has contributions inside the PAW spheres only. Hence, we can use the PAW completeness relation, Eq. (2.18), so that the first and third terms of Eq. (5.8) cancel. This finally implies that the plane-wave charge densities $\tilde{n}$ in Eqs. (5.6) and (5.7) can be neglected, so that the exchange and direct terms can be written as

$$\langle bc|V|ca\rangle = \int d\mathbf{r}d\mathbf{r}' \hat{n}_{ca}(\mathbf{r})v(\mathbf{r}-\mathbf{r}')\hat{n}_{cb}^*(\mathbf{r}') \quad (5.9)$$

and

$$\begin{aligned}\langle bc|W|aj\rangle &= \int d\mathbf{r}d\mathbf{r}' \hat{n}_{cj}(\mathbf{r}) \\ &\times W(\mathbf{r},\mathbf{r}')[\tilde{n}_{ab}(\mathbf{r}') + \hat{n}_{ab}(\mathbf{r}')]^*,\end{aligned}\quad (5.10)$$

respectively.

The augmentation charges are constructed in such a way that they restore the exact multipoles of the all-electron charge density. This implies that even though we use only augmentation charge densities, the long-range electrostatic effects are exactly accounted for. The argument laid out here also confirms that the assumption $\tilde{\phi}_c^1(\mathbf{r}) = \tilde{\psi}_c(\mathbf{r}) = 0$ everywhere in space is a valid choice. The expressions above have been implemented in the VASP code for core-conduction as well as core-valence transitions.

Direct matrix elements in a plane-wave basis

In VASP we expand all quantities in a plane wave basis. To simplify the notation, we write the charge density with the single symbol $n_{ij}(\mathbf{r})$, where it is understood that this charge density includes the augmentation charge according to the previous section. The Fourier transform of the charge density is given by

$$n_{ij}(\mathbf{r}) = \sum_{\mathbf{G}} n_{ij}(\mathbf{G} + \mathbf{q})e^{i\mathbf{r}(\mathbf{G}+\mathbf{q})}, \quad (5.11)$$

where $\mathbf{q}$ is the difference vector $\mathbf{q} = \mathbf{k}_j - \mathbf{k}_i$. Inserting this expression and the two-point Fourier transform of $W(\mathbf{r},\mathbf{r}')$ we obtain for the direct matrix element

$$\langle bi|W|aj\rangle = \int d\mathbf{r}d\mathbf{r}' n_{ij}(\mathbf{r})W(\mathbf{r},\mathbf{r}')n_{ab}^*(\mathbf{r}'), \quad (5.12)$$

$$= \frac{1}{V^3} \int d\mathbf{r}d\mathbf{r}' \sum_{\substack{\mathbf{G} \\ \mathbf{q}}} n_{ij}(\mathbf{G} + \mathbf{q})e^{i\mathbf{r}(\mathbf{G}+(\mathbf{G}'+\mathbf{q}))}W_{\mathbf{q}}(\mathbf{G}',\mathbf{G}'')e^{i\mathbf{r}(-(\mathbf{G}''+\mathbf{q})-\mathbf{G}''')}n_{ab}^*(\mathbf{G}''' + \mathbf{q}). \quad (5.13)$$

We show how the sum over $\mathbf{q}$ simplifies due to momentum conservation. As the charge densities are lattice periodic we can write them in Bloch form

$$n_{ij}(\mathbf{r}) = e^{i(\mathbf{k}_j - \mathbf{k}_i)\mathbf{r}} u_{ij}(\mathbf{r}), \quad (5.14)$$

$$n_{ab}(\mathbf{r}) = e^{i(\mathbf{k}_b - \mathbf{k}_a)\mathbf{r}} u_{ab}(\mathbf{r}), \quad (5.15)$$

where u denotes the cell-periodic part of the charge density. Next, we use the fact that momentum is conserved during the interaction. This means that if we translate the matrix element above into a diagram then momentum is conserved at each vertex so that the sum over all $\mathbf{q}$ collapses and only the term

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_j = \mathbf{k}_a - \mathbf{k}_b \quad (5.16)$$

remains. In the end, the exponential factors involving the momenta $\mathbf{k}$ and $\mathbf{q}$ cancel and the matrix element reads

$$\langle bi|W|aj\rangle = \frac{1}{V} \sum_{\mathbf{G}, \mathbf{G}'} u_{ij}^*(\mathbf{G}) W_{\mathbf{q}}(\mathbf{G}, \mathbf{G}') u_{ab}(\mathbf{G}'), \quad (5.17)$$

$$= \frac{1}{V} \sum_{\mathbf{G}, \mathbf{G}'} u_{ij}^*(\mathbf{G}) \frac{\epsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega = 0)}{|\mathbf{G} + \mathbf{q}| |\mathbf{G}' + \mathbf{q}|} u_{ab}(\mathbf{G}'), \quad (5.18)$$

where $\mathbf{k}_j, \mathbf{k}_b$, and $\mathbf{q}$ are given by Eq. (5.16) and where we have used $a(-\mathbf{G}) = a^*(\mathbf{G})$. Note that the RPA dielectric matrix is evaluated in the $\omega = 0$ limit. The $\mathbf{q} \rightarrow 0$ limit of the direct matrix elements is well defined.

We briefly mention one technicality. It is possible that the difference $\mathbf{k}_i - \mathbf{k}_j$ lies outside of the first Brillouin zone so that

$$\mathbf{k}_i - \mathbf{k}_j = \mathbf{q} + \mathbf{G}. \quad (5.19)$$

In this case, the cell periodic part of the charge density is shifted by a phase since

$$u_{\mathbf{k}_i, \mathbf{k}_j}(\mathbf{r}) = u_{\mathbf{k}_i, \mathbf{k}_i - \mathbf{q} - \mathbf{G}}(\mathbf{r}) = e^{-i\mathbf{r}\mathbf{G}} u_{\mathbf{k}_i, \mathbf{k}_i - \mathbf{q}}(\mathbf{r}). \quad (5.20)$$

To recover the correct phase of the cell-periodic part it is necessary to apply a phase $\exp(+i\mathbf{r}\mathbf{G})$ when the condition Eq. (5.19) is met.

Exchange matrix elements in a plane wave basis

Repeating the steps above we can evaluate the exchange matrix elements as

$$\langle bi|V|ja\rangle = \int d\mathbf{r} d\mathbf{r}' n_{ia}(\mathbf{r}) V(\mathbf{r} - \mathbf{r}') n_{jb}(\mathbf{r}')^*, \quad (5.21)$$

$$= \frac{1}{V} \sum_{\mathbf{G}} \frac{4\pi e^2}{|\mathbf{q} + \mathbf{G}|^2} u_{ia}^*(\mathbf{G}) u_{jb}(\mathbf{G}), \quad (5.22)$$

where we used the Fourier transform of the Coulomb kernel

$$V(\mathbf{r} - \mathbf{r}') = \frac{1}{V} \sum_{\mathbf{q}, \mathbf{G}} \frac{4\pi e^2}{|\mathbf{q} + \mathbf{G}|^2} e^{i(\mathbf{q} + \mathbf{G})(\mathbf{r} - \mathbf{r}')} \quad (5.23)$$

and where momentum conservation reduces the sum over $\mathbf{q}$ vectors just as in the previous section. In the case of finite momentum transfer, the equation above is used. In the limit $\mathbf{q} \rightarrow 0$ the procedure outlined in Sec. 4.5 is carried out. This means that for $\mathbf{q} \rightarrow 0$ we evaluate the modified matrix elements where the $\mathbf{G} = 0$ component is removed from the Coulomb kernel:

$$\langle bi|\bar{V}|ja\rangle = \frac{1}{V} \sum_{\mathbf{G} \neq 0} \frac{4\pi e^2}{|\mathbf{G}|^2} u_{ia}^*(\mathbf{G}) u_{jb}(\mathbf{G}). \quad (5.24)$$

5.2 The transition matrix elements

The next step consists in evaluating the transition matrix elements,

$$\langle a\mathbf{k}_i + \mathbf{q} | e^{i\mathbf{q}\mathbf{r}} | i\mathbf{k}_i \rangle, \quad (5.25)$$

in the PAW method. We first discuss briefly the case $\mathbf{q} \neq 0$, as it is treated in the same manner in the case of optical and core excitations. We then summarize the procedures for the case of $\mathbf{q} \rightarrow 0$ for optical excitations and core excitations separately.

$\mathbf{q} \neq 0$

As outlined in Sec. 4.6, the longitudinal transition matrix elements are used in the case of optical excitations. The optical transition matrix elements are discussed in detail in Ref. [47] and in the thesis of Harl [59]. We summarize the principal results for completeness. First, we evaluate the transition matrix elements for finite $\mathbf{q}$

$$\langle a\mathbf{k}_i + \mathbf{q} | e^{i\mathbf{q}\mathbf{r}} | i\mathbf{k}_i \rangle = \int_{\Omega} \varphi_{a\mathbf{k}_i+\mathbf{q}}^* e^{i\mathbf{q}\mathbf{r}} \varphi_{i\mathbf{k}_i}(\mathbf{r}) d\mathbf{r}, \quad (5.26)$$

$$= \int_{\Omega} B_{a\mathbf{k}_i+\mathbf{q};i\mathbf{k}_i}(\mathbf{r}) d\mathbf{r}, \quad (5.27)$$

where we have introduced the density matrix B . In the PAW method the AE wave functions φ are separated into PS parts evaluated on the entire grid and on-site AE and PS terms. The $\mathbf{k}$ dependent projectors are given by [47]

$$|p_{i\mathbf{k}_i}\rangle = e^{-i\mathbf{k}_i(\mathbf{r}-\mathbf{R}^{(\alpha)})} |p_i\rangle, \quad (5.28)$$

where $\mathbf{R}^{(\alpha)}$ is the position of the atomic sphere at ion (α) . The index of the ion position (α) is not to be confused with the index of unoccupied states a . Using this choice of the phase, the coefficient of the expansion with respect to AE and PS partial waves inside augmentation sphere (i) evaluates to

$$\langle p_i^{(\alpha)} | u_{n\mathbf{k}} \rangle = e^{i\mathbf{k}\mathbf{R}^{(\alpha)}} \langle p_{i\mathbf{k}} | u_{n\mathbf{k}} \rangle, \quad (5.29)$$

where $|p_i^{(\alpha)}\rangle$ are the projectors localized at atomic sphere (α) . Then, we obtain for B

$$B_{a\mathbf{k}_i+\mathbf{q};i\mathbf{k}_i}(\mathbf{r}) = \varphi_{a\mathbf{k}_i+\mathbf{q}}^*(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}} \varphi_{i\mathbf{k}_i}(\mathbf{r}) = u_{a\mathbf{k}_i+\mathbf{q}}^*(\mathbf{r}) u_{i\mathbf{k}_i}(\mathbf{r}), \quad (5.30)$$

$$= \tilde{u}_{a\mathbf{k}_i+\mathbf{q}}^*(\mathbf{r}) \tilde{u}_{i\mathbf{k}_i}(\mathbf{r}) + \sum_{\substack{r,s \\ (\alpha)}} \langle \tilde{u}_{a\mathbf{k}_i+\mathbf{q}} | p_{r\mathbf{k}_i+\mathbf{q}} \rangle \langle p_{s\mathbf{k}_i} | \tilde{u}_{i\mathbf{k}_i} \rangle, \quad (5.31)$$

$$\times e^{i(\mathbf{q}-\mathbf{R}^{(\alpha)})} (\phi_r^*(\mathbf{r}) \phi_s(\mathbf{r}) - \tilde{\phi}_r^*(\mathbf{r}) \tilde{\phi}_s(\mathbf{r})). \quad (5.32)$$

The term in parentheses is approximated using augmentation charges $\hat{Q}_{rs}^{l,m}$, see Sec. 2.4, so that finally

$$B_{a\mathbf{k}_i+\mathbf{q};i\mathbf{k}_i}(\mathbf{r}) = \tilde{u}_{a\mathbf{k}_i+\mathbf{q}}^*(\mathbf{r})\tilde{u}_{i\mathbf{k}_i}(\mathbf{r}) + \sum_{\substack{r,s \\ (\alpha)}} \langle \tilde{u}_{a\mathbf{k}_i+\mathbf{q}} | p_{r\mathbf{k}_i+\mathbf{q}} \rangle \langle p_{s\mathbf{k}_i} | \tilde{u}_{i\mathbf{k}_i} \rangle e^{i(\mathbf{q}-\mathbf{R}^{(\alpha)})} \hat{Q}_{rs}^{l,m}(\mathbf{r}). \quad (5.33)$$

This expression is used in the case of optical and core excitations. We now address the separate treatment of the $\mathbf{q} \rightarrow 0$ limit.

$\mathbf{q} \rightarrow 0$, Optical excitations

In the case of optical excitations the limit $\mathbf{q} \rightarrow 0$ is obtained from Eq. (5.33) by expanding the exponential factor, the pseudized cell-periodic part $\tilde{u}$, and the projectors $|p_i\rangle$ for small momenta $\mathbf{q}$. Using $Q(\mathbf{r})$ as defined in Eq. (2.43) we introduce the auxiliary quantities

$$q_{ij} = \int Q_{ij}(\mathbf{r}) d\mathbf{r}, \quad (5.34)$$

$$\tau_{ij} = \int (\mathbf{r} - \mathbf{R}^{(\alpha)}) Q_{ij}(\mathbf{r}) d\mathbf{r}, \quad (5.35)$$

$$|\beta_{a\mathbf{k}_i}\rangle = (1 + \sum_{rs} |p_{r\mathbf{k}_i}\rangle q_{rs} \langle p_{s\mathbf{k}_i}|) |\nabla_{\mathbf{k}} \tilde{u}_{a\mathbf{k}_i}\rangle \quad (5.36)$$

$$+ i(\sum_{rs} |p_{r\mathbf{k}_i}\rangle q_{rs} \langle p_{s\mathbf{k}_i}| (\mathbf{r} - \mathbf{R}^{(\alpha)})) |\tilde{u}_{a\mathbf{k}_i}\rangle - i \sum_{rs} |p_{r\mathbf{k}_i}\rangle \tau_{rs} \langle p_{s\mathbf{k}_i}| \tilde{u}_{a\mathbf{k}_i}\rangle \quad (5.37)$$

where we denote $|\beta\rangle$ with a bold symbol to emphasize that it is a vector valued quantity. We then obtain [47, 59]

$$\lim_{\mathbf{q} \rightarrow 0} \langle a\mathbf{k}_i + \mathbf{q} | e^{i\mathbf{q}\mathbf{r}} | i\mathbf{k}_i \rangle = \mathbf{q} \langle \frac{\mathbf{q}}{|\mathbf{q}|} | \beta_{a\mathbf{k}_i} | \tilde{u}_{i\mathbf{k}_i} \rangle. \quad (5.38)$$

$\mathbf{q} \rightarrow 0$, Core excitations

For excitations from the core state the $\mathbf{q} \rightarrow 0$ limit is evaluated using the transversal expression as discussed in Sec. 4.9. We thus need to evaluate

$$\frac{\langle a | \hat{\mathbf{p}} | c \rangle}{\epsilon_c - \epsilon_a} \quad (5.39)$$

within the PAW method. Expanding the conduction and core state into plane wave and on-site contribution gives

$$\langle a | \nabla | c \rangle = \langle \tilde{\varphi}_a | \nabla | \tilde{\varphi}_c \rangle + \sum_i \langle \tilde{\varphi}_a | p_i \rangle (\langle \phi_i | \nabla | \phi_c \rangle - \langle \tilde{\phi}_i | \nabla | \tilde{\phi}_c \rangle), \quad (5.40)$$

where we have used that in the PAW formalism the PAW decomposition of core states is given by Eq. (2.36). As the core states are localized entirely inside the PAW spheres all terms of the equation above are non-zero only inside the PAW spheres. We then use the completeness relation $\sum |p_i\rangle \langle \tilde{\phi}_i| = 1$ and the relation $|\tilde{\varphi}_c\rangle = |\tilde{\phi}_c\rangle$ discussed in Sec. 2.3 to cancel the first and the third terms. The final result reads [75]

$$\langle a | \nabla | c \rangle = \sum_i \langle \tilde{\varphi}_a | p_i \rangle \langle \phi_i | \nabla | \phi_c \rangle. \quad (5.41)$$

5.3 Putting all ingredients together

With all necessary components in place, we can now compute the macroscopic dielectric function $\epsilon_M(\omega)$. First, the direct and exchange matrix elements are stored in a matrix, to which a diagonal matrix of independent particle excitation energies is added, see Eq. (3.155). The resulting BSE matrix A is diagonalized, yielding the eigenvalues Ω_λ and the components of the eigenvectors $X_\lambda^{i,a}$. Combining these with the PAW transition matrix elements as evaluated above, we obtain the macroscopic dielectric function $\epsilon_M(\omega)$ where the absorption spectra are given by the imaginary part of $\epsilon_M(\omega)$. In the $\mathbf{q} \rightarrow 0$ limit this results in Eq. (4.65) for optical excitations or in Eq. (4.80) for core-level excitations.

Chapter 6

Ab-initio X-ray absorption spectroscopy using the final-state approximation

In chapters 3 through 5, we reviewed the $GW+BSE$ approach, which is the state-of-the-art method for calculating absorption spectra in both the optical and X-ray regimes. As discussed, this method is based on many-body perturbation theory, where Green's function techniques are used to derive the Bethe-Salpeter equation, which is an integral equation that is used to model excitonic excitations. The BSE is recast as an eigenvalue equation and linear response theory is then used to express the absorption spectra in terms of the eigenvalues and eigenvectors of the Bethe-Salpeter equation.

This chapter introduces an alternative approach to modeling X-ray absorption spectra that is used throughout this thesis alongside the $GW+BSE$ method - the final state approximation (FSA). In the FSA, absorption spectra are modeled by first explicitly removing a core electron from an atom in a supercell, and then recalculating the KS energies and orbitals in the presence of the core hole. The spectra are obtained by applying Fermi's golden rule, using the final state energies and orbitals.

The final-state approximation (FSA) was first introduced by von Barth and Grossmann in their studies of singularities in X-ray spectra of metals [194, 195]. In metals such as sodium, X-ray absorption spectra exhibit an asymmetry of the singularity near the threshold that was difficult to explain using a picture based on the ground state state band structure. The role of the electron hole interaction in producing this asymmetry was emphasized by Mahan who used many-body techniques and a simple model for the electron-electron interaction to predict the coefficients of the singularity at the threshold [99]. This result was later refined by Nozieres and colleagues using more advanced techniques [147, 120, 119]. In particular, Nozieres and DeDominicis derived the singularity exponents without taking recourse to perturbation theory [119]. The results by Mahan, Nozieres, and DeDominicis are often summarized as MND theory. At the same time, other researchers were using what would later be recognized as the final-state rule to compute spectra of various metals. By studying absorption spectra of model systems and of sodium Von Barth and Grossmann demonstrated the equivalence

between the final-state rule and the more formal MND theory, which bridged the gap between the formal many-body theory and the conceptually simple FSA. This established FSA as a valid alternative for studying X-ray absorption processes.

