

MANY-BODY THEORY EXPLORED OPTICAL PROPERTIES OF SELECTED 2D GROUP II-VI MONOCHALCOGENIDES

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By
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ABSTRACT

MANY-BODY THEORY EXPLORED OPTICAL PROPERTIES OF SELECTED 2D GROUP II-VI MONOCHALCOGENIDES

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Two-dimensional (2D) metal oxides (MOs) and metal chalcogenides (MChs) are emerging classes of 2D materials. Depending on the constituent elements, these materials can display various electronic and optical properties making them promising candidates in many device applications, such as solar cells and transparent circuits. Binary graphene-like structures of II-VI are the most straightforward structures of 2D MOs and MChs. We systematically examined the electronic and optical properties of selected 2D structures from this category: BeO, BaTe, CdO, CaO, CaS, MgO, SrS, SrSe and ZnO. The dynamical stability of these materials has been reported in previous studies.

In 2D semiconductors, excitonic effects dominate the optical properties. Theoretical investigation of such phenomena requires employing many-body approaches beyond standard density functional theory. We utilized a single shot of GW approximation to predict the electronic band structure and solved the Bethe-Salpeter equation in the Tamm-Dancoff approximation to consider excitonic effects.

Our results show that all structures possess indirect band gaps except ZnO and CdO. Furthermore, the considered structures have large exciton binding energies ranging from 0.72 eV in CdO to 2.84 eV in BeO. CdO has the smallest calculated optical band gap with a value of 1.43 eV. Analyzing the optical absorption spectra reveals that the CdO can absorb 7.9 % of the incident light in its optical band gap. The maximum amount of absorption appears in BeO, which can absorb 28% of incident light in the ultraviolet region.

Among the structure mentioned above, there is a close matching between the lattice constants of ZnO and MgO, promising for creating lateral and vertical heterostructures. Due to the enhanced performance resulting from mixing distinct properties of individual monolayers, van der Waals heterostructures (vdWHs) are regarded as a revolutionary class among a plethora of presently fabricated or

predicted 2D materials. Alongside vdWHs, recent studies have also reported 2D heterostructures with interlayer bonding.

Motivated by the flourishing properties of vertical heterostructures, we comprehensively examined the mechanical, electronic and optical properties of ZnO/MgO structures in four different stackings. Structural relaxation has indicated two vdWHs and two structures with interlayer binding. All considered structures are mechanically stable. In addition, phonon dispersion curves show that the AB stacking formed by placing the Mg atom on top of the O atom of the ZnO layer is also dynamically stable at zero temperature. The s orbital of Zn atom dominates the minimum of the first conduction band of these structures. The optical absorbance spectra show that strong excitonic effects reduce the optical band gap to the visible light spectrum range, and all structures can absorb around 8% of incident light.

Keywords: 2D materials, 2D metal chalcogenides and metal oxides, Optical properties, Density functional theory, Excitonic effects, Many-body theory, GW and Bethe-Salpeter equation.

ÖZET

İKİ BOYUTLU SEÇİLMİŞ GRUP II-VI KALKOJENİTLERİN OPTİK ÖZELLİKLERİNİN ÇOKLU-CİSİM TEORİLERİNE DAYANAN İNCELENMESİ

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İki boyutlu (2B) metal oksitler (MO'lar) ve metal kalkojenitler (MCh'ler), yeni ortaya çıkan 2B malzeme sınıflarıdır. Bileşenlerine bağlı olarak, bu malzemeler, güneş pilleri ve şeffaf devreler gibi birçok aygıt uygulamasında onları umut verici adaylar haline getiren çeşitli elektronik ve optik özellikler gösterebilirler. II-VI'nın ikili grafen benzeri yapıları, 2B MO'ların ve MCh'lerin en basit yapılarıdır. Bu tez çalışmasında bunların arasından seçilen 2B yapıların (BeO, BaTe, CdO, CaO, CaS, MgO, SrS, SrSe ve ZnO) elektronik ve optik özelliklerini sistematik olarak inceledik. Bu malzemelerin dinamik kararlılıkları önceki çalışmalarda rapor edilmiştir.

2B yarı iletkenlerde eksitonik etkiler optik özelliklerde baskındır. Bu tür özelliklerin teorik olarak araştırılması, standart yoğunluk fonksiyonel teorisinin ötesinde çoklu cisim yaklaşımlarının kullanılmasını gerektirir. Elektronik bant yapısını hesaplamak için tekli GW yaklaşımı kullandık ve eksitonik etkileri dikkate almak için Tamm-Dancoff yaklaşımında Bethe-Salpeter denklemini çözdük.

Sonuçlarımız, ZnO ve CdO dışındaki tüm yapıların dolaylı bant aralıklarına sahip olduğunu göstermektedir. Ayrıca, dikkate alınan yapılar, CdO'da 0.72 eV ile BeO'da 2.84 eV arasında değişen büyük eksiton bağlanma enerjilerine sahiptir. CdO, 1.43 eV değeri ile hesaplanan en küçük optik bant aralığına sahiptir. Optik soğurma spektrumlarının analizi, CdO'nun optik bant aralığında gelen ışığın %7.9'unu emileceğini ortaya koymaktadır. En yüksek soğurma, ultraviyole bölgesinde gelen ışığın %28'ini soğurabilen BeO'da görülür.

Yukarıda bahsedilen yapılar arasında, ZnO ve MgO'nun örgü sabitleri arasında, yanal ve dikey heteroyapılar oluşturmayı vaat eden yakın bir eşleşme vardır. Bireysel tek tabakaların farklı özelliklerinin karıştırılmasından kaynaklanan gelişmiş performans nedeniyle, van der Waals heteroyapıları (vdWH'ler), şu anda

üretmiş veya tahmin edilen çok sayıda 2B malzeme arasında devrim niteliğinde bir sınıf olarak kabul edilir. vdWH'lerin yanı sıra, son çalışmalar, katmanlar arası bağlanma ile 2B heteroyapılar bildirmiştir.

Dikey heteroyapıların gelişen özelliklerinden motive olarak, ZnO/MgO yapılarının mekanik, elektronik ve optik özelliklerini dört farklı istiflemede kapsamlı bir şekilde inceledik. Yapısal gevşeme, iki vdWH'yi ve katmanlar arası bağlanmaya sahip iki yapıyı gösterir. Dikkate alınan tüm yapılar mekanik olarak karardır. Ek olarak, fonon dağılım eğrileri, Mg atomunun ZnO katmanının O atomunun üstüne yerleştirilmesiyle oluşturulan AB istifinin de sıfır sıcaklıkta dinamik olarak karardır olduğunu göstermektedir. Zn atomunun s orbitali, bu yapıların ilk iletim bandının kenarını oluşturur. Optik soğurma spektrumları, güçlü eksitonik etkilerin optik bant aralığını görünür ışık spektrum aralığına indirdiğini ve tüm yapıların gelen ışığın yaklaşık %8'ini soğurabildiğini göstermektedir.

Anahtar sözcükler: 2B malzemeler, 2B metal kalkojenitler ve metal oksitler, Optik özellikler, Yoğunluk fonksiyoneli teorisi, Eksitonik etkiler, Çoklu-cisim teorisi, GW ve Bethe-Salpeter denklemi.

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Chapter 1

Introduction

In recent decades, ab-initio calculations based on density functional theory (DFT) have created a robust framework for predicting the ground state properties of materials. However, excited states become affected by the formation of quasiparticles (QP) and different coupling mechanisms between QPs. Hence, many-body methods beyond the standard DFT calculation must be employed for investigating excited states. Optical properties of materials are one of the key factors in device applications, and from the theoretical point of view, they must be studied by considering coupling between the quasi-particles. Due to their distinguished properties from bulk phases, two-dimensional materials (2D) have opened a new door in nano device engineering. Although well-established experimental techniques for measuring the optical properties of bulk phases can be employed for the inspection of light-matter interaction in 2D materials, nonetheless, pure and large-area samples must be fabricated, and then non-destructive measurement methods must be utilized. Hence, accurate theoretical predictions play a crucial role in technological advancements in the realm of 2D material. This thesis examines the optical properties of II-VI binary 2D materials using GW approximation and solving the Bethe-Salpeter equation. This chapter describes the motivation of this research. First, a brief review of the 2D materials and their optical properties is presented. Then, the importance of the current research is highlighted by explaining the properties of the considered materials.

1.1 Two Dimensional Materials

Investigating 2D materials is dated back to 1930s, when Peierls and Landau showed that flat 2D materials are thermodynamically unstable [1–3]. Despite this theoretical prediction, in 1979, Grimes and Adams experimentally observed an electron-liquid to 2D triangular electron-crystal phase transition in a sheet of electrons on a liquid-He surface [4]. Finally, a breakthrough occurred in 2004, when Novoselov and Geim et al. successfully exfoliated a single crystalline atomic layer of carbon atoms from graphite [5]. This hexagonal 2D structure of the carbon atoms is named graphene and it is shown that, intrinsic rippling stabilizes the 2D crystal structures.

Following the mechanical exfoliation of single-layer graphene, it was shown that similar technique can be employed for isolating other 2D materials [6, 7]. Furthermore, experimental and theoretical confirmed distinguished properties of 2D structures from the bulk phases [8, 9] and consequently opened a new avenue in nano-device engineering. Afterwards, the prediction and fabrication of other 2D materials with different functionalities initiated many investigations. So far, several diverse categories of 2D materials are theoretically predicted or experimentally fabricated. Examples are transitional metal dichalcogenides (TMDs) [7, 10–12], MXenes [13–15], MBenes [16–18] and binary 2D structures of group II-V [19], group III-V [20] and group IV-IV [20]. Besides, 2D materials such as silicene [21, 22], h-BN [23–25] and phosphorene [26] are already explored. Janus monolayers, where a transition metal atomic layer is sandwiched by two different chalcogen atomic layers, are another emerging category of 2D materials and have attracted interest due to their distinguished properties arising from out-of-plane structural asymmetry [27–29].

Apart from all categories above, van der Waals heterostructures (vdWHs) assembled by different monolayers are another emerging class of 2D materials [30, 31], vdWHs possess remarkable physical properties and enriched functionalities arisen by combining different properties of separate monolayers. Due to many combination possibilities, vdWHs are promising candidates for different device applications and are regarded as a revolutionary class of 2D structures [32]. Most of the early studies of vdWHs have been focused on structures assembled by graphene,

h-BN and TMDs. Graphene/h-BN vdWHs is the first fabricated member of this class [33]. vdWHs of graphene, h-BN and MoS₂ are employed for manufacturing tunnelling diodes and transistors [34, 35]. Besides, enhanced photocurrent generation in layered MoS₂ and WS₂ layers sandwiched between graphene layers have been reported [36, 37]. In addition, light-emitting diodes using quantum wells have been designed by integrating monolayers of graphene, h-BN, and TMDs [38].

Alongside vdWHs, recent investigations have reported 2D vertical heterostructures with interlayer bonding [39, 40]. For example, interlayer covalent bonding is observed in AA stacked bilayer graphene/borophene [39, 40]. Another example is SnP₃/GeP₃ heterostructures [41]. Moreover, an *ab initio* study has demonstrated the practicality of artificial manipulating the physical properties of vdWHs by employing 2D donor-acceptor heterostructures to create substantial bond-like interactions between layers [42]. Interlayer bonding in 2D heterostructures alters the properties of corresponding single layers, which is not so noticeable in vdWHs [39, 43]. Consequently, it creates a new playground for controlling electronics and optical properties.

1.2 Excitons

The concept of excitons will be discussed in more detail in the next chapter. Here, a brief description is presented to illuminate the role of this quasi-particle in the optical properties of 2D materials. In semiconductors or insulators, photo-absorption can cause an interband transition by exciting an electron from the valence band to the conduction band. The excited electron leaves a hole in the valence band that interacts with the electron via the Coulomb potential. In appropriate conditions, a bound state of electron-hole can occur. Although the binding energy of a bound state of electron-hole is much smaller than the Rydberg energy 13.6 eV, it behaves like hydrogen atoms [44] and is named exciton. Depending on the electronic properties of the materials, the excitons are categorized into two main types, Frenkel and Wannier-Mott excitons. Wannier-Mott

excitons, also called free excitons, are typically observed in semiconductors with high dielectric constant. The Coulomb interaction between electron-hole can be significantly increased in high dielectric materials, creating excitons with low binding energy and a radius higher than the lattice spacing. Frenkel excitons have a small radius and large binding energy and usually appear in insulators and molecular crystals. The stability of the excitons at high temperatures depends on their binding energies. Therefore, only excitons with binding larger than $k_B T \approx 0.025$ eV are observable at room temperature. The stability of the excitons at high temperatures depends on their binding energies. Therefore, only excitons with binding larger than 0.025 eV are observable at room temperature.

1.3 Optical Properties of Two Dimensional Materials

The flourishing properties of 2D materials make them promising candidates for a wide range of applications in the next-generation nanodevices [45], specifically in optoelectronics [46]. Here two main essential features that distinguish the optical properties of 2D materials from the bulk structures are explained.

Thinking of the small thickness of 2D materials, one of the peculiar properties of 2D materials is related to the amount of light that they can absorb. Experimental measurements are shown that for photon energies above 0.5 eV, graphene possesses a spectrally flat optical absorbance around 2.3% and very small reflectance ($< 0.1\%$) [47, 48]. Its opacity ¹ at low-frequency limit can be determined by $\pi\alpha$, where α is the Sommerfeld fine-structure constant $1/137$ [48]. At first glance, the amount of absorbance of graphene seems to be small. However, it is equivalent to the absorbance of 20 nm thick Si or 5-10 nm thick GaAs, which are widely used absorbers in solar cells [49, 50]. The absorbance in TMDs is more noticeable as they can absorb 5–10 % incident sunlight in a thickness of less than 1 nm.

The other exciting effect in 2D semiconductors is the formation of Wannier-Mott

¹The opacity O is defined as $O=(1-T)$, where T is the transmittance

excitons with considerable binding energies [51]. Due to the quantum confinement effects that reduce dielectric screening, excitons in 2D semiconductors have binding energies large enough to prevent thermal dissociation [52]. Initially, theoretical calculations had predicted high exciton binding energies in monolayer TMDs. The first experimental measurement of the exciton binding energy of a 2D structure is reported in 2014, where the exciton binding energy of the MoSe₂ on graphene substrate is measured [53]. In this experiment, the optical and electronic band gaps are obtained using scanning tunnelling and photoluminescence spectroscopy, respectively. The obtained exciton binding energy, the difference between the electronic and optical band gaps, has a value of 0.55 eV, which is orders of magnitude greater than in typical bulk semiconductors. It shows that the optical properties of 2D semiconductors are dominated by tightly bounded excitons [50].

1.4 Metal Oxides and Metal Chalcogenides

Initial works on 2D materials focused on efficiently experimentally fabricable structures, such as graphene and common TMDs (MoS₂, MoSe₂, WS₂, WSe₂) and various properties of these structures are thoroughly investigated [54]. As it is pointed out in previously, currently, many 2D materials are fabricated or predicted. Among them, metal oxides (MOs) and metal chalcogenides (MChs) are emerging classes of 2D materials [55, 56]. Their bulk phases have a long history in device application. This section briefly highlights the application of MOs and MChs ².

In essence, electronic devices, such as display screens, are invisible circuits [57], where optical transparency is incorporated with high carrier mobilities. Optical transparency requires band gaps wider than 3.3 eV. Since a large band gap prevents effective doping, it was thought that optical transparency is conflicting with high electron conductivity [58]. Nevertheless, it is shown that this conflict does not exist in the case of MOs. Examples are n-type doped In₂O₃, SnO₂ and

²Although oxygen is also in the chalcogen group, here and in the rest of the thesis, we used chalcogen for group VI materials other than oxygen.

ZnO. Devices such as light-emitting diodes and bipolar transistors operate based on p-n junctions. In this sense, the observation of p-type (hole) conductivity in CuAlO₂ is considered significant progress [58, 59] and has extended the application of transparent oxide semiconductors in optoelectronics [60–64]. In MOs, 2p orbitals of the oxygen atoms from the valence band maximum (VMB) and the conduction band minimum (CBM) are usually dominated by the s orbital of metals. Lattice distortions have an insignificant effect on the spherical symmetry of the s orbital of CBM. Therefore, the electron transport properties are adequate for device applications even in the amorphous state of MOs [65]. This property distinguishes MOs from commonly used Si semiconductors, where as a consequence of spatially directional sp^3 hybridization, the carrier mobilities significantly decrease in the amorphous state. Furthermore, MOs can display various electronic, optical and magnetic properties depending on their crystal structures and constituent elements. This make them promising alternatives in applications where the traditional wide band-gap semiconductors, such as GaN [66] and SiC [67], are inadequate [61]. MChs possess electronic and optical properties similar to MOs, and more importantly, they are amenable to p-doping [68]. Apart from the transparent electronic devices, some MOs and MChs can be employed in visible light and solar spectrum devices. The most notable example is CdTe which has a band gap of around 1.5 eV and is already utilized for fabricating high-efficiency solar cells [69–71].

Binary II-VI are the simplest class of MOs and MChs. Investigating the optical properties of II-VI monolayers is the main topic of this thesis.

1.5 II-VI Semiconductors

Different applications of bulk and nanostructures group II-VI elements are already demonstrated in several studies. Monolayers of these materials are also examined using *ab-initio* calculations, and it is shown that CaS, SrS, SrSe, BaTe, BeO, MgO, CaO, ZnO, and CdO possess planar graphene-like structures are dynamically stable [72]. These theoretical predictions motivated experimental studies [73] and inspired the investigation of various properties and possible applications of these

materials [74–77]. As it is pointed out, examining the properties of group II-VI structures have been an active research field for the last two decades. For instance, different phases of ZnO have been studied substantially, being the most intriguing structures among the aforementioned materials. Several technological applications of ZnO in different bulk and powder phases are already revealed. For example, the wurtzite structure, the most stable ZnO phase, is a wide band gap (3.37 eV) semiconductor and exhibits strong piezoelectric properties [78]. Besides, thin films of wurtzite ZnO possess a strain tunable bandgap [79]. The adjustability of the band gap and lattice constant of ZnO by the number of layers is also demonstrated experimentally [80]. Also, reducing the number of layers causes the transformation into graphene-like structures [81, 82]. Experimentally, nonpolar ZnO monolayers initially have been observed on Pd(111) [83] surface and later on Ag(111) [84] and graphene [85]. Moreover, free standing ZnO multi and monolayers are already fabricated [86–88]. Optoelectronics [89], hydrogen storage [90] and selective photoreduction of CO₂ [80] are some of the potential applications based on ZnO monolayer.

CdO has cubic rocksalt structure in the bulk phase and possesses a direct band gap at Γ point that decreases from 2.31 eV at 0 K to 2.18 eV at 300 K [91]. CdO thin films are fabricated by pulsed laser deposition. These structures have high infrared transmission transparent contact [92, 93] and they are suitable for optoelectronic applications. The dynamical, thermal and mechanical stability of monolayer CdO has been confirmed theoretically [94, 95]. Furthermore, a direct to indirect band gap transition under strain is reported [96] for monolayer CdO. In addition, 2D combinations of CdO with ZnO and CdS have been reported as good candidates for water splitting [97, 98].

Nanostructures of BeO have attracted lots of interest after theoretical predictions of BeO nanotube [99, 100] followed by experimental observation of monolayer BeO [73, 101]. It is shown that the magnetic properties of monolayer BeO are tunable by introducing vacancies and doping by transition metals [102].

Owning ionic bonds, MgO is a wide gap material (7.8 eV) and has a high thermal conductivity [103]. Several methods have been employed for the fabrication of MgO thin films [103–109]. It is shown that the band gap of thin films decreases by more than 60% compared to the bulk phase [103]. Exceptionally,

square lattice monolayer MgO and CaO are also reported experimentally [110], and a first principle calculation has shown the stability of corresponding buckled 2D structures [111]. SrSe and SrS are other members of this family. It is shown that hole doping induces ferromagnetism in these theoretically predicted monolayers [74]. Furthermore, the high piezoelectric strain [77] of these materials is already pointed out.

Motivated by the remarkable properties of the monolayer II-VI, we first investigated their optical properties by employing the many-body approaches beyond the standard DFT calculations. Then, inspired by the promising properties of ZnO/MgO heterostructures (see 4.1) and close lattice matching between the graphene-like ZnO and MgO, we presented a comprehensive study of mechanical, electronic and optical properties of bilayer structures formed by them.

1.6 Thesis Organization

After this introduction, in chapter 2, the theoretical framework required for studying optical properties is briefly reviewed. Chapter 3 presents a systematic study of the optical properties of II-VI monolayers. In chapter 4, we focused on the ZnO/MgO heterostructures. Finally, chapter 5 summarizes the main achievements and the conclusion of this research.

Chapter 2

Theory and Computational Methods

2.1 Introduction

This chapter presents a brief review of the theoretical background of the methods used in the thesis. First, the many-body problem of a system consisting of electrons and nuclei is described. Then the main challenges and approaches for obtaining ground state properties of the system are explained. Afterwards, the procedures for investigating excited states where quasi-particles arose are motivated and introduced.

2.2 The Many-Body Problem

In classical mechanics, solids can be modeled as a lattice of interacting nuclei vibrating around fixed lattice points. However, investigating electronic properties

is only feasible by a quantum mechanical approach. The time dependent many-body Schrödinger equation for describing a solid is given by:

$$\hat{H}\Psi(\vec{r}, \vec{R}, t) = \hat{E}\Psi(\vec{r}, \vec{R}, t) \quad (2.1)$$

Where, Ψ is the wave function, $\vec{r}$ refers to positions of electrons and $\vec{R}$ shows nuclei (Ions). For a system consisting of N_e electrons and N_n nuclei, the Hamiltonian operator can be explicitly writing as:

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_e} \sum_i^{N_e} \nabla_i^2 - \frac{\hbar^2}{2M_I} \sum_I^{N_I} \nabla_I^2 + \frac{1}{2} \sum_j^{N_e} \sum_i^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \\ & - \sum_I^{N_n} \sum_i^{N_e} \frac{Z_I e^2}{|\vec{R}_I - \vec{r}_i|} + \frac{1}{2} \sum_J^{N_n} \sum_I^{N_n} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} \end{aligned} \quad (2.2)$$

The terms in the left side of the equation 2.2 describe kinetic energy of electrons (T_e), kinetic energy of nuclei (T_n), electron-electron interactions (V_{ee}), nuclei-electron interactions (V_{ne}) and nuclei-nuclei interactions (V_{nn}), respectively. Equation 2.1 has $3(N_e + N_I)$ spatial variables. Beside, for a system with N_e electron Slater determinant required to describe the fermionic wave function has dimension of $N_e \times N_e$ for each single-particle basis set. Therefore, with M being the total number of single-particle basis, the number of required Slater determines is given by:

$$\binom{M}{N_e} = \frac{M!}{N_e! (M - N_e)!} \quad (2.3)$$

This is typically a huge number. For instance, in the case of single carbon, which has 12 electrons, if we use 24 basis functions for orbitals, the number of Slater determinants becomes 2704156. Therefore, approximation methods are necessary for dealing with equation 2.1.

2.3 Born-Oppenheimer Approximation

The adiabatic theorem of quantum mechanics states that if the given perturbation acts slowly and there is a gap between the current eigenvalue and the rest of Hamilton's spectrum, the system will remain in its instantaneous eigenstate. Due to the significant difference between the mass of an electron and the masses of atomic nuclei, electron-nuclei interaction has a negligible effect on the position of nuclei. Therefore it is possible to decouple the electronic and nuclei wave function. The wave function of the system can be written as a product of the wave function of electrons and nuclei. This is known as the Born-Oppenheimer approximation [112, 113]. Besides, the core electrons are tightly bound to the nuclei, and it is possible to consider them as a single core. The Hamiltonian of this ion-core describes the lattice structure and vibrational properties, while the electronic Hamiltonian gives the electronic and optical properties. As it was explained before, because of electron-electron interaction, solving the electronic part of the Schrödinger equation is still computationally expensive, and further approximations are required.

2.4 Hartree-Fock Approximation

Consider a system of many interacting individuals. It is possible to approximate the interaction of an individual with others by an averaged effect. This approach is called mean-field, or self-consistent field theory. In the case of the many-body electronic system, we can assume that each electron interacts with the background potential, which is the average of its interactions with all other electrons. Hartree method approximates the ground-state many-body electron wave function as the product of single electron wave functions [114, 115]. In the Hartree units, $\hbar = m_e = e = 1$, the Schrödinger equation of a single electron in the effective potential is given by:

$$\left(-\frac{\nabla^2}{2} + \sum_n^{N_I} V_{ne} \left(\vec{r} - \vec{R}_n \right) + \sum_{j \neq i}^{N_e} \int \frac{|\phi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \right) \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \quad (2.4)$$

equation 2.4 must be solved self consistently. It starts with a trial wave function and utilizes the variational method to minimize the energy. Nevertheless, this approach neglects electron correlations, and more importantly, the fermionic nature of electrons is also ignored in the Hartree method. The Hartree-Fock (HF) method [115, 116] solves this problem by introducing the electronic wave function by a single Slater determinant [117]. HF wave function is given by:

$$\Psi_{HF} = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_2(\vec{r}_1) & \cdots & \phi_{N_e}(\vec{r}_1) \\ \phi_1(\vec{r}_2) & \phi_2(\vec{r}_2) & \cdots & \phi_{N_e}(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_{N_e}) & \phi_2(\vec{r}_{N_e}) & \cdots & \phi_{N_e}(\vec{r}_{N_e}) \end{vmatrix} \quad (2.5)$$

Furthermore, another potential term is added to the Hartree Hamiltonian to consider local exchange effects:

$$V_{ex} = - \sum_{j \neq i}^{N_e} \int \frac{\phi_j^*(\vec{r}') \phi_i(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (2.6)$$

A linear combination of Slater determinants of single-electron orbitals is usually used in practical applications of the HF method. These methods are called configuration interaction methods. A schematic diagram of the HF method is shown in Figure 2.1.

If we consider all Slater determinants of a complete set of single-particle basis functions, the HF can precisely describe the ground state of the many-body problem. However, as it was pointed out before, the high computational cost prevents practical applications. Considering a limited number of Slater determinants, correlation effects will be neglected. Therefore, it is necessary to change the point of view and utilize a method that can consider all terms of the 2.2 effectively.

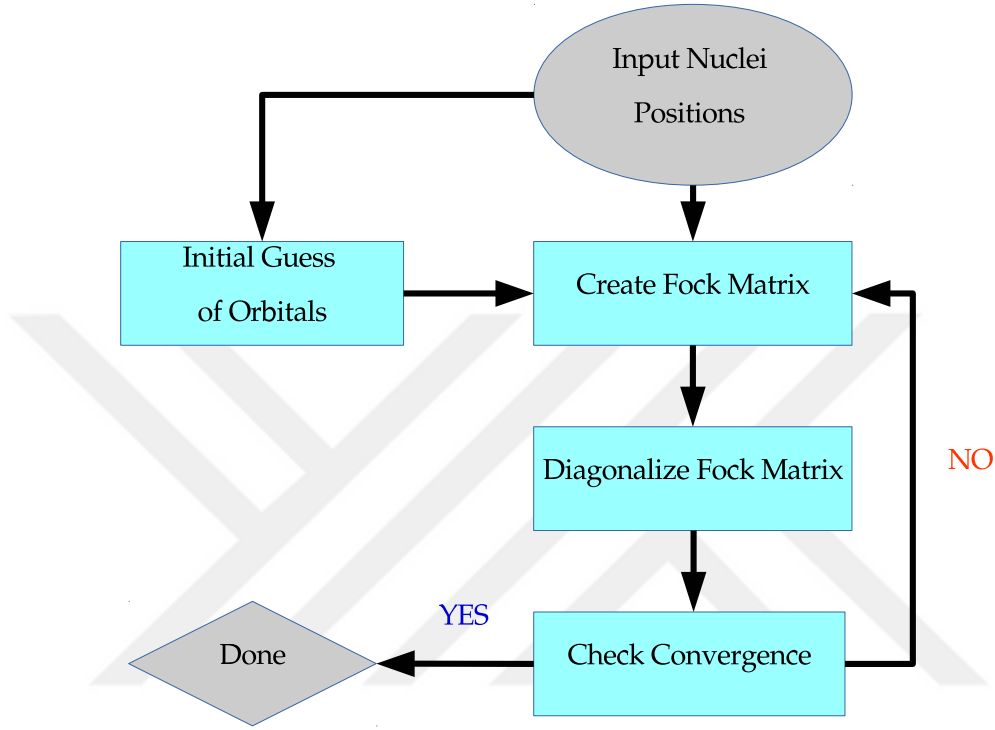


Figure 2.1: Flowchart illustrating the HF method

2.5 Thomas-Fermi Theory

Almost simultaneous to the HF approach, Thomas and Fermi proposed a method for investigating the many-body electronic problem, where instead of the wave functions, they used electron density as the variable [118, 119].