As we will show below when we discuss the results, while the spectra modeled with this method are comparable to those obtained with the more sophisticated BSE approach, they are not identical. However, the FSA offers a significant advantage in computational efficiency compared to the GW +BSE method, since it is only as expensive as a ground state DFT calculation. Therefore, the FSA can be applied to much larger systems. It also provides flexibility in physical parameters, since the charge removed from the core state or the electron charge added to the conduction bands can be adjusted freely. For these reasons, the FSA serves as an ideal complement to the GW +BSE approach.

6.1 Theory

We now provide a reasoning that connects the seemingly ad-hoc FSA to the more rigorous and formal framework of MND theory where we follow closely the arguments in Ref. [194]. Starting point is the imaginary part of the macroscopic dielectric constant including changes that have been made when an electron is excited from a core state (Sec. 4.9):

$$\epsilon_M(\omega) = 1 - \frac{4\pi e^2}{V} \sum_{a,b} \frac{\langle a|\hat{\mathbf{p}}|c\rangle \langle b|\hat{\mathbf{p}}|c\rangle^*}{\epsilon_c - \epsilon_a} [L(\omega)]_{c,a}^{c,b}. \quad (6.1)$$

In deriving the absorption spectra from MBPT the spectral representation of L is inserted which leads to Eq. 4.80. Instead, in MND theory the correlation function $L(\omega)$ is obtained from the Fourier transform of the time dependent two-particle correlation function, that is,

$$[L(\omega)]_{c,a}^{c,b} = \int e^{i\omega t} [L(t)]_{c,a}^{c,b} dt = \int e^{i\omega t} \langle \Psi_0 | A_b^\dagger(t) c^\dagger(t) c(0) A_a(0) | \Psi_0 \rangle dt, \quad (6.2)$$

where we have written the creation and annihilation operators of the conduction band electrons with an uppercase A and where c denotes the core state operators. In MND theory, the correlation function $L(t)$ is written as a product [119]

$$L(t) = G_{ab}(t)C(t), \quad (6.3)$$

of the conduction band electron Green's function G and the core Green's function C . The transient conduction band electron Green's function obeys a Dyson-like equation

$$G_{ab}(\tau, t) = G_{ab}^0(\tau) - \sum_{a'b'} \int_t^0 G_{aa'}^0(\tau - \tau') V_{a'b'} G_{b'b}(\tau'; t) d\tau', \quad (6.4)$$

where V is the potential of the core-hole.

Consider the equilibrium case $t \rightarrow \infty$. Instead of solving the Dyson equation, we self-consistently solve the KS equations where the core-hole potential is included by removing one core electron from one atom in a supercell at the beginning of the self-consistency cycle. Self-consistently solving the KS equations in the presence of the core-hole results in final state KS energies and wave functions $\epsilon_i^{\text{fs}}, \varphi_i^{\text{fs}}$. The KS energies and orbitals obtained from a calculation without the core hole are termed initial state KS energies and orbitals. The final state

energies and wave functions approximately account for the renormalization of the KS energies and orbitals due to the core hole. Additionally, by this procedure screening effects due to the rearrangement of valence electrons around the core hole are taken into account. Out of the final state energies and orbitals we then construct a final state conduction band Green's function G^{fs} that we use to approximate the transient Green's function G in Eq. (6.3). As in the KS formalism the electrons are non-interacting the Green's function is diagonal and reads

$$G_{ab}^{\text{fs}}(t) = e^{i\epsilon_a^{\text{fs}}t} \delta_{ab}, \quad (6.5)$$

while the core energies and wave functions are unaffected due to the frozen core approximation that is used in the present implementation of the PAW method. The approximate two-particle final state correlation function L^{fs} then reduces to

$$[L^{\text{fs}}(\omega)]_{c,a}^{c,b} = e^{i(\epsilon_a^{\text{fs}} - \epsilon_c)t} \delta_{ab}. \quad (6.6)$$

Correspondingly, the final state KS energies and orbitals $\epsilon_i^{\text{fs}}, \varphi_i^{\text{fs}}$ are used when evaluating the transition matrix elements. When this result is inserted into the Fourier transform (6.2) we obtain the macroscopic dielectric function

$$\epsilon_M(\omega) = 1 - \frac{4\pi e^2}{V} \sum_a \left| \frac{\langle a^{\text{fs}} | \hat{\mathbf{p}} | c \rangle}{\epsilon_c - \epsilon_a^{\text{fs}}} \right|^2 \frac{1}{\epsilon_a^{\text{fs}} - \epsilon_c + \omega - i\delta}, \quad (6.7)$$

where the infinitesimal $-i\delta$ was added to recover the analytical properties of $L(\omega)$. The absorption spectra are obtained from the imaginary part so that the final result reads

$$\text{Im}\epsilon_M(\omega) = -\frac{4\pi^2 e^2}{\omega^2 V} \sum_a \left| \langle a^{\text{fs}} | \hat{\mathbf{p}} | c \rangle \right|^2 \delta(\epsilon_c - \epsilon_a^{\text{fs}} - \omega), \quad (6.8)$$

where we have absorbed the denominators of the transition matrix elements into ω^2 . This result gives us the X-ray absorption spectrum in the FSA. To implement Eq. (6.8) in the PAW method we use the result of Sec. 5.2:

$$\text{Im}\epsilon_M(\omega) = -\frac{4\pi^2 e^2}{\omega^2 V} \sum_a \left| \sum_i \langle \tilde{\varphi}_a^{\text{fs}} | p_i \rangle \langle \phi_i | \nabla | \phi_c \rangle \right|^2 \delta(\epsilon_c - \epsilon_a^{\text{fs}} - \omega), \quad (6.9)$$

The index a runs over all unoccupied states considered in the calculation. Due to the requirement of using supercells the total number of unoccupied states can reach values of $10^3 - 10^4$.

6.2 Summary of core constraining approaches

As mentioned at the beginning of this chapter, the FSA method offers some flexibility as the amount of charge removed from the core state during the self-consistency cycle can be adjusted freely. Additionally, the excited electron can be placed into one of the conduction bands, added to the background charge, or removed entirely from the simulation cell. Thus several methods have been derived from the FSA that use this flexibility by imposing different physically motivated constraints on the core and conduction band occupancies. We provide here an overview of the commonly employed methods where we follow the reviews of Michelitsch and Reuter [110], Klein *et al.* [76], and Jana and Herbert [72].

In the following, total energies are denoted by an uppercase E and KS eigenenergies by a lowercase ϵ . A subscript “fs” or “i” will indicate whether the energies are final or initial state energies, respectively. The occupancies of the core and conduction band states are given in the form $\epsilon_a^{fs}(n_c, n_a)$ which in this instance means the final state KS energy of conduction band a obtained by constraining the core and conduction band occupancy to n_c and n_a , respectively, when performing a self-consistent calculation.

Δ self consistent field and related methods

In the Δ self consistent field (Δ SCF) method [11, 193, 55] the transition energy $\omega_{ac} = \epsilon_a - \epsilon_c$ is obtained from total energy differences as

$$\omega_{ac}^{\Delta\text{SCF}} = E^{\text{fs}}(n_c = 0, n_a = 1) - E^{\text{i}}(n_c = 1, n_a = 0). \quad (6.10)$$

Note that the constraint is applied to each individual conduction band so that in Δ SCF a separate SCF calculation has to be performed for each included conduction band. That is, if N conduction bands are included when calculating the spectra, then N SCF calculations need to be carried out to obtain each separate $E^{\text{fs}}(n_c = 0, n_a = 1)$. While this constraint renders this method prohibitive for large systems and solid state calculations with multiple $\mathbf{k}$ -points, Δ SCF is one of the standard methods to calculate X-ray excitation spectra of molecules [117] where it is on occasion on par with more sophisticated techniques [18, 82].

From Δ SCF several variants have emerged, such as Slaters transition state (TS) [163] and the generalized TS (GTS) [198] methods for which the transition energies are given by

$$\omega_{ac}^{\text{TS}} = \epsilon^{\text{fs}}(n_c = 1/2, n_a = 1/2) - \epsilon^{\text{i}}(n_c = 1/2, n_a = 1/2), \quad (6.11)$$

$$\omega_{ac}^{\text{GTS}} = \left[\frac{1}{4} \epsilon_a^{\text{fs}}(n_c = 1, n_a = 0) - \frac{3}{4} \epsilon_a^{\text{i}}(n_c = 1/3, n_a = 2/3) \right] \quad (6.12)$$

$$- \left[\frac{1}{4} \epsilon_c^{\text{fs}}(n_c = 1, n_a = 0) - \frac{3}{4} \epsilon_c^{\text{i}}(n_c = 1/3, n_a = 2/3) \right]. \quad (6.13)$$

In contrast to Δ SCF, the TS and GTS transition energies are obtained from the final state KS eigenvalues of the corresponding constrained DFT calculation. Note, that two calculations need to be performed for GTS. Again, the constraints are applied to each conduction band separately and the self-consistency has to be determined N times, if N conduction bands are included.

Transition potential and related methods

One possibility to simplify the calculations is to neglect the excited electron entirely, that is, setting the occupation $n_a = 0$ in the TS variant of the preceding section. Then, instead of calculating N different conduction band constrained final states only one final state calculation is necessary. The commonly used approaches that use this constraint are the transition potential (TP) [168, 66, 182] and full core-hole (FCH) [177, 64, 90] methods. The TP method is sometimes referred to as half-core hole (HCH) method [137, 70, 90] as the final state is determined self-consistently including half of a core hole. Additionally, Michelitsch and Reuter [110] introduced the generalized TP (GTP) method as an analogue to the GTS method listed

in the previous section. The constraints of these three methods are as follows:

$$\omega_{ac}^{\text{FCH}} = \epsilon_a^{\text{fs}}(n_c = 0, n_a = 0) - \epsilon_c^{\text{i}}(n_c = 0, n_a = 0), \quad (6.14)$$

$$\omega_{ac}^{\text{TP}} = \epsilon_a^{\text{fs}}(n_c = 1/2, n_a = 0) - \epsilon_c^{\text{i}}(n_c = 1/2, n_a = 0), \quad (6.15)$$

$$\omega_{ac}^{\text{GTP}} = \left[\frac{1}{4} \epsilon_a^{\text{fs}}(n_c = 1, n_a = 0) - \frac{3}{4} \epsilon_a^{\text{i}}(n_c = 1/3, n_a = 0) \right] \quad (6.16)$$

$$- \left[\frac{1}{4} \epsilon_c^{\text{fs}}(n_c = 1, n_a = 0) - \frac{3}{4} \epsilon_c^{\text{i}}(n_c = 1/3, n_a = 0) \right]. \quad (6.17)$$

Neutral transition potential methods

The methods listed in the last section have the disadvantage that the simulation cell is not charge neutral. A charge neutral variant of the FCH method was devised by Prendergast and Galli [137] by placing the excited electron into the lowest unoccupied molecular orbital (LUMO) in the case of molecules or lowest conduction band (LCB) in the case of solids. This method is called excited electron and core hole (XCH). The charge neutral variants of the methods of the preceding section are

$$\omega_{ac}^{\text{XCH}} = \epsilon_a^{\text{fs}}(n_c = 0, n_{\text{LUMO/LCB}} = 1) - \epsilon_c^{\text{i}}(n_c = 0, n_{\text{LUMO/LCB}} = 1), \quad (6.18)$$

$$\omega_{ac}^{\text{XTP}} = \epsilon_a^{\text{fs}}(n_c = 1/2, n_{\text{LUMO/LCB}} = 1) - \epsilon_c^{\text{i}}(n_c = 1/2, n_{\text{LUMO/LCB}} = 1), \quad (6.19)$$

$$\omega_{ac}^{\text{XGTP}} = \left[\frac{1}{4} \epsilon_a^{\text{fs}}(n_c = 1, n_{\text{LUMO/LCB}} = 1) - \frac{3}{4} \epsilon_a^{\text{i}}(n_c = 1/3, n_{\text{LUMO/LCB}} = 1) \right] \quad (6.20)$$

$$- \left[\frac{1}{4} \epsilon_c^{\text{fs}}(n_c = 1, n_{\text{LUMO/LCB}} = 1) - \frac{3}{4} \epsilon_c^{\text{i}}(n_c = 1/3, n_{\text{LUMO/LCB}} = 1) \right]. \quad (6.21)$$

We note that the FCH, TP (or HCH), and XCH methods have been used extensively in X-ray spectroscopies of water where it is still debated which of these methods yields the best agreement with experiment [43].

6.3 Final state approximation in practice

We now summarize how FSA approximation are performed in practice in the present work. An FSA calculation involves two steps. First, a supercell of sufficient size must be created to reduce the interaction between neighboring core holes. The size of the supercell has to be determined each time a new material is investigated, as the size of the supercell depends on the material in question: While around 100 atoms are needed for diamond [173] and wurzite AlN [111] only 32 are sufficient for GaN [89]. Keep in mind that the density of the $\mathbf{k}$ -point sampling must remain constant during this procedure. If the unit cell is sampled with, say, $20 \times 20 \times 20$ $\mathbf{k}$ points, then the $2 \times 2 \times 2$ supercell should be sampled using $10 \times 10 \times 10$ $\mathbf{k}$ -points, etc.

In the second step the FSA is carried out. A minimal working INCAR has the following form

NBANDS = 512 #The total number of included conduction bands.

ICORELEVEL = 2 #Flag that activates the FS calculation.

CSHIFT = 0.2 #Broadening in eV

CLNT = 1 #Species from which the core electron is excited.

$\text{CLN} = 1$ #Principle quantum number of excited electron.
 $\text{CLL} = 0$ #Angular quantum number of excited electron.
 $\text{CLZ} = 1$ #Charge removed from core state.
 $\text{NELECT} = \text{total number of valence electrons} + n_{\text{LUMO/LCB}}$ #Charge added to the LUMO or LCB.
 $\text{CLE} = -268.77$ #Core-eigenstate energy ϵ_c in Eq. (6.8)

The core hole charge n_c (CLZ) is a freely adjustable parameter. The results of chapter 7 of Part II were obtained by removing an entire electron from the excited atom by setting $n_c = 1$. In chapter 8 of Part II examples will be shown where n_c is set to values different from 1. Additionally, the amount of charge added to the LUMO/LCB, $n_{\text{LUMO/LCB}}$, can be controlled with the parameter **NELECT** that sets the total number of valence electrons in the system. By default, $\text{CLZ}=1$ and $\text{NELECT} = \text{number of valence electrons} + 1$ so that one electron is removed from the core shell and an extra electron is added to the LUMO. This choice of parameters corresponds to the XCH method of Sec. 6.2. By adjusting **CLZ** (i.e. n_c) and **NELECT** (i.e. $n_{\text{LUMO/LCB}}$), it is possible to select other methods of Sec. 6.2 in which the electron is removed or added from the core state and to the LUMO. For example, the XTP method is selected by setting $\text{CLZ} = 0.5$ and $\text{NELECT} = \text{number of electrons} + 0.5$. In particular, the FCH method that is used extensively in Part II is selected with $\text{CLZ} = 1$ and $\text{NELECT} = \text{number of valence electrons}$.

This completes the part, where we have introduced the necessary theory and the methods used in this thesis.

Part II

Results

Chapter 7

Results on reference materials

This chapter presents excerpts from Ref. [184]. In accordance with the rules of the University of Vienna for cumulative theses, I describe here how I contributed to this publication.

The original paper was published in October 2022 in the journal *Physical Review Letters* B and is entitled "X-ray absorption using the projector augmented-wave method and the Bethe-Salpeter equation". The copyright is held by the American Physical Society.

With the help and guidance of my co-authors Alexey Tal and Georg Kresse, I have largely independently performed this study. The implementation was done by me under the guidance of Georg Kresse, and I produced all the numerical results. I wrote most of the original manuscript, with my co-authors providing inputs for the academic writing process. At all stages of the research project, my co-authors provided valuable feedback and constructive criticism on the results, on my analysis, and on the drafts of the manuscript.

I do not include the theoretical part of Ref. [184] as it is sufficiently covered in chapters 2 to 7 of this thesis. Only the sections dealing with the computational methods, the results, and the conclusion are included.

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7.1 Introduction

X-ray Absorption Spectroscopy (XAS) experiments probe the transition probability of exciting an electron from a core state to a conduction band state. XAS spectra furnish information about the local chemical environment of the probed atom, e.g. coordination number or oxidation state [203]. However, experimental XAS spectra are difficult to interpret without theoretical input.

To simulate XAS spectra, two fairly simple *ab initio* approaches exist. In the initial-state approximation, the XAS spectrum is calculated via Fermi's golden rule, where the initial state is a core state and the final state a conduction band state. In the final-state approximation [195, 141, 130, 97, 143], the final-state wavefunction is calculated self-consistently using Kohn-Sham Density Functional Theory (DFT) [65] by removing one core electron and placing it in the conduction bands.

These methods have a couple of drawbacks. In the initial-state approach, electrons and holes are independent particles and any interactions between them are neglected. In the final-state approach, supercells are required to avoid spurious interactions between core-holes located in different unit cells. For this reason, this approach is here called Supercell Core-Hole (SCH) method. Further, it is assumed that the approximate density functionals remain valid for excited states. Finally, the excited electron is usually placed into the conduction band edge, and it is implied that the resulting renormalized one-electron energies for all conduction bands will be a good approximation for the XAS fine structure.

By looking at these restrictions an approach is desirable which addresses some of the shortcomings of the SCH method. In particular, an accurate description of the electronic structure is needed, ideally including many-body correlations for the interaction of electrons and holes.

The state-of-the-art approach that resolves both issues is the $GW+BSE$ method. It combines *ab initio* ground state electronic structure calculations with techniques of Many-Body Perturbation Theory (MBPT) [125]. By calculating the one-particle Green’s function G , various one-body properties can be obtained, e.g. quasiparticle band gaps and quasiparticle energies [68].

For a description of the mutual interaction of the electrons and holes, one needs to go beyond one-particle theory and solve the equation of motion for the two-particle Green’s function – the Bethe-Salpeter Equation (BSE) [156, 105]. The BSE is an integral equation that can be recast into an eigenvalue equation, where the exchange and the screened attraction of electrons and holes are incorporated in the resulting BSE matrix. The BSE approach has first been applied to optical spectra of semiconductors in the late seventies [58]. *Ab initio* based approaches to the BSE followed in the late nineties [17, 7, 186, 146].

In these approaches, the orbitals are usually obtained from a standard ground state DFT calculation. In the second step, the Green’s function is calculated using the DFT orbitals and one-electron energies. Many-body correlation effects are included by replacing the Kohn-Sham exchange-correlation potential with the self-energy in the GW approximation and by solving the Dyson equation for the interacting Green’s function. The one-electron energies are then updated by equating them to the poles of the resulting interacting Green’s function. In most cases, a single iteration is performed. Finally, the two-particle BSE is set up and solved. Often one refers to this approach as $GW+BSE$.

The $GW+BSE$ approach has been extended from the optical to the X-ray regime by covering excitations from core levels to the conduction band. The earliest implementation was presented by Shirley *et al.* [158, 165] within a pseudopotential scheme. This work culminated in the OCEAN package [189, 49, 161]. Further adaptations within all-electron full-potential methods were established by Olovsson *et al.* in **exciting** [123] and subsequently by Laskowski *et al.* in WIEN2K [88]. To the best of our knowledge, most available electronic structure codes that implement the Projector Augmented-Wave (PAW) methodology calculate XAS spectra via the supercell core-hole method [48, 52, 108, 29, 138]. We note that in a recent version of the OCEAN code [191], an augmentation technique reminiscent of the PAW methodology is used for the calculation of transition matrix elements.

In this work, we present an implementation of the $GW+BSE$ scheme in the PAW method for X-ray absorption spectra. We derive the BSE in the PAW scheme and show what modifications must be made for core states. Our implementation is tested by calculating XAS spectra for the K -edges of one prototypical covalent system (diamond), two 2D van-der-Waals layered materials (graphite and hexagonal boron-nitride), and four ionic materials with shallow core states (the lithium-halides LiF, LiCl, LiBr, and LiI). We benchmark our results against spectra obtained either by a pseudopotential or an all-electron implementation of the BSE and point out where the $GW+BSE$ implementation within PAW shows improvements. We furthermore compare our results with experiment and a previously presented implementation of the SCH method [75].

Finally, we show that previously obtained SCH spectra of the lithium-halides can be improved by adding the electron to the background charge instead of the lowest conduction band. We argue that the improvement comes from a reduction of self-interaction errors. We then connect this explanation to the $GW+BSE$ approach by investigating how the spectra change if the

exchange term of the BSE is omitted.

In Sec. 7.2 we summarize the computational methods, followed by a presentation of the results in Sec. 7.3. In Sec. 7.4 we present the improved SCH spectra for the lithium-halides and the discussion of the suggested self-interaction effect. Finally, we summarize and conclude this work in Sec. 7.5.

7.2 Computational Methods

7.2.1 Numerical details

All *ab initio* electronic structure calculations were performed with the all-electron plane-wave code VASP [84], which uses the PAW-implementation of Kresse and Joubert [85]. The workflow is the following.

We start with a standard DFT calculation, yielding the Kohn-Sham energies and Kohn-Sham orbitals. In all DFT calculations we used the exchange-correlation functional by Perdew, Burke, and Ernzerhof [131]. The energy cutoffs are listed in Table 7.1. We perform a single-shot *GW* calculation (G_0W_0) to calculate the quasiparticle energies and the dynamic screened interaction in momentum space $W_{\mathbf{G},\mathbf{G}'}(\omega)$. The static approximation for W is made at the beginning of the BSE calculation. Note that the orbitals are kept fixed at the DFT level. After a convergence study for LiF, the energy cutoff of the response function is set to 150 eV in all systems. Then, the BSE eigenvalue equation is set up using the *GW* quasiparticle energies and the PBE orbitals. Finally, the BSE equation is solved and the BSE dielectric function is calculated.

We reiterate that in this work we only investigate *K*-edges. Furthermore, transitions from valence states to conduction states are excluded from the calculations. The number of conduction bands included in the transitions is 8 in diamond, 12 in graphite, 12 in *h*-BN, and 15 in all four lithium-halides. These values are chosen so that the modeled spectra firstly reproduce all relevant peaks and secondly cover the same energy range as the experimental spectrum.

We employ the shifted grid technique in all *GW*+BSE calculations [149] to reduce the computational demand and still obtain highly accurate spectra. First, we generate all irreducible $\mathbf{k}$ -points $\mathbf{k}_{1,\dots,L}$ and corresponding weights $w_{1,\dots,L}$ of an $n \times n \times n$ $\mathbf{k}$ -mesh. Then, we perform L independent calculations with an $m \times m \times m$ $\mathbf{k}$ -mesh, where the $\mathbf{k}$ -point grid is shifted by one of the L irreducible $\mathbf{k}$ -points. This procedure generates all $\mathbf{k}$ -points of a regular $(m \cdot n) \times (m \cdot n) \times (m \cdot n)$ $\mathbf{k}$ -mesh. Finally, we average the L so obtained dielectric functions, $\varepsilon = \sum_i^L w_i \varepsilon_i / \sum_i^L w_i$.

For diamond, graphite, and *h*-BN we compare the *GW*+BSE spectra to those of the SCH calculations implemented previously [75]. In all SCH calculations the supercells contain 128 atoms. Previous publications observed converged results for these supercells [173, 75]. In Table 7.2 we list the $\mathbf{k}$ -meshes used in the *GW*+BSE and SCH calculations.

In the available experimental absorption spectra of graphite [27] and of boron in *h*-BN [93], the incoming radiation was incident at an angle α of 40° and 45° to the surface normal, respectively. In these cases, we have averaged the imaginary parts of the perpendicular and parallel components of the dielectric function according to absorption $\propto \cos(\alpha)^2 \varepsilon_{xx}^{(2)} + \sin(\alpha)^2 \varepsilon_{zz}^{(2)}$,

System	E_{cut} (eV)
diamond, graphite	434.9
<i>h</i> -BN	400.0
LiF	487.7
LiCl	262.4
LiBr	216.3
LiI	175.6

Table 7.1: Plane-wave energy cutoffs used in the present work for the plane-wave expansion of the orbitals.

Method	BSE	BSE	BSE	SCH	SCH
System	n	L	$m \times m \times m$	atoms	$\mathbf{k}$ -points
diamond	3	4	$10 \times 10 \times 10$	128	$9 \times 9 \times 9$
graphite	4	12	$16 \times 16 \times 4$	128	$4 \times 4 \times 2$
<i>h</i> -BN	3	4	$12 \times 12 \times 4$	128	$5 \times 5 \times 3$
lithium-halides	3	4	$10 \times 10 \times 10$	128	$8 \times 8 \times 8$

Table 7.2: Table of $\mathbf{k}$ -meshes used for the shifted grid technique and for the supercell core-hole calculations (SCH). Shifted grid technique: an $n \times n \times n$ mesh results in L irreducible $\mathbf{k}$ -points. Meshes of size $m \times m \times m$ are then shifted by these L different $\mathbf{k}$ -points, creating an $(m \cdot n) \times (m \cdot n) \times (m \cdot n)$ $\mathbf{k}$ -mesh. All meshes are centered at the Γ -point. For the SCH calculations we specify both the supercell size (number of atoms) and the $\mathbf{k}$ -point grids.

where $\varepsilon_{xx}, \varepsilon_{yy}$ are the in-plane and ε_{zz} the out-of-plane components of the dielectric function. Details on the polarization are missing for the K -edge of nitrogen in *h*-BN [134]. For this system we have weighted each component by a factor 1/3.

In all the presented spectra for C, B, and N, an energy-independent Lorentzian broadening of 0.3 eV is applied. To facilitate comparison of our spectra with the results of other authors a reduced broadening of 0.1 eV is used for the lithium-halides.

Finally, we note that neither the GW +BSE nor the SCH method can quantitatively determine the onset of absorption, hence the energy axes of the modeled spectra are always shifted in order to obtain best agreement with the experimental spectra.

7.2.2 Model dielectric function approach

In the GW +BSE approach, the screened interaction W is the output of the G_0W_0 step. Since we perform single-shot GW calculations, W is calculated in the RPA approximation from the PBE orbitals and eigenvalues. GW calculations are computationally demanding, scaling with the fourth power of the system size and quadratic with the number of $\mathbf{k}$ -points [96]. We investigate whether W can be obtained cheaper and still sufficiently accurately by using the model dielectric function approach [25]. In this approach, a standard DFT calculation is done as a preparatory step. Then, the G_0W_0 step is skipped and the screened interaction is instead calculated via $W = \varepsilon^{-1}v$, where ε^{-1} is approximated by a diagonal model dielectric function.

In this work, we use the model dielectric function

$$\varepsilon_{GG}^{-1}(\varepsilon_{\infty}^{-1}, \mu) = 1 - (1 - \varepsilon_{\infty}^{-1})e^{-G^2/4\mu^2}, \quad (7.1)$$

with $G = |\mathbf{G}|$. It was shown that this model dielectric function yields reasonable results for the diagonal of the dielectric function [25, 32, 174] as well as for optical spectra [25, 174]. Additionally, it has only two parameters. In the preceding equation, the macroscopic dielectric function ε_{∞} is obtained by averaging the diagonal elements of the macroscopic dielectric tensor corresponding to W in the GW calculations. The screening parameter μ (in $\text{\AA}^{-1}$) results from a fit of the model-dielectric function to $\varepsilon_{GG}^{-1}(\mathbf{q} \rightarrow 0, \omega = 0)$, where the long-range and short-range limits are set to $1/\varepsilon_{\infty}$ and 1, respectively.

This approach is tested for diamond and B in h -BN and compared to the parameter-free GW +BSE spectra. Furthermore, we need to assess how well this approach approximates the diagonal elements of W . To do this, we also show for these two systems GW +BSE spectra where the off-diagonal elements of W have been set to zero in the BSE step.

In summary, we compare for diamond and B in h -BN three spectra: a GW +BSE spectrum using the full screened interaction including off-diagonal elements, a GW +BSE spectrum using only the diagonal elements of W , and finally a BSE spectrum using the model dielectric function.

7.3 Results

7.3.1 Diamond

In Fig. 7.1 we compare the K -edge of diamond using the present PAW- GW +BSE implementation with experiment [98], a pseudopotential BSE implementation [165], and an SCH-spectrum. Comparing the modeled spectrum to experiment, we see that the positions of the peaks agree very well, but the spectrum lacks intensity towards higher energies. Interestingly, the differences between the theoretical and experimental spectra seem to be mostly a "background" present in the experimental spectrum: for instance, the intensity modulations around the individual peaks follow the experimental intensity modulations exceedingly well. This is most obvious around the minimum at 302 eV: both to the left and right-hand side, the experimental and theoretical spectrum change by roughly the same amount. The background consistently increases from the leftmost first peak towards the right, and can be roughly modeled by a parabolic curve with the onset of the parabola located around the onset of absorption. The same discrepancy will be noticeable for all spectra that we show in the present work. We are not certain about the origin of the discrepancy, but speculate that it is related to multiple scattering events involving core-conduction band pairs at other sites, or alternatively high energy valence-conduction band pairs. Both are not accounted for by the present level of theory.

Returning to the diamond spectrum, we note that in the experimental spectrum at around 290 eV a slight, most likely excitonic peak is visible. Compared to the other spectra our result shows a slight shoulder located at around the same energy (see arrow in Fig. 7.1). To show that this feature is not an artifact of the shifted grid technique, we plot in an inset up to the first maximum at 291 eV the result of a calculation using a standard non-shifted $18 \times 18 \times 18$

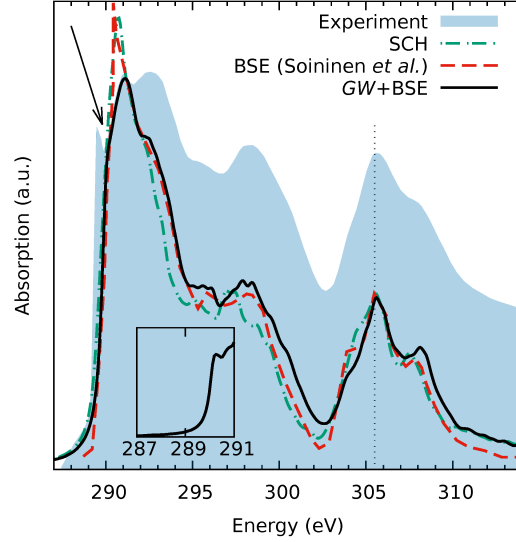


Figure 7.1: XAS spectra of K -edge of C in diamond. *Blue filled curve*: experiment [98]. *Black curve*: $GW+BSE$ spectrum, this work. *Green dash-dotted curve*: SCH calculation. *Red dashed line*: BSE-spectrum from [165]. *Arrow*: Location of the excitonic shoulder in the $GW+BSE$ spectrum. *Inset*: $GW+BSE$ result using an $18 \times 18 \times 18$ $\mathbf{k}$ -mesh and a reduced Lorentzian broadening. All modeled XAS-spectra are centered and adjusted in scale on the peak at 305.5 eV (dotted line).

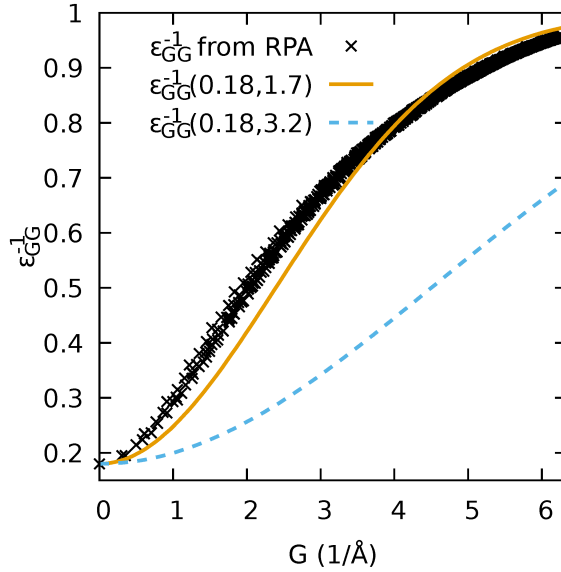


Figure 7.2: Inverse dielectric function ε_{GG}^{-1} of diamond. *Crosses*: Inverse dielectric function $\varepsilon_{GG}^{-1}(\mathbf{q} \rightarrow 0, \omega = 0)$ at the RPA level. *Orange line*: model dielectric function $\varepsilon_{GG}^{-1}(0.18, 1.7)$, see Eq. (7.1), where μ is given in $1/\text{\AA}$. *Blue broken line*: $\varepsilon_{GG}^{-1}(0.18, 3.2)$. All lines intercept the y -axis at $\varepsilon_{\infty}^{-1} = 0.18$.

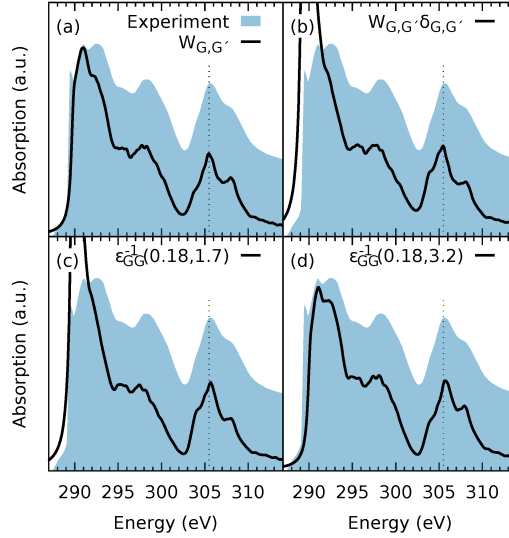


Figure 7.3: K -edge spectrum of C in diamond, comparing experiment [98] (*blue filled curves*) to $GW+BSE$ spectra, using different approximations for the screened interaction W : (a) W from G_0W_0 step, (b) same as panel (a) excluding off-diagonal elements, (c) model dielectric function $\varepsilon_{GG}^{-1}(0.18, 1.7)$, see Eq. (7.1), where μ is given in $1/\text{\AA}$. (d) model dielectric function $\varepsilon_{GG}^{-1}(0.18, 3.2)$, μ adjusted to fit experiment.

$\mathbf{k}$ -point mesh. Clearly, this spectrum also shows a peak. To make it better visible we have reduced the Lorentzian broadening in this calculation to 0.2 eV.

In summary, for the case of diamond the present spectrum agrees very well with the experimental spectrum for all peak positions. Even small features in the experimental spectrum are resolved. However, deviations are observed for the absolute intensities of the peaks. We attribute this to the lack of background in the theoretical modeling caused by multiple scattering events in the experiment.

In Fig. 7.3 we compare the experiment to four $GW+BSE$ spectra. In each panel, we use a different approximation for the screened interaction, as outlined in the computational methods section. All spectra are centered on and adjusted in scale to the peak of the experimental spectrum at 305.5 eV, marked by a vertical dotted line. Comparing the results obtained by including (panel (a)) or excluding (panel (b)) off-diagonal elements of W , we see that the magnitude of the first peak is vastly overestimated when only the diagonal elements are included. In panel (c) we use a model-dielectric function $\varepsilon_{GG}^{-1}(0.18, 1.7)$. As in panel (b), the first feature is overestimated. In panel (d) we use a model-dielectric function with unchanged $\varepsilon_{\infty}^{-1}$ and the screening parameter adjusted to $\mu = 3.2 \text{ \AA}^{-1}$. Increasing μ restores the amplitude of the first peak to that of panel (a).

Neglecting the off-diagonal elements of the screened interaction from panel (a) to panel (b) in Fig. 7.3 or only using the diagonal model-dielectric function in panel (c) overestimates the first peak and redshifts the peak at 297 eV slightly to the left. In Fig. 7.2 we plot the diagonal elements of the RPA dielectric matrix as well as the model dielectric functions $\varepsilon_{GG}^{-1}(0.18, 1.7)$

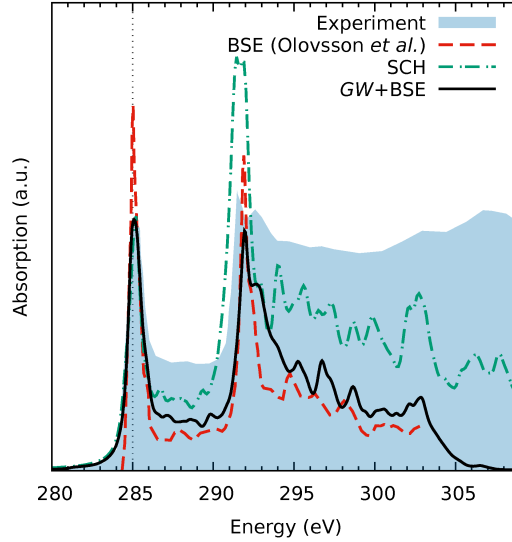


Figure 7.4: XAS spectra of the K -edge of C in graphite. *Blue filled curve*: experiment [27]. *Black curve*: $GW+BSE$ spectrum, this work. *Green dashed curve*: BSE-spectrum from [159]. *Red dash-dotted curve*: SCH calculation. All modeled spectra are centered at 285 eV and adjusted in height to match the integral over the first peak.

and $\varepsilon_{GG}^{-1}(0.18, 3.2)$. From this plot we see that for a given wave vector G increasing μ decreases ε_{GG}^{-1} and hence decreases $W = \varepsilon^{-1}v$.