The main idea of the Thomas-Fermi approach is to write all terms in the many-body Hamiltonian as functionals of electron density. Explicitly, the electron density is given by:

$$n(\vec{r}) = \sum_i^{N_e} |\phi_i(\vec{r})|^2 \quad (2.7)$$

However, the kinetic energy term of electrons is challenging. Therefore, as an approximation, the kinetic energy of uniform electron gas is employed in the TF

method. The total energy as a functional of the electron density has the form:

$$E[n] = A_k \int d\vec{r} n^{\frac{5}{3}}(\vec{r}) + \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int d\vec{r} V_{ext}(\vec{r}) n(\vec{r}) \quad (2.8)$$

Where, $A_k = \frac{3}{10} \left((3\pi^2)^{\frac{2}{3}} \right)$. The first term in 2.8 is kinetic energy, the second term is associated with electron-electron interaction, and the last term represents electron-nuclei interaction.

The TF approach reduces the many-body problem to a minimization problem where the functionals are only dependent on electron density, with only three degrees of freedom. Because the total number of electrons is fixed and imposes a constraint, it is possible to determine $n(\vec{r})$ by utilizing the Lagrange multiplier method:

$$F[n(\vec{r})] = E[n(\vec{r})] - \mu N_e \quad (2.9)$$

Despite reducing the complexity of the problem, the TF approach neglects the exchange and correlation effects. However, the basic idea of this seminal work is the core of the DFT theory.

2.6 Density Functional Theory

More than three decades after the TF theory, a scientific breakthrough occurred. Two theorems by Hohenberg and Kohn[120] and reformulation of many-body electronic Hamiltonian in terms of functional of electron density by Kohn and Sham [121], made the accurate solution of the problem possible. Walter Kohn received the Nobel Prize in chemistry for his contributions in developing DFT.

2.6.1 Hohenberg-Kohn Theorems

Theorem 1: The external potential is (to within a constant) uniquely defined by a functional of electron density. Therefore ground state properties of the system can be directly determined by $n(\vec{r})$.

Theorem 2: The electron density that minimizes the energy functional is the exact ground state density of the system. This theorem is the direct result of the variational principle.

Mathematically the expectation value of the electronic part of the Hamiltonian is given by:

$$\langle \Psi_e | \hat{H} | \Psi_e \rangle = \langle \Psi_e | \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} | \Psi_e \rangle \quad (2.10)$$

and gives the following results:

$$E_{ne} = \langle \Psi_e | \hat{V}_{ne} | \Psi_e \rangle = \int n(\vec{r}) V_{ne}(\vec{r}) d\vec{r}$$

$$E_{ee} = \langle \Psi_e | \hat{V}_{ee} | \Psi_e \rangle = \iint \frac{n(\vec{r}, \vec{r}')}{2|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \quad (2.11)$$

$$K_e = \langle \Psi_e | \hat{T}_e | \Psi_e \rangle = -\frac{1}{2} \int \Psi_e^* \nabla^2 \Psi_e d\vec{r}$$

The term $n(\vec{r}, \vec{r}')$ in equation 2.11 is related to the probability of finding another electron at position $\vec{r}'$, given that there is an electron at position $\vec{r}$. This term can be written as $n(\vec{r}, \vec{r}') = n(\vec{r})n(\vec{r}') + \Delta_n$. It is possible to write the expectation value of the kinetic energy operator in terms of electron density, but first, it is necessary to describe Kohn-Sham (KS) equations [121] that facilitate the practical application of DFT.

2.6.2 Kohn-Sham Equations

The central assumption in the KS equations [121] is that it is possible to assume a fictitious non-interacting system of electrons that has the same electron density as

the interacting system. By replacing the wave function of the interaction system with those of the non-interacting system and using the kinetic energy operator of the fictitious system, the expectation value of the kinetic energy in equation 2.11 takes the form:

$$K_e = -\frac{1}{2} \sum_i^{N_e} \int \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) d\vec{r} + \Delta_k \quad (2.12)$$

Δ_k shows the difference in the kinetic energies of two interacting and non-interacting systems. Where $\phi_i^*(\vec{r})$ are called KS orbitals. The total energy becomes:

$$\begin{aligned} E[n(\vec{r})] = & -\frac{1}{2} \sum_i^{N_e} \int \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) d\vec{r} + \int n(\vec{r}) V_{ne} d\vec{r}' \\ & + \frac{1}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}' + \Delta_k + \Delta_n \end{aligned} \quad (2.13)$$

The summation of the last two terms is called the exchange-correlation function:

$$E_{XC} = \Delta_k + \Delta_n \quad (2.14)$$

Up to now, there was only Born-Oppenheimer approximation in driving the equations. For practical use, the term E_{XC} is assumed to be a functional of the electron density and equation 2.13 is called KS functional. In practice, the DFT starts with an initial guess for density and uses KS orbitals to minimize the KS functional.

2.7 Practical Implementation of DFT

This section presents a summary of the technical issues regarding practical DFT calculations.

2.7.1 Local Density Approximation

As it is mentioned before, the E_{XC} must be approximated in terms of electron density. The first and most straightforward way for this is using the electron density of homogeneous electron gas (*Jellium*). Since exchange and correlation have local effects within this approach, it is called local density approximation (LDA):

$$E_{XC}^{LDA}(n\vec{r}) = \int n(\vec{r}) \epsilon_{XC}(n(\vec{r})) d\vec{r} \quad (2.15)$$

Where ϵ_{XC} is the electron density of homogeneous electron gas. Because the electron density of Jellium is constant, LDA overestimates the correlation energy and underestimates exchange [122].

2.7.2 Generalized Gradient Approximation

LDA gives about 10% error in the exchange energies of atomic and molecular systems [123]. In order to give a better description of binding energies, which are essential in chemical application, it is necessary to correct the errors arising from LDA. It is done within the framework of general gradient approximation (GGA) by considering E_{XC} as functional of electron density and its derivatives. Explicitly:

$$E_{XC}^{GGA} = E_{XC}^{GGA}[n(\vec{r}) \nabla(n(\vec{r}))] \quad (2.16)$$

Several forms for GGA are proposed. Examples are: Becke(B88) [123] which reproduce an improved $1/r$ asymptotic behavior of electron density, Perdew and Wang (PW91) [124], which has better accuracy in the description of delicate magnetic effects and Perdew, Burke, and Enzerhof (PBE) [125]. PBE improves the performance of BB3 and provides a smoother potential, and gives an accurate description of the linear response of the uniform electron gas. Another example

of GGA functionals is AM05 [126] that promotes proper treatment of systems with electronic surfaces. An improved PBE type GGA is PBEsol [127] that gives more precise equilibrium properties of densely packed solids and their surfaces. PBE type functionals are the widely used GGA in the field of solid-state. It must be pointed out that all above density functional are designed for spin-polarized cases as well.

2.7.3 Plane-Wave Basis Sets

The other query in the KS equation is selecting the type of KS orbitals. To address this, we utilize the assumption that the atoms are arranged in well-defined lattices in solids. In order to take a finite size structure, it is sufficient to impose periodic boundary conditions. This assumption facilitates the use of the Bloch theorem. The wave function of the Schrödinger equation for a periodic lattice can be written as a plane wave modulated by a periodic function:

$$\begin{aligned}\Psi_k &= u(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \\ u(\vec{r}) &= u(\vec{r} + \vec{R})\end{aligned}\tag{2.17}$$

Where $\vec{k}$ is a wave vector confined to the first Brillouin Zone and $\vec{R}$ is the lattice vector. It is possible to expand the periodic function $u(\vec{r})$ in terms of a Fourier series. By selecting the reciprocal lattice vector as the basis of Fourier expansion, we can rewrite Ψ_k in equation 2.17:

$$\Psi_k = \sum_{\vec{G}} c_{\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G}) \cdot \vec{r}}\tag{2.18}$$

Most DFT programs use a plane-wave basis for KS orbitals. The exact results can be obtained if an infinite number of expansion terms are employed. In practice, only plane waves with kinetic energies less than a predefined cutoff are

selected. However, a careful convergence test must be performed for selecting the appropriate cutoff energy. A schematic diagram of the Kohn-sham method is shown in Figure 2.2.

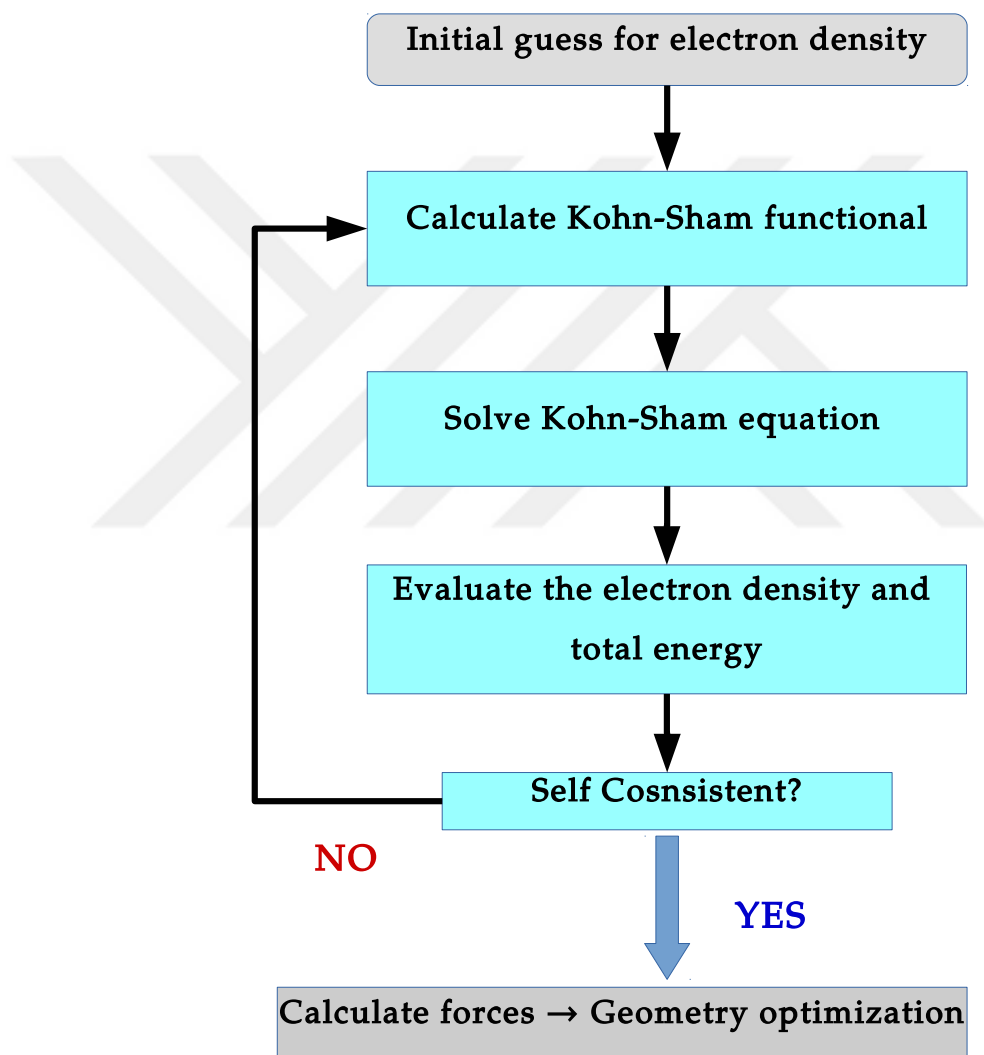


Figure 2.2: Flowchart illustrating the Kohn-Sham approach

In the case of finite size systems such as molecules, the plane wave basis is inefficient, and usually Gaussian orbitals are used. Describing the electronic structure of a single molecule with plane waves demands considering a large vacuum around the molecule to eliminate the interactions between periodic images. However, in

these circumstances, the number of plane waves dramatically increases. To summarize, we write the Schrödinger equation for a single KS orbital at a specific $\vec{k}$ (in Hartree units) :

$$\left(-\frac{1}{2} \nabla^2 + V_{ext}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{XC} \right) \phi_{i,\vec{k}}(\vec{r}) = E_{i,\vec{k}}^{KS} \phi_{i,\vec{k}} \quad (2.19)$$

The third term in equation 2.19 is called Hartree term (V_H).

2.7.4 Projector Augmented-Wave Method

There are situations, such as spatially strongly localized, where the number of plane waves needed for describing the actual wave function may be very large. More importantly, near the ion cores, the number of required plane waves exceeds the practical limit due to rapid oscillations of the wave function. The projected augmented wave (PAW) [128] approach is one of the most used methods for overcoming this problematic behaviour. The main idea of the PAW method is to map the all-electron (AE) wave function to a fictitious pseudo wavefunction (PS) via a linear transformation operator. In order for AE and PS to be different only in the region close to the ionic core, the transformation operator is defined as:

$$\mathcal{T} = 1 + \sum_{\vec{R}} \tilde{\mathcal{T}}_{\vec{R}} \quad (2.20)$$

where $\tilde{\mathcal{T}}_{\vec{R}}$ is an atom-centred contribution that is non-zero only within some spherical augmentation region $\Omega_{\vec{R}}$. Within $\Omega_{\vec{R}}$, each PS function can be expanded into partial waves:

$$|\tilde{\Psi}\rangle = \sum_i |\tilde{\phi}_i\rangle c_i \quad (2.21)$$

Therefore, within $\Omega_{\vec{R}}$ the corresponding AE wave function has the following form:

$$\begin{aligned} |\Psi\rangle &= \mathcal{T} |\tilde{\Psi}\rangle = \sum_i |\phi_i\rangle c_i \\ |\Psi\rangle &= |\tilde{\Psi}\rangle - \sum_i |\tilde{\phi}_i\rangle c_i + \sum_i |\phi_i\rangle c_i \end{aligned} \quad (2.22)$$

Since the transformation operator is linear, the expansion coefficients in equation 2.22 are the scalar product of the PS and the projector functions:

$$c_i = \langle \tilde{p}_i | \tilde{\Psi} \rangle, \langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{i,j} \quad (2.23)$$

Therefore, the transformation operator between the valence wave functions and fictitious PS can be written as:

$$\mathcal{T} = 1 + \sum_i \left(\langle \phi_i | - \langle \tilde{\phi}_i | \right) | \tilde{\phi}_i \rangle \quad (2.24)$$

and the AE wave function can be obtained from the PS wave function using the following transformation:

$$|\Psi\rangle = |\tilde{\Psi}\rangle + \sum_i (\langle \phi_i | - \langle \tilde{\phi}_i |) | \tilde{\phi}_i \rangle \langle \tilde{\Psi} | \quad (2.25)$$

In the above equation, the partial waves are radial functions multiplied by the spherical harmonics and PS wave functions can be expanded using plane waves. The PAW method is usually used with the frozen core approximation, where the core states are assumed to be independent of the environment, and there are precalculated based on pseudopotential defined for individual atoms. Using the Bloch theorem, the PS wave function can be written as:

$$|\tilde{\Psi}_{n,\vec{k}}\rangle = e^{i\vec{k}\cdot\vec{r}} |\tilde{u}_{n,\vec{k}}\rangle \quad (2.26)$$

where n shows the band index.

2.8 Linear Optical Properties

In the experiments, one usually measures the macroscopic quantities, defined as averages over the crystal's unit cell. Maxwell's equations describe the interactions of electromagnetic fields and matter. The key to investigating optical properties is the dielectric function of the considered structure. The macroscopic dielectric function, which is a 3×3 tensor, relates the electric field inside the material to an applied electric field:

$$\vec{D} = \vec{\epsilon} \vec{E} \quad (2.27)$$

In ab-initio calculation, the directly accessible quantity is the microscopic dielectric function. We need to start with the linear response theory to introduce the concept of the frequency-dependent microscopic dielectric function and relate it to the corresponding macroscopic quantity. For sufficiently weak perturbation, one may assume that the total change in potential $\delta V_{tot}(\vec{r}, t)$ in the material is linearly connected to the external potential by:

$$\delta V_{tot}(\vec{r}, t) = \int \epsilon^{-1}(\vec{r}, \vec{r}', t - t') \delta V_{ext}(\vec{r}', t') d\vec{r}' dt' \quad (2.28)$$

or similarly:

$$\delta V_{ext}(\vec{r}, t) = \int \epsilon(\vec{r}, \vec{r}', t - t') \delta V_{tot}(\vec{r}', t') d\vec{r}' dt' \quad (2.29)$$

In the above equation, the $(t - t')$ dependence of the dielectric function ϵ is a result of time translation symmetry. The similarity between the 2.29 and 2.27 is that the field $\vec{D}$ is related to external charges or potential and causes field $\vec{E}$ inside the material. For homogeneous systems that are invariant under infinitesimal spatial translations, the dielectric function takes the form $\epsilon(\vec{r} - \vec{r}', t - t')$. In the frequency space, for a periodic lattice with translation vector $\vec{R}$, the dielectric function holds the following condition:

$$\epsilon(\vec{r}, \vec{r}', \omega) = \epsilon(\vec{r} + \vec{R}, \vec{r}' + \vec{R}, \omega) \quad (2.30)$$

Moreover, in the momentum space, from the equation 2.30, we can obtain:

$$\epsilon(\vec{q}, \vec{q}', \omega) = \epsilon(\vec{r}, \vec{r}', \omega) e^{i(\vec{q} - \vec{q}') \cdot \vec{r}} \quad (2.31)$$

The equation above indicates that $\epsilon(\vec{q}, \vec{q}', \omega) = 0$ unless $\vec{q} - \vec{q}'$ is a reciprocal lattice vector $\vec{G}$. Therefore, it is convenient to restrict the vectors $\vec{q}$ and $\vec{q}'$ to first Brillouin zone of the crystal. Taking the time Fourier transforms of 2.29 and going to momentum and frequency space, we get:

$$\delta V_{ext}(\vec{q} + \vec{G}) = \sum_{\vec{G}'} \epsilon_{\vec{G}\vec{G}'}(\vec{q}, \omega) \delta V_{tot}(\vec{q} + \vec{G}') \quad (2.32)$$

where, the following notation is used:

$$\epsilon_{\vec{G}\vec{G}'}(\vec{q}, \omega) \equiv \epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}', \omega) \quad (2.33)$$

The off-diagonal elements of the dielectric matrix are the results of the crystal's inhomogeneous charge distribution and are called local field effects.

In the self-consistent field approach of DFT, it is necessary to connect the external perturbation to the electron density. The polarizability ($\chi(\vec{r}, \vec{r}', t - t')$) relates the induced charge density ($n_{ind}(\vec{r}, t)$) to the external perturbation:

$$\delta n_{ind}(\vec{r}, t) = \int \chi(\vec{r}, \vec{r}', t - t') \delta V_{ext}(\vec{r}', t') d\vec{r}' dt' \quad (2.34)$$

To simplify the notation, we can present equation 2.34 in the following form :

$$\delta n_{ind} = \chi \delta V_{ext} \quad (2.35)$$

Similarly, the independent-particle polarizability (χ^0) relates the total perturbing potential to the resulting change in the electron density:

$$\delta n_{ind} = \chi^0 \delta V_{tot} \quad (2.36)$$

In the formalism of the KS equation, the change in the total potential becomes:

$$\delta V_{tot} = \delta V_{ext} + \delta V_H + \delta V_{XC} = \delta V_{ext} + V_C \delta n_{ind} + K_{XC} \delta n_{ind} \quad (2.37)$$

where V_C is the bare Coulomb interaction and K_{XC} is the functional derivative of exchange-correlation potential :

$$K_{XC}(\vec{r}, \vec{r}') = \frac{\delta^2 V_{XC}(\vec{r}, \vec{r}')}{\delta n(\vec{r}) \delta n(\vec{r}')} \quad (2.38)$$

By combining equations 2.34, 2.35 and 2.37, it is possible to connect the polarizability to independent-particle polarizability:

$$\chi = (1 - \chi^0 V_C - \chi^0 K_{XC})^{-1} \chi^0 \quad (2.39)$$

It must be pointed out that in equation 2.39 matrix notation is used and matrix inversion is required. Using equation 2.39 and 2.30 the dielectric function can be written as :

$$\epsilon^{-1} = 1 + (V_c + K_{XC})\chi \quad (2.40)$$

In the so-called random phase approximation (RPA), the contribution of the exchange-correlation term is neglected, and the dielectric function becomes :

$$\epsilon^{-1} = 1 + V_C(1 - \chi_0 V_C)^{-1} \chi_0 \quad (2.41)$$

In RPA, the Fourier transform of the frequency-dependent symmetric dielectric matrix is given by [129, 130] :

$$\epsilon_{\vec{G}, \vec{G}'}(\vec{q}, \omega) = \delta_{\vec{G}, \vec{G}'} - \frac{4\pi e^2}{|\vec{G} + \vec{q}| |\vec{G}' + \vec{q}|} \chi_0 \quad (2.42)$$

In the above equation, the omega has the dimension of energy, and in the Adler-Wiser formalism [131, 132], the irreducible polarizability matrix in the independent particle picture is given by :

$$\chi_{\vec{G}, \vec{G}'}^0(\vec{q}, \omega) = \frac{1}{V} \sum_{n, n', \vec{k}} 2w_{\vec{k}}(f_{n'\vec{k}+\vec{q}} - f_{n\vec{k}}) \frac{|\langle \Psi_{n'\vec{k}+\vec{q}} | e^{i(\vec{q}+\vec{G})} | \Psi_{n\vec{k}} \rangle|^2}{\epsilon_{n'\vec{k}+\vec{q}} - \epsilon_{n\vec{k}} - \omega - i\eta} \quad (2.43)$$

where V is the unit of the primitive cell, $w_{\vec{k}}$ is the k-point weight, n is the band index, Ψ represents the Bloch wave, η is an infinitesimal positive number, and $f_{n\vec{k}}$ displays the Fermi weight, which is 1 for occupied and zero for unoccupied states.

The inverse of macroscopic dielectric function ($\epsilon_{infty}(\vec{q}, \omega)$) is equal to the inverse of the long wavelength limit ($\vec{q} \rightarrow 0$) of the full microscopic dielectric matrix [133]:

$$\frac{1}{\epsilon_{\infty}(\vec{q}, \omega)} = \lim_{q \rightarrow 0} \epsilon_{0,0}^{-1}(\vec{q}, \omega) \quad (2.44)$$

The above relation is due to off-diagonal terms in the dielectric matrix (local field effects). By neglecting local field effects the macroscopic dielectric function can be approximated as:

$$\epsilon_{\infty}(\vec{q}, \omega) = \sum_{\alpha, \beta} \hat{q}_{\alpha} \epsilon_{\alpha\beta} \hat{q}_{\beta} \approx \lim_{q \rightarrow 0} \epsilon_{0,0}(\vec{q}, \omega) \quad (2.45)$$

The imaginary part of the 3×3 tensor dielectric tensor $\epsilon_{\alpha\beta}$, is defined as [129]:

$$\epsilon_{\alpha,\beta}^{(2)}(\omega) = \frac{4\pi e^2}{V} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,\vec{k}} 2w_{\vec{k}} \delta(\varepsilon_{c,\vec{k}+\vec{q}} - \varepsilon_{v,\vec{k}} - \omega) \times \left\langle u_{c,\vec{k}+\hat{e}_{\alpha}q} \middle| u_{v,\vec{k}} \right\rangle \left\langle u_{c,\vec{k}} \middle| u_{v,\vec{k}+\hat{e}_{\beta}q} \right\rangle \quad (2.46)$$

where $\vec{k}$ is restricted to the irreducible Brillouin zone, $\hat{e}_{\alpha}$ is a unit vector in the Cartesian direction α and $|u\rangle$ shows the cell periodic part of the Bloch state. The indexes v and c stand for valence and conduction bands, respectively. The real part of the dielectric tensor $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ can be calculated using the Kramers-Kronig relation:

$$\epsilon_{\alpha\beta}^{(1)}(\omega) = 1 + \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\epsilon_{\alpha\beta}^{(2)}(\omega') \omega'}{\omega'^2 - \omega^2} d\omega' \quad (2.47)$$

where $\mathcal{P}$ means Cauchy principal value.

Other frequency-dependent optical properties can be determined using imaginary and real parts of the complex dielectric function. The refractive index that shows the ratio of the speed of light to the phase velocity of light inside the medium $n = \frac{c}{v_p} = \frac{2\pi f}{qc}$ is given by :

$$n(\omega) = \left(\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2} \right)^{\frac{1}{2}} \quad (2.48)$$

Since v_p can be greater than the speed of light, in general, the refractive index can be smaller than 1. Besides, the refractive index can be negative in the case

of metamaterials that possess negative permeability and permittivity (dielectric constant) [134]. Similar to the refractive index, to describe the absorption of light inside the material, the extinction coefficient is defined as:

$$\kappa(\omega) = \left(\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2} \right)^{\frac{1}{2}} \quad (2.49)$$

For most of the materials, κ is positive. However, for an active laser medium where the incident light becomes intensified, κ can be less than zero. The refractive index and extinction coefficient present the real and imaginary parts of the complex refraction index. The quantity that is usually measured in the experiments is the absorption coefficient:

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c} \left(\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1 \right)^{\frac{1}{2}} \quad (2.50)$$

The absorption coefficient relates the intensity of light inside the material to the intensity of incident light I_0 via the Beer-Lambert law. For light traveling in the x direction, the intensity as a function of depth x is given by :

$$I = I_0 e^{-\alpha(x)} \quad (2.51)$$

The energy-loss function is related to the inverse of the dielectric function:

$$L(\omega) = \text{Im}\left(\frac{-1}{\epsilon(\omega)}\right) \quad (2.52)$$

The reflectivity (reflectance) defines the ratio of the reflected power to incident power :

$$R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (2.53)$$

Similarly, transmittance $T(\omega)$ shows the amount of the transmitted light, and absorbance $A(\omega)$ gives the portion of the absorbed light, and the following relation holds:

$$A(\omega) + T(\omega) + R(\omega) = 1 \quad (2.54)$$

$T(\omega)$ and $A(\omega)$ can also be obtained using n and k [135]. For 2D materials, more straightforward equations for these quantities can be obtained by employing optical conductivity. According to Maxwell's equations, for bulk materials, the optical conductivity can be obtained using the dielectric function [136] :

$$\sigma_{3D}(\omega) = i\epsilon_0\omega(1 - \epsilon(\omega)) \quad (2.55)$$

where ϵ_0 is the permittivity of vacuum. In ab-initio studying 2D materials, a large vacuum thickness is considered for eliminating the interaction between the layer and its periodic image. Therefore, for removing the effect of vacuum thickness, the in-plane optical conductivity is defined as [137] :

$$\sigma_{2D}(\omega) = L\sigma_{3D}(\omega) \quad (2.56)$$

where L is the slab thickness (thickness of the layer + vacuum thickness). By defining $\tilde{\sigma} = \frac{\sigma_{2D}}{\epsilon_0 c}$ (unitless), it is possible to calculate $R(\omega)$, $A(\omega)$ and $T(\omega)$ [137]:

$$\begin{aligned} R &= \left| \frac{\frac{\tilde{\sigma}}{2}}{1 + \frac{\tilde{\sigma}}{2}} \right|^2, \\ A &= \frac{Re(\tilde{\sigma})}{\left| 1 + \frac{\tilde{\sigma}}{2} \right|^2}, \\ T &= \frac{1}{\left| 1 + \frac{\tilde{\sigma}}{2} \right|^2} \end{aligned} \quad (2.57)$$

Furthermore, for 2D materials, the amount of reflected light from the layer is very small and absorbance can be approximated by [138]:

$$A(2\pi f) = \frac{2\pi f}{c} L \epsilon_2(2\pi f) \quad (2.58)$$

where f is the frequency of the incident light, and L is the length of the simulation box perpendicular to layer's plane (thickness of the layer plus vacuum distance).

2.9 GW Approximation

2.9.1 Excited States and Self-Energy

Demonstrated the approach for obtaining ground state properties now we can turn our attention to excited states. The many-body perturbation theory (MBPT), a branch of quantum field theory, deals with excitations that give rise to quasi-particles. The most well-known of these excitations are the collective vibration of atoms due to finite temperature, and their quasi-particles are known as phonons. In a many-electron system, electrons are correlated with strong Coulomb interaction. Due to exchange and correlation effects, a positive charge cloud forms around an electron. The combination of electron and positively charged cloud behave like a single particle which is called quasi-particle. The interaction between these quasi-particles is screened Coulomb interaction and thus is weaker than the interaction between electrons. Figure 2.3 shows a schematic representation of quasi-particle formation. The main concern of this thesis is the optical properties, where usually there is a significant difference between the experimental results and DFT prediction [139]. In this case, an electron becomes excited to a conduction band and thus leave a Coulomb hole in the valence band. The interactions between electrons and holes create another type of quasi-particles. Different types of quasi-particles are possible depending on the number of electrons and holes that form a quasi-particle. The most important one is the quasi-particle formed by a single electron-hole pair, called an exciton. Before considering these excitonic effects, it is necessary to investigate quasi-particle energies before excitation due to interacting with photons. Exciton formation after photon absorption is illustrated in Figure 2.5. Interestingly the main approach for investigating quasi-particle effects was developed almost simultaneously with the KS equation. In 1965 Hedin [140] formulated a method based on Green's function for investigating self energies.

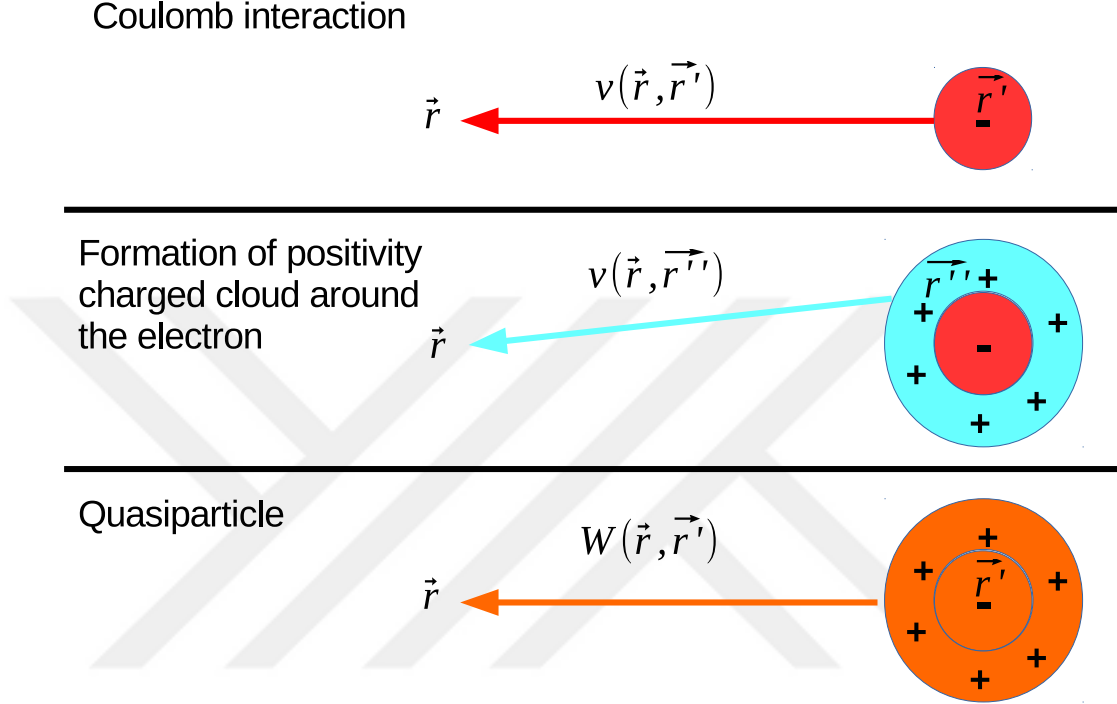


Figure 2.3: Formation of a quasi-particle is schematically represented. Here $v(\vec{r}, \vec{r}')$ is the bare Coulomb potential due to single electron and $W(\vec{r}, \vec{r}')$ is the screened Coulomb potential. Upon an electron removal a positively charged cloud is formed around the electron. The combination of an electron and positively charged clouds forms a quasi-particle

2.9.2 Many-Body Green's Function

As it is described before, DFT only gives an accurate description of ground states, and MBPT explains excited states. One of the concepts that are required to describe the many-electron problem is Green's function. Although this term is similarly used in mathematics as the kernel of convolution for finding the inverse of a differential operator, it has a more general meaning in MBPT. In MBPT, single-particle Green's function is propagator that defines the probability of finding a particle at position $\vec{r}$ and time t considering a particle at $\vec{r}'$ and t' . Let Ψ_N be the ground state wave function of non-relativistic N electron system; the single-particle Green's function is given by [141]:

$$G(\vec{r}, t; \vec{r}', t') = -\frac{i}{\hbar} \langle \Psi_N | \hat{T} [\hat{\psi}(\vec{r}, t) \hat{\psi}^*(\vec{r}', t')] | \Psi_N \rangle \quad (2.59)$$

Where $\hat{T}$ is the time ordering operator (latest on the left side), $\hat{\psi}$ and $\hat{\psi}^*$ are particle annihilation and creation operators in second quantization.

If we use Heisenberg picture for time evaluation of operators we can rewrite the Green's function as [139, 142]:

$$\begin{aligned} G(\vec{r}, t; \vec{r}', t') &= -\frac{i}{\hbar} \langle \Psi_N | \psi(\vec{r}) e^{-i\hat{H}(\frac{t-t'}{\hbar})} | \Psi_N^* \rangle \Theta(t-t') + \\ &\frac{i}{\hbar} \langle \Psi_N | \psi(\vec{r}) e^{-i\hat{H}(\frac{t-t'}{\hbar})} | \Psi_N^* \rangle \Theta(t-t') = \\ &G^e(\vec{r}, t; \vec{r}', t') - G^h(\vec{r}, t; \vec{r}', t') \end{aligned} \quad (2.60)$$

where, $\Theta(t-t')$ is the step function. For $t > t'$ equation 2.60 describes the propagation of an additional electron, and for $t < t'$, it describes the propagation of a hole. We can write electron density in terms of Green's function:

$$n(\vec{r}, t) = \langle \Psi_N^* | \hat{\psi}(\vec{r}, t) \hat{\psi}(\vec{r}, t) | \Psi_N \rangle = -i\hbar G(\vec{r}, t; \vec{r}, t + \eta) \quad (2.61)$$

where η is an infinitesimal small positive number and introduced to keep the correct ordering of the field operators. This term will appear in some of the equations described afterwards.

2.9.3 Spectral Function

In order to relate Green's function to experimental measurements, we should introduce spectral or so-called Lehmann representation of the Green's function. For a stationary system with $\tau = t - t'$ and considering a complete set of the basis of $N+1$ or $N-1$ derive the following expression for G :

$$\begin{aligned} G(\vec{r}, \vec{r}'; \tau) &= \frac{-i}{\hbar} \sum_i \psi_i^{N+1}(\vec{r}) \psi_i^{*N+1}(\vec{r}') e^{-i\varepsilon_i^{N+1} \frac{\tau}{\hbar}} \Theta(\tau) \\ &+ \frac{i}{\hbar} \sum_i \psi_i^{N-1}(\vec{r}) \psi_i^{*N-1}(\vec{r}') e^{-i\varepsilon_i^{N-1} \frac{\tau}{\hbar}} \Theta(-\tau) \end{aligned} \quad (2.62)$$

In equation 2.62, ε_i^{N+1} and ε_i^{N-1} are the energy required to add and remove one electron from the system, respectively. Fourier transform of equation 2.62 gives the Lehmann representation of Green's function:

$$G(\vec{r}, \vec{r}'; \omega) = \sum_i \frac{\psi_i^{N+1}(\vec{r}) \psi_i^{*N+1}(\vec{r}')}{\hbar\omega - \varepsilon_i^{N+1} + i\eta} + \sum_i \frac{\psi_i^{N-1}(\vec{r}) \psi_i^{*N-1}(\vec{r}')}{\hbar\omega - \varepsilon_i^{N-1} - i\eta} \quad (2.63)$$

The photocurrent, which is measured in the photoemission spectroscopy experiment, is the probability of emitting an electron with kinetic energy ω . It is related to spectral function, which is given by [143]:

$$A(\vec{r}, \vec{r}'; \omega) = \sum_i \psi_i(\vec{r}) \psi_i^*(\vec{r}') \delta(\hbar\omega - \varepsilon_i) \quad (2.64)$$

Using the spectral function, we can rewrite equation 2.63 as:

$$G(\vec{r}, \vec{r}'; \omega) = \int_{-\infty}^{\infty} \frac{A(\vec{r}, \vec{r}'; \omega')}{\hbar\omega - \hbar\omega' + \text{sgn}(\hbar\omega - \mu) i\eta} d\omega' \quad (2.65)$$

Where, $\min(\varepsilon_i^{N-1}) \leq \mu \leq \max(\varepsilon_i^{N+1})$. When N goes to infinity, μ is the chemical potential.

Now we can reformulate the spectral function:

$$A(\vec{r}, \vec{r}'; \omega) = -\text{sgn}(\hbar\omega - \mu) \frac{1}{\pi} \text{Im} (G(\vec{r}, \vec{r}'; \omega)). \quad (2.66)$$

In an infinite system of particles, the sharp peaks that arise from the delta function in the spectral function create Lorentzian peaks. The inverse of the width of these peaks give the quasi-particle lifetimes.

2.9.4 Hedin's Equations

In 1965 Hedin [140] derived integro-differential equations that describe the many-electron problem exactly. These are five sets of equations that relate effective potential Coulomb potential (W), polarizability (P), Green's function (G), self-energy (Σ) and vertex function (Γ). These equations can not be solved numerically. Instead, by analytic iteration, it is possible to obtain approximate equations

which can be solved self-consistently. Before writing Hedin's equations, it is necessary to introduce a notation used for simplification in writing the equations. For any integer j , We define:

$$\begin{aligned} j &\rightarrow (\vec{r}_j, t_j) \\ j^+ &\rightarrow (\vec{r}_j, t_j + \eta) \\ dj &\rightarrow d\vec{r}_j dt_j \end{aligned} \tag{2.67}$$

By using the notations in equation 2.67, Hedin's equations can be written as:

$$\begin{aligned} \Gamma(123) &= \delta(12) \delta(13) - \int \frac{\delta \Sigma(12)}{\delta G(45)} G(56) \Gamma(673) G(74) d4d5d6d7 \\ P(12) &= -i \int G(13) \Gamma(342) G(41) d3d4 \\ W(12) &= v(12) + \int v(13) P(34) W(42) d3d4 \\ \Sigma(12) &= i \int G(13) W(1^+4) \Gamma(324) d3d4 \end{aligned} \tag{2.68}$$

$$G(12) = G_0(12) + \int G_0(13) \Sigma(34) G(42) d3d4$$

The last equation is the Dyson equation for Green's function and G_0 the Green's function of the noninteracting system. The function v in equation 2.68 shows the Coulomb interaction. As a first approximation, we can assume that Γ is diagonal:

$$\Gamma(123) = \delta(12) \delta(13) \tag{2.69}$$

this neglects vertex correction. In other words, the change in the potential due to excitation is neglected. Under this assumption, the self-energy becomes:

$$\Sigma = iG(12) W(1^+2) \tag{2.70}$$

Equation 2.70 shows the reason for calling this approach *GW* approximation. Within this approximation, the polarizability and vertex function are given by:

$$\begin{aligned} P(12) &= -iG(12) G(21) \\ \Gamma(123) &= \delta(12) \delta(13) \end{aligned} \tag{2.71}$$

2.9.5 Practical Application of GW method

Using self-energy as the perturbation to the noninteracting system, we can write the Schrödinger equation for a quasi-particle, which is called Dyson equation [144–146].

$$\left(-\frac{1}{2}\nabla^2 + V_{ext} + V_H\right) \phi_{i,\vec{k}}^{QP}(\vec{r}) + \int \Sigma(\vec{r}, \vec{r}', E_{i,\vec{k}}^{QP}) \phi_{i,\vec{k}}^{QP}(\vec{r}') d\vec{r}' = E_{i,\vec{k}}^{QP} \phi_{i,\vec{k}}^{QP}(\vec{r}) \quad (2.72)$$

In equation 2.72, $E_{i,\vec{k}}^{QP}$ is the quasi-particle energy. The self-energy operator in the Dyson equation is a nonlocal term and depends on the quasi-particle energies. Therefore, equation 2.72 is a generalized eigenvalue problem, and it has a higher-order complexity than the KS equation. Furthermore, the orbitals of the Dyson equation can not be calculated exactly. The reason is that the self-energy itself is a solution of Hedin's integro-differential equations [140], and as it was described before, each iteration level gives an approximation for self-energy. In order to simplify equation 2.72, Duffy and Chong [146] proposed using the KS orbitals instead of the exact quasi-particles orbitals. Conceptually, this approach is similar to the assumption used in the time-independent perturbation of quantum mechanics, where the basis of unperturbed Hamiltonian is used to expand the eigenstate of the perturbed system. Using KS orbitals, we can rewrite equation 2.72 as:

$$\left(-\frac{1}{2}\nabla^2 + V_{ext} + V_H\right) \phi_{i,\vec{k}}(\vec{r}) + \int \Sigma(\vec{r}, \vec{r}', E_{i,\vec{k}}^{QP}) \phi_{i,\vec{k}}(\vec{r}') d\vec{r}' = E_{i,\vec{k}}^{QP} \phi_{i,\vec{k}}(\vec{r}) \quad (2.73)$$

Comparing equation 2.73 with the KS equation, we see that the exchange-correlation potential is omitted in GW, and a new term that describes the self-energy of quasi-particles and nonlocal effects is considered. Equation 2.73 follows a different path from the KS equation. The main aim of the KS equation was to determine electron density and energy eigenvalues. Moreover, the KS orbitals are also determined by solving the KS equation. Equation 2.73 utilizes KS orbitals to determine the self-energy of the quasi-particles.

Now we can turn our attention to Σ . The GW approximation uses equation 2.70,

and each level of iteration gives a higher-order correction. At the first level :

$$\Sigma_0 = -iG_0W_0 \quad (2.74)$$

where G_0 is the Green's function of the noninteracting, KS system and W_0 is the first approximation for screened or effective Coulomb interaction. The spectral representation of G_0 is given by:

$$G_0(\vec{r}, \vec{r}', \omega) = \sum_{n, \vec{k}}^{\text{all}} \frac{\phi_{i, \vec{k}}(\vec{r}) \phi_{i, \vec{k}}^*(\vec{r}')}{\omega - \varepsilon_{n, \vec{k}} + \text{sgn}(\varepsilon_{n, \vec{k}} - \mu) i\eta} \quad (2.75)$$

The upper index in the summation in Equation 2.75 is highlighted because it plays a vital role in the practical application. The number of KS orbitals is infinite. However, in practice, only a limited number of them are obtained. The accuracy of the GW calculation depends on this highlighted upper limit. Using equations 2.61, 2.70 and Hedin's equations 2.68, it is useful to write different levels of approximations obtained from self-energy:

$$\begin{aligned} \Sigma(1, 1) &= n(\vec{r}) \\ \Sigma_{HF} &= iG_0v \\ \Sigma_{G_0W} &= iG_0W \end{aligned} \quad (2.76)$$

The above relations show that all the self-energy expansion includes the HF potential. Therefore, GW approximation is the Hartree-Fock approach where the screened Coulomb interaction is used instead of pure Coulomb interaction.

In the approach of Duffy and Chong [146], the quasi-particle energies are obtained by adding a correction to KS energies. In the approach of Duffy and Chong, the quasi-particle energies are obtained by adding a correction to KS energies. To illustrate this approach clearly, we can write:

$$\begin{aligned} & \left(-\frac{1}{2} \nabla^2 + V_{ext} + V_H + V_{XC} \right) \phi_{i, \vec{k}}(\vec{r}) + \\ & \underbrace{\int \left(\Sigma(\vec{r}, \vec{r}', E_{n, \vec{k}}^{QP}) - V_{XC} \right) \phi_{i, \vec{k}}(\vec{r}') d\vec{r}'}_{\Delta\Sigma} = E_{i, \vec{k}}^{QP} \phi_{i, \vec{k}}(\vec{r}) \end{aligned} \quad (2.77)$$

We can see that the KS equation appears in the first part of equation 2.77. By taking the expectation value and using bra-ket short notation we obtain:

$$E_{i,\vec{k}}^{QP} = E_{i,\vec{k}}^{KS} + \text{Re} \left\langle \phi_{i\vec{k}}^{KS} \left| \Delta \Sigma \right| \phi_{i\vec{k}}^{KS} \right\rangle \quad (2.78)$$

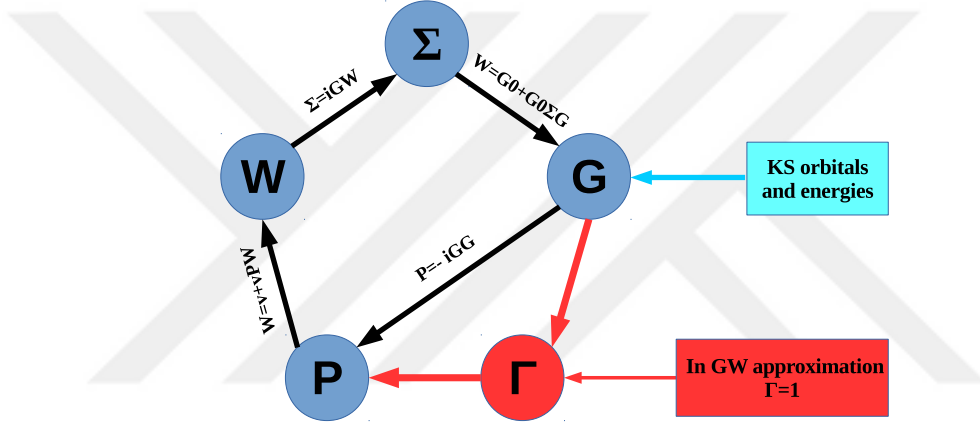


Figure 2.4: Hedin's pentagon and the workflow of GW approximation starting from KS energies and orbitals is shown. Here the variables on the left side of the equations are the variables for the next step of the iteration.

We are using the KS wave functions, and on this basis, $\Delta \Sigma$ is not diagonal. Furthermore, the diagonal elements might have small imaginary parts due to the difference between the KS and QP orbitals. For this reason, the real part of the expectation value of $\Delta \Sigma$ is considered in equation 2.78. A schematic diagram that illustrates GW approximation utilizing Hedin's equations is presented in Figure 2.4. By using Taylor expansion, it is possible to solve equation 2.78 iteratively:

$$E_{i,\vec{k}}^{N+1} = E_{i,\vec{k}}^N + Z_{i,\vec{k}}^N \text{Re} \left(\left\langle \phi_{i\vec{k}}^{KS} \left| -\frac{1}{2} \nabla^2 + V_{ext} + V_H + \Delta \Sigma \right| \phi_{i\vec{k}}^{KS} \right\rangle \right) \quad (2.79)$$

where

$$Z_{i,\vec{k}}^N = \left(1 - \left\langle \phi_{i\vec{k}}^{KS} \left| \frac{\partial(\Sigma(E_{i,\vec{k}}^N))}{\partial(\omega)} \right| \phi_{i\vec{k}}^{KS} \right\rangle \right)^{-1} \quad (2.80)$$

with $N = 0$, $E_{i,\vec{k}}^0$ is the KS energy and $E_{i,\vec{k}}^1$ is the quasi-particle energy in G_0W_0 approximation. For the successive iterations, equation 2.79 uses quasi-particle energies obtained at each step to calculate the Green's function for the next step:

$$G_N(\vec{r}, \vec{r}', \omega) = \sum_{n,\vec{k}}^{all} \frac{\phi_{i,\vec{k}}(\vec{r})\phi_{i,\vec{k}}^*(\vec{r}')}{\omega - E_{n,\vec{k}}^N + \text{sgn}(E_{n,\vec{k}}^N - \mu)i\eta} \quad (2.81)$$

Iterations higher than $N=0$ are called GW_0 approximation [147, 148].

2.9.6 Bethe-Salpether Equation

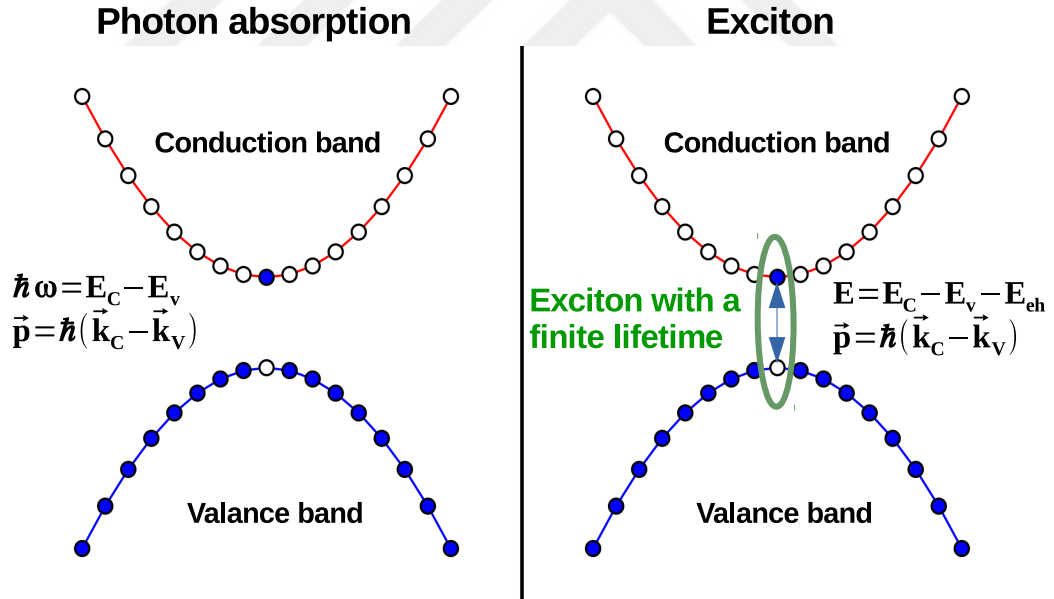


Figure 2.5: An electron becomes excited from a valence band to a conduction band in photoabsorption and leaves a hole in the valence band. In such a process, energy and momentum are conserved. The Coulomb attraction between the electron and hole establishes a bound state and creates a quasi-particle called an exciton. The exciton lowers the total energy of the excited system.

The excitation of an electron can be described by the GW approximation

that yields QP energies. However, as it is illustrated in Figure 2.5, optical absorption is not a single particle process. An excited electron leaves a hole that can interact with the electron, the bound state of the electron-hole is called an exciton. The exciton formation lowers the QP band gap obtained by the GW approximation. In order to describe the electron-hole pair, it is necessary to start with the two-particle Green's function $G(12;1'2')$. According to the notation introduced in equation 2.67, the two-particle Green's function depends on four time variables. The time ordering determines electron-electron, electron-hole and hole-hole pairs. Here, we are interested in electron-hole pairs, where there are two different possible time orderings. The first case is $t_1, t_1' > t_2, t_2'$ which describes hole-particle, and the second case is $t_1, t_1' < t_2, t_2'$, which describes particle-hole amplitudes [143]. To describe the motion of the two-particle Green's function, we need to introduce the electron-hole correlation function [149]:

$$L(12;1'2') = -G(1,2,1'2') + G(1,1')G(2,2') \quad (2.82)$$

The Bethe-Salpeter equation (BSE) [141, 150] is a Dyson equation for the two-particle correlation function that describes the electron-hole excitation:

$$L(12;1'2') = G(12')G(21') + \int G(13)G(3'1')K(34';3'4)L(42;4'2')d(33'4'4) \quad (2.83)$$

Considering both types of time ordering described above, the BSE can be written as a set of generalized eigenvalue equations [151–153]:

$$\begin{aligned} (E_{c,\vec{k}+\vec{Q}} - E_{v,\vec{k}})A_{v,c,\vec{k}}^{(S,\vec{Q})} + \sum_{v',c',\vec{k}'} K_{v,c,\vec{k},v',c',\vec{k}'}^{AA}(\vec{Q})A_{v',c',\vec{k}'}^{(S,\vec{Q})} \\ + \sum_{v',c',\vec{k}'} K_{v,c,\vec{k},v',c',\vec{k}'}^{AB}(\vec{Q})A_{v',c',\vec{k}'}^{(S,\vec{Q})} = \Omega^{S,\vec{Q}}A_{v,c,\vec{k}}^{(S,\vec{Q})} \\ (E_{c,\vec{k}+\vec{Q}} - E_{v,\vec{k}})B_{v,c,\vec{k}}^{(S,\vec{Q})} + \sum_{v',c',\vec{k}'} K_{v,c,\vec{k},v',c',\vec{k}'}^{BB}(\vec{Q})A_{v',c',\vec{k}'}^{(S,\vec{Q})} \\ + \sum_{v',c',\vec{k}'} K_{v,c,\vec{k},v',c',\vec{k}'}^{BA}(\vec{Q})A_{v',c',\vec{k}'}^{(S,\vec{Q})} = -\Omega^{S,\vec{Q}}B_{v,c,\vec{k}}^{(S,\vec{Q})} \end{aligned} \quad (2.84)$$

where the eigenvalue $\Omega^{S,\vec{Q}}$ is the exciton energy, $\vec{Q}$ denotes the momentum

transform required in an indirect transition, E shows the QP energies obtained in the GW step, subindices v and c refer to valence and conduction bands, K^{AA} and K^{BB} are the electron-hole interaction kernels, and K^{AB} and K^{BA} ($K^{BA} = -(K^{AB})^*$) describe the coupling between resonant ($v \rightarrow c$) and antiresonant ($c \rightarrow v$) transitions.

Neglecting resonant and antiresonant coupling and considering only time ordering $t_1, t_1' > t_2, t_2'$, which is equivalent to valence to conduction transition with $E_v < E_c$ the equation 2.84 simplifies to a single eigenvalue equation:

$$(E_{c,\vec{k}+\vec{Q}} - E_{v,\vec{k}})A_{v,c,\vec{k}}^{(S,\vec{Q})} + \sum_{v',c',\vec{k}'} K_{v,c,\vec{k},v',c',\vec{k}'}^{AA}(\vec{Q})A_{v',c',\vec{k}'} = \Omega^{S,\vec{Q}}A_{v,c,\vec{k}}^{(S,\vec{Q})} \quad (2.85)$$

Equation 2.85 is known as the Tamm-Dancoff approximation (TDA), which is the widely used method in investigating the optical properties of solid. It is shown that TDA gives absorption results in agreement with experimental measurements for solids such as Si, C and LiF. However, TDA is valid when the electron-hole interaction is small compared with the QP gap, and it might break down for confined systems such as organic molecules and nanotubes. In TDA the excitonic state can be written as a linear combination of electron and hole states:

$$|S\rangle = \sum_{v,c,\vec{k}} A_{v,c,\vec{k},\vec{Q}}^S |v, \vec{k}\rangle \otimes |c, \vec{k} + \vec{Q}\rangle \quad (2.86)$$

The TDA is usually considered with the assumption ($\vec{Q} = 0$), and only direct transitions are evaluated, which is consistent with the small momentum carried by a photon ($p = \frac{E}{c}$). With all mentioned simplification, the explicit form of the electron-hole interaction kernel in equation 2.85 is given by:

$$K^{AA} = \langle c, v' | v_c | v, c' \rangle + \left(\frac{i}{-2\pi} \right) \int_{-\infty}^{\infty} e^{-i\eta\omega} \langle c, v' | W | v, c' \rangle \\ \times \left[\frac{1}{\Omega_S - \omega - (E_c^{QP} - E_v^{QP}) + i\eta} + \frac{1}{\Omega_S - \omega - (E_c^{QP} - E_v^{QP}) + i\eta} \right] \quad (2.87)$$

where η is a positive real infinitesimal. The solution of TDA provides the eigenvalues (Ω^S) and coupling coefficients ($A_{v,c,\vec{k}}^S$) that can be used for calculating the

imaginary part of the frequency-dependent dielectric function [153]:

$$\epsilon_2(\omega) = \frac{16\pi e^2}{\omega^2} \sum_S \left| \sum_{v,c,\vec{k}} A_{c,v,\vec{k}}^S \hat{\lambda} \cdot \langle v, \vec{k} | \hat{V} | c, \vec{k} \rangle \right|^2 \delta(\omega - \Omega_S) \quad (2.88)$$

where $\hat{\lambda}$ is the polarization vector of the light, and $\hat{V}$ is the single-particle velocity operator. By using the imaginary part of the dielectric function, it is possible to calculate other optical properties utilizing the relations described in section 2.8.