From all these observations we conclude that the off-diagonal elements of the screened interaction are indispensable for an accurate description of excitonic peaks of localized core states. Neglecting off-diagonal elements of $\varepsilon_{GG'}^{-1}$ amounts to the neglect of local-field effects [68, 146]. Local-field effects describe the microscopic variation of the screening field induced by a homogeneous electric charge. Although adjusting the screening length in the model dielectric function can mimic the effect of local-field effects on the spectra, this remains a rather *ad hoc* approach. Also, the model dielectric function after adjustment of μ clearly does not follow the *ab initio* results, compare Fig. 7.2. As to why the off-diagonal components are relevant, we note that one makes similar observations for small molecules and in general for strongly localized states. The diagonal approximation in momentum space is not adequate when dealing with a mixture of localized and itinerant states, whereas it accounts well for transitions involving only band-like itinerant states. This is an important observation that most likely exposes and underlines the limits of a simple diagonal screening approach.

7.3.2 Graphite

In Fig. 7.4 we present a comparison of our PAW- $GW+BSE$ result of the K -edge of graphite to experiment [27], to an all-electron full-potential BSE spectrum [124], and an SCH-spectrum. In Ref. [124] perpendicular and parallel components are shown separately, so we have averaged them in the same way as our result. The $GW+BSE$ and SCH peaks have been adjusted in height to the first peak in experiment. Since the spectrum of Olovsson *et al.* [124] has been calculated using less broadening, we have adjusted its height to approximately match the

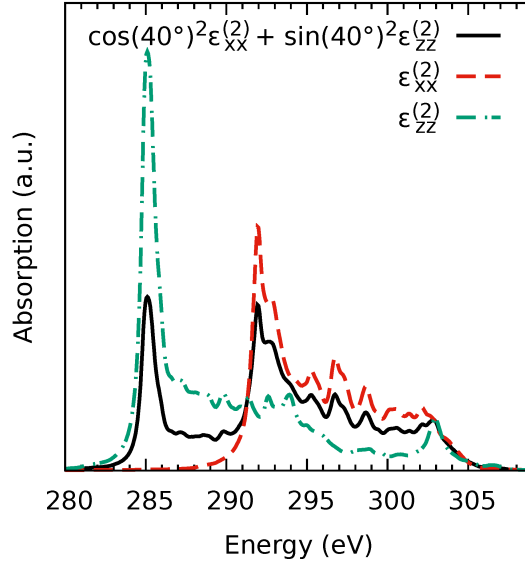


Figure 7.5: Imaginary parts of in-plane and out-of-plane components of the dielectric function for the K -edge of C in graphite. *Black curve*: averaged components, Absorption $\propto \cos(40^\circ)^2 \varepsilon_{xx}^{(2)} + \sin(40^\circ)^2 \varepsilon_{zz}^{(2)}$. *Red dashed curve*: in-plane component, $\varepsilon_{xx}^{(2)}$. *Green dash-dotted curve*: out-of-plane component, $\varepsilon_{zz}^{(2)}$.

integral over the first peak. Comparing the PAW-GW+BSE spectrum of this work and the all-electron result of Ref. [124] we see that both results can match the energy difference of the experimental peak positions at 285 eV and 292 eV.

Graphite is a 2D van-der-Waals material and we show the in-plane and out-of-plane components of the imaginary parts of the dielectric function in Fig. 7.5: The peak at 285 eV can be fully attributed to the out-of-plane component $\varepsilon_{zz}^{(2)}$.

While our result as well as the spectrum from Ref. [124] can reproduce the intensity ratio of the peaks at 287 eV and 292 eV reasonably well, the SCH spectrum overestimates the second peak. We also note the difference in amplitude of our result and experiment in the ranges 285-292 eV and from 292 eV upwards. Furthermore, above 305 eV, we find no intensity, whereas the experimental signal remains quite substantial. As before, the experimental data show a substantial background at higher energies that is lacking in our theoretical calculations. We note that as for diamond the fine-structure of the experimental XAS spectrum is very well resolved in our theoretical calculations: the peaks at 292, 293, 295, 296, and 303 eV are also visible in the experimental spectrum at least as slight humps.

In Ref. [124], it was suggested that the double-peak structure at 292 eV and 293 eV is due to a breaking of degeneracy induced by the electron-phonon interaction. While we cannot exclude that electron-phonon coupling will enhance the splitting, we clearly observe two peaks even in the absence of any lattice distortions. In the previous BSE calculations of Ref. [124] this feature was not discernible. Ref. [124] also discusses the controversy concerning the σ_2^* peak. It is mentioned that some studies interpret this peak as a delocalized bandlike contribution [28]. If we interpret the shoulder in our spectrum tentatively as the σ_2^* peak, then an explanation

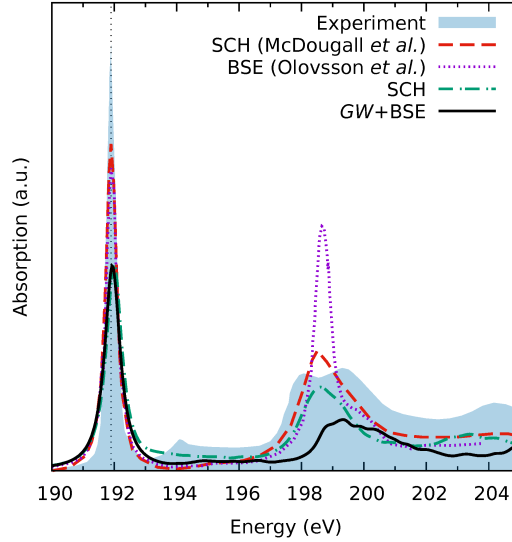


Figure 7.6: XAS spectra of the K -edge of B in h -BN. *Blue filled curve*: experiment [93]. *Black curve*: $GW+BSE$ spectrum, this work. *Green dashed curve*: SCH-spectrum from [109]. *Violet dotted curve*: BSE-spectrum from [124]. *Green dash-dotted curve*: SCH-spectrum. All modeled spectra are centered at 192 eV and adjusted in height to match the integral over the first peak.

might be given why we can see the shoulder in our spectrum and not in the work of Ref. [124]: delocalized states are necessarily localized in reciprocal space. The shifted grid technique can sample the reciprocal space sufficiently accurately to capture this feature. Olovsson *et al.* on the other hand, used a $11 \times 11 \times 3$ $\mathbf{k}$ -mesh. While this grid is sufficiently dense to reproduce the main features, it might not be sufficient to resolve the fine structure.

7.3.3 Hexagonal boron-nitride

7.3.3.1 Boron

In Fig. 7.6 we compare an experimental K -edge spectrum of boron in h -BN [93] to the XAS spectrum obtained with the present PAW- $GW+BSE$ implementation and to an all-electron full-potential BSE spectrum [124]. We also show two SCH spectra, one obtained with an all-electron APW implementation [109] and an SCH spectrum calculated using the implementation presented previously [75]. All spectra have been adjusted in height such that the integrals over the first peak match. All methods reproduce the distance between the exciton peak at 192 eV and the center of the double peak structure, located at 199 eV, while no spectrum can reproduce the double-peak structure or the smaller peak at 194 eV. The latter peak may be caused by double-electron excitations [37, 206]. In this case, neither the SCH nor the $GW+BSE$ implementation presented in this work can capture that feature. As for graphite, the double peak structure has been attributed to a breaking of the degeneracy induced by the electron-phonon interaction [75, 124]. Here our results are unambiguous: without the inclusion of electron-phonon couplings one cannot reproduce the double-peak structure. We note that the experimental double peak is also much more pronounced and distinct than in

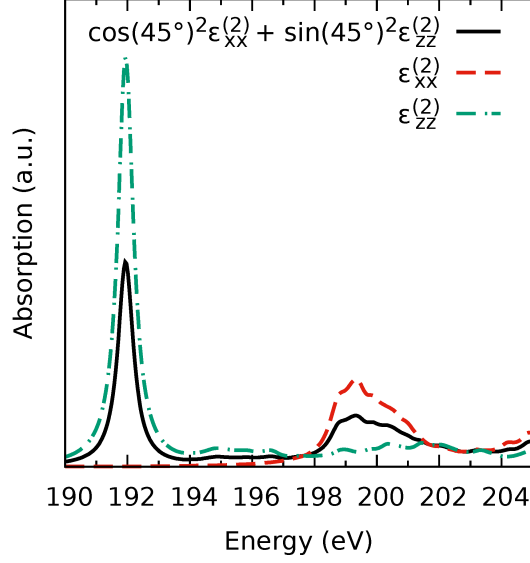


Figure 7.7: Imaginary parts of in-plane and out-of-plane components of the dielectric function for the K -edge of B in h -BN. *Black curve*: averaged components, Absorption $\propto \cos(45^\circ)^2 \varepsilon_{xx}^{(2)} + \sin(45^\circ)^2 \varepsilon_{zz}^{(2)}$. *Red dashed curve*: in-plane component, $\varepsilon_{xx}^{(2)}$. *Green dash-dotted curve*: out-of-plane component, $\varepsilon_{zz}^{(2)}$.

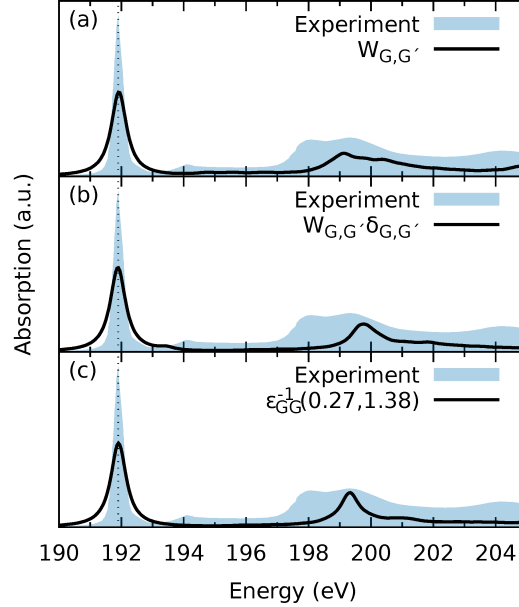


Figure 7.8: K -edge of B in h -BN, comparing different approaches to the screened interaction W . (a) W from G_0W_0 step. (b) same as panel (a), excluding off-diagonal elements. (c) Model dielectric function $\varepsilon_{GG}^{-1}(0.27, 1.38)$, see Eq. (7.1), where μ is given in $1/\text{\AA}$. *Blue filled curve*: experiment [93].

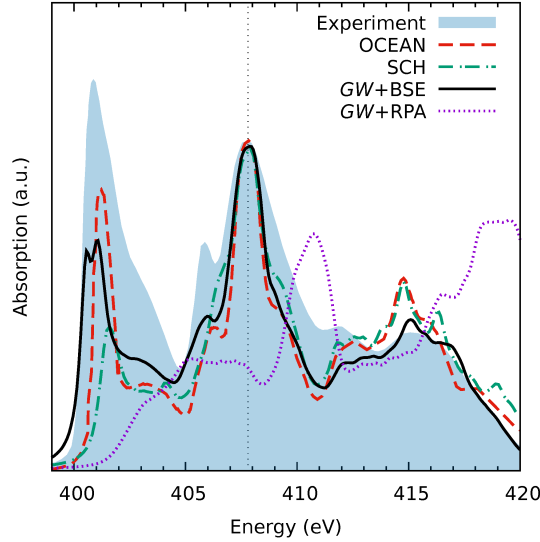


Figure 7.9: XAS spectra of the K -edge of N in h -BN. *Blue filled curve*: experiment [134]. *Black curve*: $GW+BSE$ spectrum, this work. *Red dashed curve*: OCEAN BSE-spectrum, extracted from [191]. *Green dash-dotted curve*: SCH-spectrum. *Violet dotted curve*: $GW+RPA$ spectrum. All simulated spectra, except for $GW+RPA$, are centered on the maximum at 408 eV.

graphite.

As for graphite, we also show the in-plane and the out-of-plane components of the imaginary parts of the dielectric function in Fig. 7.7. Here we see that the strong peak at 192 eV corresponds to the out-of-plane component, while the features around 199 eV are attributable to the in-plane components.

In Fig. 7.8 we compare the experiment to BSE spectra. As for diamond, we use different approximations for the screened interaction, as outlined in the section on computational methods and as explored for diamond before. We use either (a) W including off-diagonal elements, or (b) excluding off-diagonal elements, or (c) a model dielectric function $\epsilon_{GG}^{-1}(0.27, 1.38)$. Here, only the $GW+BSE$ spectrum including the off-diagonal elements [panel (a)] can reproduce the energy difference between the first peak at 192 eV and the middle of the double peak structure located at 199 eV. The model dielectric function or using the diagonal elements of W only can not reproduce the position of the center of the double peak structure. However, the model-dielectric function approach performs slightly better, since in that case the second peak is redshifted by approximately 0.1 eV toward the center of the double peak at 199 eV.

7.3.3.2 Nitrogen

In Fig. 7.9 we show an experimental K -edge spectrum of nitrogen in h -BN [93], a modeled spectrum using the current PAW- $GW+BSE$ implementation, a spectrum obtained via the OCEAN package [191], and an SCH-spectrum. Compared to the SCH-spectrum, we are able to better reproduce the energy separation between the π^* resonance at 401 eV and the σ^* peak

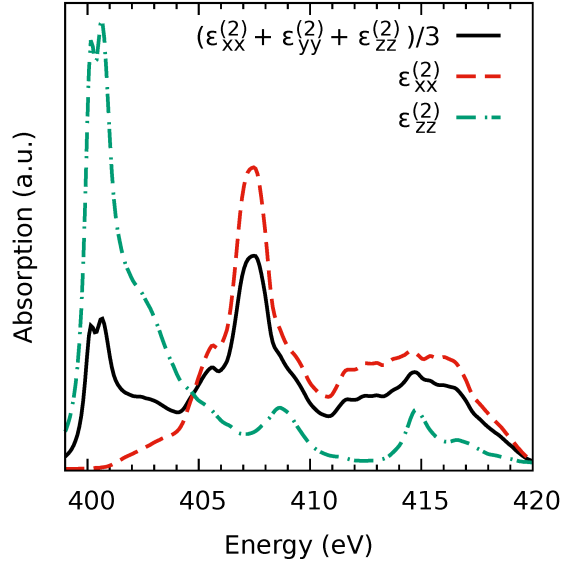


Figure 7.10: Imaginary parts of in-plane and out-of-plane components of the dielectric function for the K -edge of N in h -BN. *Black curve*: average of all components, $\frac{1}{3}(\epsilon_{xx}^{(2)} + \epsilon_{yy}^{(2)} + \epsilon_{zz}^{(2)})$. *Red dashed curve*: in-plane component, $\epsilon_{xx}^{(2)}$. *Green dash-dotted curve*: out-of-plane component, $\epsilon_{zz}^{(2)}$.

at 408 eV. Furthermore, the $GW+BSE$ spectrum shows a shoulder at 403 eV and a pronounced side-peak at 406 eV. These experimental features are missing in the SCH spectrum. We also see that the shape of the first peak of the $GW+BSE$ spectrum agrees better with experiment. Comparing our results with the results obtained by OCEAN we see that both spectra agree overall. Slight improvements can be seen in our spectrum regarding the peak at 401 eV and the side-peak at 406 eV: in the OCEAN spectrum these are redshifted with respect to experiment by ≈ 0.1 eV.

Again, we show the in-plane and out-of-plane components in Fig. 7.10. Analogously to graphite, we see that the first peak at 401 eV can be attributed to the out-of-plane component and is identified with the π^* resonance.

We want to briefly discuss the influence of the direct terms on XAS spectra and plot to this end in Fig. 7.9 a $GW+RPA$ spectrum. The latter is obtained by omitting the direct terms in the $GW+BSE$ Hamiltonian. Note that we employ in this work the Tamm-Dancoff approximation, and that in principle a treatment beyond Tamm-Dancoff is needed to obtain a full RPA spectrum. However, as was shown in a previous publication [149], omitting the direct terms restores the symmetry of resonant-resonant and antiresonant-resonant matrix elements. This means that we strictly speaking do not use the Tamm-Dancoff approximation in the calculation of the $GW+RPA$ spectrum. Overall, including the direct term shifts the peaks downward by about 4 eV ($420 \rightarrow 415$ eV, $411 \rightarrow 408$ eV, and $405 \rightarrow 401$ eV). $GW+RPA$ is not able to reproduce the spectrum. In particular, the excitonic peak at 401 eV is missing from the $GW+RPA$ spectrum. This is analogous to results for optical transitions [125, 150, 181, 40]. $GW+RPA$ results for the K -edges of diamond, graphite, hBN , and LiF can be found elsewhere [165, 160].

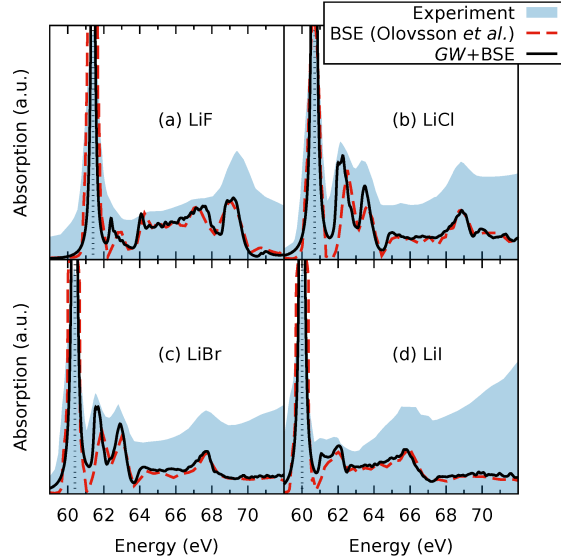


Figure 7.11: XAS spectra for the K -edge of lithium in four lithium-halides. *Blue filled curves*: experiment [56]. *Black curves*: $GW+BSE$ spectra, this work. *Red dashed lines*: BSE spectra from [123]. All modeled spectra are centered on the vertical dashed line in each panel.

7.3.4 Lithium-halides

In Fig. 7.11 we show the results for the XAS spectra of four lithium-halides with shallow core-states: LiF, LiCl, LiI, and LiBr. In each panel we compare our PAW- $GW+BSE$ results to experiment [56] and to an all-electron full-potential BSE spectrum [123]. The XAS-spectra of this work as well as those of Olovsson *et al.* can reproduce the edge-positions and the fine structure found in the experimental spectrum, however, our result better matches the peak positions of some features. This can likely be attributed to the fact that in the GW step we calculate quasiparticle energies of each conduction band individually, while in the spectra of Olovsson *et al.* the bands were rigidly shifted via a scissor operator. We note that we also used a much finer $\mathbf{k}$ -point sampling. Using a finer grid can also change the shape and slightly the position of some peaks.

7.4 Self-interaction effects in SCH calculations

The main issue that we will discuss in this paragraph is the dependence of the SCH method on where one places the excited electrons. To this end, we collect calculated SCH spectra for diamond, N in h -BN, and lithium-halides in Fig. 7.12. The technical details for the supercell calculations are collected in Table 7.2.

We start with a brief discussion of the SCH method as it is commonly used in quantum chemistry and solid state physics. The most refined approach is to create a potentially fractional core-hole, and at the same time add a fractional charge to a conduction band state and perform a self-consistent DFT calculation. Ideally, self-consistent calculations should be performed for any of the many possible conduction band states. Then the transition probability from the groundstate into the excited state is calculated and the spectrum is obtained by combining

all these calculations, where the excitation energy is given by the energy difference between the groundstate and the excited state and the amplitude by the transition probability. This requires many DFT calculations and is highly impractical for solids since it is impossible to place the electron in a selected conduction band if many $\mathbf{k}$ -points are used. So in practice, in solids, the excited electrons are only placed into the conduction band edge or, even simpler, treated as negative background charge [64, 137].

All yet reported SCH spectra of this work have been obtained by adding the core electron back to the conduction band edge, performing a single self-consistent DFT calculation and then calculating the transition probabilities into all available conduction band states. In quantum chemistry, this approach is sometimes more specifically referred to as eXcited electron and Core-Hole method (XCH) [137]. Placing the electron into the background charge, hence essentially omitting the excited electron density distribution in the self-consistent calculations, is sometimes referred to as the Full Core-Hole (FCH) method, since a full electron is removed from the core [64].

At this point, it is expedient to study these two approximations, XCH method, and the FCH method, for the materials scrutinized here. In the case of diamond and *h*-BN, panels (a) and (b) of Fig. 7.12 show that the XCH and FCH spectra are almost identical — compare red and green dashed lines. This implies that the electron that we place into the conduction band is well approximated by a homogeneous background charge. This in turn suggests that the localization of the excited electron is not very sizeable in the XCH method for diamond and *h*-BN.

However, this is not the case for the lithium-halides, Figs. 7.12(c)-(f). Here we observe significant differences between placing the electron into the conduction band edge or into the background, again compare red and green line. Compared to the experimental spectrum and *GW*+BSE, the homogeneous background method (FCH, green line) yields clearly improved results for the peak positions compared to the more often used XCH method (red line). The peak positions for LiCl, LiBr, and LiI are in almost perfect agreement with the *GW*+BSE results, whereas for the XCH method the higher energy excitations are far too close to the main peak. Obviously, placing the excited electron into the lowest conduction band and then calculating the entire spectrum is not a good approximation for the lithium-halides, but works reasonably well for diamond and *h*-BN. To rule out finite-size effects we repeated the same procedure for LiBr using a supercell containing 250 atoms. The differences persisted even with this larger supercell.

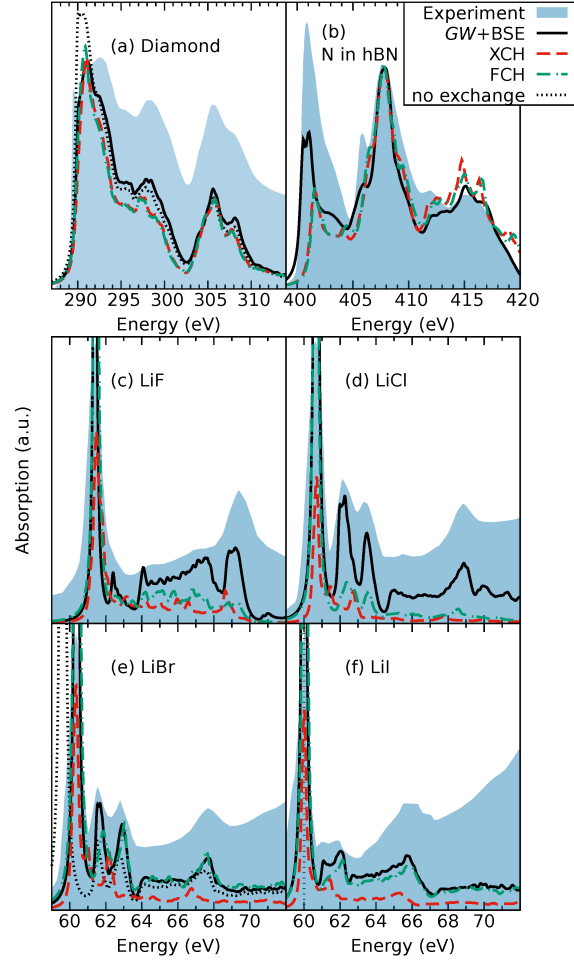


Figure 7.12: XAS spectra for the K -edges of various systems. We show experimental spectra [56, 98, 134] (*blue filled curves*), spectra using the current $GW+BSE$ implementation (*black curves*), XCH spectra where the electron was added to the lowest conduction band (*red dashed curve*), and FCH spectra where the electron was added to the background charge (*green dash-dotted curves*). In panels (a) and (e) we also show with a dotted line $GW+BSE$ spectra without exchange term.

We will now try to explain why the SCH method often works well and when it tends to fail. The first crucial point is that the SCH method yields a reasonable approximation to the BSE, in particular, to the crucial term that describes the electrostatic interaction between the core-hole and the excited conduction band electrons. This is related to the W term (direct term) in the BSE method. In the SCH method, a core-hole is created and all the other valence electrons will screen this local core-hole. The screening of the valence electrons is described by the static DFT dielectric function, so effectively the conduction band electrons see an effective screened core-hole $\int \varepsilon^{-1}(r', r)/|r - r_c| d^3r$, if the core-hole is positioned at r_c . This implies that the SCH method mimics the effects of the direct term in the BSE very well. The successes and failures of the SCH method are then mainly related to the self-interaction of the conduction band electron.

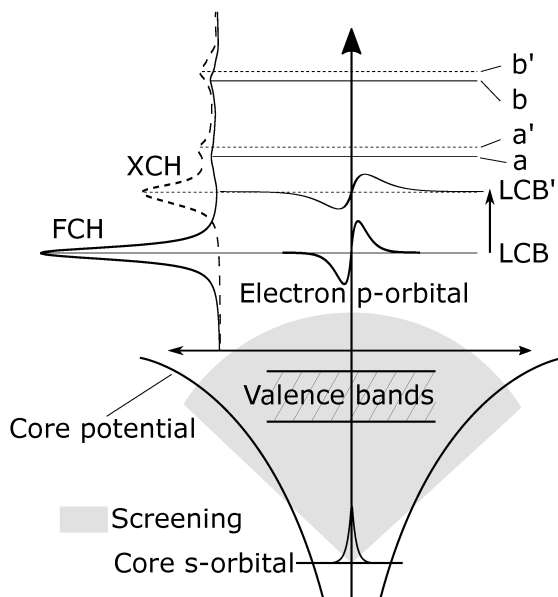


Figure 7.13: Sketch describing how the self-interaction error of the additional electron in XCH method can change the spectra. See text for description.

This will be discussed by inspecting the scheme shown in Fig. 7.13. The FCH spectrum of the K -edge of Li in Li-halides is schematically shown vertically in the left part of the figure. The Lowest Conduction Band (LCB) level is indicated by the line labeled LCB . For the FCH method, this level is unoccupied, since the excited electron is moved to the homogeneous background. To represent the orbital of the excited conduction band electron we show schematically a p -like orbital. In the XCH method, this orbital LCB becomes occupied with a single electron that essentially experiences the screened Coulomb potential (see above). The resulting localized charge density is added to the total charge density and in turn this further modifies the Hartree and DFT exchange-correlation potentials. Unless the DFT functional is canceling the self-interaction error, this will lead to a sizeable self-interaction of the electron. In particular, this self-interaction error is more substantial, if the conduction band electron is strongly localized, as it is for the Li-halides.

The self-interaction error in turn causes two effects: first, it shifts the energy level of the conduction band electron up from the initial energy to the new energy LCB' . Second, it delocalizes the electron, which we have visualized by spreading out the p -orbital. These effects negatively impact the spectrum of the XCH method, as shown schematically in the left part of the figure. The delocalization reduces the oscillator strength, in turn reducing the amplitude of the first peak. The upshift of the eigenvalue on the other hand shifts the position of the peak to higher energies. Furthermore, this conduction band electron somewhat screens the core-hole. The energies of higher lying unoccupied conduction band states are then determined in the presence of the screened core-hole potential and the potential of the added electron. This also shifts their energies upwards from a, b to a', b' . However, since these states are necessarily orthogonal to the lowest conduction band state and since these states are also not as well localized as the lowest conduction band state, the energy shift $a \rightarrow a'$ is much smaller than from $LCB \rightarrow LCB'$. This negatively impacts the calculated spectrum and results in a too small energy separation between the main peak (LCB') and the other peaks

(a' and b').

To summarize, the main issue with the conventional XCH method is that the conduction band edge is shifted upwards due to self-interaction errors present in most semi-local DFT functionals. If the additional electron is placed into the background this problem is not observed. Note that self-interaction is unphysical and would not be present for the exact DFT functional. One might well argue that the conventional XCH methods in combination with DFT functionals that are not self-interaction free is bound to be fairly inaccurate for localized excitons.

At this point, we want to quantify the mechanism outlined above. We do this by calculating the energy differences of the bands corresponding to the DFT conduction band minimum and DFT valence band maximum at the Γ -point. We have obtained these values for the DFT, FCH, and XCH calculations for LiBr of Fig. 7.12(e). These values are 4.94 eV (DFT), 3.37 eV (FCH), and 4.41 eV (XCH). The additional electron in the XCH method shifts the energy of the lowest conduction band upward by approximately 1 eV relative to the valence band edge. This orbital shift to higher energies in the XCH method will shift the onset of absorption by the same amount, as outlined in the previous paragraphs.

To make a connection to the GW +BSE approach and to further substantiate our claims we have also investigated how the exchange terms contribute to the GW +BSE spectra. We first discuss the effect of the exchange term in general. The exchange term has a positive sign and is related to the change of the Hartree potential. It accounts for the repulsive electrostatic interaction of the individual electron-hole pairs, see Eq. (5.2). If the electron-hole pairs are strongly localized, then including the exchange term will shift oscillator strengths to higher energies. Conversely, omitting the exchange term for strongly localized electron-hole pairs shifts the spectrum to lower energies. We now discuss the effect of the exchange term on excitons in particular. Above we have argued that self-interaction Hartree effects come into play for strongly localized excitons. Hence, for excitons involving conduction band states where the Hartree self-interaction is large, we should also see a noticeable energy-shift of the excitonic peaks when the exchange term is omitted.

In panel (a) and (e) of Fig. 7.12, we show the GW +BSE results for diamond and Li in LiBr where the exchange terms were omitted (black dashed line). For diamond this hardly changes the spectrum, in agreement with the observation that the XCH and FCH method are very similar. For LiBr though, the first peak, and the first peak only, is shifted towards the left by almost 1 eV. This is also very close to the difference between the XCH and FCH methods. It confirms that the excitation into the first conduction band state in LiBr creates a strongly localized exciton, whereas all the other excitations in LiBr as well as in diamond are fairly delocalized, in line with our previous arguments.

A final note is in place: in the BSE method changes of the Hartree potential are considered for all excitations individually. On the other hand, in the XCH method, one places the electron into the lowest conduction band and assumes that changes of the Hartree potential for this case mimic the changes of the Hartree potential if one would place the electrons into other conduction band states. This is obviously a crude approximation if the lowest conduction band state is strongly localized, whereas the other states are delocalized. It seems wiser to leave changes of the potential related to the occupation of the lowest conduction band entirely out, as done for the FCH method.

7.5 Summary and Conclusion

In the present work, we have discussed how to implement the BSE within the PAW methodology for the calculation of X-ray absorption spectra. After reviewing the basic theory, we have detailed how to evaluate the matrix elements of the BSE Hamiltonian and explained how the expressions need to be modified when core states are included. In particular, we have discussed that we approximate the overlap charge densities involving core states using augmentation charges only. This suffices, since the augmentation charges are designed to describe long-range electrostatic interactions essentially exactly. However, for the transition probabilities, we use the exact all-electron core orbitals and the all-electron partial waves corresponding to the conduction band electrons. We have tested our implementation on four materials classes: a covalent system (diamond), two 2D van-der-Waals layered materials (graphite and *h*-BN) and four ionic systems with shallow core states (Li-halides).

For diamond we found that our result could reproduce all relevant peak positions very well. Compared to other theoretical spectra our spectrum features an additional shoulder at around 290 eV, which we assign to the excitonic peak of the experimental spectrum. As was the case for the supercell core-hole method and previous BSE calculations, our spectrum lacks intensity at higher energies. This seems to be mostly related to a background that is present in the experimental data but missing at the level of theory that is commonly used. The origin of the lack of background in the present theories is not entirely clear to us, but could be related to interactions with core-conduction band pairs at other sites or the admixture of core-valence pairs.

For diamond we have also investigated the influence of different approximations to the screened interaction W on the spectrum. We found that the off-diagonal elements of the screened interaction play an important role for accurate predictions of the individual peaks in the X-ray absorption spectrum. Neglecting the off-diagonal components leads to a quite significant deterioration of the results compared to experiment. This also means that simplified approaches that attempt to model the screening using a diagonal model lead to inaccurate results.

In graphite the peak positions and intensity ratios also match the experiments well. In our results, we found a shoulder in the σ^* peak that can be tentatively assigned to the σ_2^* peak, suggested by some authors to be related to a delocalized bandlike contribution [28]. So strictly speaking, electron-phonon coupling may not be required to explain the splitting of the σ^* peak. However, we also do not doubt that the splitting will be enhanced by electron-phonon coupling, as suggested by other authors [124].

For the boron K -edge in *h*-BN we found again good agreement with experiment and previous BSE and supercell calculations. The results for the nitrogen K -edge are somewhat more notable. The $GW+BSE$ approach is able to describe all relevant peaks observed experimentally, while the supercell core-hole calculation lacks important features in the spectrum. Specifically, the distance between the π^* and σ^* peaks is in excellent agreement with experiment as well as state-of-the-art results of other authors.

For the Li-halides we found again excellent agreement between the BSE results and experiment. Compared to previous BSE spectra employing a scissor shift, a slight but noticeable improvement of the peak positions is observed. We have tentatively related this to improved quasiparticle energies, as our calculations rely on the G_0W_0 band structures, whereas previous

calculations only employed a scissor-corrected DFT band structure. We also note that our vastly improved $\mathbf{k}$ -point sampling may have positively impacted our predicted spectra.

Finally, we have carefully scrutinized the supercell core-hole method for diamond, h -BN, as well as the Li-halides. As discussed, the supercell core-hole method comes in two variants, one where the excited electron is placed in the conduction band edge, and the other where the electron is treated as a homogeneous background charge. For diamond and h -BN, both approaches yield almost identical results. For the halides, treating the excited electron as a background charge gives much-improved peak positions almost on par with the BSE. We have tried to argue that the self-interaction errors of present density functionals are the most likely explanation for the failure of the supercell core-hole method with the excited electron in the lowest conduction band. Self-interaction erroneously pushes the first excitonic peak to too high energies.

In summary, the present work shows that excellent predictions for X-ray absorption spectra are possible using the PAW method and the BSE approach.

Chapter 8

Results on single-walled carbon nanotubes

In this Chapter we reproduce in its entirety Ref. [185] where results on single-walled carbon nanotubes are discussed. In accordance with the rules of the University of Vienna for cumulative theses, I describe here how I contributed to this publication.

The article was published in February 2025 in the journal Physical Review Research and is entitled "Core-hole induced misalignment between Van-Hove singularities and K-edge fine structure in carbon nanotubes". Copyright is held by the publisher the American Physical Society.

I performed the numerical calculations, took primary responsibility for the analysis, and wrote most of the text for the final manuscript. At all stages of the project, my coauthors provided valuable feedback and criticism on my results and analysis. Specifically, Alexey Tal, Pedro Melo and Georg Kresse provided feedback on the theoretical calculations. Ryosuke Senga, Kazu Suenaga, and Thomas Pichler provided the experimental data and further insight from an experimental perspective. All coauthors provided feedback on the manuscript.

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8.1 Introduction

Single-wall carbon nanotubes (SWCNTs) are cylindrical sheets of graphene [71] with unique mechanical, optical, and transport properties that make them interesting for current and future device applications [60, 152, 176, 192, 128]. Characteristic of the one-dimensional nature of SWCNTs are the Van Hove singularities (VHSs) visible in their electronic ground-state density of states (DOS) [148]. These VHSs play an important role in discussing the transport and optical properties of SWCNTs [31, 30, 164] and their applications in opto- or microelectronics, see e.g. [95, 116, 151, 205, 139, 73].

X-ray absorption spectroscopy (XAS) was used to study the unoccupied DOS of metallicity-sorted [83], diameter-sorted [10], and mainly (6,5)/(6,4)[20] SWCNTs. These studies have shown a fine structure in the absorption edges. Recently, Senga *et al.* [153] used electron energy loss spectroscopy (EELS) to measure *K*-edges of isolated SWCNTs and found that different chiralities can be distinguished by their unique fine structure in the absorption edges. Kramberger *et al.* [83] first used the VHSs to interpret the fine structure in the *K*-edge. This relationship was demonstrated by superimposing a suitably shifted conduction band DOS on the absorption spectrum and associating the first (second, etc.) peak in the fine structure with the first (second, etc.) VHS. This approach was used to explain results on a single (6,5) SWCNT [153] where it was possible to assign the peaks in the fine structure to the individual VHSs. However, while it was possible to assign each peak in the fine structure to a VHS, a misalignment was visible. In these studies [83, 10, 20, 153] the misalignment was attributed to core-hole effects, *i.e.* effects induced by creating the core-hole and, in particular, the formation of excitons. These effects are missing in an independent picture based on the ground-state DOS.