Chapter 3

Optical Properties of Selected 2D Group II-VI Materials

3.1 Electronic Properties of II-VI Monolayers from DFT

3.1.1 Computational Details of the DFT Calculation

In order to determine ground state properties of considered materials, we have performed ab-initio calculations in the framework of pseudopotential plane wave method based on (DFT) [120, 121, 154–157]. The PAW type pseudopotentials (PAW) [158, 159] are used to account for the electron-ion interaction. The exchange and correlation effects are taken into account by using Perdew-Burke-Ernzerhof (PBE) functional based on generalized gradient approximation (GGA) [160]. All computational parameters are selected after performing careful convergence tests. Accordingly, a plane-wave basis set with an energy cutoff of 520 eV is used in the total energy and geometry optimization calculations. Layers are placed in x-y plane and, Γ centered $25 \times 25 \times 1$ Monkhorst-Pack k-point mesh is used for Brillouin zone (BZ) sampling and the tetrahedron method with

Blöchl corrections [161] is employed for BZ integration. In order to eliminate the interaction between the layers and their periodic images, a vacuum of 15 Å is introduced between the slabs. Atomic coordinates are fully relaxed by setting a convergence criterion of 0.01 eV/Å for the minimization of Hellmann–Feynman forces on each atom.

The computational resources for this work were provided by the High Performance and Grid Computing Center (TRGrid e-Infrastructure) of TUBITAK ULAKBIM, Turkish Academic Network and Information Center. The total available number of nodes was 8, with each node being connected to 24 cores, resulting total of 192 cores, and each core held 4800 MB of memory. The maximum time limit for a single job was restricted to 15 days.

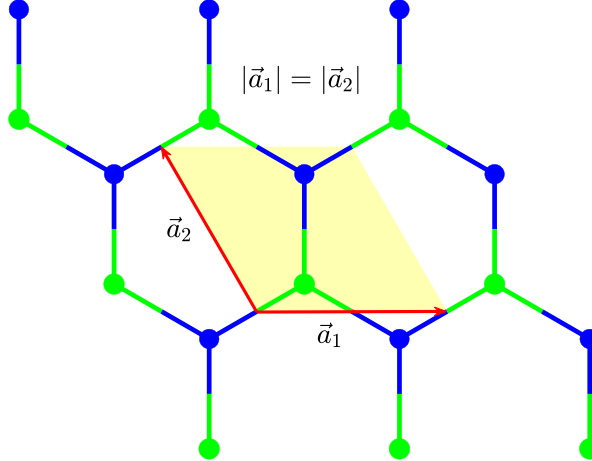


Figure 3.1: General lattice structure of II-VI monolayers. Layers are placed in x-y plane.

3.1.2 Results of the DFT Step

The calculated lattice constants and band gaps from different methods are summarized in Table 3.3 and the electronic band structures and density of states

DOS obtained using GGA are presented in Figure 3.2. Our DFT results for band gaps and lattice constants are in good agreement with previously reported results [19]. All of the structures investigated here possess indirect bandgaps except the CdO and ZnO, which have direct bandgaps at Γ point. Among these materials, SrS, SrSe, BaTe and CaS possess a flat top valence band that creates sharp peaks in their DOS. These sharp peaks and existing d orbitals in ZnO and CdO make the commonly used band-partial DOS representation limited. Therefore, to get more detailed insight into electronic properties, we utilized another representation and decomposed bands into the contribution of each element and corresponding orbitals. The results are presented in Figures 3.3, 3.4 and 3.5. From these figures, we can deduce several features of band structures. The p orbitals of oxygen and chalcogen atoms form the top valence bands of mono-oxides and mono-chalcogenide, respectively. The first conduction bands are mainly formed by the s orbitals of the metal atoms. The s orbitals of the chalcogen and oxygen atoms have similar contributions near the Γ point. From Figures 3.4 and 3.3, we can see that flat valence bands of SrS, SrSe, BaTe, and CaS are formed by the p_z orbital of chalcogen atoms in the entire BZ, and p_x and p_y orbitals contribute similarly near the M-K path (edge of BZ). As it is clear from Figure 3.3, although the top valence band of indirect bandgap monolayers BaO and MgO are assembled by the p_z orbital, at Γ point where the direct band gap is located, the p_x and p_y orbital are formed the valence band. The opposite of this happened in the case of CaO, where only p_z orbital is included in valence band at Γ point. Figure 3.5 shows that near the Γ point, the orbital configuration of the band structures of direct bandgap monolayers, CdO and ZnO, are similar to BeO and MgO and consist p_x and p_y orbitals.

The contribution of each orbital in band structure determines the possible optical transition. Figure 3.6 shows the xx and zz components of the imaginary part of the frequency-dependent dielectric tensor. $\text{Im}(\epsilon_{xx})$ and $\text{Im}(\epsilon_{zz})$ are related to perpendicular and parallel incident light, respectively. As discussed above, near the Γ point where the direct band gap is located, the valence band of SrS, SrSe, BaTe, CaS and CaO are formed by the p_z orbital, and consequently, $\text{Im}(\epsilon_{zz})$ precedes the $\text{Im}(\epsilon_{xx})$. For ZnO, CdO, MgO and BeO $\text{Im}(\epsilon_{zz})$ start before the

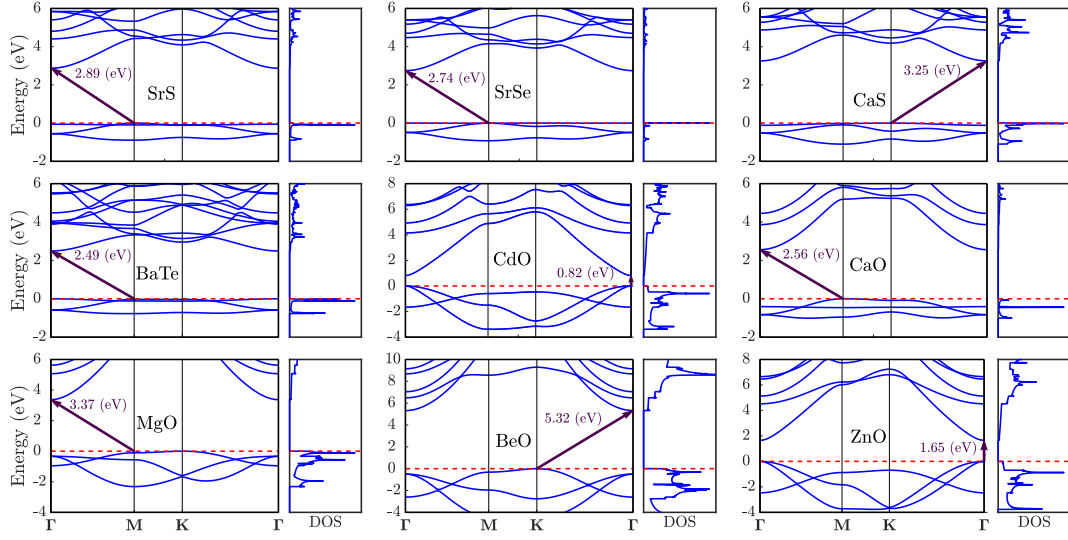


Figure 3.2: Band structures of II-VI monolayers obtained using DFT-GGA.

$\text{Im}(\epsilon_{zz})$. As it is pointed out, DFT fails to describe excited states accurately. The rest of this chapter investigates the electronic and optical properties using methods beyond standard DFT.

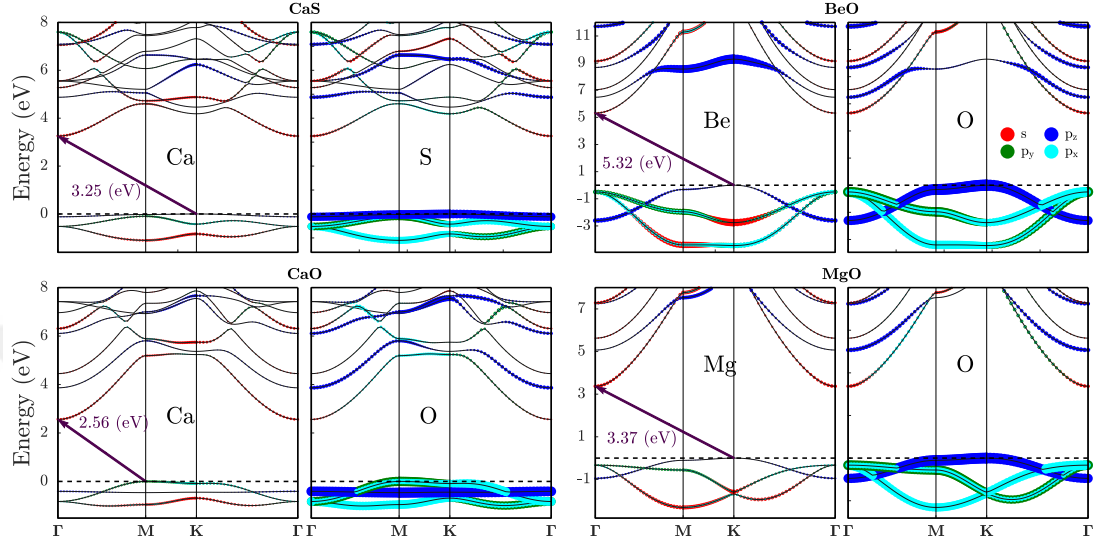


Figure 3.3: Orbital projected band structures of each element of CaS, BeO, CaO and MgO. The radii of filled circles are scaled according to the contribution of each orbital, and black dashed lines are plotted as a guide for the eye.

3.2 Electronic Properties of II-VI Monolayers from GW+BSE

3.2.1 Computation Details and Remarks on the GW Calculation

In this section, a detailed description of the GW calculation is presented. We calculated quasiparticle (QP) energies utilizing a single shot GW approximation (G_0W_0) and investigated excitonic effects within TDA. Several factors can affect the obtained QP energies from G_0W_0 and exciton effects in BSE. Therefore, it is necessary to select reasonable parameters after performing convergence tests and according to available computational resources. The main parameters are the number of unoccupied bands considered in calculating QP energies, the number of considered k points, the energy cutoff for the response function in G_0W_0 and the number of frequency grid points which must be selected according to the number

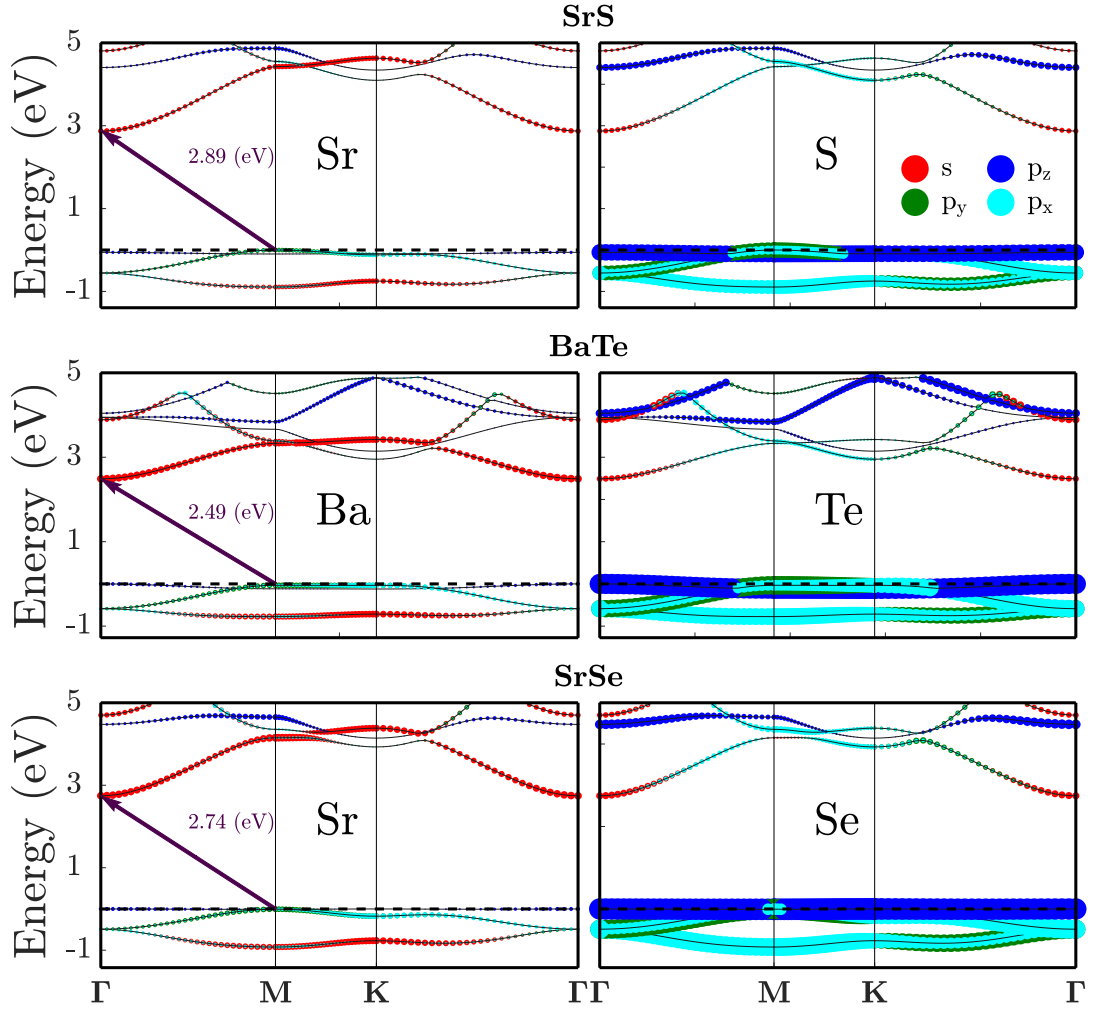


Figure 3.4: Orbital projected band structures of each element of SrS, SrSe and BaTe. The radii of filled circles are scaled according to the contribution of each orbital, and black dashed lines are plotted as a guide for the eye.

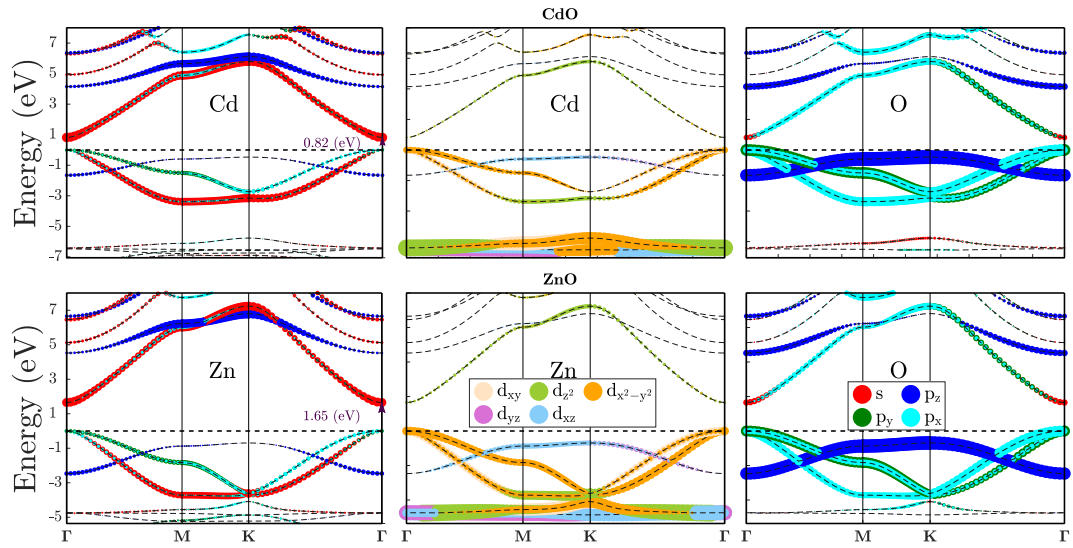


Figure 3.5: Orbital projected band structures of each element of CdO and ZnO. The radii of filled circles are scaled according to the contribution of each orbital, and black dashed lines are plotted as a guide for the eye. Due to the presence of d orbitals in Cd and Zn, to clearly present the contribution of the d orbitals, an extra panel is considered for d orbitals.

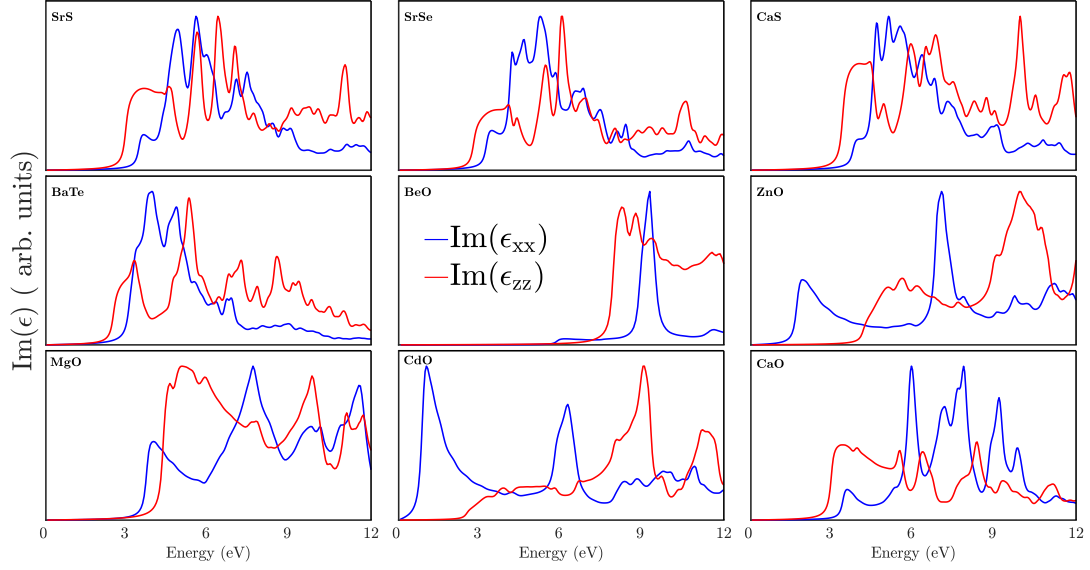


Figure 3.6: Imaginary part of the frequency depended dielectric function of II-VI monolayers calculated by DFT-GGA. Here, $\text{Im}(\epsilon_{zz})$ and $\text{Im}(\epsilon_{xx})$ are related to incident light parallel and perpendicular to layers, respectively.

of k to avoid noise in the self-energies and density of states. Furthermore, in the case of the 2D structures, the amount of the vacuum distance considered above the slab is critical because of the long-range nature of Coulomb interaction. Previous studies of QP energies of monolayer MoS_2 have shown that Coulomb truncation is critical for obtaining convergence of the GW band energy corrections [162, 163]. However, truncating Coulomb interaction is not implemented in our work, and interaction between periodic images must be controlled by increasing the vacuum above the 2D layer. When the vacuum level increases, the number of plane waves and consequently the computational time increase. A general trend that is observed in previous reports is increasing the QP band gap by increasing the vacuum distance and decreasing the QP band gap by increasing the number of k-points [162–166]. An example of the effect of changing number of k-points and vacuum distance on the QP energies of MoS_2 is presented in Figure 3.7. Furthermore, it is shown that converged BSE results can only be achieved using a very dense k-point mesh [163], i.e. up to $300 \times 300 \times 1$. Nevertheless, the excessive memory requirement precludes using very dense k-point mesh and a

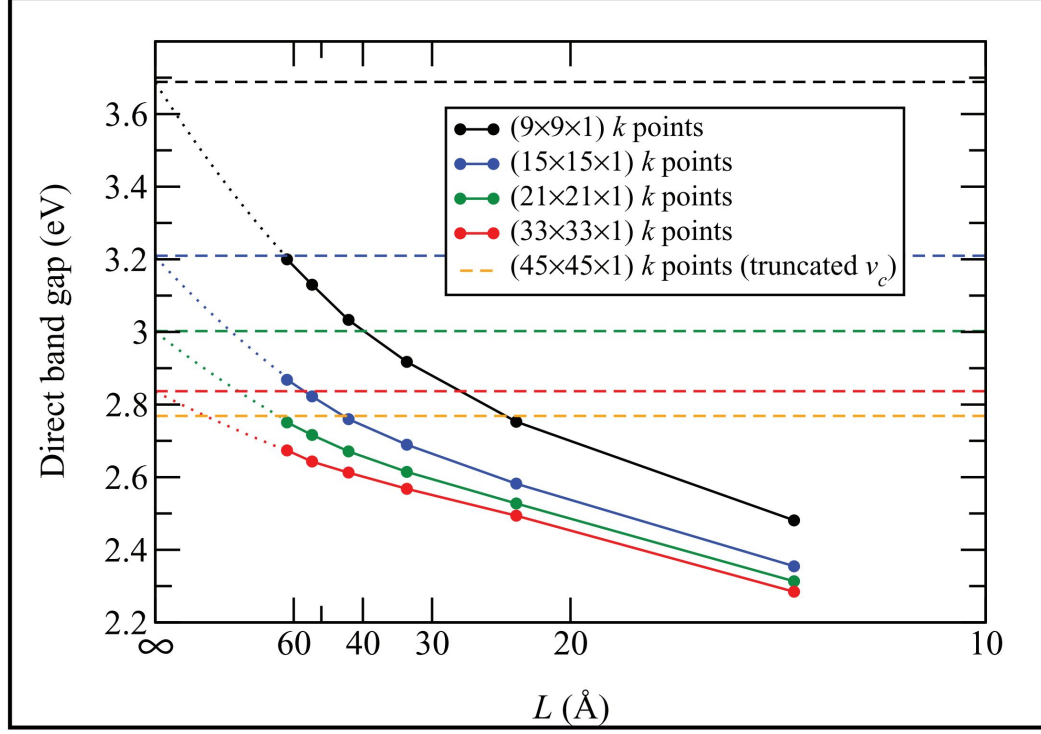


Figure 3.7: An example of the effect of the k-points sampling and vacuum distant (L) on the direct G_0W_0 band gap. Dashed horizontal lines indicate the calculated values with the truncated Coulomb interaction. This calculation has been carried out using 200 bands and a cutoff of 3.7 Ry (50.34 eV). This figure is taken from reference [162]; after permission from the publisher.

large vacuum distance above the slab. The main objective of this search is to investigate frequency-dependent optical properties where the density of k-point mesh plays a crucial role [165–167]. Therefore, considering our computational resources, we considered 15 Å vacuum distance above the layers and performed convergence tests for other parameters.

To illustrate the effect of the increasing vacuum level on the computational time of the G_0W_0 step, in Figure 3.8 we presented an example of the effect of the vacuum thickness on computation time of G_0W_0 step for SrS and SrSe. From Figure 3.8 it can be deduced that increasing the vacuum distance from 15 Å to 30 Å boosts the computational time six times. Following the approach presented

in reference [168], fixing the vacuum distance, we performed convergence for the number of empty bands and energy cutoff.

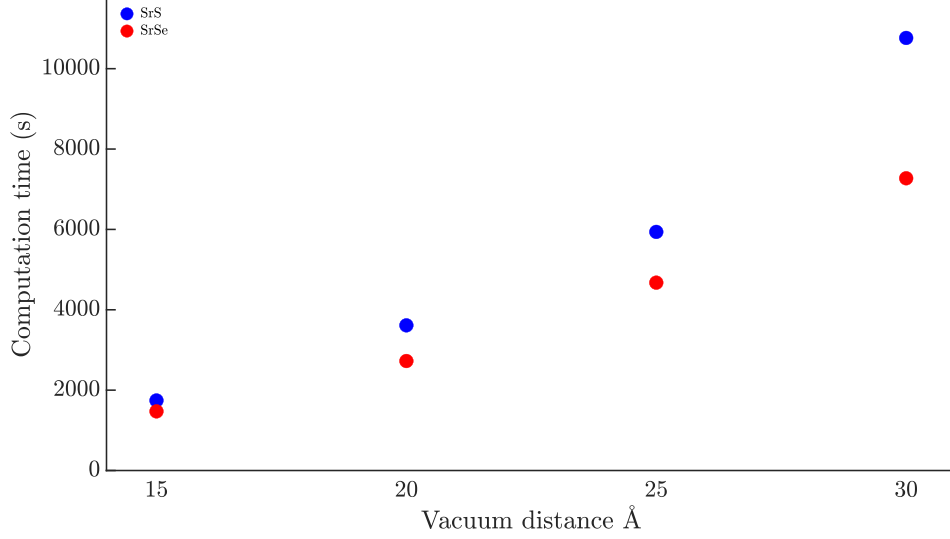


Figure 3.8: The effect of the increasing vacuum distance above the layer on the computation time of GW step for SrS (blue dots) and SrSe (red dots). In these calculations a Γ centered $6 \times 6 \times 1$ k-point mesh is used. The number of bands has been set to 1344 and plane wave energy cutoff is chosen as 273 eV and 240 eV for SrS and SrSe, respectively.

Convergence tests for number of empty bands for total number of bands and screened cutoff can be done using a small number of k-points [168]. The default value of screened cutoff is $\frac{2}{3}$ of plane wave energy cutoff. We aimed to decrease the error in the bandgap to less than 0.1 eV. To accomplish this, we selected a $6 \times 6 \times 1$ k-point mesh and performed the following steps:

1. Keeping numebr of bands as 1344 and number of frequency gird points equal to 256, plane wave energy cutoff is gradually increased from the maximum value of energy cutoff in the pseudo potential. We calculated the QP bandgaps at high symmetry points. An example of this convergence test for ZnO is presented in Figure 3.9, and the results for the rest of the

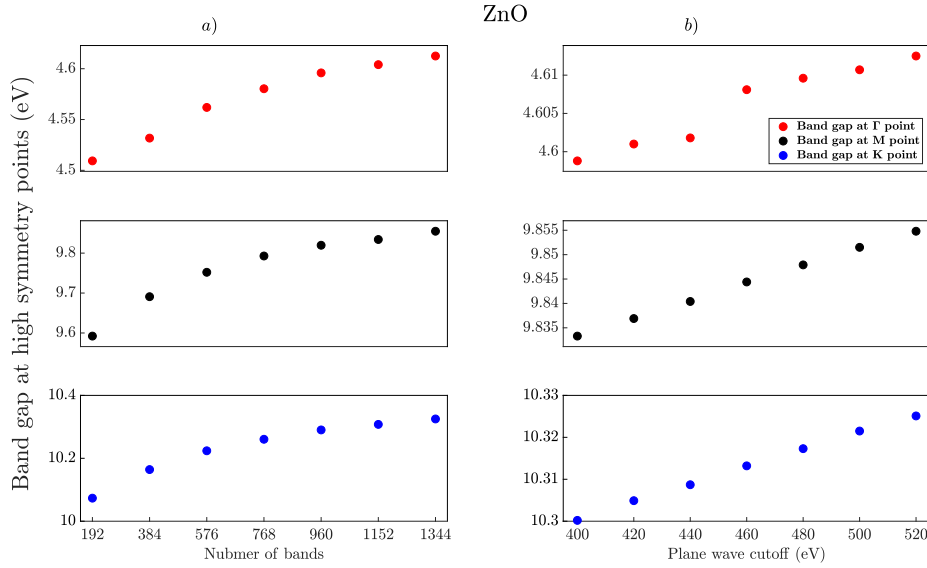


Figure 3.9: Convergence of the quasiparticle band gap for ZnO with respect to a) number of bands and b) the screened cutoff (2/3 of the plane wave cutoff). Number of frequency points is equal to 256.

materials are given in Appendix A. The difference between the maximum and minimum of used plane wave energy cutoffs for all materials are given in Table 3.1.

2. Keeping plane wave energy cutoff equal to the maximum value used in the previous step and number of frequency grid points equal to 256, the number of bands gradually increased from 192 to 1344. An example of the results of this step is also shown in Figure 3.9, and the results for the rest of the materials are provided in the appendix. The difference between the maximum and minimum of used plane wave energy cutoffs values is given in Table 3.2.

The maximum difference between the QP energies obtained from the maximum and minimum considered number of bands is equal to 0.430 (eV), which belongs to BeO at Γ point, while the minimum of this value is 0.0634 (eV), which belongs to BaTe at K point. The maximum difference between the QP energies obtained from the maximum and minimum assumed plane wave energy cutoff is equal

Table 3.1: Minimum and maximum values of considered plane wave cutoff (Min_E and Max_E), absolute value of the difference between these values (Δ) at high symmetry points, and selected plane wave cutoff (U_E) are presented. Number of bands is 1344 and the number of frequency points is 256 for all cases.

	Min_E (eV)	Max_E (eV)	$\Delta\Gamma$ (eV)	ΔM (eV)	ΔK (eV)	U_E (eV)
BaTe	190	310	0.0086	0.0187	0.0187	210
BeO	400	520	0.0727	0.0850	0.0653	420
CaO	400	520	0.0041	0.0061	0.0081	420
CaS	270	390	0.0144	0.0170	0.0285	279
MgO	400	520	0.0170	0.0153	0.0164	420
CdO	400	520	0.0180	0.0155	0.0065	420
ZnO	400	520	0.0137	0.0215	0.0249	420
SrS	260	380	0.0243	0.0370	0.0253	273
SrSe	230	350	0.0163	0.0290	0.0211	240

to 0.0850 (eV), which belongs to BeO at M point, while the minimum of this value is 0.0041, which belongs to CaO at Γ point. These results show that QP energies are more sensitive to the considered number of bands. Therefore, we selected 1344 bands and an energy cutoff slightly larger than the default values. The selected values for plane wave energy cutoffs are given in Table 3.5. A Γ centered $24 \times 24 \times 1$ k grid is used in our main calculation. This k-point mesh is selected according to our computational resources and considering the symmetry of the honeycomb lattices to include all high symmetry points. The number of frequency grid points has been set to 256.

On top of the above discussions, we would like to point out a particular limitation of the current study. Here, the GW calculations have been carried out using DFT wave functions as the starting point. Previous studies have suggested that for materials with d or f orbital shells, employing the wave functions of the DFT+U [169, 170] or HSE methods can improve the accuracy of the GW estimation [171–176]. The HSE method imposes an increased computational cost, whereas the DFT+U method enhances the accuracy of the results with a minor increase in the computational time. However, it is essential to note that the Hubbard U correction was originally introduced to correct the underestimated

Table 3.2: Fixed values of plane wave cutoff (E_{cutoff}) used in convergence tests for the number of bands and difference between the quasi particle energies obtained with 1344 bands and 192 bands (ΔM) at high symmetry points. In all cases the number of frequency point is 256.

	E_{cutoff} (eV)	$\Delta\Gamma$ (eV)	ΔM (eV)	ΔK (eV)
BaTe	310	0.2110	0.1495	0.0634
BeO	520	0.4304	0.3440	0.3372
CaO	520	0.3093	0.3011	0.2039
CaS	390	0.2543	0.1575	0.0981
MgO	520	0.4028	0.3946	0.4029
CdO	520	0.1905	0.2039	0.2854
ZnO	520	0.1032	0.2626	0.2518
SrS	380	0.3162	0.3473	0.1130
SrSe	350	0.2658	0.2957	0.0758

band gap of DFT to match with experimental results. Various approaches have been proposed for determining DFT+U parameters from the first principle calculation [177–182]. The effect of Hubbard+U correction on the band gap of graphene-like ZnO is investigated previously [183], and it is pointed out that further experimental data is required for the correct selection of the DFT+U parameters using the ab initio approach. Consequently, a range of parameters is presented. In the specific case of bulk ZnO considering 160 bands for the band summation, it is shown that $\text{GW}_0 + U_d$ improves the calculated band gap of bulk ZnO [173]. On the other hand, it is demonstrated that by increasing the number of unoccupied bands considered in the G_0W_0 calculation, the band gap converges to the experimental value, but $\text{LDA}+U+\text{G}_0\text{W}_0$ converges more rapidly than the $\text{LDA}+\text{G}_0\text{W}_0$ [184]. Furthermore, a similar effect is reported in the case of transition metal oxide perovskites, and the effect of the converged number of bands in the results of GW calculations is highlighted [185] and only in the cases that the standard DFT is not able to open the gap, DFT+U is used. Therefore, although we emphasize the importance of the considered initial orbitals in GW calculations, in this study, we relied on careful convergence tests for selecting the parameters and used DFT wave functions as explained in the previous chapter.

3.2.2 Electronic Properties of II-VI Monolayers from G_0W_0

The calculated lattice constants and band gaps from different methods are summarized in Table 3.3. Comparing calculated bandgaps by using GGA functional and G_0W_0 , the minimum difference occurs in CdO, whereas the maximum difference arises in the case of BeO. Here, the most noteworthy results are those obtained from G_0W_0 calculations. As pointed out in the first chapter, among the considered materials here, different phases of ZnO have been extensively studied due to their wide range of applications. Monolayer ZnO is fabricated using the atomic layers deposition (ALD) method on the graphene substrate, and the optical band gaps were reported as 4.03 eV, 3.78 eV and 3.22 eV using 10, 20 and 200 ALD cycles, respectively [85]. Furthermore, it was pointed out that the thinnest ZnO monolayer has an optical band gap up to 4.0 eV. These results are also confirmed in a recent study where ZnO is fabricated on graphene oxide [186]. The optical band gap is related to photon absorption, where the excitonic effects play a critical role in the case of 2D materials in a manner that the exciton binding energies significantly reduce the QP band gaps. By considering 100 empty bands and $40 \times 40 \times 1$ k-point mesh, Attaccalite et al. have reported QP band gap of 3.01 eV and optical band gap of 1.51 eV for g-ZnO [187]. Another study on g-ZnO has estimated QP bandgap of 3.18 eV and optical bandgap of 1.72 eV [89] using 400 empty bands and $20 \times 20 \times 1$ k-points mesh. In both cases, the screened Coulomb interactions were truncated [188]. Our result for the QP band gap and optical band gap of ZnO are 4.19 eV and 2.84 eV, respectively. The obtained optical band gap in our study is 1 eV more than previous results and closer to experimental reports. This improvement is in line with the considered number of unoccupied bands, as the same effect is also confirmed in the case of bulk ZnO [184], where it was shown that 3000 conduction bands are required to obtain converged Coulomb-hole self-energies. The reason for deviations from the experimental value is likely the Coulomb interaction between periodic images due to the periodic boundary condition used. As previously highlighted, the calculated QP band gap can be improved by increasing the vacuum distance considered between the layers [162, 163, 168]. Besides, the estimated value of the optical band gap is smaller than the experimental value. As it is explained

Table 3.3: Calculated in plane lattice constants (a_{LDA} , a_{GGA}) (in Å) using LDA and GGA functionals, band gaps (in eV) based on LDA, GGA functionals and G_0W_0 , energy shift Δ_E for scissors operator (in eV) .

Material	a_{LDA}	a_{GGA}	E_g (LDA)	E_g (GGA)	E_g (G_0W_0)	Δ_E
SrS	4.76	4.85	2.81	2.89	5.41	2.54
SrSe	4.95	5.06	2.69	2.74	5.11	2.36
CaS	4.48	4.57	3.30	3.25	5.95	2.70
BaTe	5.61	5.73	2.46	2.49	4.50	2.01
CdO	3.59	3.68	0.73	0.82	2.15	1.33
CaO	3.71	3.78	2.63	2.56	5.04	2.48
MgO	3.25	3.30	3.51	3.37	6.6	3.23
BeO	2.64	2.68	5.51	5.32	8.91	3.60
ZnO	3.21	3.29	1.69	1.65	4.19	2.54

before, increasing the vacuum thickness or truncating the Coulomb interaction that removes image effects directly increases the QP bandgap and subsequently the optical bandgap. Therefore, the overall results obtained here are justified, and we can expect the QP energies to be underestimated, although the amount of dispersion depends on the materials. In the next section the accuracy of the results is examined by comparing the universal scaling law between the exciton binding energy and QP band gap.

In Figure 3.10, the band structures obtained from DFT-GGA (red lines) and G_0W_0 calculations (shown with dotted lines) are presented. GGA band structures are plotted for comparison purposes after applying a scissor operation. All conduction bands are shifted up until the edges of the first conduction band of DFT-GGA results reached to first conduction band calculated in G_0W_0 step. The amount of this shift corresponds to the difference between the band gap values obtained from GGA and G_0W_0 (see Table 3.10). Also, the corresponding density of states (DOS) are displayed in a separate panel right to the band structures in Figure 3.10. The same scissors operator was applied to the conduction part of the DOS of the GGA bands. Comparing these band structures shows that both GGA and G_0W_0 bands are completely similar. This remarkable resemblance of the two band structures in all cases confirms that the G_0W_0 approach, which takes into account the effect of self-interaction, principally corrects the band gap

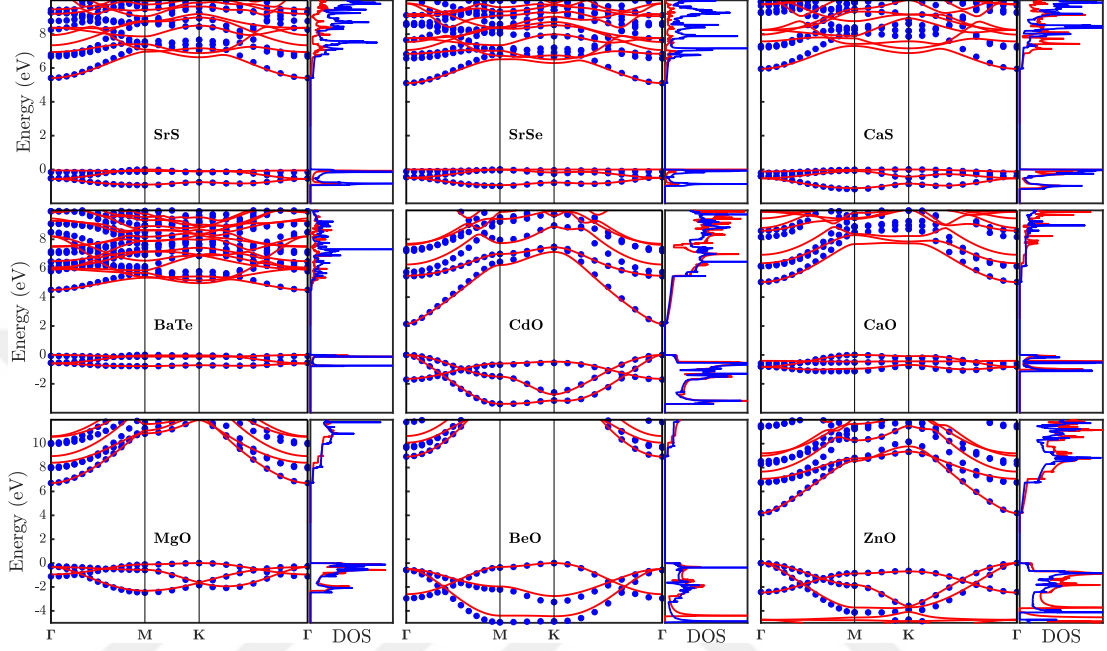


Figure 3.10: Calculated band structures by using GGA functional (red lines), and G_0W_0 (green dots). Fermi level is set to zero. The conduction bands of GGA are shifted up by difference between the bandgap of QP and GGA ($\Delta_E = E_{G_0W_0} - E_{GGA}$), so that the conduction band edges of band structures coincides for easy comparison. The density of states (DOS) are also shown on the right panel next to the band structures.

underestimation of GGA-based calculated bands.

Analysis of band structures given in Figure 3.10 reveals that the top valence band of the studied monochalcogenides studied here is extremely flat. Accordingly, a very sharp peak appeared around the valence band edge in DOS in these systems. This heightened DOS around Fermi energy might be pretty outstanding for optical excitations. Meanwhile, the top valence bands exhibit a dispersion in mono oxides, yet there is a sharp peak in DOS slightly below the Fermi energy. Another essential characteristic of the band structures of these materials is that in all of them, the smallest band gap for direct transition is located at the Γ point. These direct transitions are critical in the BSE calculation.

Table 3.4: Indirect QP band gap ($E_{G_0W_0}$), positions of the VBM and CBM in the BZ, direct QP band gap $E_{G_0W_0}^d$, first BSE eigenvalue E_{BSE} , and exciton binding energy (in eV) E_x for perpendicular incident light. All direct band gaps belong to Γ - Γ .

Material	$E_{G_0W_0}$ (eV)	VBM-CBM	$E_{G_0W_0}^d$ (eV)	E_{BSE} (eV)	E_x (eV)
SrS	5.41	M - Γ	5.59	3.89	1.70
SrSe	5.11	M - Γ	5.24	3.70	1.54
CaS	5.95	K - Γ	6.15	4.36	1.79
BaTe	4.50	M - Γ	4.59	3.27	1.32
CdO		Γ - Γ	2.15	1.43	0.72
CaO	5.04	M - Γ	5.62	3.36	2.26
MgO	6.70	K - Γ	6.98	4.55	2.43
BeO	8.91	K - Γ	9.49	6.65	2.84
ZnO		Γ - Γ	4.19	2.84	1.35

3.3 Optical Properties of II-VI Monolayers from GW+BSE

In order to determine excitonic effects in the photo absorption process, we solve BSE in TDA [149, 189, 190, 190] utilizing the obtained QP energies and wave functions of G_0W_0 step. It is shown that the discrepancy between the results estimated utilizing TDA and full BSE is negligible for Si [191]. TDA is used for examining excitonic effect in 2D structures such as ZrS_2 and HfS_2 [192], antimonene and bismuthene [193] and PtS_2 [194]. The reliability of TDA is also confirmed for a series of molecules [195].

Due to the excessive memory requirement for solving the BSE, a limited number of valence and conduction bands are usually considered for calculating excitonic effects. Here we selected the number of valence bands considering the distances between the lower valence and the top valence band. The number of unoccupied bands is selected considering the distance between the minimum conduction band and higher empty bands. The chosen values are summarized in Table 3.5. Furthermore, the indirect transitions are neglected and the simplified

Table 3.5: Selected number of occupied bands (N_O), number of valence bands (N_v) and energy cutoff for different materials.

Material	N_O	N_v	E_c (eV)
SrS	4	16	273
SrSe	4	16	240
CaS	4	16	279
BaTe	4	16	210
CdO	8	12	420
CaO	4	16	420
MgO	3	16	420
BeO	3	16	420
ZnO	8	12	420

form of TDA is used:

$$\begin{aligned}
 \left(\varepsilon_{c\vec{k}}^{\text{QP}} - \varepsilon_{v\vec{k}}^{\text{QP}} \right) A_{v\vec{k}}^S + \sum_{v'c'\vec{k}'} \left\langle v\vec{k} \left| K_{e-h} \right| v'c'\vec{k}' \right\rangle A_{v'c'\vec{k}'}^S \\
 = \Omega^S A_{v\vec{k}}^S
 \end{aligned} \tag{3.1}$$

indices c and v show to conduction and valence bands respectively, $A_{v\vec{k}}^S$ and Ω^S are expansion coefficients of the exciton wave function and corresponding eigenvalues, K_{e-h} is the kernel which describes electron-hole interactions (see [190] and previous chapter). An excitonic eigenstate is given by:

$$|S\rangle = \sum_{v\vec{k}} A_{v\vec{k}}^S |v\vec{k}\rangle \tag{3.2}$$

According to equation 3.2, visualizing coupling coefficients ($A_{v\vec{k}}^S$) can provide information about the electron-hole pairs that contribute more to the specific exciton wave function, defined by $|S\rangle$. In Figure 3.11, the absolute values of BSE coupling coefficients for the first bright excitons are displayed in fatband representation [196] together with the G_0W_0 band structure. Bright excitons are BSE eigenvalues with non-zero oscillator strength. The oscillator strengths describe the intensity of the transition for specific excitonic states and are proportional to the sum of the momentum matrix elements [191, 197]. Evidently, the couplings are substantial near the Γ point where the direct bandgap is located. In the case of SrS, SrSe and BaTe the first bright excitons is created by coupling the last

valence band and first conduction band. According to Figure 3.4, the last valence band of these structures are formed by p_z orbitals, therefore the first bright exciton is created by the incident light parallel to x-y plane. Since the perpendicular incident light is more important in 2D materials we plotted BSE fatbands for this case in Figure 3.12. The first exciton eigenvalues for perpendicular incident light are presented in Table 3.5. The exciton binding energies are calculated from difference between the exciton eigenvalues and corresponding QP energies. From Figure 3.11, we can see that ZnO and CdO which possess direct band gap and the maximum coupling appears exactly at Γ point where the band gap is located. For the rest of materials that have indirect band gaps the coupling is strong near the gamma point which is due to neglecting indirect transitions. Interestingly, there are large coupling between second and third valence bands (holes) and the first conduction band (electrons).

Through a simplified model, a universal scaling had been predicted for 2D semiconductors [165, 166], and a linear relation between exciton binding energies and QP band gaps with a slope of 0.25 was obtained. Furthermore, fitting a line to computational and experimental results is estimated to have a slope of 0.27. in Figure 3.13 the binding energies versus QP energies are presented. Overall, our results are in agreement with the computationally predicted slope. It is shown that vacuum thickness has no substantial effect on the optical bandgap (BSE eigenvalue) [165]. Therefore slight deviations in our results from the predicted slope are related to the QP underestimation bandgaps due to the vacuum thickness. To further examine the level of accuracy of the results obtained in this study, in Table 3.6, we compared our results for MgO, CdO and CaO with the recently published report where the QP energies are calculated using a vacuum distance same as our study and Coulomb interaction is truncated. In ref [198], a smaller number of k-points ($15 \times 15 \times 1$) and 700 empty bands are considered. Comparing the direct GW band gaps shows that our results are 12.24%, 0.08%, and 0.01% smaller in the case of CdO, CaO and MgO, respectively. The smaller values obtained in this work are due to the Coulomb interaction, although the increased number of bands partially cancels the overall errors. On the other hand, comparing the ratio of direct QP energies to exciton binding energies in Table 3.6

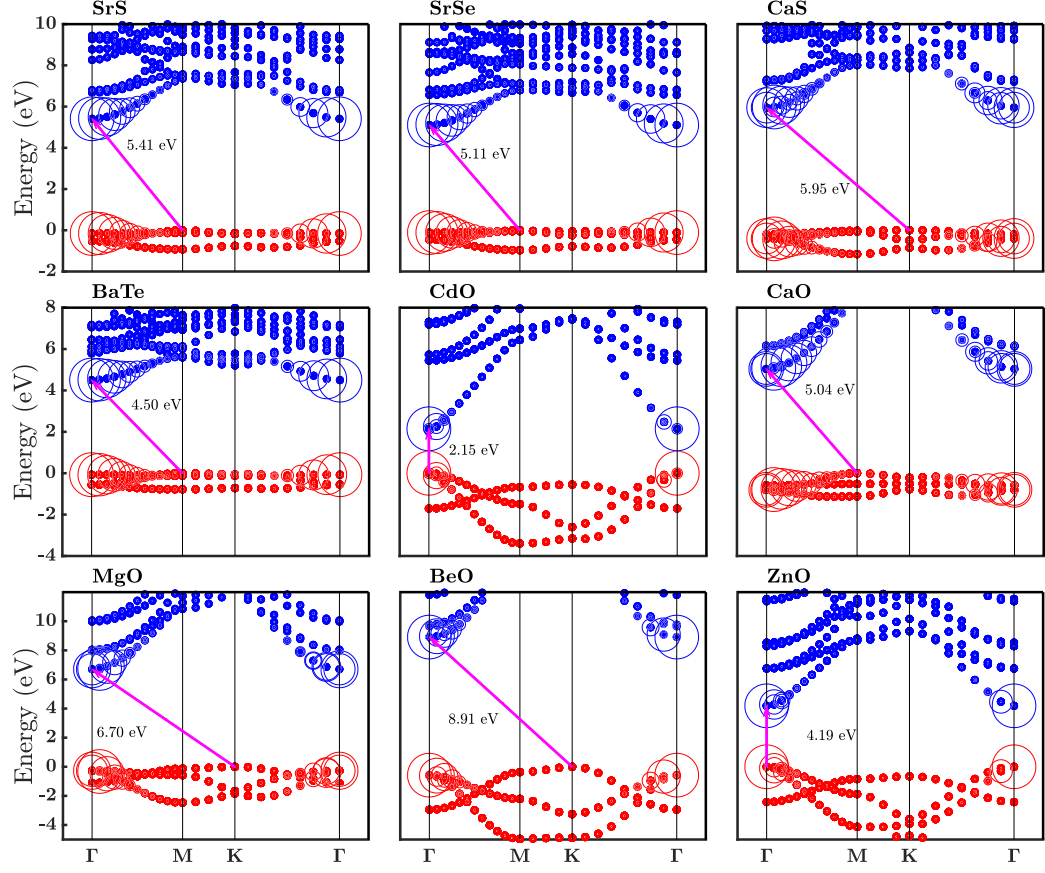


Figure 3.11: Fatband representation for absolute values of electron- hole coupling coefficients (circles) on top of G_0W_0 band structures.

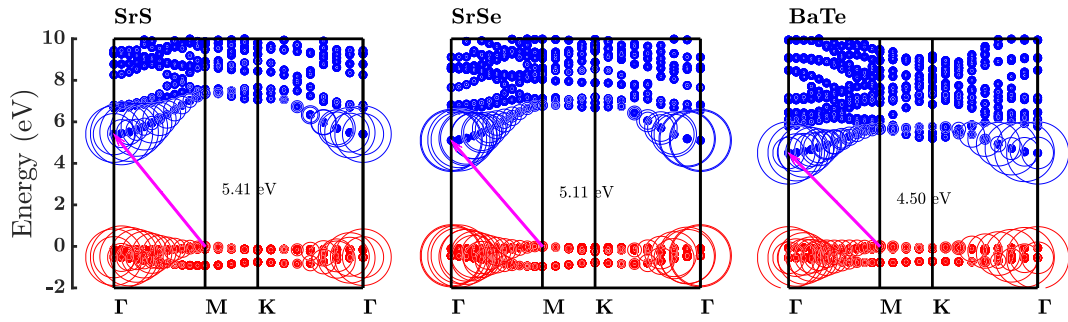


Figure 3.12: Fatband representation for absolute values of electron- hole coupling coefficients (circles) on top of G_0W_0 band structures for SrSe, SrS and BaTe for the first bright exciton of the perpendicular incident light.

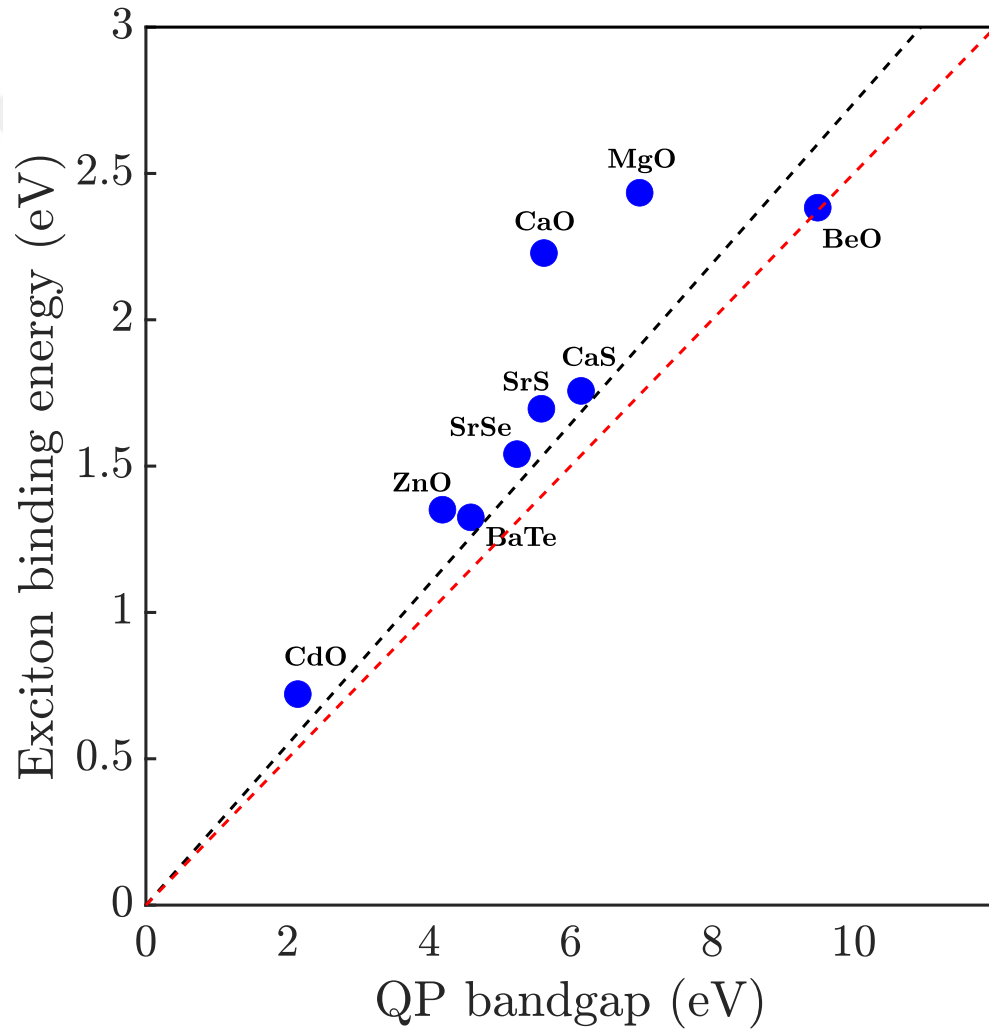


Figure 3.13: Exciton binding energies versus QP energies. The slope of red dashed line is 0.25 and the slope of black dashed line is 0.27, these values are theoretical and computational predictions of reference [166].

Table 3.6: Our results for lattice constant (a_{GGA}), direct G_0W_0 bandgap ($E_{G_0W_0}^d$), optical bandgap (E_{BSE}) and the ratio of the exciton binding energy E_x to direct G_0W_0 band gap are compared with the results of ref [198]. Here N_b is the total number of bands included in G_0W_0 , N_O is the number of the valence bands included in BSE and N_v is the number of conduction bands in the BSE step. In our calculation, the vacuum separation is 15 Å and a $24 \times 24 \times 1$ k-point mesh is used. The same thickness is used in previous work [198], but the Coulomb interaction is truncated and a $15 \times 15 \times 1$ mesh is used.

Material	a_{GGA} (Å)	N_b	N_O	N_v	$E_{G_0W_0}^d$ (eV)	E_{BSE} (eV)	$\frac{E_x}{E_{G_0W_0}^d}$
CdO							
This work	3.68	1344	8	12	2.15	1.43	0.34
Ref [198]	3.66	700	5	5	2.40	1.27	0.47
CaO							
This work	3.78	1344	4	16	5.62	3.40	0.40
Ref [198]	3.78	700	5	5	6.08	3.71	0.39
MgO							
This work	3.30	1344	3	16	6.98	4.54	0.35
Ref [198]	3.30	700	5	5	7.12	4.63	0.35

reveals a much larger deviation in the previously reported results for CdO. It is attributed to the coarse k-point mesh used in the previous study [198]. As pointed out before, BSE results are less sensitive to vacuum distance and more susceptible to the density of k-point mesh.

By comparing the magnitude of the oscillator strengths, it is possible to determine the dark and bright excitons. The dark excitons are those with zero or negligible oscillator strengths. It has been shown that dark excitons can considerably influence the optical response of 2D materials [52]. For instance, close energy between the dark and bright exciton significantly decreases the photoluminescence of MoS₂ [199]. Two main types of dark excitons are related to the spin or momentum forbidden transitions [52, 200], where radiative recombination is impossible. Since the effects of spin polarization and finite momentum are not considered in our approach, the dark excitons in this study (see Fig. 3.13) are related to small matrix elements of momentum operator [201]. From figure 3.14 it can be noticed that in all cases, there is not any dark exciton in the vicinity of the

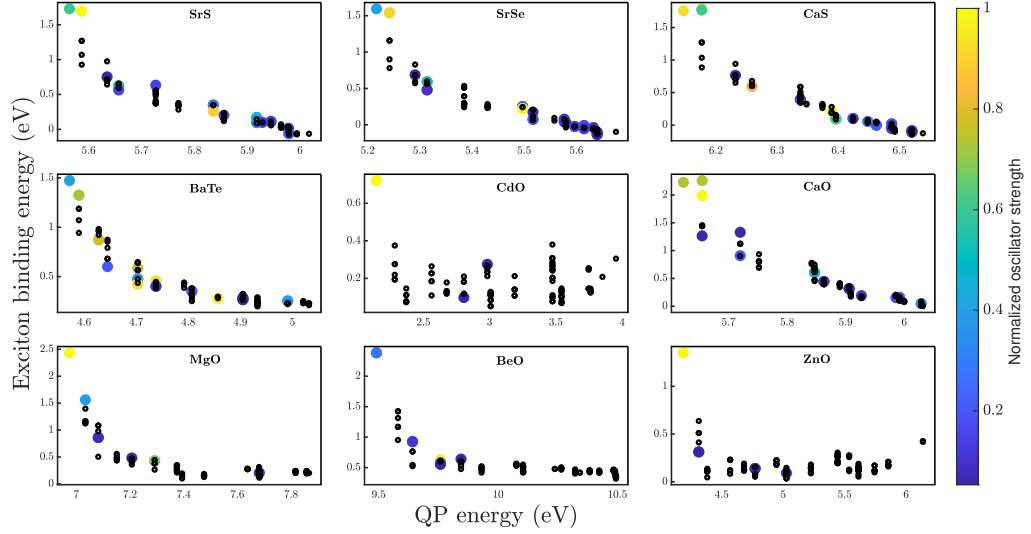


Figure 3.14: The exciton binding energies versus exciton eigenvalues. The color bar shows the normalized oscillator strengths and black circles are used for displaying excitons with negligible oscillator strengths (less than 0.05 after normalization with respect to maximum).

foremost bright exciton. However, it must be noted that the first bright exciton of SrS, SrSe and BaTe are accessible by incident light parallel to the layers. The other interesting case, which is more noticeable in the case of mono-oxides, is that the majority of the excitons are dark, and there is a small number of optically accessible (bright) excitons.