To account for core-hole effects previous studies [180, 197, 48, 114] have used methods based

on the final-state approximation [195, 141]. These methods remove an electron from the inner shells and add it to the lowest conduction band. A supercell is needed to reduce spurious interactions between excited atoms. The electronic ground-state is then determined self-consistently using Kohn-Sham density functional theory (DFT) [65, 81]. Finally, the spectrum is calculated by Fermi's golden rule using the orbitals determined in the presence of the core-hole.

When Refs. [180, 197, 48, 114] were published, experiments were performed on bundles of SWCNTs or diameter-sorted SWCNTs. The modeled spectra had to be averaged and only tentative conclusions could be drawn from experiments: Titantah *et al.* [180] demonstrated that core-hole effects must be considered to recreate the shape of the experimental spectra. Wessely *et al.* [197] extended the final-state method to include dynamical effects by using Mahan-Nozières-deDominicis theory [99, 121]. They concluded that the position of the absorption edge is significantly affected by chirality, while the energy separation between π^* and σ^* peaks varies for metallic and semiconducting SWCNTs. Mowbray *et al.* [114] concluded that the fine structure arises from localized molecular states perpendicular to the tube axis. Finally, Gao *et al.* [48] showed that core-hole effects should be considered to correctly assign peaks in the diameter-sorted spectra to semiconducting or metallic SWCNTs. Gao *et al.* [48] also discussed the spectra's diameter- and chirality dependence by equating the energy differences between the peaks in the fine structure with those of the VHSs. By deriving the VHSs from a zone-folding dispersion relation it is assumed that core-hole effects are negligible. So far it has not been possible to compare simulated and experimental spectra of isolated SWCNTs.

While the final-state approximation yields reliable spectra it also has some drawbacks. It is based on ground-state theory while removing a core-electron creates an excited state. Self-consistently solving the Kohn-Sham equations including the additional core-hole can reproduce some many-body effects, such as the screening by valence electrons or the electron-hole attraction. In contrast, many-body perturbation theory (MBPT) methods are derived for excited states and therefore treat both effects explicitly [107, 42]. For modeling spectra using MBPT, the state of the art is the GW + Bethe-Salpeter equation method (GW +BSE) [125, 105]. In this approach, the screened Coulomb attraction between electrons and holes is approximated using the random-phase approximation (RPA) [23, 144]. Several implementations apply the GW +BSE method to X-ray spectra [123, 88, 189, 190]. Recently, Unzog *et al.* [184] presented an X-ray BSE implementation within the VASP code. They showed that in bulk carbon systems (diamond, graphite) GW +BSE can resolve features missing in spectra based on the final-state approximation. To the best of our knowledge, GW +BSE has not yet been applied to study XAS spectra of SWCNTs. However, using GW +BSE, Spataru *et al.* [166] obtained excellent results for optical spectra of small-diameter SWCNTs.

In this chapter, we present X-ray spectra of isolated SWCNTs using the final-state approximation and the GW +BSE method. We compare our results to the experimental spectra measured for individual SWCNTs by Senga *et al.* [153]. We will show that the VHSs rarely align with the peaks at the absorption edge. We suggest that these differences arise from effects induced by the confinement along the circumference which affect weakly bound excitons. This will be shown by studying the excitonic properties of a graphene supercell that reproduces the same periodic boundary conditions as the (6,5) SWCNT.

We first summarize our methods in Sec. 8.2. The results are presented in Sec. 8.3. In Sec.

Table 8.1: Table listing radii and the BSE parameters used for modeling K -edge spectra of semiconducting SWCNTs.

Chirality	(6,5)	(9,1)	(8,3)	(8,4)	(11,0)	(10,2)
Radius (Å)	3.5	3.8	3.9	4.2	4.3	4.4
Unit cell length (Å)	41.1	41.1	42.4	11.4	4.3	24.0
$1 \times 1 \times n$ $\mathbf{k}$ -points	2	2	2	8	18	4
Bands used for W_0	2000	2100	1500	900	260	1400
Complex frequencies	24	20	14	24	20	20
Unoccupied bands	1200	1400	1200	405	170	1000

8.3.1, experiments are compared to modeled spectra. In Sec. 8.3.2, we discuss in detail the absorption edge of the (6,5) SWCNT. We discuss the excitonic properties of the graphene supercell in Sec. 8.3.3. A discussion follows in 8.4, and the chapter is concluded in Sec. 8.5.

8.2 Methods

The plane-wave code VASP [84, 85] was used to calculate the spectra. The SWCNTs were placed into tetragonal cells with an inter-tube separation of at least 6 Å. The geometries were then relaxed using the Perdew, Burke, Ernzerhof (PBE) functional [131] until forces converged below 0.01 eV/Å.

The orbitals were calculated using the hybrid functional PBE0($\alpha = 0.24$) [132, 38, 5]. Using this fraction of exact exchange $\alpha = 0.24$, the G_0W_0 bandgaps are reproduced, which closely match band gap values deduced from experiment [183, 202]. This approach allows us to obtain more accurate orbitals than found via the PBE functional. In particular, this choice better reproduces the band dispersion of the unoccupied bands which affects the localization and hence the binding energy of the exciton. As will be shown in Fig. 8.2, using PBE orbitals and energies misestimates the band dispersion and hence the localization of the exciton. This results in underestimated amplitude ratios and unsatisfactory relative peak positions. Conduction band DOS and band structures are also computed with PBE0($\alpha = 0.24$). Note that in Ref. [83] PBE was used to calculate the conduction band DOS.

The method based on the final-state approximation used in this study is the full core-hole (FCH) method. In the FCH method, the excited electron is not added to the lowest conduction band but to the background charge [110]. It was shown that X-ray absorption spectra are improved with this procedure [184]. To calculate FCH spectra we use an implementation presented previously [75]. The electronic states were determined using PBE0 and we denote these spectra as FCH. The spectra converged with a supercell size of 7 nm along the tube axis and for all FCH spectra only the Γ point was sampled.

To calculate GW +BSE spectra we use the core-hole BSE methodology as implemented by Unzog *et al.* [184]. To determine the screened interaction, we made use of the low-scaling GW algorithm of Kaltak *et al.* [74]. As it accurately describes the screening and yields good bandgaps within G_0W_0 , we use the RPA based on PBE for the screening in the BSE which we denote as W_0^{PBE} . In the set-up of the Bethe-Salpeter eigenvalue equation the PBE0($\alpha=0.24$)

ground-state energies and orbitals are used. In the following, we call these spectra BSE for short. When BSE calculations are performed on top of G_0W_0 @PBE, the intensity of the first peak is way underestimated to the rest. Using PBE0 orbitals and energies yields qualitatively better results. We believe PBE0 orbitals are better approximations for the Dyson orbitals, but orbital selfconsistent GW calculations are prohibitive for the systems considered here. In Tab. 8.1 we list the computational parameters used for the BSE spectra.

As usual, we made the static approximation for the screened interaction when solving the BSE. A soft projector augmented-wave (PAW) [21] pseudopotential was used for carbon ("C_s_GW") and the plane-wave cutoff for orbitals and the cutoff of the response function were set to 300 eV and 150 eV, respectively. We used the Tamm-Dancoff approximation [36, 175] for all BSE spectra and excluded excitations from valence to conduction band states. We calculated the BSE dielectric function in the $\mathbf{q} \rightarrow 0$ limit, see Eq. (29) of [184].

We point out that the EELS experiments of Senga *et al.* [153] involve a finite momentum transfer due to the large convergence and collection angles of 42.5 mrad and 33 mrad, respectively. However, in the valence-loss spectrum of Fig. 3b of Ref. [153] we see mostly dipole-allowed E_{ii} transitions while additional multipolar contributions such as intraband excitations or activation of dark excitons [154] are hardly visible. Therefore, the EELS setup of Ref. [153] is dipole-dominated which allows us to directly compare the FCH and BSE results with the EELS spectra.

Within the PAW approach implemented in VASP the core states are frozen [21, 84], and absolute core energies are not computed. Instead, the spectra are shifted by aligning the first peak of the modeled spectra with the first peak observed in experiments. The modeled spectra are obtained by averaging the three diagonal components of the imaginary dielectric tensor, and a Lorentzian broadening of 0.2 eV (full width at half maximum) was applied to all modeled spectra.

8.3 Results

8.3.1 Spectra

In this section, we compare our results to the experiments and relate the VHSs to the peaks at the absorption edge. Kramberger *et al.* [83] used the conduction band DOS to compare the positions of the VHSs with the peaks at the absorption edge. We show instead for each SWCNT the initial state (IS) spectrum. The IS spectrum is obtained from the conduction band DOS in the absence of the hole by weighing each conduction band energy by the dipole transition matrix element from the core state to the corresponding conduction band state. It is important to note that this method is equivalent to the independent particle (IP) approximation, a common term in the many-body community, and we will use both terms (IP and IS) interchangeably. To find the correspondence between the VHSs and the peaks in the IP spectrum we followed Kramberger *et al.* [83] and shifted each IP spectrum so that the first VHS aligns with the first peak at the absorption edge.

The spectra of individual SWCNTs are shown in Fig. 8.1. Since the computational complexity of the FCH method is that of a DFT calculation we used it to model spectra of all semiconducting SWCNTs investigated in Ref. [153]. In (6,5), (8,3), (9,2), (8,4), and (11,1) FCH can resolve the most pronounced peaks of the fine structure visible in the experimental absorp-

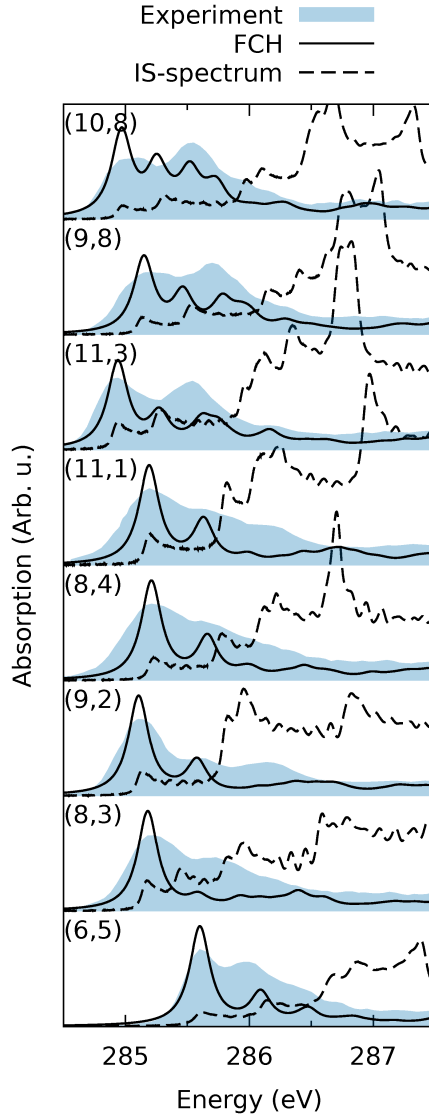


Figure 8.1: Comparison of experimental and modeled K -edge absorption spectra of isolated SWCNTs. *Red lines*: Experiments by Senga *et al.* [153]. *Black solid lines*: FCH spectra using PBE0, see Sec. 8.2 for details. *Black dashed lines*: Initial state spectra, *i.e.* the PBE0 DOS where each conduction band energy is weighted by the transition probability from the core state to the corresponding conduction band state. The SWCNTs are arranged so that the radius decreases from top to bottom. All FCH spectra are shifted to align the first peaks in the experimental and modeled spectrum and scaled such that the area below the first peak of modeled and experimental spectra are approximately equal.

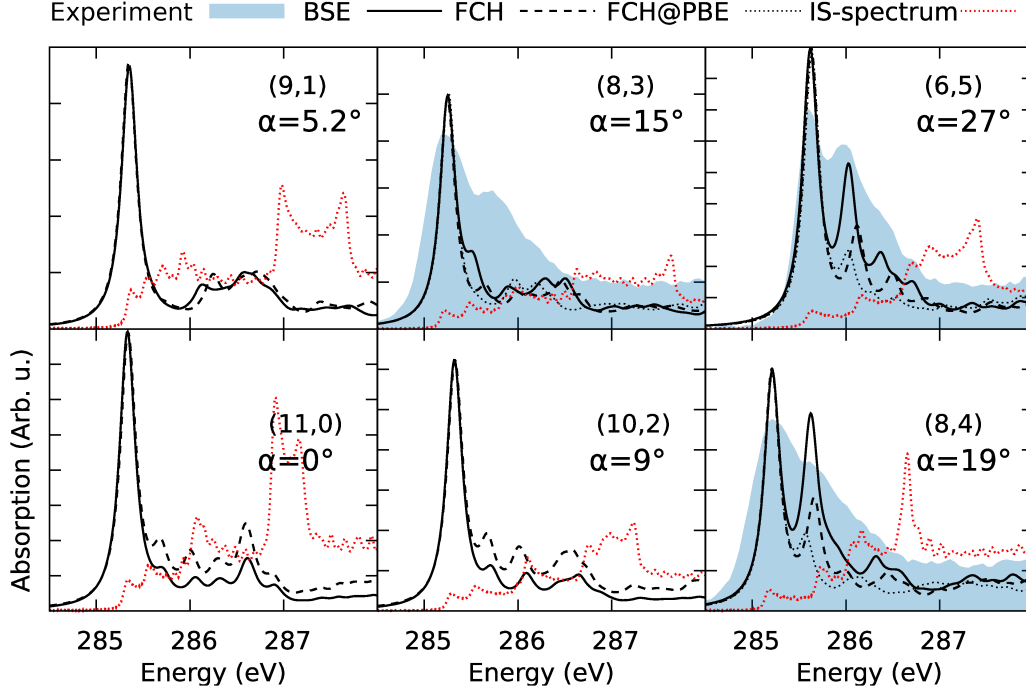


Figure 8.2: Comparison of modeled K -edge spectra of isolated SWCNT with their initial state spectra. *Black solid lines*: BSE spectra using PBE0 orbitals and energies and W_0^{PBE} in the BSE Hamiltonian. *Black dashed lines*: FCH spectra using PBE0. The BSE and FCH methods are explained in Sec. 8.2. *Red dotted lines*: Initial state spectra. *Blue filled areas*: Experimental spectra of Senga *et al.* [153]. All modeled spectra are shifted to align the first peaks in experimental and modeled spectra. The modeled spectra are scaled such that the area below the first peak of the modeled and experimental spectra are approximately equal.

tion edges. The relative positions of the second peaks are generally in better agreement with experiment than the third and fourth peaks. In the measured spectra of (9,8), (10,8), and (11,3) we can see two broad peaks in the absorption edge which we interpret individually as two close by peaks. The FCH spectra can tentatively replicate these features although the first two peaks are slightly too far apart. The energy separations of the third and fourth peaks in the FCH spectra more closely match the corresponding broad second peak in experiment. The broad peak formed by the third and fourth peaks aligns with the corresponding peak for the (10,8) spectrum while it is blueshifted in (9,8) and (11,3).

Comparing IS and FCH spectra, we can see that the positions of the VHSs are significantly shifted from the peaks of the fine structure. If core-hole effects were negligible, then the relative positions of the VHSs should closely match the energies of the peaks at the absorption edge. The large mismatch between absorption peaks and VHSs in the IS spectra shows instead that core-hole effects significantly alter the conduction band energies. A systematic shift of the VHSs relative to the absorption peaks as a function of radius is not visible from Fig. 8.1.

We proceed with the BSE results. The high computational requirements of the BSE approach prohibit us from calculating spectra of all SWCNTs investigated in Ref. [153]. Therefore, we

present in Fig. 8.2 BSE and FCH spectra for a subset of chiralities. The average radius of the SWCNTs in the top (bottom) row is 3.8 Å (4.3 Å). In each figure, we indicate the chiral angle of the SWCNTs [148]. For chiralities (9,1), (11,0), and (10,2) we have no experimental data at our disposal. The BSE spectra give slightly better relative peak positions for (8,4) and (6,5). This is particularly evident for the chirality (6,5), where BSE accurately matches the positions of all four sub-peaks in the absorption edge, whereas these features are blueshifted with FCH. Additionally, the amplitude of the second peak in (6,5) and (8,4) is higher in BSE compared to FCH. The improvement of BSE over FCH aligns with the findings of Unzog *et al.* [184] for reference bulk systems. Although G_0W_0 on top of PBE rectifies the peak positions, it does not change the intensity distribution between the peaks. This issue is also visible in BSE calculations, whenever PBE orbitals are used, and motivates our choice to start BSE calculations from PBE0 orbitals and eigenvalues.

Our choice to describe the orbitals using hybrid functionals is motivated by comparing the FCH spectra obtained with PBE and PBE0 functionals shown in Fig 8.2. While the spectrum based on PBE orbitals shows an overall similar peak structure, some of the secondary peaks are shifted and the amplitudes are underestimated.

Similarly to the FCH results, comparing the peaks in the BSE spectra to the VHSs in the IS spectra reveals large discrepancies for all systems. A particularly large difference can be seen for (9,1) where the IS spectrum shows four VHS in the range 285 eV to 286 eV. Both modeled spectra of (9,1) show instead only a single broad peak. By inspecting Fig. 8.2 we could infer whether the shift of a peak at the absorption edge with respect to the VHS is correlated with the chiral angle. As with the curvature above, we do not observe a systematic correlation.

In discussing optical spectroscopies of SWCNTs they are separated into two families depending on whether $(n-m) \bmod 3$ is equal to 1 or 2 [155, 33]. By inspecting Figs. 8.1 and 8.2, we can also exclude that misalignment between peaks at the absorption edge and VHSs is only found in one of those families or that one family shows more misalignment than the other.

8.3.2 (6,5) fatband structure

These findings indicate that the relationship between VHSs and the peaks at the absorption edge is more complicated than suggested by Kramberger *et al.* [83]. In that work each peak in the fine structure is identified with one particular VHS. To understand how to relate the VHSs with the peaks at the absorption edge we investigate the fatband structure [25] of the (6,5) SWCNT. In the BSE formalism, the exciton is formed by all possible electron-hole pairs. The so-called BSE coupling coefficients quantify how much a particular electron-hole pair contributes to the exciton. Since the core state is fixed in our calculations we can use the BSE coefficients to infer which conduction band states contribute more strongly. In the fatband structure, the squared magnitudes of the BSE coupling coefficients of a state within a given band and at a given $\mathbf{k}$ -point are drawn as circles superimposed on the band structure.