In order to examine optical properties, in Figure 3.15 we plotted the imaginary parts of the dielectric function obtained from DFT, G_0W_0 and BSE calculations for perpendicular incident light ($\epsilon_{I_{xx}}$) and parallel incident light ($\epsilon_{I_{zz}}$). The complex and frequency-dependent dielectric function describes how light interacts when propagating through matter. While its real part depicts the dispersion effects, the imaginary part illustrates the optical absorption. First of all, as expected from the comparison of calculated band structures from GGA-based DFT and G_0W_0 , the dissimilarity between the DFT and G_0W_0 based optical absorption is only their starting edge. As we did for conduction bands in Figure 3.10, we can compare the G_0W_0 based ϵ_I by a constant shifting of the standard DFT

results. Apart from this shift, DFT and G_0W_0 results exhibit similar characteristics. The ϵ_I obtained in BSE step shows different behavior mainly due to excitonic effects and the decreased number of bands that are included in the calculations, the latter case is more evident in higher photon energies.

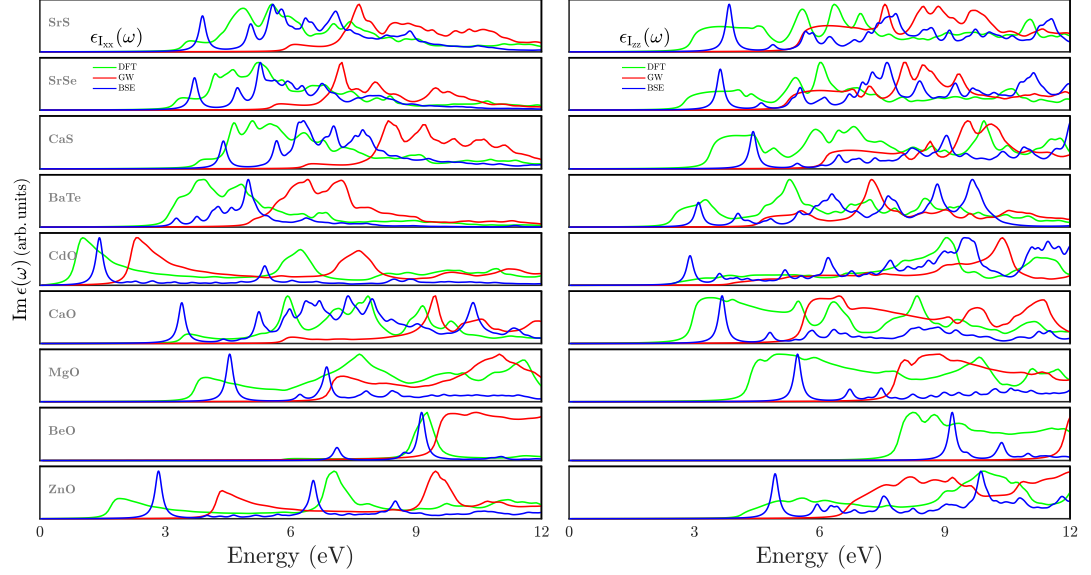


Figure 3.15: Imaginary parts of dielectric function obtained from DFT, G_0W_0 and BSE calculations (green, red and blue lines, respectively) for two different polarizations.

After comparing the results of different methods, we focus on the dielectric functions obtained in the BSE step, which are the most meaningful results of our calculations. In Figure 3.16, we presented the imaginary part obtained in BSE and oscillator strength corresponding to each BSE eigenvalue. In all of the considered structures, the most considerable oscillator strength appeared at the energy where the first maximum of the $\text{Im}(\epsilon)$ is located. As it is expected, the subsequent non-zero oscillator strengths are precisely in accordance with the peaks and shoulders of the dielectric function. In all of the configurations, the first peak of the $\text{Im}(\epsilon_{xx})$ precedes the first peak of the $\text{Im}(\epsilon_{zz})$, except SrS and SrSe and BaTe.

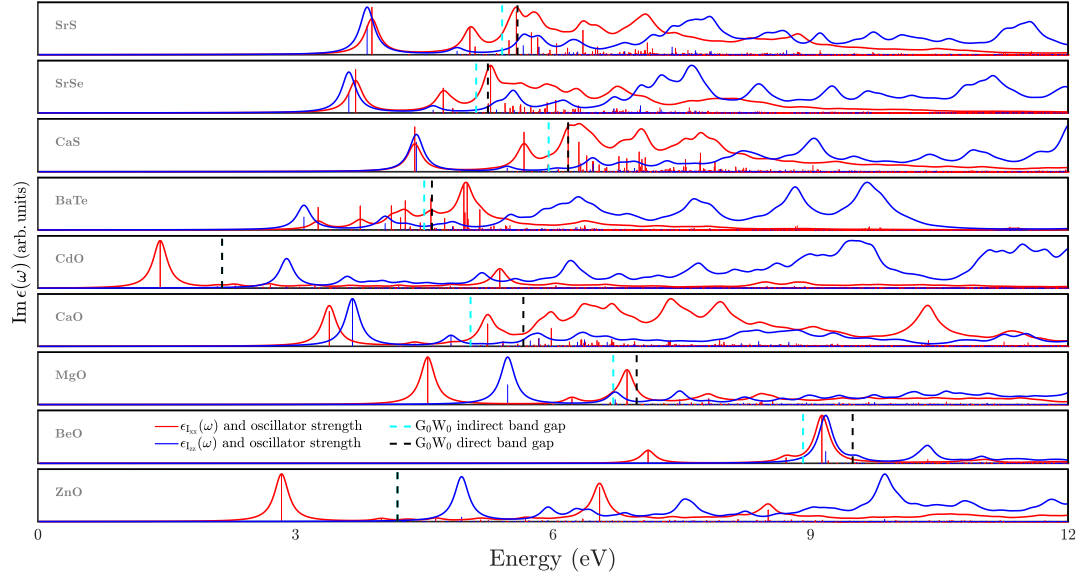


Figure 3.16: Imaginary parts of the dielectric function obtained from BSE for in-plane and perpendicular incident light (blue and red curves, respectively), oscillator strengths (blue and red vertical lines, respectively) and positions of the G_0W_0 direct and indirect band gap (black and cyan dashed vertical line, respectively).

By comparing the magnitude of the oscillator strengths, it is possible to determine the dark and bright excitons. The dark excitons are those with zero or negligible oscillator strengths. It has been shown that dark excitons can considerably influence the optical response of 2D materials [52]. For instance, close energy between the dark and bright exciton significantly decreases the photoluminescence of MoS2 [199]. Two main types of dark excitons are related to the spin or momentum forbidden transitions [52, 200], where radiative recombination is impossible. Since the effects of spin polarization and finite momentum are not considered in our approach, the dark excitons in this study (see Figure 3.14) are related to small matrix elements of momentum operator [201]. From Figure 3.14 it can be noticed that in all cases, there is not any dark exciton in the vicinity of the foremost bright exciton. However, it must be noted that the first bright exciton of SrS, SrSe and BaTe are accessible for incident light parallel to the layers. The other interesting case, which is more noticeable in the case of mono-oxides,

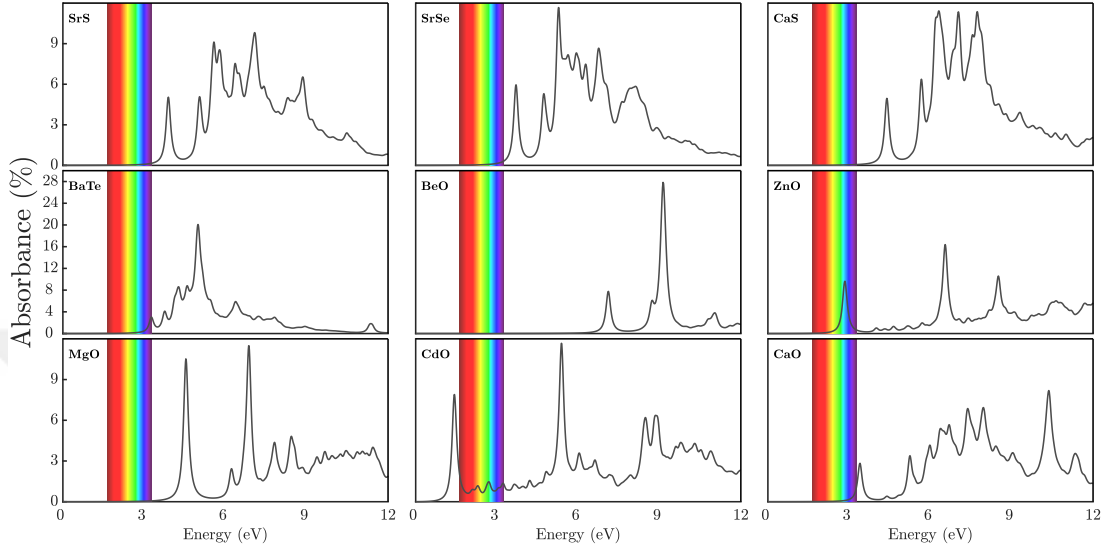


Figure 3.17: Optical absorbance of II-VI monolayers for perpendicular incident light. The visible light spectrum is also shown (from 1.63 eV to 3.26 eV) for reference.

is that the majority of the excitons are dark, and there is a small number of optically accessible (bright) excitons.

The percentage of light that 2D materials can absorb is quantified by the optical absorbance, as described in the previous section. In Figure 3.17 we presented the absorbance for the considered material. Among the considered material, the absorbance spectrum of BeO has a sharp peak (28%) in the ultraviolet region, and minimum absorbance belongs to CaO, which can absorb maximum 8% of incident light in the ultraviolet region. The absorbance spectra of SrS and SrSe, and CaS have similar behaviours. The absorbance spectrum of ZnO has a sharp peak in the visible light region, and in energy equal to 2.84 eV, it can absorb 9.6% of the incident light. Besides, CdO has an optical band gap of 1.43 eV with the maximum absorbance of 7.9%.

3.4 Optical Properties of ZnO and CdO Revisited

In the previous sections, we showed that monolayer ZnO has an optical band gap of 2.84 eV, which is larger than the earlier reports 1.51 eV [187] and 1.71 [89]. Besides, in the case of CdO, according to the data presented in Table 3.6, there is a considerable deviation from the universal scaling law in the results obtained by truncating Coulomb interaction [198]. In this section, we revisited the optical properties by increasing the vacuum distance to 30 Å and the number of bands to 1440. The increased vacuum thickness partially removes the effect of the long-range Coulomb interaction. In order to make the computations feasible with our computational resources, a Γ centered $19 \times 19 \times 1$ k-pointed mesh is employed. Furthermore, a similar set of parameters are used in the next chapter, where we studied ZnO/MgO heterostructures. Furthermore, in the case CdO, in BSE step we used 5 unoccupied and 5 occupied bands to compare our results with the previous report.

3.4.1 ZnO

The results obtained using different parameter sets for ZnO are compared in Table 3.7. Using a vacuum distance of 30 Å and $19 \times 19 \times 1$ k-point mesh raises the direct band gap by 0.17 eV. As previously mentioned, we expect a slight decrease in bandgap by reducing the number of k-points; however, the increased number of bands may partially cancel the effect of k-point density. The exciton binding energy is increased by 0.2 eV. Nonetheless, the optical bandgap has a tiny change of 0.03 eV, which is in line with the previous discussion about the small effect of vacuum distance on the optical band gap. Overall, these results confirm the impact of the number of bands on QP energies. In Figure 3.18, we compared the optical absorbance obtained by two different parameter sets to get more insight into the effect of selected parameters. The overall behaviour of the absorbance in the visible light region is similar, and the difference between the two curves is a slight shift in position and the magnitude of the first peak. However,

Table 3.7: Direct G_0W_0 bandgap ($E_{G_0W_0}^d$), optical bandgap (E_{BSE}) and the exciton binding energy E_x of ZnO compared using different k-point meshes and vacuum distances. Here d is the vacuum thickness, N_k is the number of k-points in each in-plane direction, N_b is the total number of bands included in G_0W_0 , N_O is the number of the valence bands included in BSE and N_v is the number of conduction bands in the BSE calculation.

d (Å)	N_k	N_b	N_O	N_v	$E_{G_0W_0}^d$ (eV)	E_{BSE} (eV)	E_x (eV)
15	24	1344	8	12	4.19	2.84	1.35
30	19	1440	8	12	4.36	2.81	1.55

as the energy increases, the dissimilarities become more evident, specifically in the third peak of the results obtained using $24 \times 24 \times 1$ k-points. This can be traced back to the impact of the k-point density on the accuracy of the imaginary part of the dielectric function that involves integration over the first BZ.

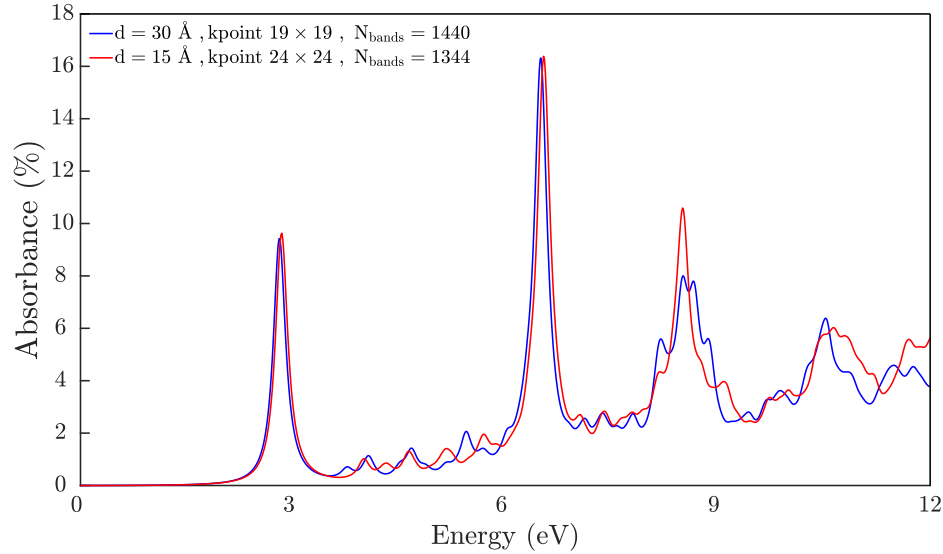


Figure 3.18: Optical absorbance of ZnO for perpendicular incident light calculated with different vacuum thicknesses.

3.4.2 CdO

In Table 3.8, we compared the results obtained from different parameter sets for CdO. Using a vacuum distance of 30 Å and $19 \times 19 \times 1$ k-point mesh raises the direct band gap by 0.12 eV and the exciton binding energy is increased by 0.18 eV. However, the optical bandgap has a smaller decrease of 0.06 eV. This is also in line with the previous discussion about the small effect of vacuum distance on the optical band gap. All in all, these results confirm the impact of the number of bands on QP energies and the effect of the density of k-point mesh on optical bandgap. In Figure 3.19, we compared the optical absorbance obtained by two different parameter sets to get more insight into the effect of selected parameters. The overall behaviour of the absorbance close to the first and second peaks. However, as the energy increases, the dissimilarities become more evident, in this case the main reason is reduced number of the considered bands considered in the BSE step.

Finally, from the Table 3.8 we can deduce that by using parameters the ratio of the exciton binding energy to QP is increased to 0.4 which is smaller than previously reported value 0.47 [198] but it is closer to predicted universal value 0.25.

Table 3.8: Direct G_0W_0 bandgap ($E_{G_0W_0}^d$), optical bandgap (E_{BSE}) and the exciton binding energy E_x of CdO compared using different k-point meshes and vacuum distances. Here d is the vacuum thickness, N_k is the number of k-points in each in-plane direction, N_b is the total number of bands included in G_0W_0 , N_O is the number of the valence bands included in BSE and N_v is the number of conduction bands in the BSE calculation.

d (Å)	N_k	N_b	N_O	N_v	$E_{G_0W_0}^d$ (eV)	E_{BSE} (eV)	E_x (eV)
15	24	1344	8	12	2.15	1.43	0.72
30	19	1440	5	5	2.27	1.37	0.9

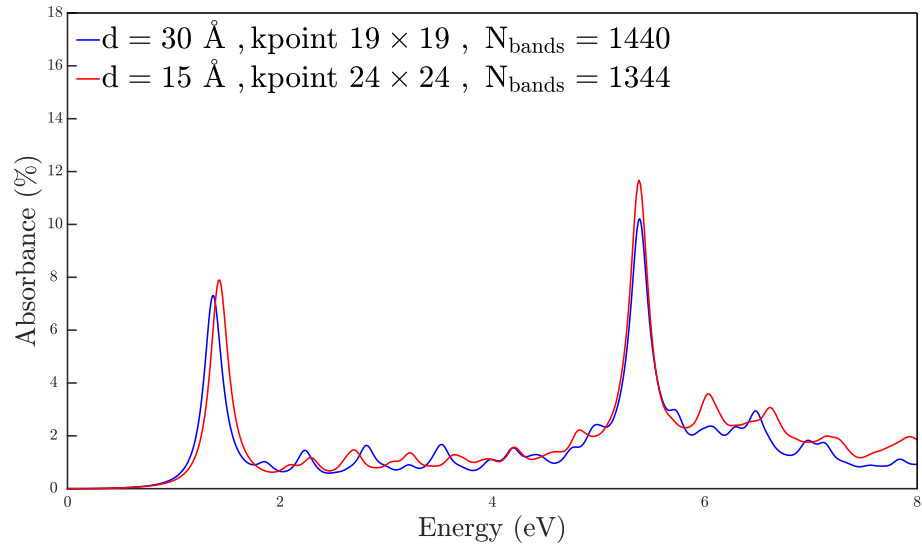


Figure 3.19: Optical absorbance of CdO for perpendicular incident light calculated with different vacuum thicknesses.

Chapter 4

Optical Properties of 2D Heterostructures Formed by ZnO and MgO Monolayers

4.1 Introduction

Currently, layered structures of ZnO and MgO have been utilized in various electronic devices. ZnO/MgO dielectrics for metal-insulator-metal capacitor [202], field-effect transistor [203] and Au/MgO/ZnO metal-insulator-semiconductor ultraviolet light emitters are currently fabricated [204]. Besides employing bilayer MgO/ZnO, a smaller leakage current and increased shunt resistance are attained in organic photovoltaics, and it is shown that MgO increases the short circuit current density and fill factor in such devices [204]. Due to their intriguing properties, in recent years, ZnO-based van der Waals heterostructures (vd-WHs) have attracted many researchers, for example the tunability of band gap in WSe₂/ZnO [205], stanene/ZnO [206], ZnO/PtSSe [207], MoSSe/ZnO [208], BP/ZnO [209] and ZnO/ZnX (X = S, Se, Te) [210] are already pointed out and their applications as photocatalytic for water splitting have been investigated [211–215]. Also, it is shown that microspherical MgO/ZnO bilayer can

enhance the stability of self-powered lead-halide perovskite photodetectors and elevate carrier transport [216]. Besides, a recent study is revealed that internal piezoelectric polarization fields form robust excitons at the 2D interface of non-polar MgZnO/ZnO heterostructures [217].

A previous study by C. E. Ekuma et al. has only presented the electronic and optical properties of MgO/ZnO and MgO/ZnO/MgO heterostructures [218] in one possible stacked structure using HSE06 hybrid functional and shown that MgO is an excellent dielectric gate oxide for encapsulating ZnO-based optoelectronic devices. Motivated by prospering properties of MgO/ZnO structures and theoretically predicted close lattice match between graphene-like MgO and ZnO, in this chapter, we systematically investigated mechanical and optical properties of bilayer heterostructures formed by MgO and ZnO monolayers.

4.2 DFT Study of ZnO/MgO Heterostructures

We considered four different stacking for assembling heterostructures of MgO/ZnO. Relaxed structures of the considered configurations are shown in Figure 4.1. The Mg atom is placed on top of the Zn atoms in the structure named AA_I. In the AA_{II} structure, the O atom, which is in the same plane as the Mg atom, is placed on top of the Zn atom. This structure can be constructed from the AA_I by rotating the top layer by 60° through the rotation axis through the O–O bond perpendicular to the plane and then moving it along the armchair direction, Mg shifts towards the neighbour O, by a bond length. We conducted DFT calculations to study the mechanical and dynamical stability of the considered structures, and then we calculated their ground state electronic properties.

4.2.1 Computational Details

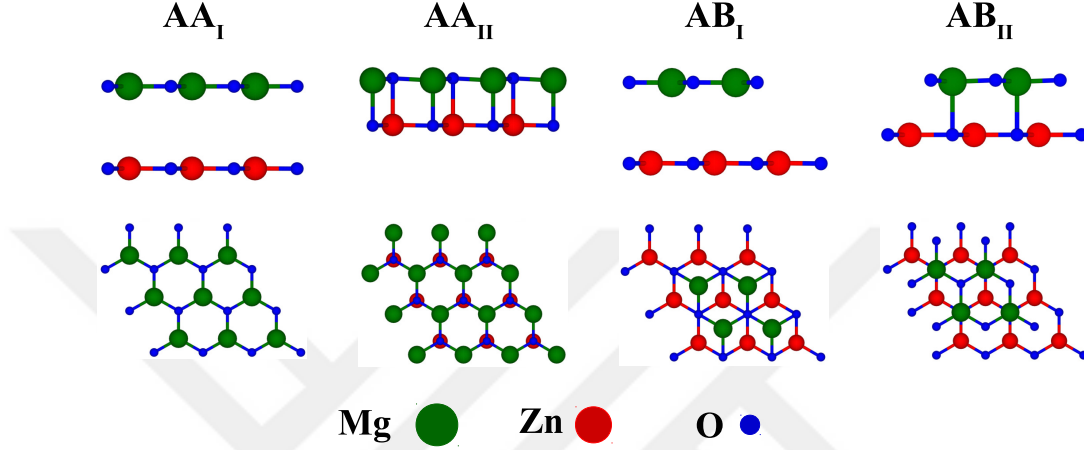


Figure 4.1: Side and top views of the relaxed structures of the considered heterostructure. Here we used subindex **I** for van der Waals heterostructures and subindex **II** for heterostructures with interlayer binding.

AB_I structure is formed by shifting the atoms of the upper plane of AA_{II} structure along the armchair direction, Mg shifts away from the neighbor O towards the center of the hexagon of the lower layer by a bond length. The last structure named AB_{II} is formed by moving the atoms of the upper plane of AA_I structure along the armchair direction, Mg shifts towards the nearest neighbour O atom by a bond length.

All calculations in this study are carried out using the PAW for DFT calculations within the PBE functional [128, 219], and in order to gain a better approximation for vdW interactions, we employed optB86b-vdW functional [220–222]. All computational parameters have been selected after conducting careful convergence tests. For relaxing the structures, a Γ point centered $25 \times 25 \times 1$ Monkhorst-pack k-point mesh is used for sampling the BZ. The kinetic energy cutoff for the plane-wave basis is set to 500 eV. Energy is converged with a tolerance of 10^{-8} eV, and Hellmann–Feynman forces on each atom are minimized to be less than 10^{-3}

Table 4.1: Calculated in-plane lattice constant (**a**), interlayer distance (**h**), binding energy (**E_{bind}**) and elastic constants (**C₁₁**) and (**C₁₂**) (both in **Nm⁻¹**) for different stackings.

Configuration	a (Å)	h (Å)	E _{bind} (meV)	C ₁₁	C ₁₂
AA _I	3.28	3.76	-92.23	217.62	66.53
AA _{II}	3.36	2.18	-806.49	166.56	49.13
AB _I	3.28	3.53	-113.61	216.76	66.10
AB _{II}	3.32	2.36	-436.53	191.33	59.15

eV/Å. Layers are placed in x-y plane, and in order to eliminate the interaction between the layers and their periodic images, a vacuum of 30 Å is considered in z direction above the layers. Subsequently, a $5 \times 5 \times 1$ supercell and $5 \times 5 \times 1$ k-point mesh are used for calculating phonon dispersions. Force constants are calculated using density functional perturbation theory [223], and PHONOPY [224] code is used for computing the phonon frequencies.

4.2.2 Stability Analysis

Lattice parameters of the relaxed structures are given in Table 4.1. The difference between the in-plane lattice constants of AA_I and AB_I structures are very small (0.02 Å), but AA_I has a slightly larger interlayer distance which is in agreement with the earlier reported value [218].

The interlayer distance of these configurations is larger than their in-plane the lattice constant, which shows a typical van der Waals bond distance. On the other hand, the obtained interlayer distances of AA_{II} and AB_{II} structures are smaller than their in-plane lattice constants by about 1 Å. In AA_{II} and AB_{II} configurations, the Mg atom is placed on top of the O atom of the underlying ZnO layer. The bond length of Mg-O bond is 2.07 Å and 1.87 Å in its bulk form, rock salt crystal, and in monolayer MgO, respectively [19]. Therefore, the calculated interlayer distances of these structures are slightly larger than the bond length of the rock salt structure. Thus, while AA_I and AB_I structures can be considered

as vdWHs, there is an interlayer bonding in AA_{II} and AB_{II} configurations. We estimated the binding energies of ZnO/MgO heterostructures using the following formula:

$$E_{\text{bind}} = E_{\text{tot}} - (E_{\text{ZnO}} + E_{\text{MgO}}) \quad (4.1)$$

where E_{tot} is the total energy of the heterostructure, E_{ZnO} and E_{MgO} are the energies of the ZnO and MgO monolayers, respectively. The calculated binding energies are summarized in Table 4.1. The calculated negative binding energies confirm the thermodynamic stability of all structures. The considerable binding energies of the AA_{II} and AB_{II} structures indicate a considerable interaction between the layers. To study the mechanical stability of considered materials, we computed elastic constants using the energy-strain method [225]. We used the open-source program VASPKIT [226] for pre-and post-processing steps of calculating elastic constants. In terms of elastic constants, C_{ij} , the criteria for mechanical stability of a 2D hexagonal lattice are given by [227, 228]:

$$\begin{aligned} C_{11} &> 0 \\ C_{11} &> |C_{12}| \end{aligned} \quad (4.2)$$

All configurations are mechanically stable using the above conditions and obtained elastic constants given in Table 4.1.

Finally, to examine the dynamical stability of the considered structures, we calculated the phonon dispersion curves as presented in Figure 4.2. Our results show that AB_{II} has no imaginary phonon frequency and is dynamically stable at zero temperature. AA_{II} structure possesses many imaginary phonon frequencies, and its phonon band structure is not presented here (see Appendix B). The AA_{II} structure is dropped from the analysis in the rest of this chapter. AA_I and AB_I have imaginary optical phonon frequencies near the Γ point. These imaginary frequencies might be cleared by effects like temperature, strain, doping etc. An illustration of this kind of transition is the surface-functionalized ZnO nanostructures [218, 229]. Other examples are the bulk structures of perovskites

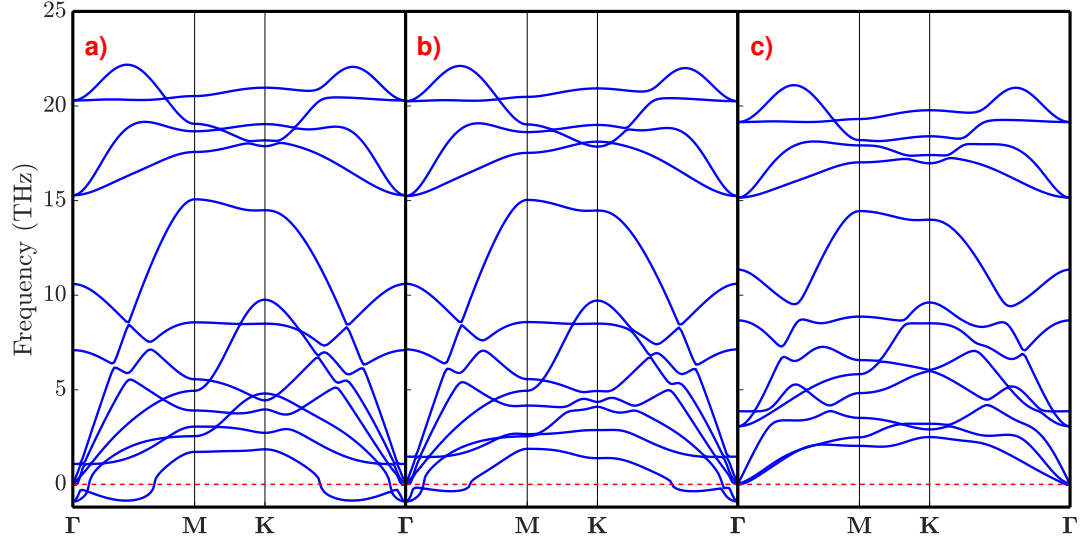


Figure 4.2: Calculated phonon dispersion curves for AA_I (a), AB_I (b) and AB_{II} (c).

that possess imaginary frequencies at their ground states, but temperature-dependent DFT calculations verified their dynamical stabilities at high temperatures [230, 231].

In addition to the stability of AB_{II} structure, employing the calculated phonon frequencies, it is practicable to compare its thermal conductivity κ with the monolayer ZnO approximately. A first-principle investigation within the framework of Boltzmann transport theory has reported a very low κ of $4.5 \text{ Wm}^{-1}\text{K}^{-1}$ for monolayer ZnO at room temperature [232]. κ of the MgO is obtained as $64 \text{ Wm}^{-1}\text{K}^{-1}$ utilizing the same procedure [233]. Here we utilize the Slack equation [234–236] to assess the thermal conductivity of the AB_{II} structure. According to the Slack equation, the κ can be approximated by the following expression:

$$\kappa = B \frac{\bar{M} \Theta_D^3 \delta n^{\frac{1}{3}}}{\gamma^2 T} \quad (4.3)$$

where B is a physical constant, $\bar{M}$ is the average mass of the atoms inside the primitive cell, Θ_D is the Debye temperature, δ^3 is the volume per atom, n is the number of the atoms inside the unit cell, T is the temperature, and γ is the high-temperature limit of the Grüneisen parameter of acoustic modes. Using $\bar{M}$

in atomic mass units and δ in Å, the constant B must be set to 3.6×10^{-6} to get κ in $\text{Wm}^{-1}\text{K}^{-1}$. The following expression can approximate the Debye temperature:

$$\frac{1}{\Theta_D^3} = \frac{1}{2} \left(\frac{1}{\Theta_{\text{TA}}^3 + \Theta_{\text{LA}}^3} \right) \quad (4.4)$$

In the above equation, the variable Θ_i ($i = \text{TA}, \text{LA}$), which is defined for the transverse (TA) and longitudinal (LA) acoustic modes, given by:

$$\Theta_i = \frac{\hbar \omega_{i,\text{max}}}{k_B} \quad (4.5)$$

where $\hbar$ is the reduced Planck's constant, k_B is the Boltzmann constant, and $\omega_{i,\text{max}}$ indicates the maximum angular frequency of the LA or TA mode. For all 2D materials, the Grüneisen parameter can be approximated as 2; it is shown that this value can give a reasonably good estimation for the trend of 2D materials [236]. Following reference [232], here we used the vdW diameter of the oxygen atom (3.04 Å) for the thickness of the layer. Accordingly, the obtained κ for ZnO and AB_{II} structures are $2.75 \text{ Wm}^{-1}\text{K}^{-1}$ and $11.14 \text{ Wm}^{-1}\text{K}^{-1}$, respectively. These results show that κ of the AB_{II} structure is less than monolayer ZnO and MgO.

4.3 Electronic Properties of ZnO/MgO Heterostructures from DFT calculations

In this section, we examined the electronic structures of ZnO/MgO heterostructures. The calculated DFT band structures are shown in Figure 4.3, and the band gap values are summarized in Table 4.2. AA_I and AB_I structures possess direct band gap at the Γ point, but AB_{II} has an indirect band gap. The location of the maximum valence band (VBM) and the minimum of the conduction band (CBM) of the structures indexed by I and II are the same as the ZnO and MgO monolayers, respectively. The DFT band gap of the AA_I is 1.58 eV, which is larger than of AB_I structure by a small amount of 0.01 eV. The indirect band gap of AB_{II} is 1.87 eV. This different characteristic of the band gap is another result of the inter-layer bonding in AB_{II} structure.

The DFT band gap of the AA_I is 1.58 eV, which is larger than of AB_I structure by a small amount of 0.01 eV. The indirect band gap of AB_{II} is 1.87 eV. This different characteristic of the band gap is another result of the inter-layer bonding in AB_{II} structure. For this structure, the direct band gap, which is essential in our BSE analysis, is found at the Γ point and has a value of 2.13 eV. The LDA band gaps for ZnO and MgO have been reported as 1.68 eV and 3.68 eV, respectively [19]. Compared with the large band gap of MgO, the band gaps of the investigated heterostructures are reduced by 57.07% in the case of AA_I, 57.33% in AB_I and 49.20% in AB_{II}. The DFT band gap of the AB_{II} structure is 0.19 eV larger than the ZnO monolayer.

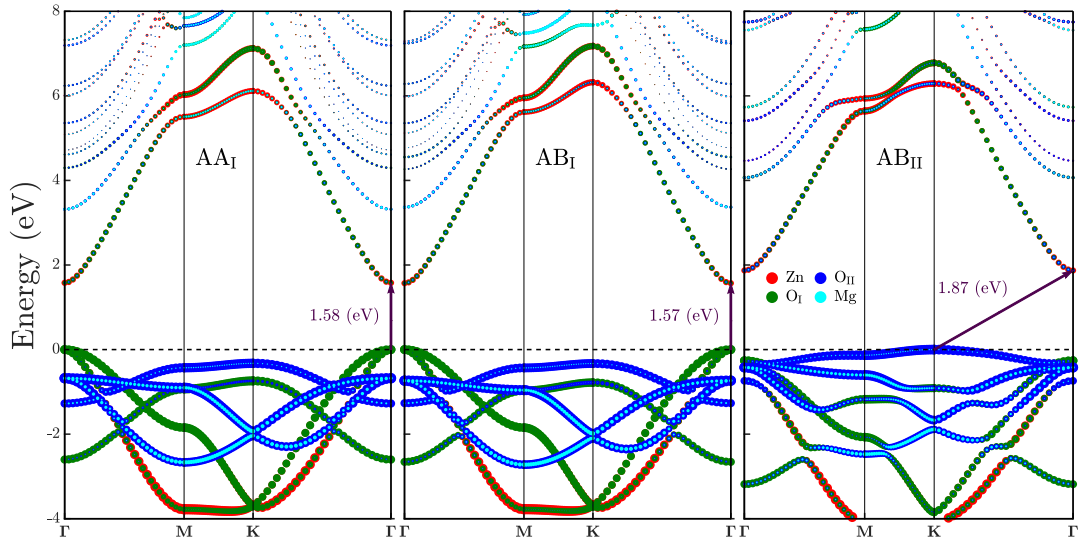


Figure 4.3: Electronic band structures of AA_I, AB_I and AB_{II}. The band energies are shifted so that the maximum of the valence band is located at E=0 eV. The arrows show the band gap.

Table 4.2: Calculated DFT band gap (E_{vdW}), G_0W_0 band gap ($E_{\text{G}_0\text{W}_0}$), first BSE eigenvalue (E_{BSE}) and exciton binding energies (E_{exc}). All energies are in eV. The direct band gap of the AB_{II} structure (4.42 eV) is used for calculation of the exciton binding energy.

Structure	E_{vdW}	$E_{\text{G}_0\text{W}_0}$	E_{BSE}	E_{exc}
AA_{I}	1.58	3.73	2.50	1.23
AB_{I}	1.57	3.70	2.49	1.21
AB_{II}	1.87	4.07	3.05	1.37

The contribution of each atom in the band structure is also displayed in Figure 4.3. It is possible to determine the band alignment types of the considered heterostructures using the obtained band structures. The band alignment of a bilayer structure formed by two different layers A and B can be determined according to the position of VBM, and CBM of each layer [237]. In straddling (type-I) heterostructures $\text{VBM}_{\text{A}} < \text{VBM}_{\text{B}} < \text{CBM}_{\text{B}} < \text{CBM}_{\text{A}}$, hence, electrons and holes are confined in the same region, which can lead to radiative recombinations that are desirable for applications such as light-emitting diodes. In staggered (type-II) heterostructures, $\text{VBM}_{\text{A}} < \text{VBM}_{\text{B}} < \text{CBM}_{\text{A}} < \text{CBM}_{\text{B}}$, therefore VBM and CBM of the type-II heterostructures are located in different layers that enables the separation of electrons and holes. Type-II heterostructures are promising for applications such as photo-detection, photovoltaics, solar cells and lasers. In our cases, as it can be seen from Figure 4.3 in the structures labeled by I, $\text{VBM}_{\text{MgO}} < \text{VBM}_{\text{ZnO}} < \text{CBM}_{\text{ZnO}} < \text{CBM}_{\text{MgO}}$ and thus these structures possess type-I band alignment. Previously type-I band alignment has been predicted for the AA_{I} structure [218], which is consistent with this result. On the other hand, in the AB_{II} structure, $\text{VBM}_{\text{ZnO}} < \text{VBM}_{\text{MgO}} < \text{CBM}_{\text{ZnO}} < \text{CBM}_{\text{MgO}}$ that demonstrates type-II band alignment.

Also, we plotted the total density of states (DOS) and orbital decomposed DOS for each atom in Figure 4.4. It must be pointed out that spheres with Wigner-Seitz radii are used to calculate the partial DOS (PDOS). Since it is impossible to fill the volumes with the non-overlapping spheres and the presence of a large

vacuum above the slab, the values of the PDOS do not sum up precisely to the total DOS.

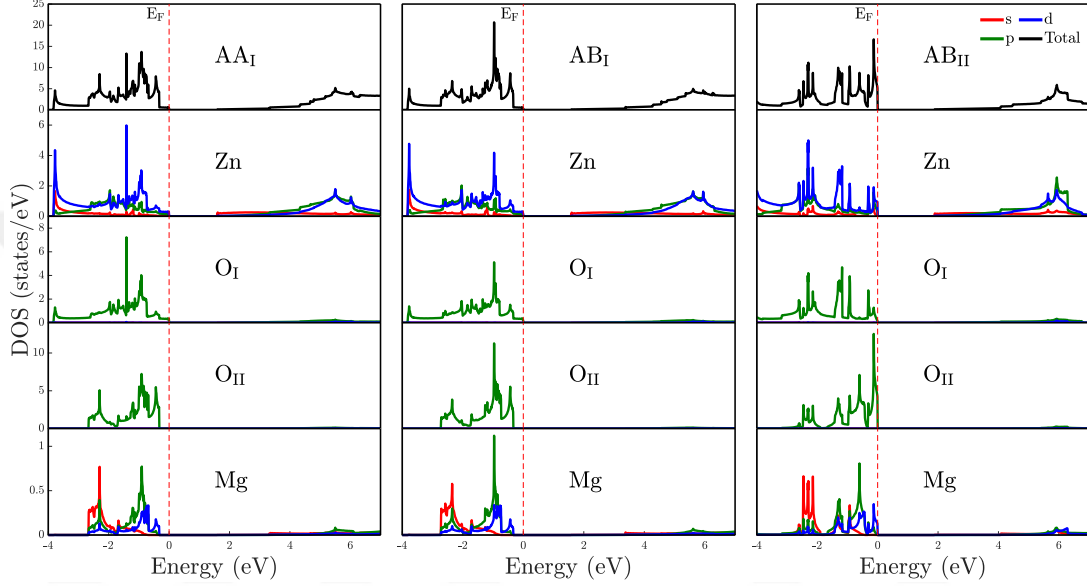


Figure 4.4: Total and partial density states of AA_I , AB_I and AB_{II} structures. Here, O_I and O_{II} are the oxygen atoms in the same layer with Zn and Mg atoms, respectively.

Figure 4.4 shows that in the AB_{II} structure, the top of the valence band is dominated by the orbitals from the MgO layer. Whereas, in the systems labeled by I, the orbitals of the atoms in the ZnO layer assemble the top of the valence band. The Zn atom contributes most to the first conduction band in all structures. These results show that the MgO layer enhances the electron collection in the bonded bilayer, and the ZnO layer serves as an electron transfer layer.

To further understand the nature of the charge transfer in considered structures, we calculated Bader's charges associated with each atom. In Bader analysis, the charge assigned to each atom is estimated using the minima of the charge density between the atoms [238–240]. The obtained Bader charges are presented in Table 4.3. The total charge density is calculated by adding valence and core charges and assuming the charge density maxima is located at the atomic centers [238–240]. The Bader charges are reported as charge transfer on each atom concerning their atomic configurations. Therefore, a negative charge represents

electron surplus, while a positive charge means depletion.

Table 4.3: Calculated Bader charges for each atom in different configurations. O_I and O_{II} are the atoms on ZnO and MgO layers, respectively.

Configuration	Zn	O_I	O_{II}	Mg
AA _I	1.191	-1.199	-1.628	1.636
AB _I	1.187	-1.199	-1.625	1.637
AB _{II}	1.186	-1.242	-1.586	1.642

The Bader charges of the structures labeled by I reveal that approximately 1.19 e is donated by the Zn atom to the O atom in the same layer, which received 1.2 e in total. The charge transfer is slightly larger in the MgO layer as 1.64 e of Mg charge is transferred to O in the same layer, acquiring 1.63 e in total. Hence, there is only 0.01 e transfer from the MgO layer to ZnO in these structures. This result also verifies their vdW character of interlayer interaction in AB_I and AA_I structures. On the other hand, a more mixed situation is observed in the AB_{II} structure. Similar to previous cases, Zn donates 1.19 e and Mg gives away 1.64 e, approximately. However, the O atom of the ZnO layer obtains 1.24 e while the MgO layer O only draws 1.59 e. Therefore, the charge transfer from the MgO layer to ZnO is slightly larger and increases to 0.04 e. This can be elucidated by comparing the bond length of AB_{II} configuration with other structures. According to the lattice parameters summarized in Table 4.1, AB_{II} has a smaller inter-layer separation, and metal atoms are closer to the inter-layer O atoms. These results show a more robust interaction between the layers in AB_{II} structure compatible with bonded inter-layer nature of the heterostructure.

4.4 Electronic and Optical Properties of ZnO/MgO Heterostructures from G_0W_0+BSE

Up to now, we have outlined the electronic properties of the considered structures at the standard DFT level. At this point, we focus on excited states and excitonic

effects for optical properties.

4.4.1 Computational Details of the G_0W_0 and BSE Steps

Following the discussions presented in the previous chapter, we conducted convergence tests to select the parameters for the GW step. An example of convergence tests for choosing the number of bands and plane wave energy cutoff is presented in Figure 4.5. The G_0W_0 band gap is very susceptible to the number of empty bands. Still, the energy cutoff value has an insignificant effect on the band gap of the materials considered in this study. We selected 800 bands and an energy cutoff of 400 eV for plane-wave energy, while 2/3 of this value is used for the energy cutoff for the response function. Following the results of references [162, 165, 166], we selected $19 \times 19 \times 1$ k-point mesh and a vacuum of 30 Å for all structures. The number of frequency grid points is set to 160. We considered 6 occupied bands and 12 conduction bands for solving the BSE. Parameters similar to those selected here were previously used to derive scaling universality between QP band gap and exciton binding energy of 2D materials [165, 166].

4.4.2 QP Band Structures of ZnO/MgO Heterostructures

The band structures estimated using G_0W_0 procedure are depicted in Fig. 4.7. The band gap of the AA_I and AB_I structures by 57.64% and 57.57%, respectively. For the AB_{II} configuration, the indirect band gap is increased by 54.05%, and the direct band gap is risen by 51.81%. These comparable ratios show the equivalent nature of the electron-hole interaction in considered systems. As discussed in detail in the previous chapter, the results of the GW-BSE procedure are sensitive to the computational parameters used. Hence, it is necessary to be careful about the exact quantitative comparison between the results obtained in this work and previous literature reports. The G_0W_0 band gap of monolayer ZnO has been reported to be 4.87 [241], 3.18 [89], 3.01 [187], and 3.98 [242]. In section 3.4.1,

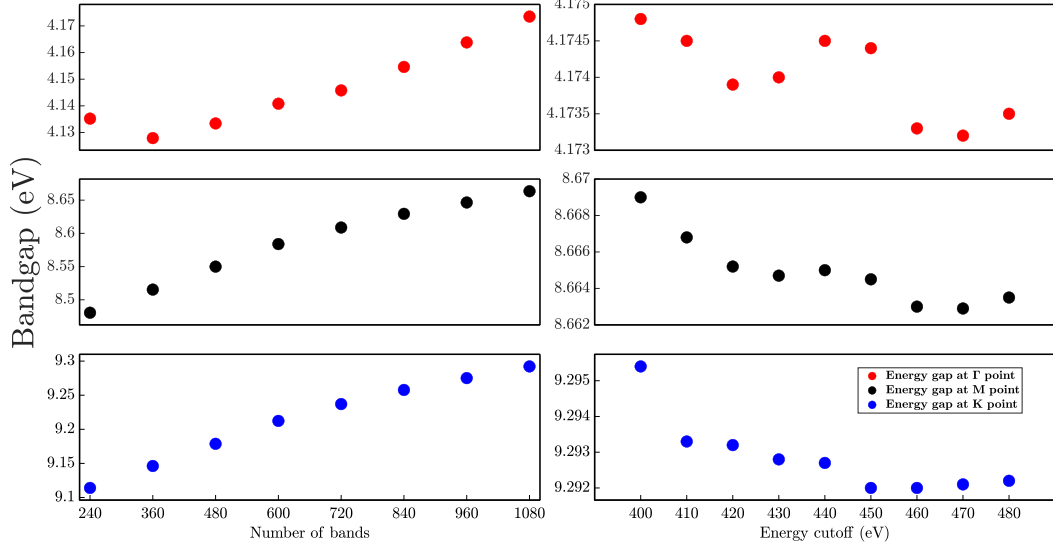


Figure 4.5: Examples of quasiparticle energy convergence tests for AB_I structure with respect to number of bands (left) and energy cutoff (right). For the convergence test of the number of bands, the energy cutoff has been set to 480 eV. For the energy cutoff, 1080 bands are used. In both cases, the number of (imaginary) frequency grid points is chosen as 160, and a vacuum of 30 Å is considered.

employing similar parameters that are used here, we obtained the QP band gap of ZnO as 4.36 eV. Compared with this value, the calculated G_0W_0 band gaps of the AA_I , AB_I and AB_{II} are smaller by 0.63 eV, 0.66 eV and 0.29 eV, respectively. AB_{II} possesses a broader direct band gap by 0.06 eV. The first BSE eigenvalues, E_{BSE} , which are used for the estimation of exciton binding energies, are also reported in Table 3.3. Compared with the exciton binding energy of monolayer ZnO, all MgO/ZnO heterostructures have slightly smaller exciton binding energies. The obtained direct QP band gap ($E_{G_0W_0}^d$), first BSE eigenvalue (E_{BSE}) and exciton binding energies (E_{exc}) of MgO/ZnO heterostructures are compared with monolayer ZnO in Figure 4.6. The first bright exciton of the AB_{II} structure has binding energy (E_{exc}) of 1.37 eV, which is the maximum among all heterostructures.

In Fig. 4.7, the absolute value of BSE coupling coefficients for the first BSE eigenvalue are plotted in fatband representation [196] on top of the G_0W_0 band structure. Apparently, the couplings are strong near the Γ point where the direct

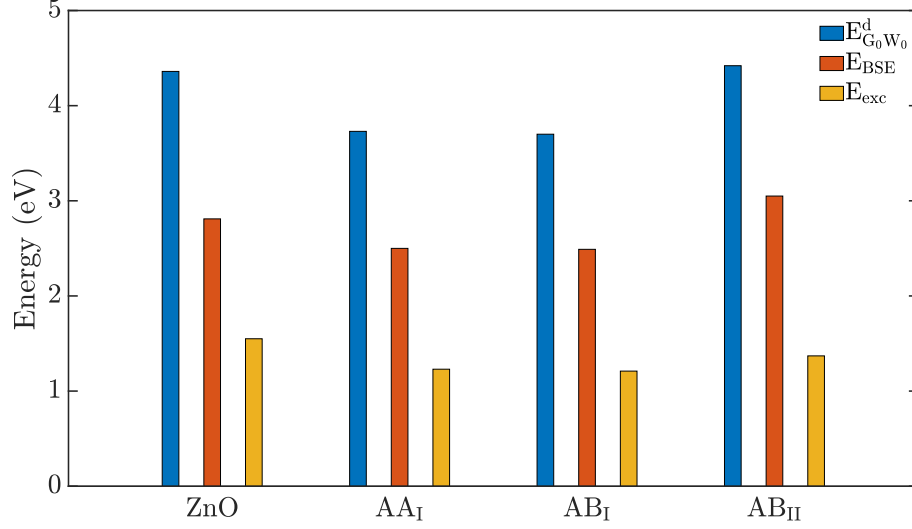


Figure 4.6: QP band gap ($E_{G_0W_0}^d$), first BSE eigenvalue (E_{BSE}) and exciton binding energies (E_{exc}) of MgO/ZnO heterostructures and monolayer ZnO.

band gap is located. It must be pointed out that the first BSE eigenvalue is degenerate in all structures. This is due to the symmetry of the structures, so x and y polarized lights have the same BSE eigenvalues. In the structures labeled by **I**, only two valence bands from the edge of the valence band (bands number 13 and 12) have large coupling values. In the AB_{II} structure, couplings are also noticeable between the third valence band and the first conduction band near the Γ point.

To get more insight into the coupling between electrons and holes, in Fig 4.8, we plotted the absolute values of normalized coupling coefficients between the lowest conduction band (band number 14) and the top three valence bands. The maximum coupling between the two top valence bands and the first conduction band is located at the Γ point in all structures. By moving to the edge of the BZ, the coupling coefficients between the second VB and first CB band disappear faster than those of VBM (band number 13) and CBM (band number 14). For AA_I and AB_I, couplings are insignificant near the Γ point and edges of the BZ. In AB_{II}, the couplings have considerable values near the Γ point. These behaviours

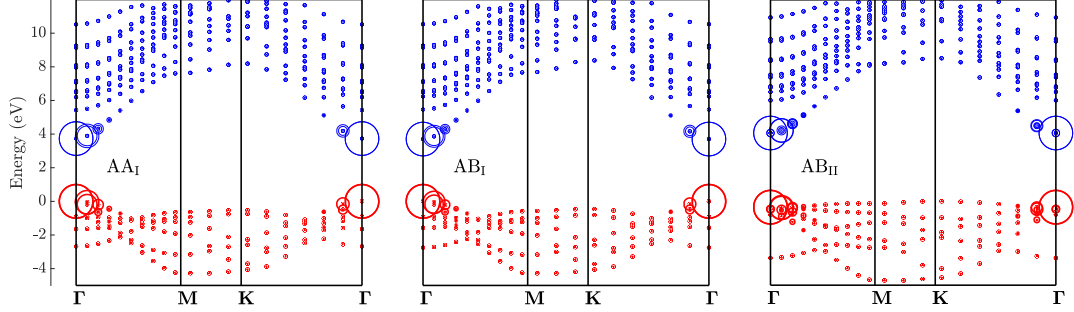


Figure 4.7: The band structures calculated by G_0W_0 approach. The circles show the absolute value of the BSE coupling coefficients. The radii of the circles are scaled according to the maximum coupling coefficient and the gap between the band structure.

are directly related to the shape of the band structure. For example, in AB_I and AA_I , the minimum distance between the third VB and first CB is located where the maximum coupling coefficient is observed.

4.4.3 Optical Properties of ZnO/MgO Heterostructures

The imaginary part of the frequency-dependent dielectric functions ($\text{Im}(\epsilon_x)$) obtained in DFT, GW and BSE steps for x-polarized incident light are presented in Fig. 4.9. The dielectric function of AA_I and AB_I structures are very similar. In these two structures, the blue shifts due to QP effects are reduced by 42.79% and 43.19%. Accordingly, the first peaks of the dielectric functions have appeared in the middle of the visible spectrum. Moreover, the dielectric functions retain a shoulder near the outer edge of the violet light. For x-polarized light, the QP blue shift in the AB_{II} structure is reduced by 46.27%, and the maximum of the $\text{Im}(\epsilon_x)$ is located in the middle of the violet light spectrum. Analogous to other structures, $\text{Im}(\epsilon)_x$ of AB_{II} also has a shoulder near the first peak, which is located at the outer edge of the violet light spectrum.

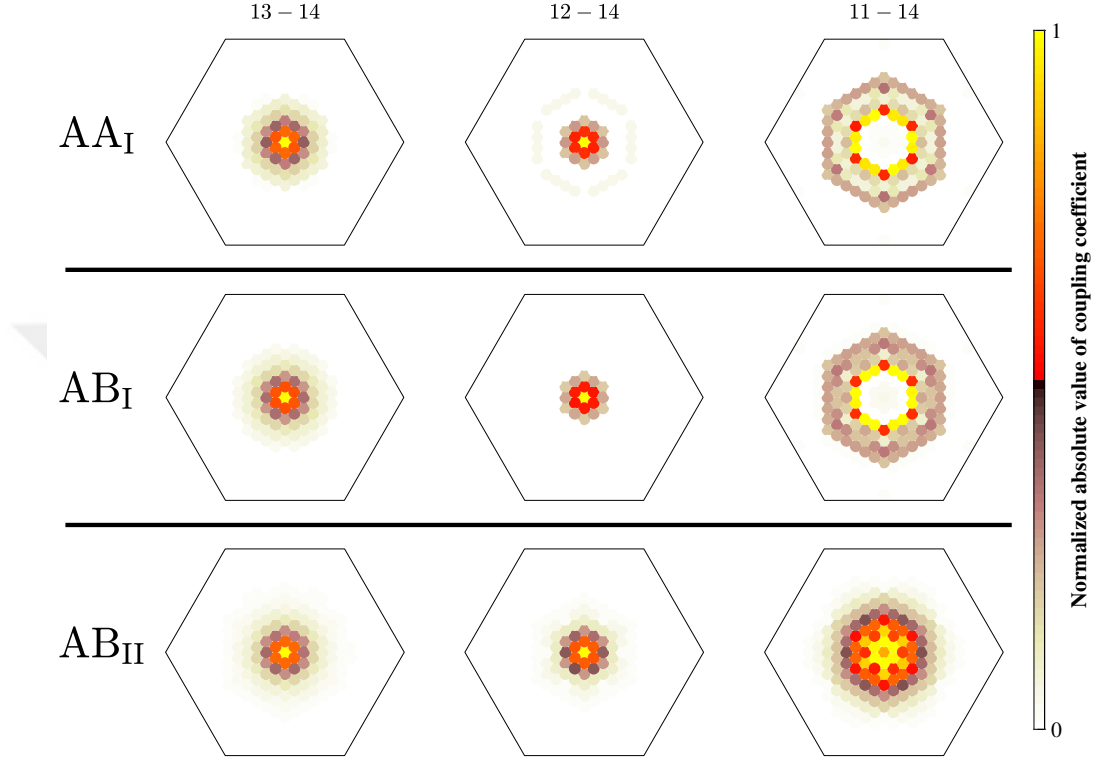


Figure 4.8: Distribution of absolute value of electron-hole coupling coefficients for direct transitions from top three valence bands from the edge (bands number 13, 12 and 11) to first conduction band (band number 14). Hexagons show the first Brillouin zone.

The excitonic effects are also evident in Figure 4.10, where the optical absorbance calculated from different methods is shown. Similar to the imaginary part of the dielectric function, the frequency-dependent absorbance spectra calculated from BSE have a single sharp peak in the visible light region, while there are no such behaviours in the results of the DFT and G_0W_0 .