We point out differences of about 50-100 meV between the centers of some circles, *i.e.*, the conduction band energies used in the BSE Hamiltonian, and the corresponding states in the band structure. We attribute these differences to the separate treatment of the $|\mathbf{q} + \mathbf{G}| = 0$ singularity of the Coulomb interaction in reciprocal space $V = 4\pi/|\mathbf{q} + \mathbf{G}|^2$, where $\mathbf{G}$ are the reciprocal lattice vectors and $\mathbf{q} = \mathbf{k} - \mathbf{k}'$. For the BSE spectra, the singularity correction of

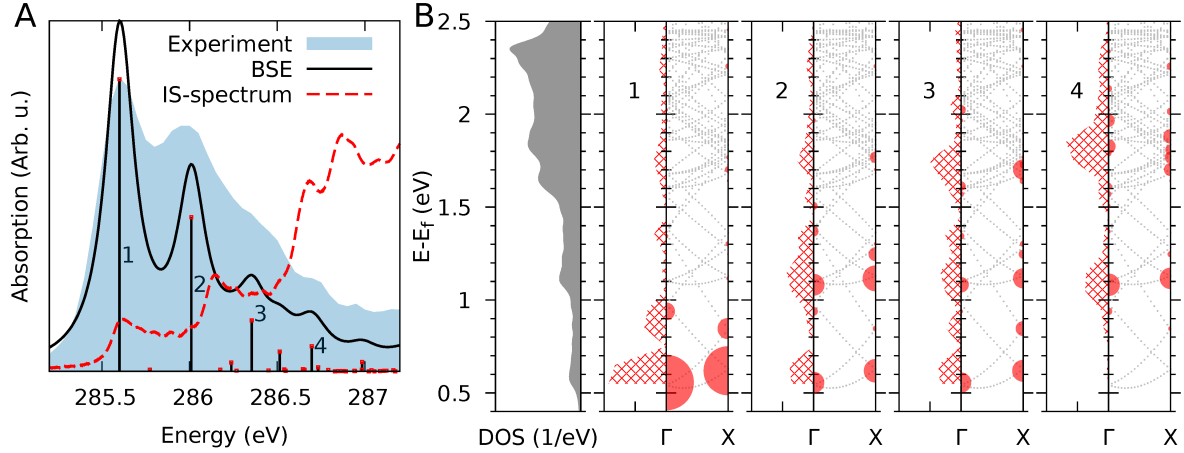


Figure 8.3: The fatband structure of the (6,5) absorption edge. Panel **A**: Enlarged view of the absorption edge. *Blue filled area*: Experiment by Senga *et al.* [153]. *Black solid line*: BSE spectra using PBE0 orbitals and energies and W_0^{PBE} in the BSE Hamiltonian, see Sec. 8.2. The BSE excitations are shown as black lines. The first four bright transitions are labeled 1-4. *Red dashed line*: Initial state spectrum. Panel **B**: Fatband structures of the first four bright excitations of panel A. *Gray shaded area*: Initial state spectrum. *Panels 1-4*: BSE fatband structures of transitions 1-4 of panel A. The PBE0 band structure is shown with gray dots. The radii of the red circles are proportional to the square of the BSE coefficients. We show histograms of the fatband structures with red-shaded areas. Only contributions at Γ and X are shown, as $\mathbf{k}$ -point sampling in the BSE was limited to these two $\mathbf{k}$ -points.

Massidda, Posternak, and Baldereschi [106] was used in two cases: in the determination of the PBE0 ground-state orbitals and energies and when solving the BSE. In contrast, when calculating the band structures, the Coulomb interaction was truncated according to Spencer and Alavi [167], as only truncated Coulomb kernels allow for an interpolation to dense $\mathbf{k}$ -point grids.

We present in panel A of Fig. 8.3 an enlarged view of the absorption edge. We have marked with labels 1-4 the excitations corresponding to the four brightest absorption peaks visible in the fine structure. We can see a small shift of the second VHS in the IS spectrum to the second excitation (labeled 2) in the BSE spectrum, while the third and fourth VHSs are significantly blue-shifted with respect to the corresponding BSE excitations (3 and 4).

The fatband structures of the first four bright transitions 1-4 shown in panel A are shown in panel B. For the excitation 1, the bands of the first VHS at around 0.75 eV contribute the most. This contribution of the first VHS is in line with a simple correspondence between a peak in the fine structure and a particular VHS. We can also see some contributions of higher-lying conduction band states which decrease in strength with increasing energy.

We also see a very sizeable contribution from the edge of the Brillouin zone that does not fit with the simple picture of the exciton being related to a single VHS. The exciton is rather formed by linearly combining low-energy states with progressively less contributions from higher energy states. This is exactly what one would expect from a local exciton build from upwards dispersing π^* -bands. The specifics of the band structure and Brillouin zone do not

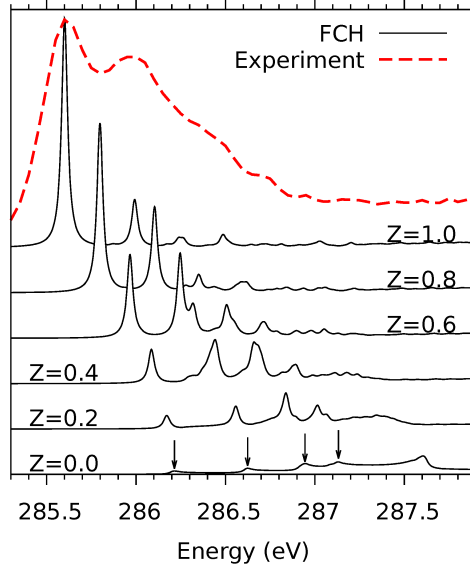


Figure 8.4: Increasing the core-hole charge in FCH spectra of chirality (6,5). *Black lines:* FCH spectra using PBE, with core-hole charge indicated. *Red line:* Experiment [153]. All spectra are shifted and scaled equally, with the shift chosen to align the first peak of the $Z = 1$ spectrum with the first peak in experiment. Arrows mark the first four VHSs in the $Z = 0$ spectrum.

matter. This will also be later confirmed by the exciton wavefunction analysis.

Investigating the fatband structure of excitation 2 we can see that the bands of the second VHS located at 1.1 eV are strongly involved in forming the exciton. However, we can also see additional contributions of conduction band states from the first VHS. The histogram further shows that the contributions from the first and second VHS are approximately equal in magnitude. This pattern holds for the excitations 3 and 4 as well. Because of the mutual orthogonality of the wavefunctions of different excitations, this pattern is a direct consequence of the first exciton involving orbitals from higher energies. Likewise, since the second exciton involves orbitals at even higher energies, for those to then be orthogonal to the first and second exciton, they also need to involve contributions from orbitals related to the first and second VHS. This means that the excitations generally involve conduction band states across multiple VHSs. Therefore, we have to consider that a wide range of transitions into different VHSs are coupled to form one exciton. It is therefore difficult to predict peak positions at the absorption edge only from the relative distances of VHSs. On the contrary, a perfect match between VHSs and a peak at the absorption edge is coincidental because the excitonic energy results in a complex manner from the transitions to different VHSs.

It could be argued that in cases where close alignment between a VHS and a peak in the fine structure is found, only states from that particular VHS are involved. We, however, emphasize that we need to conclude that multiple VHSs contribute, although the energy difference between the first and second peak seemingly often matches the energy difference between the first and the second VHS. Even in this case, conduction band states across multiple VHSs contribute to the exciton.

To investigate how core-hole effects change the VHSs we show in Fig. 8.4 FCH spectra for chirality (6,5), where the core-hole charge Z is incrementally increased from 0 to 1 atomic unit. For this result, we use FCH based on PBE orbitals. By comparing the spectra with $Z = 1$ and $Z = 0$ we conclude firstly that the first and second exciton have binding energies of 0.6 eV and 0.2 eV, respectively. Second, we again conclude that core-hole effects are significant, as the downward shift is comparable in magnitude to the separation between adjacent VHSs. Third, the shifts of the VHS are not uniform as different VHSs are shifted to varying degrees. Finally, large shifts of oscillator strength into the first four VHS are visible upon increasing Z . These shifts make it difficult to determine which states in the $Z = 0$ spectrum contribute to a particular absorption peak in the $Z = 1$ spectrum. This further supports the conclusion above that a wide range of transitions form one exciton. We note that the π^* response around 287.6 eV disappears when the core-hole charge is switched on. It is tempting to attribute the increase in oscillator strength of the first four VHSs to states from the π^* peak. However, when we re-examine the fatband structure in Fig. 8.3 we see that none of the first four absorption peaks have significant contributions from the corresponding VHS here located at 2.5 eV in the IS spectrum.

8.3.3 Graphene supercell

We now investigate why conduction band states across multiple VHSs are involved in creating a particular excitonic transition. To eliminate curvature effects we map the unit cell of the SWCNT onto a graphene supercell, where the basis vectors are the chiral and translation vectors $\mathbf{C}$ and $\mathbf{T}$, respectively, and $\mathbf{k} = k_c \mathbf{K}_1 + k_t \mathbf{K}_2$, where $\mathbf{K}_1, \mathbf{K}_2$ are the reciprocal lattice vectors along the circumference and nanotube axis, respectively [148]. Along the tube axis k_t is sampled on a fine grid, whereas along the circumference $k_c = 0$. This way, the boundary conditions of the SWCNT are reproduced, *i.e.*, infinite extent along the nanotube axis and confinement along the circumference with an added periodic boundary condition. The results below were obtained for a graphene supercell corresponding to the chirality (6,5). When both k_c and k_t are finely sampled we recover the K -edge spectrum of graphene. In contrast to the SWCNTs, the π^* response of graphene is dominated by a single excitonic transition [67]. We display the charge density of this exciton in panel A of Fig. 8.5.

The spectra and charge densities of the excitons are collected in Fig. 8.5. In panel B we show the BSE spectra of the (6,5) SWCNT and supercell with red and black dashed lines, respectively. Both spectra are multiplied by the volume of the cell and shifted by the energy of the conduction band edge. We can see that the supercell spectrum also exhibits the characteristic fine structure observed in the absorption edge of the SWCNT spectrum. The supercell spectrum is however blueshifted with respect to the SWCNT spectrum and the amplitude of the first peak is decreased. We attribute these effects to the curvature of the SWCNT which reduces the dispersion of the π^* bands [19] and in turn increases the binding energy of the exciton. We mark the first two excitations of the SWCNT and supercell spectra with $\{1,2\}$ and $\{1',2'\}$, respectively.

In panel C, we show the charge densities of the first two bright excitations in the (6,5) SWCNT and in the supercell. The hole was fixed at the excited atom highlighted with a red dot (black in greyscale). The charge densities corresponding to the first (1 and 1') and second (2 and 2') bright peaks are presented in the first and second columns, respectively. For the SWCNT, we show the charge densities obtained from FCH and BSE methods.

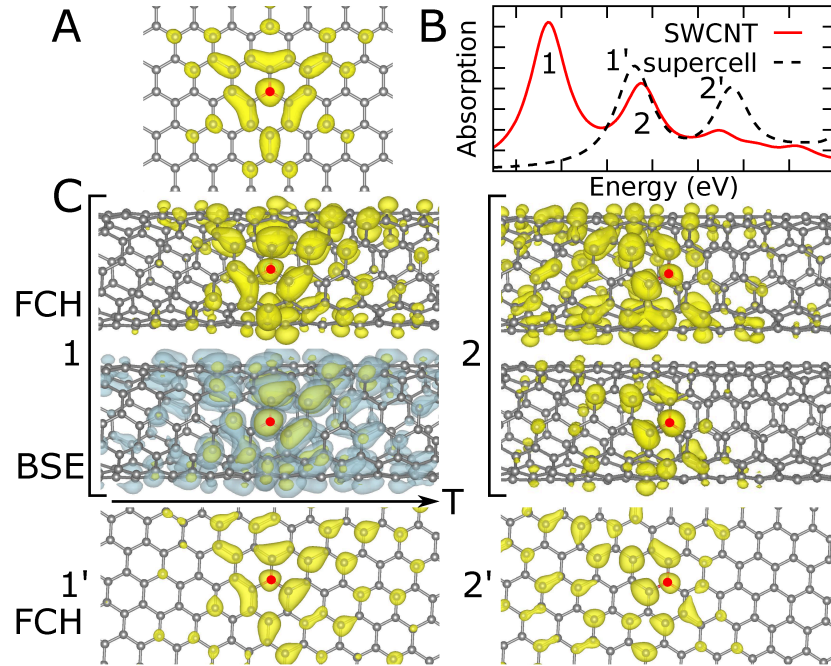


Figure 8.5: Comparison of spectra and wavefunctions of a (6,5) SWCNT and a corresponding graphene supercell. Panel **A**: Charge density of the exciton in graphene. Panel **B**: BSE spectra of the SWCNT (*red solid line*) and the equivalent graphene supercell (*black dashed line*). Panel **C**: Charge densities of the excitons corresponding to excitations 1 and 2 in panel B using FCH (top row) and BSE (middle row). The excitons of transitions 1' and 2' of panel B (supercell) are shown in the bottom row. The core-excited atom is marked with a red dot (black in greyscale) and the value of the yellow isosurface is set to $5 \times 10^{-4}e$ throughout. The blue isosurface is set to $1 \times 10^{-4}e$. The direction of the translation vector $\mathbf{T}$ of the supercell is indicated in the figure. The charge density plots were generated with VESTA [112].

We first investigate the charge densities in the first column corresponding to the peaks 1 and 1' of panel B. We can see that the excitons corresponding to peaks 1 and 1' closely resemble the exciton of graphene shown in panel A. In particular, all three excitons demonstrate approximately the same symmetry and localization. The BSE charge density is more localized than the FCH charge density, though. To facilitate the comparison between FCH and BSE we provide a second isosurface with a smaller value which emphasizes the symmetry better.

While the first exciton resembles the exciton in graphene, excitons 2 and 2' are much more extended. Curvature effects are absent in the graphene supercell model. Therefore, we attribute this extended shape entirely to the $\mathbf{k}$ -point sampling in the supercell, which reproduces the boundary conditions of the SWCNT.

The difference between the first and second excitons can be explained as follows. We determine the bound states of the core-hole potential while considering the boundary conditions in the SWCNT. The core-hole potential is strong enough that the first bound state has a large binding energy. It is sufficiently strongly bound that the first exciton is not affected by the confinement along the circumference and hence completely localized near the core-hole. Its shape is then determined by a few nearest neighbors of the excited atom so that the exciton resembles the exciton in graphene. In contrast, the second exciton has a reduced binding energy and a more delocalized wavefunction. For the second exciton, the confinement along the circumference must be considered, resulting in a wavefunction that is not determined by the nearest neighbors but exhibits the extended shape visible in Fig. 8.5.

In short, strongly bound excitons resemble the exciton in graphene, while reducing the binding energy of an exciton results in a shape that adapts to the periodic boundary conditions. To test this idea we use the FCH method which allows us to adjust the core-hole charge Z and hence the binding energy $\sim Z^2$. We show in Fig. 8.6 the charge densities of the first bound state in the graphene supercell using PBE orbitals and different values for Z . The excited atom is marked with a red dot (black in greyscale). The value $Z = 0.7$ leads to a state with about half the binding energy of the $Z = 1$ state. The continuous change from a shape resembling the exciton in graphene to an extended shape is evident.

To relate these results to the previous section we plot in Fig. 8.7 the fatband structures of the first two excitations of the graphene supercell, *i.e.*, excitations 1' and 2' in panel B of Fig. 8.5. Comparing Fig. 8.7 with Fig. 8.3 we see the same structure: the first excitation couples bands mostly from the first VHS, while the second excitation couples bands from many VHSs. Therefore, we can attribute the fatband structures 2, 3, and 4 of Fig. 8.3 to a failure of a simple model of a localized exciton resembling the exciton in graphene. In these cases, conduction bands from many different VHSs contribute to form the extended excitons.

8.3.4 Exciton character

In this section we investigate the character of the excitons in more detail. Excitons are classified into Frenkel [44, 45] or Wannier-Mott [196, 113] excitons, the former corresponding to the atomic limit where electron and hole are found on the same atom and the latter to large separations between electron and hole. An intermediate model is the charge-transfer (CT) exciton [78] that is encountered in molecular [79, 207, 35] or ionic crystals [126, 77, 204, 2]. An exciton is identified as a CT-exciton when the electron and hole are localized at different molecules or molecular subunits [78, 201].

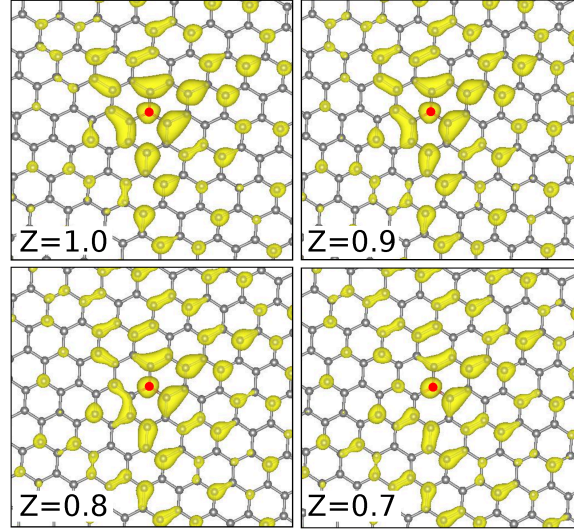


Figure 8.6: Charge density of the lowest energy exciton in a graphene supercell that reproduces the boundary conditions of a (6,5) SWCNT. The value of the core-hole charge Z is indicated in each panel. The charge density plots have been obtained using FCH based on PBE orbitals, see text for details. The excited atom is marked with a red dot (black in greyscale) and the charge density plots were generated with VESTA [112].

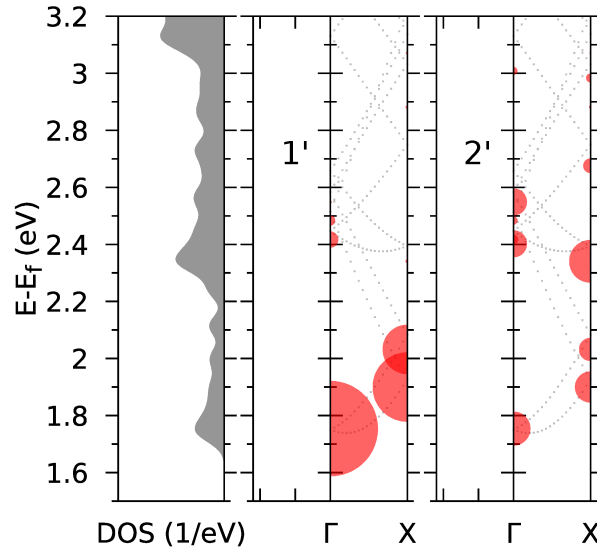


Figure 8.7: The BSE fatband structures of the first two bright transitions (1' and 2') of the graphene supercell spectrum shown in panel A of Fig. 8.5. The radii of the red circles are proportional to the amplitude square of the BSE coefficients. The initial state spectrum is shown with gray dots.

We quantified the electron localization by determining the dipole moments $\mathbf{p} = \sum_{i \in V} \rho(\mathbf{r}_i)(\mathbf{r}_i - \mathbf{r}_{\text{exc}})$ of bright excitons in semiconducting chiral and zig-zag SWCNTs, where the excited atom was the reference point $\mathbf{r}_{\text{exc}}$. The analysis shows that all first bright excitons have a vanishing dipole moment, and additionally, the charge density is maximal at the excited atom. It is therefore fairly evident that the first excitons have Frenkel character.

In contrast, higher bright excitons have a finite dipole moment of about 1-2 eÅ. The component of the dipole moments along the nanotube axis is in all cases much larger than the component perpendicular to it (pointing upward in Fig. 8.5). This suggests that these excitons have a CT character, implying that the center of the electronic charge is to some extent shifted to neighboring atoms. However, it was shown previously that a non-vanishing dipole moment is not sufficient to assign CT character [133]. For example, in molecular crystals, the localization of the charge distribution can be changed by shifting the hole which results in zero net dipole moment on average [35]. To test this, we excited the hole at the nearest neighbor along the tube axis of the marked atom in Fig. 8.5. We found that the dipole moment then points to the right, while it originally pointed towards the left. This suggests that the net polarization is zero in an experiment where multiple neighboring atoms are excited. Since the dipole moment is zero on average, the core excitons of higher excitations in SWCNTs are better described as charge resonance states [133].

8.4 Discussion

In Sec. 8.3, we inferred that core-hole effects are strong since they significantly alter the spectrum from the initial state (IS) approximation. Nevertheless, it is hard to deny that the VHSs in the IS spectra often seem to align well with the position of the quasiparticle (QP) peaks in the experimental spectrum. Here, we argue that the separation between VHSs in the IS spectrum determines whether the IS spectrum is a good approximation to the QP spectrum. Our argument relies on the orthogonality of excitons and is complemented by a formal approach based on pseudopotential theory.

We begin with the *K*-edge of graphene, where a *single* bound exciton dominates the π^* response [67]. The remaining π^* part of the spectrum is featureless and roughly forms a parabolic band. In SWCNT, the first exciton closely resembles the first exciton of graphite, as shown above (see Fig. 8.5). As the first exciton is localized in real space, it is necessarily a linear combination of π^* conduction band states. States from the bottom of the conduction band dominate the exciton, but states from higher energies also contribute, as shown in Fig. 8.3: as one moves further upwards from the bottom of the conduction band, the contributions of the conduction band states to the first exciton decay with the energy separation.

We have seen above that the second and third peaks in the excitonic spectrum contain significant contributions from the original second and third VHS, but they also contain some contributions from the 1st VHS. This is a consequence of the orthogonality condition. As the first exciton contains contributions from the entire π^* band (including contributions from the 2nd and 3rd VHS), mutual orthogonality requires that states at higher energies also contain some admixture from the 1st VHS.

From this picture, the following conclusion emerges. If the energy separation between the VHS is large, then the 1st bound exciton will be predominantly formed from conduction band

states close to the first VHS, with little contributions from higher VHS. The second peak in the spectrum, which needs to be orthogonal to the 1st bound exciton (and thus the 1st VHS), will now be dominated by states from the second VHS, and so on. Hence, in this case, the IS picture is at least qualitatively a good approximation to the spectrum.

Conversely, if the energy separation between the VHSs is small, the first exciton will have strong contributions from the second VHS and potentially even further VHS. As orthogonality to the first exciton must be maintained, states from the first VHS will contribute significantly to the second as well as other exciton. In this case, the IS picture will not necessarily correspond well with the QP spectrum.

To make this more explicit, we briefly relate these observations to the orthogonalized plane-wave (OPW) method [63] as formulated by Phillips and Kleinman [135]. We summarize the important points and adapt the notation of Ziman [208]. In the OPW method, an ansatz is made for the conduction band states $|\psi\rangle$ by orthogonalizing a linear combination of plane-waves $|\phi\rangle$ to the core-states $|b_t\rangle$:

$$|\psi\rangle = \left[1 - \sum_t |b_t\rangle\langle b_t| \right] |\phi\rangle. \quad (8.1)$$

This procedure results in an effective Hamiltonian (in atomic units) for the pseudo-orbital ϕ

$$H_{\text{eff}}(E) = -\frac{1}{2}\Delta + V + \underbrace{\sum_t (E - E_t) |b_t\rangle\langle b_t|}_{\Gamma(E)}, \quad (8.2)$$

where V is the attractive potential of the nuclei [135, 208]. The Hamiltonian is now expressed in terms of the effective pseudopotential $\Gamma(E) = V + V_R$, where $V_R = \sum_t (E - E_t) |b_t\rangle\langle b_t|$. As the conduction band energies E are always larger than the core state energies E_t , V_R is a positive, *i.e.*, a repulsive potential that compensates the attractive potential of the nuclei V [135].

We can readily adapt the formalism to K -edge excitations. The carbon $1s$ hole is localized at the nucleus, and can be approximated by a positive point charge $V(+1)$ located at one of the nuclei. The potential $V(+1)$ leads to one excitonic bound state with a negative charge, and we can mimic the combined potential of the positive core charge and the bound exciton in exactly the same manner as in the OPW theory, Eq. (8.2), but with a single bound state t :

$$H_{\text{eff}} = -\frac{1}{2}\Delta + V(+1) + (E - E_t) |b_t\rangle\langle b_t|, \quad (8.3)$$

where E_t is the energy of the bound exciton.

The effective potential felt by electrons at higher energies is then the sum of the original attractive $V(+1)$ potential plus the repulsive potential caused by the requirement of orthogonalization. As discussed before, if the bound exciton is predominantly made up of states in the first VHS, the overall potential experienced by the "remaining" electrons is weak. Hence, the rest of the spectrum is dominated by the effects imposed by the quantization of electronic states in the circumferential direction, and concomitantly, the second peak in the spectrum is dominated by states from the 2nd VHS, etc.

We note that this concept, matter of fact, shows again that the 2nd peak will always contain contributions from the 1st VHS, as the wave function ψ , by construction, possesses contributions from the first bound exciton due to the projection in Eq. (8.1). From experience, it is known that the OPW concept is accurate in the limit that the bound state is localized and much lower in energy than the remaining states. Hence, if the energy separation between the VHS is large, and the bound exciton is dominated by a linear combination of the 1st VHS only, the core hole is mostly screened ($\Gamma(E) \approx 0$), and the remaining QP states resemble the IP spectrum.

Summarizing, we argue that the energy difference between VHSs determines whether an approach based on VHSs in the IP spectra leads to satisfactory predictions for the QP peaks. This is also illustrated in Fig. 8.2. For the (6,5) chirality, the first three VHSs are widely spaced, resulting in absorption spectra that qualitatively match the IS spectra. Conversely, for the (9,1) chirality, the first four VHSs are close together, and the actual QP absorption spectrum does not quite resemble the IS spectrum. To make this failure for (9,1) more apparent, we show in Fig. 8.8 spectra with an increasing core-hole charge (for the (6,5) tube the corresponding results are shown in Fig. 8.4). The first four VHSs in the IS spectrum and their corresponding peaks in the FCH spectrum are marked with arrows, highlighting the large discrepancies: upon increasing the core-hole charge Z , the local exciton is formed as a linear combination of the conduction band π^* orbitals. The exciton separates from the remaining peaks and shifts down in energy. Remarkably even in this case, the separation between the 2nd, 3rd and 4th peaks in the final QP spectrum is quite similar to the separation between the corresponding three peaks in IS sp the IP approximation ($Z = 0.0$). However, the final spectrum also shows additional fine structure beyond the 4th peak that is absent in the IP picture.

Within this framework, we can also understand the results on C_{60} fullerenes where the absorption spectrum closely resembles the IS spectrum [122]. The VHSs in the IS spectrum are at least 1 eV apart, almost twice the value of the separation between the first three VHSs in (6,5) where the qualitative picture was shown to hold. In this case, the gaps between the VHSs are so large that hardly any states of the second VHS contribute to the first exciton. In other words, the orthogonalization contribution $(E - E_t)|b_t\rangle\langle b_t|$ can largely compensate for the attractive core-hole potential.

We emphasise, however, that even if the energy separation between the VHSs is large, the IS spectra are at best qualitatively correct. For a quantitative comparison, core-hole effects should be included, since the peaks visible in the spectrum are always linear combinations of many states of at least one, but often several, VHSs. Furthermore, the exact position of the resonances depends on a balance between the effects caused by the partially shielded core hole and the quantisation of the electronic states around the tube-circumference.

8.5 Conclusion

In this chapter, we have modeled X-ray spectra of isolated SWCNTs and compared them with experimental EELS spectra [153]. We used the supercell approach in a version we call the Full Core Hole (FCH) method, as well as the Bethe-Salpether approach (BSE). In both methods, we used the global hybrid functional PBE0 either as a starting point for BSE or in the FCH calculation, since it provides improved orbitals and a better description of the band

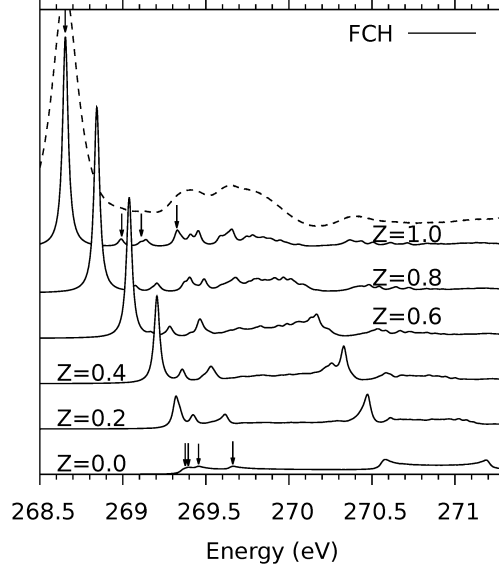


Figure 8.8: Increasing the core-hole charge in FCH spectra of chirality (9,1). *Black lines*: FCH spectra using PBE, with core-hole charge indicated. *Black dashed line*: $Z = 1$ spectrum using a broadening 0.2 eV (full-width half maximum) and scaled by a factor 6 for easier comparison with Fig. 8.2. Arrows mark the first four VHSs in the $Z = 0$ spectrum and their corresponding peaks in the $Z = 1$ spectrum.

dispersion.

The FCH and the BSE spectra are in reasonable agreement with each other. The spectra show also satisfactory agreement with the experimental data, with the BSE demonstrating slightly better alignment with the experimental results. The core-hole effects are very significant both, in the FCH and the BSE method. Specifically, core-hole effects lead to a significant shift of the intensities from higher energies to low energy excitations, but they also change the energy difference between the peaks significantly. So the common approach to compare excitation energies in the independent particle picture with experimental excitation energies seems to be at least somewhat questionable. To investigate the excitonic effects in more detail, we used a fatband analysis. This shows that conduction band states from multiple VHSs contribute to one exciton.

To investigate whether curvature effects are strong, we also performed graphene supercell calculations with a $\mathbf{k}$ -point sampling chosen to mimic the quantization effects imposed on the electronic states around the circumference of the tube. We found that the core-hole spectra are very similar for graphite and nanotubes. However, the curvature reduces the bandwidth, which in turn increases the excitonic effects in carbon nanotubes. Overall, the spectra are nevertheless only slightly different for "quantized" graphite and nanotubes.

A key finding of the present study is that the first exciton is strongly localised in all nanotubes and has a similar character and electron charge density distribution as in graphene. It is best described as a Frenkel exciton. In graphene, however, no additional QP peaks are visible, neither experimentally nor theoretically. It is therefore clear that the additional peaks in the core-hole spectrum, must be a result of the effects imposed by the quantisation of the

electronic states around the circumference of the tube. However, all our results suggest that there is no simple one-to-one correspondence between the independent particle spectrum and the full QP spectrum. For example and as mentioned above, a fatband analysis shows that the QP peaks contain orbital contributions from many VHS and the position of the peaks is different for the IP spectrum and the spectrum including core-hole effects. Although the details differ between the spectra with and without core-hole effects, we have been able to find a theoretical motivation why, for all but the first bound exciton, there is usually a strong similarity for the VHS and the higher energy peaks in the QP spectrum. This theoretical motivation is based on the orthogonalised plane wave method. As described above, the first exciton is bound and the requirement of orthogonalisation of the higher excitons to the first exciton implies that the core hole is "screened" at higher excitation energies by the first exciton. Thus, at higher excitation energies the positions of the QP peaks are often quite close to the positions of the VHS. Whether this picture is correct depends on whether the bound first exciton is predominantly composed of states in the first VHS or not. If the VHS have a large energy difference, then there is often a close match between the positions of the VHS in the IP spectrum and the QP peaks in the full core-hole spectrum. However, for an accurate description, it seems expedient to perform full BSE calculations, ideally starting from PBE0 orbitals.

Part III

Summary and conclusion

In this thesis we implemented the BSE for X-ray absorption spectra in VASP and then used the BSE and the density functional theory based FSA to calculate spectra of reference materials and single wall carbon nanotubes.

VASP is a code based on the projector augmented-wave (PAW) methodology and in the first part of this thesis we laid out in great detail how the quantities that are needed to set up the BSE eigenvalue equation have to be formulated in the PAW formalism. In particular, we showed how the PAW augmentation charges are the central quantities of the matrix elements for excitations of core to conduction band states. In the first part we additionally summarized the many-body perturbation theory techniques needed to compute the *GW*-BSE spectra. We introduced the main quantities of MBPT, such as the Green’s function and the self-energy, which lead to Hedin’s *GW* approximation and the quasiparticle energies. We then derived the BSE equation and showed how it can be recast as an eigenvalue equation. Finally, we showed how to use the linear response formalism to obtain XAS spectra including excitonic effects.

We then applied the *GW*-BSE and the FSA to reference spectra where the BSE and FSA approaches agreed excellently with experiment. The BSE could in some cases (diamond, h-BN) resolve features that were absent in the FSA. This confirms the *GW*+BSE approach as the state-of-the-art to obtain X-ray spectra. We then investigated whether the screened interaction can be approximated by a diagonal model, either by neglecting the off-diagonal elements of the screened interaction matrix, or by using a parameter dependent model for the diagonal elements. We found in both cases considered (diamond, h-BN) that such a diagonal model is insufficient and that the parameters of the diagonal model had to be significantly altered by hand to reproduce the ab-initio spectra. We concluded that the off-diagonal elements, or local-field effects, play a large role in core excitation spectra.

We then analyzed the FSA in more detail and found that FSA spectra can be improved if the excited core electron is not added to the lowest conduction bands as it is commonly done, but added to the background charge. We suggested that FSA spectra are influenced by the self-interaction effects that the additional electron in the conduction band experiences. This self-interaction error alters the energy of the additional electron in the lowest conduction band and hence alters the absorption spectrum. By instead including the electron to the background charge this self-interaction effect is mitigated and the spectra improved. Using the notation of previous authors we called these spectra full core hole (FCH) spectra. The improvement is quite significant as in the case of LiF the FCH spectra are on par with the BSE results.

In the second part of this thesis we used our methods to explain the fine structure seen in EELS results of semiconducting carbon nanotubes. To interpret the experimental data, experimentalists matched the first VHS seen in the ground state DOS to the first peak seen in experiment. While each VHS in the DOS could be assigned to a particular peak in the fine structure, there was still a mismatch. We then used a combined BSE and FCH approach to show that the mismatch between the VHSs in the DOS and the fine structure peaks is due to the strength of the core-hole potential and the requirement that successive exciton states are orthogonal. To support our argument we used the formalism of the orthogonalised plane wave method. In this formalism, the requirement that the core state must be orthogonal to the conduction states leads to a pseudopotential that weakens the core hole effect, where this pseudopotential depends on the energy difference between the core state and the next VHS. Using both approaches, we argued that when the VHSs are close in energy, the discrepancy

between the VHSs in the DOS and the peaks in the fine structure is large. On the other hand, when the energy separation between VHSs is large, an approach based on the ground state DOS gives satisfactory results.

Two conclusions can be drawn from the results of this thesis. Firstly, the agreement of all our results with the corresponding experimental spectra underlines a point that was already made in the introduction: only by using the advanced computational methods of theoretical spectroscopy can we hope to account for all the different processes that influence the XAS spectra. However, reproducing the spectra is only a first step towards an understanding of the X-ray absorption process. The second conclusion of this thesis is that our results highlight the need to use *complementary methods* and to perform *computational experiments* to obtain a complete physical picture.

In Sec. 7.4 we established FCH as a valid alternative to the BSE approach only by performing computational experiments: we added and removed the electron from the lowest conduction band and turned on and off the electron-hole interaction in the BSE spectra. Then, our study of SWCNT spectra in chapter 8 demonstrated the need to use both computational experiments and complementary methods. The computationally inexpensive and flexible FCH method allowed us to calculate spectra of many different carbon nanotubes and to emphasize the importance of core hole effects. By varying the core hole charge, we were able to understand how core hole effects alter the spectra and to show how weakly bound excitons are affected by the periodic boundary conditions. On the other hand, the more accurate BSE approach yielded spectra in better agreement with experiment, increasing the confidence in our results. Finally, the BSE fatband structure analysis provided the necessary insights from many-body perturbation theory as to why the VHS in the DOS only sometimes align with the fine structure peaks. Only by using this dual approach were we able to fully explain the carbon nanotube spectra.

In conclusion, this thesis has shown that the many body perturbation theory based BSE approach is the state-of-the-art technique for modeling accurate XAS spectra. Furthermore, we have shown that by combining the BSE approach with the DFT-based FCH method we were able to gain a deeper understanding of how the spectra are shaped by core exciton effects. These tools of theoretical spectroscopy, along with measurements from fourth-generation X-ray facilities, will enable XAS to address future challenges in materials science.

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