To further examine the excitonic effects, we plotted oscillator strengths along with the imaginary part of the dielectric function corresponding to x-polarized and z-polarized lights obtained from BSE calculation in Figure 4.11. The oscillator strengths describe the intensity of the transition for BSE eigenvalues and are proportional to the sum of the momentum matrix elements [191, 197]. In all of the considered structures, the most significant oscillator strength emerged at the

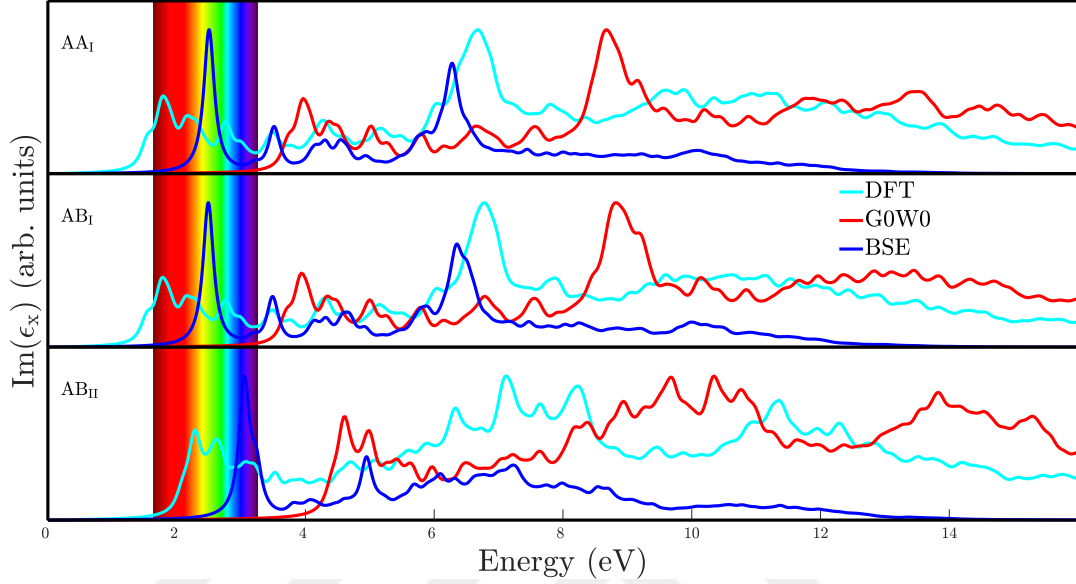


Figure 4.9: The imaginary part of the dielectric function for x-polarized incident light for AA_I and AB_I and AB_{II} configurations. Cyan, red and blue curves are the results of the DFT, G₀W₀ and BSE calculations. The visible light spectrum is also shown (from 1.63 eV to 3.26 eV) for the reference.

energy where the first maximum of the $\text{Im}(\epsilon_x)$ is located. As it is expected, the next non-zero oscillator strengths are precisely following the peaks and shoulders of the dielectric function. In all of the configurations, the first maximum of the $\text{Im}(\epsilon_x)$ is located before first peak of the $\text{Im}(\epsilon_z)$. In the AA_I and AB_I structures, the first peak of the $\text{Im}(\epsilon_z)$ is located after the second maximum of $\text{Im}(\epsilon_x)$. In the AB_{II} structure, the first peak of the $\text{Im}(\epsilon_z)$ is located close to the visible light range and appears before the second peak of the $\text{Im}(\epsilon_x)$. The optical absorbance of the considered structures for the perpendicular incident light is presented in Figure 4.10. All structures retain a single absorbance peak at the optical band gap and possess optical absorbance values similar to ZnO. It must be highlighted that the AB_{II} structure has an indirect band gap, and the top valence band is almost flat near its maximum. Because only direct transitions are considered in this study, and phonon-assisted transitions are neglected, the absorbance of the AB_{II} might show different behaviour at high temperatures.

Finally, the spectral distribution of the dark and bright excitons is presented

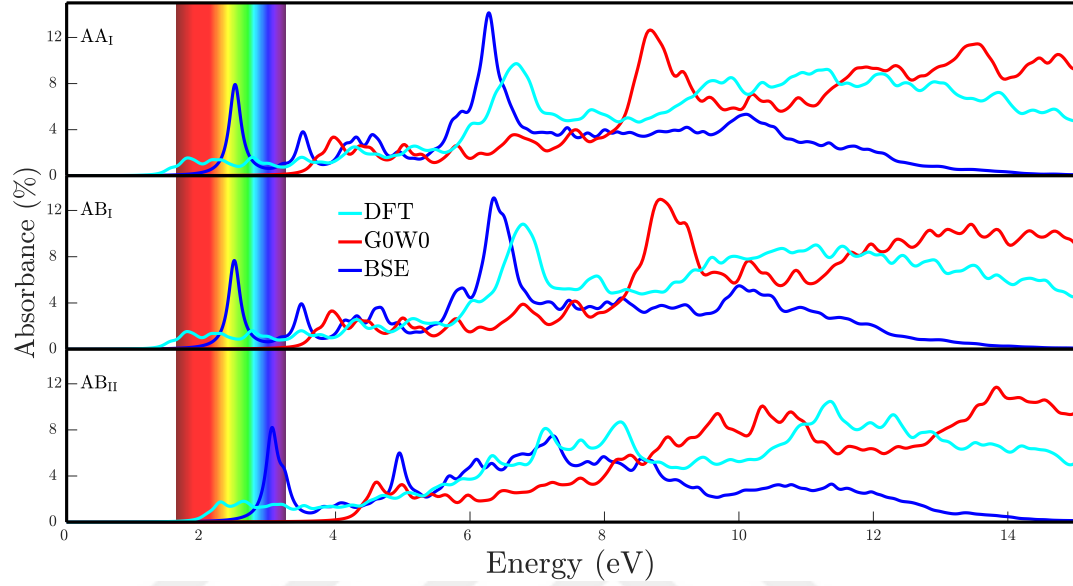


Figure 4.10: The optical absorbance for x-polarized incident light for AA_I and AB_I and AB_{II} configurations. Cyan, red and blue curves are the results of the DFT, G_0W_0 and BSE calculations. The visible light spectrum is also shown (from 1.63 eV to 3.26 eV) for the reference.

in Figure 4.12). As it is discussed in the previous chapter, close energy between the dark and bright excitons can affect the photoluminescence of the nanostructures [168, 243]. Our results reveal that there is not any dark exciton close to the first BSE eigenvalue of the AA_I and AB_I structures. The first dark exciton of AB_{II} structure appears near the third BSE eigenvalues.

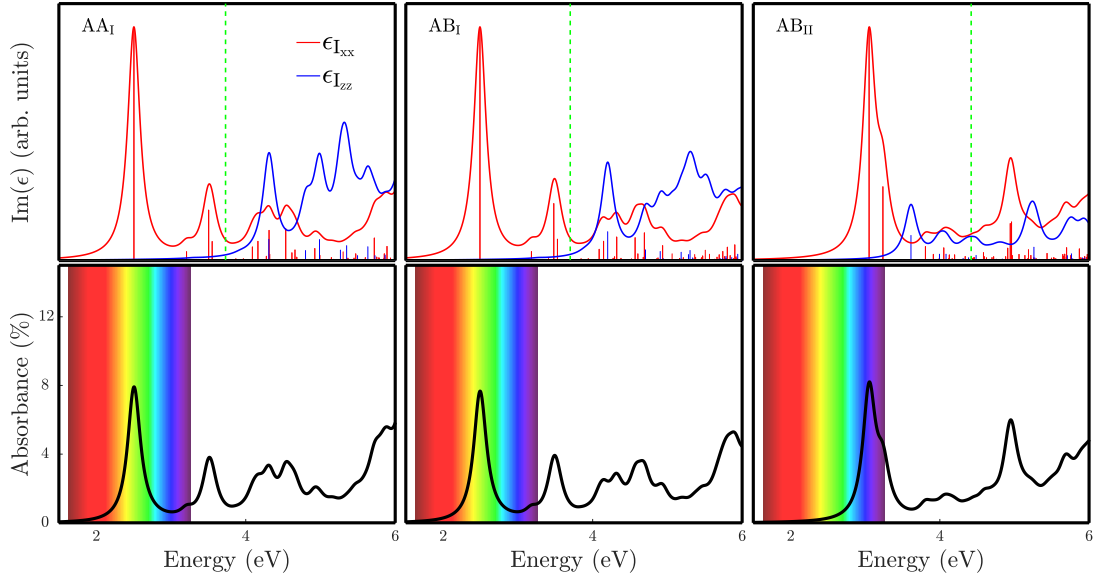


Figure 4.11: (Upper row) The imaginary part of the dielectric function for x- and z-polarized incident lights from BSE calculation. Vertical blue and red lines show the oscillator strengths for x- and z-polarized light, respectively. Dashed green lines show the position of direct G_0W_0 band gap. (Bottom row) Optical absorbance for perpendicular incident light calculated in BSE step.

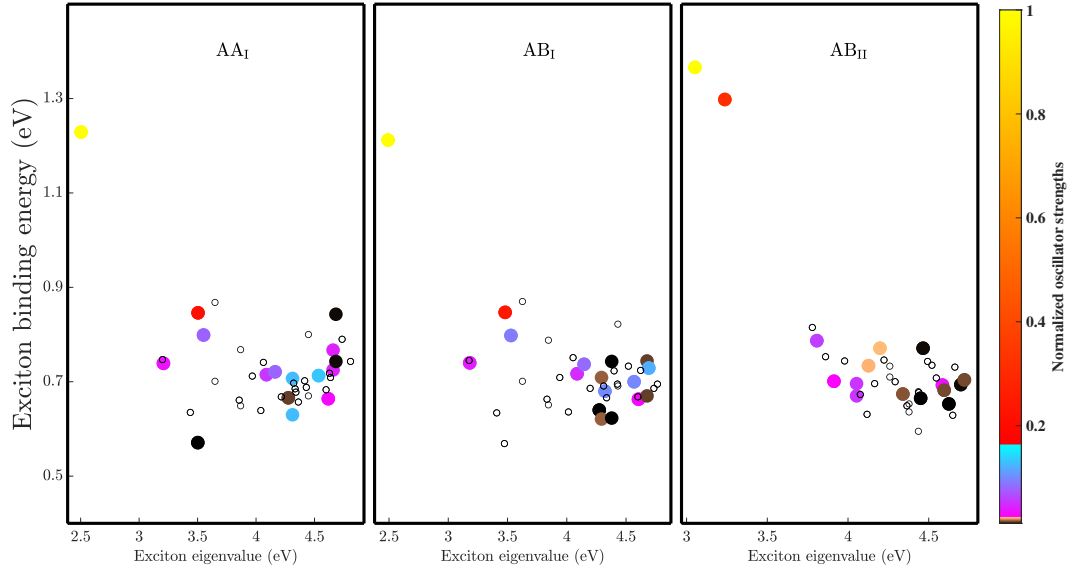


Figure 4.12: The exciton binding energies versus exciton eigenvalues for x-polarized incident light. The color bar shows the normalized oscillator strengths and open black circles are used for displaying zero oscillator strengths.

Chapter 5

Conclusion

Employing GW approximation and solving BSE in TDA, we systematically investigated the optical and electronic properties of nine binary graphene-like II-VI structures: BeO, BaTe, CdO, CaO, CaS, MgO, SrS, SrSe and ZnO.

Our band structure results based on DFT show that in metal oxides, p_x and p_y orbitals of oxygen atom dominate the top valence band, and the s orbital of the metal atom forms the minimum conduction band. In metal chalcogenide, the p_z orbital of the chalcogen atom forms the highest valence. Like metal oxides, the s orbital atom creates the minimum conduction band. These features are directly reflected in the dielectric function as the out-of-plane dielectric function of the metal chalcogenides precedes the in-plane dielectric function.

After performing careful convergence tests, we calculated the GW band structures. The results are very similar to the DFT band structures, and they can be generated by a constant shift equal to the difference between the GW and DFT band gaps. Among the considered materials, the maximum calculated QP band gap is 8.91 eV, which belongs to BeO and the CdO has the minimum QP band gap, equal to 2.15 eV. In alkaline earth metal oxides, the band gap decreases by increasing the atomic number of the metal (Be, Mg, Ca). Group IIB (Zn, Cd) oxides obey a similar trend but have smaller band gaps.

The calculated exciton binding energies show large exciton binding energies ranging from 0.72 eV in CdO to 2.84 eV in BeO. Analysis of BSE coupling coefficients

shows that except for SrS, SrSe and BaTe, the first bright exciton of all other materials is degenerated and formed by coupling between the p_x and p_y orbitals of the valence band and the s orbital of the conduction band. In the case of SrS, SrSe and BaTe, the first bright exciton is formed by coupling between the valence pz and conduction s orbital and arises with parallel incident light. To assess the accuracy of the obtained results, we compared our results with the previously reported scaling universality between the QP band gap and exciton binding energies. Our results are in line with the theoretical prediction. The most considerable deviations are observed in MgO and CaO. These deviations are due to the Coulomb interaction between the periodic images that causes underestimation of the QP band gap. However, as discussed in chapter 3, this effect doesn't significantly affect the optical band gap. Examination of optical absorbance spectra shows that CdO can absorb 7.9% of incident light at its optical band gap, which is close to the energy of the maximum intensity of solar radiation (1.4 eV). Thus CdO is a promising material for solar cells. Besides, ZnO has an optical band gap of 2.81 eV, located in the blue light spectrum. It possesses a sharp absorbance peak in this band gap and can absorb around 9.6% of incident light. The maximum observed absorbance is 28% which occurs in BeO in the ultraviolet region. In chapter 4, we presented a comprehensive study of mechanical, electronic and optical properties of ZnO/MgO vertical heterostructures in four various stackings. Structural relaxations demonstrated two van der Waals and two structures with interlayer binding. We examined their thermodynamic, mechanical, and dynamical stabilities of considered configuration. Although, all systems are thermodynamically and mechanically stable, but phonon dispersion revealed the instability of AA_{II} structures. Other structures have good dynamic stabilities. Remarkably, the AB_{II} structure has no imaginary phonon frequency and thus is stable in zero Kelvin.

Furthermore, we studied the nature of the charge transfer utilizing Bader charge analysis. All structures are n-type semiconductors, and a small amount of charge is transferred from the MgO layer to the ZnO layer.

The DFT band structures show that AA_I and AB_I have direct band gaps, whereas AB_{II} has an indirect band gap. Besides, type-I and type-II band alignments are observed for the structures indexed by I and II, respectively. In all structures, the

s orbital of the Zn atom forms the minimum conduction band. In AA_I and AB_I structures, the orbitals of the O atom of the ZnO layers form the valence band, whereas, in the AB_{II} structure, the orbitals of the Mg atom form the top valence band. Thus in AB_{II}, the ZnO layer acts as the electron transfer layer. Analysis of the absorbance spectra obtained using the GW+BSE approach shows that the structure indexed by I have a close optical band gap in the middle of the visible light range, and AA_{II} owns an optical band gap in the inner verge of violet light. Furthermore, all structures can absorb around 8% of incident light.

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Appendix A

Convergence Tests for Selecting Parameters of G_0W_0

Here the conducted convergence tests for determining plane wave energy cutoff and the number of bands used in G_0W_0 are presented. In all cases, a Γ centered $6 \times 6 \times 1$ k-point mesh is used for sampling the Brillouin zone, 15 Å vacuum is considered above the layers, and the number of frequency points has been set to 256.

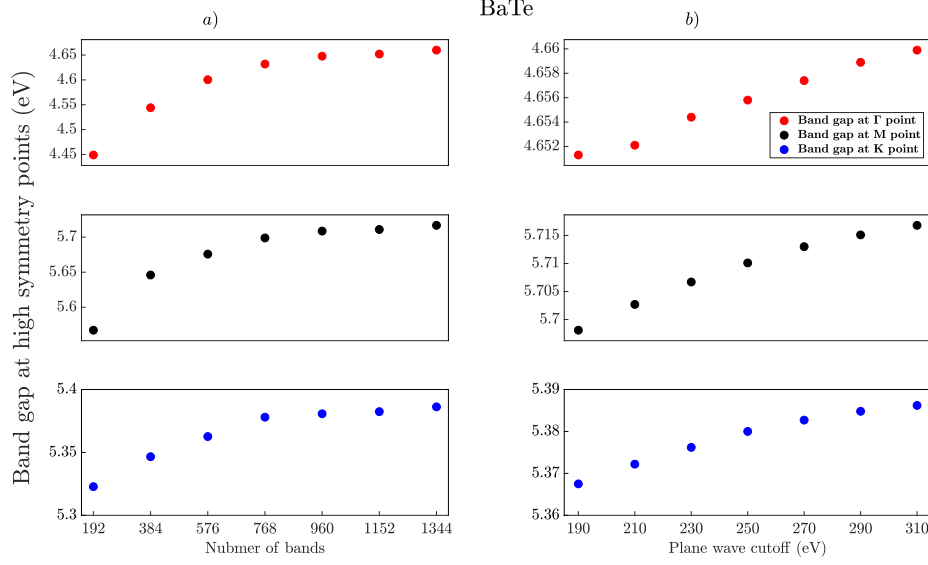


Figure A.1: Convergence of the quasiparticle band gap for BaTe with respect to a) number of bands and b) the screened cutoff (2/3 of the plane wave cutoff).

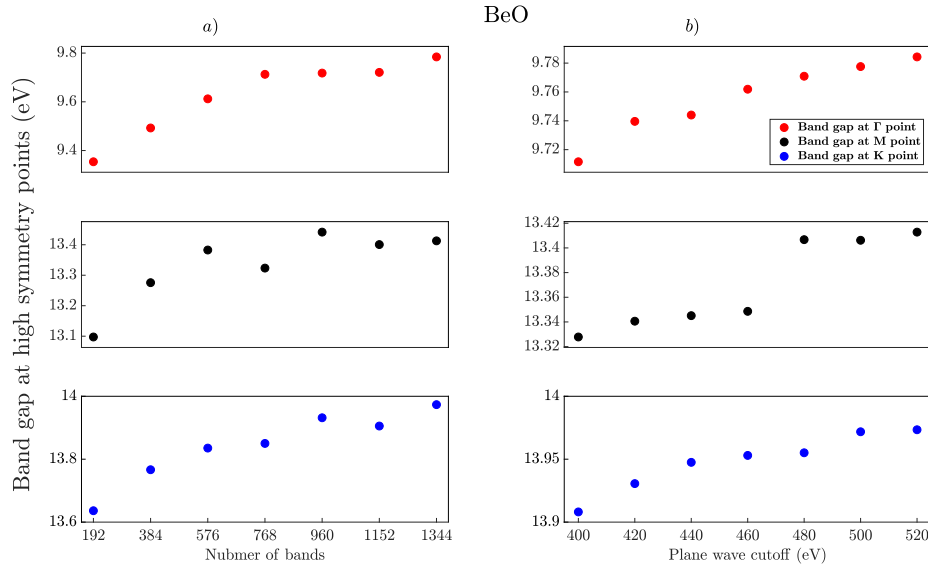


Figure A.2: Convergence of the quasiparticle band gap for BeO with respect to a) number of bands and b) the screened cutoff (2/3 of the plane wave cutoff).

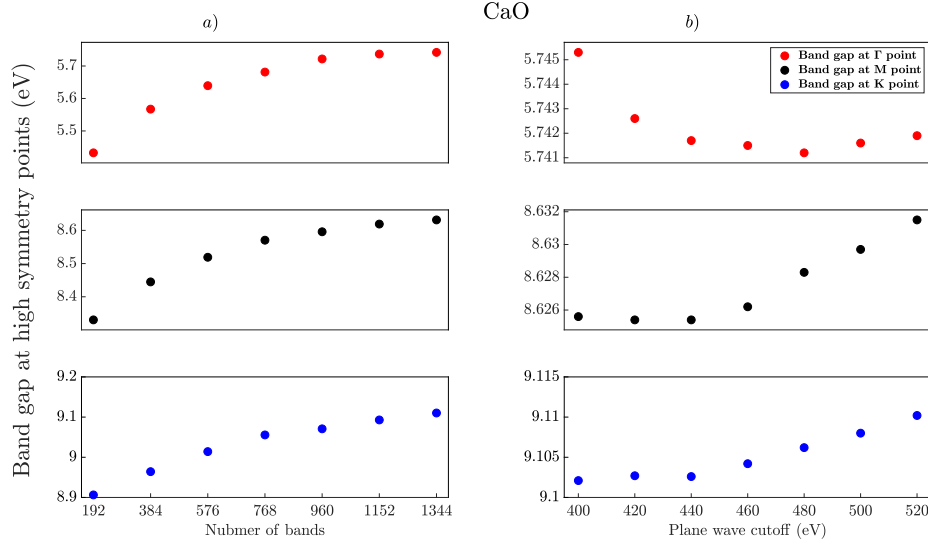


Figure A.3: Convergence of the quasiparticle band gap for CaO with respect to a) number of bands and b) the screened cutoff (2/3 of the plane wave cutoff).

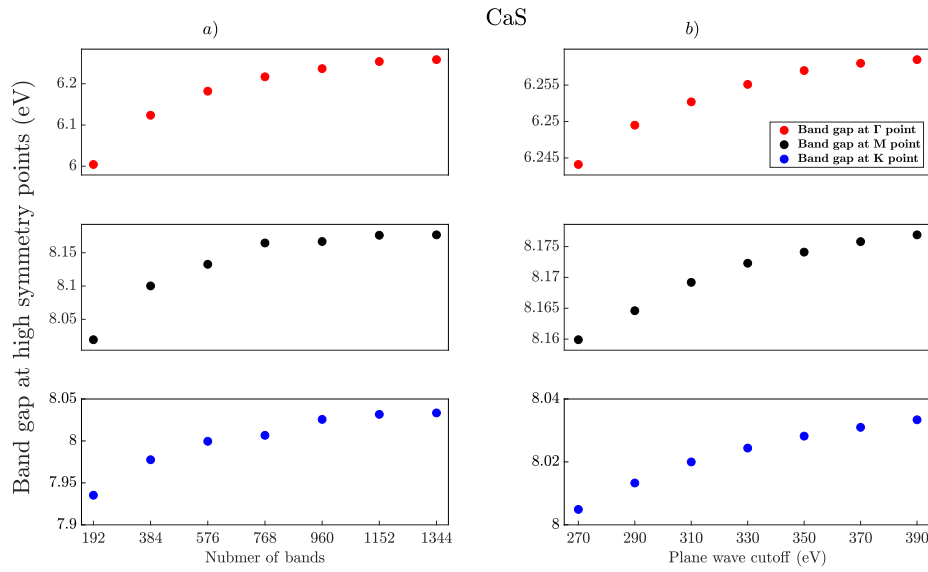


Figure A.4: Convergence of the quasiparticle band gap for CaS with respect to a) number of bands and b) the screened cutoff (2/3 of the plane wave cutoff).

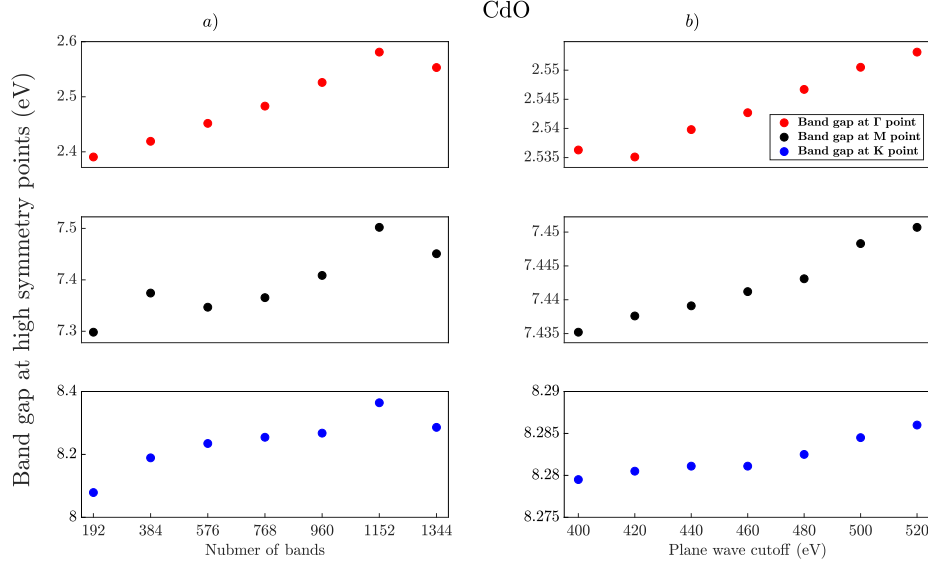


Figure A.5: Convergence of the quasiparticle band gap for CdO with respect to a) number of bands and b) the screened cutoff (2/3 of the plane wave cutoff).

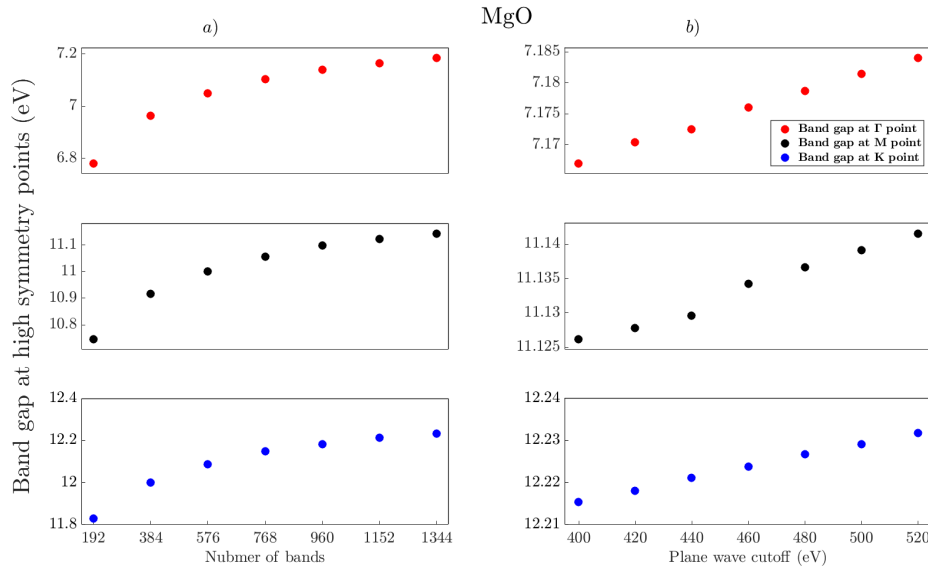


Figure A.6: Convergence of the quasiparticle band gap for MgO with respect to a) number of bands and b) the screened cutoff (2/3 of the plane wave cutoff).

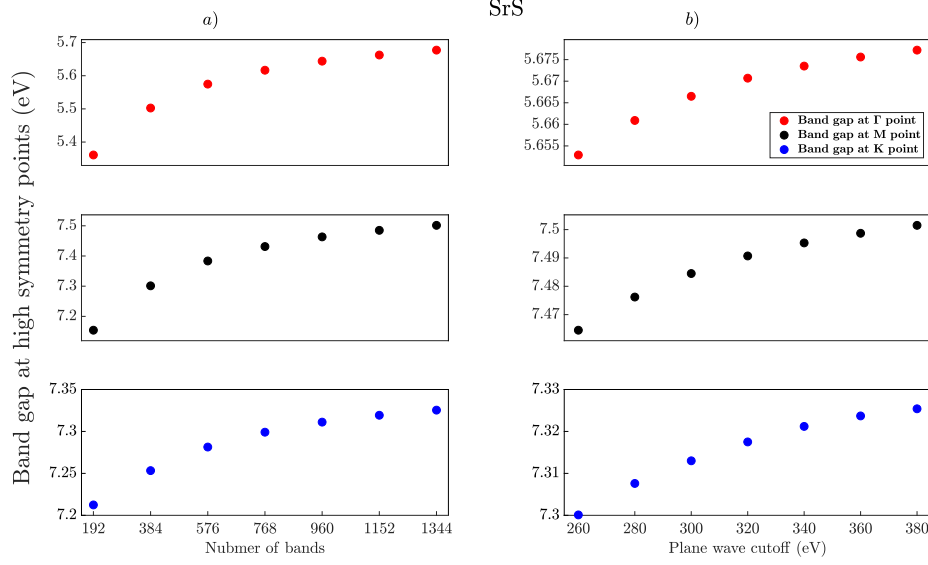


Figure A.7: Convergence of the quasiparticle band gap for SrS with respect to a) number of bands and b) the screened cutoff ($2/3$ of the plane wave cutoff).

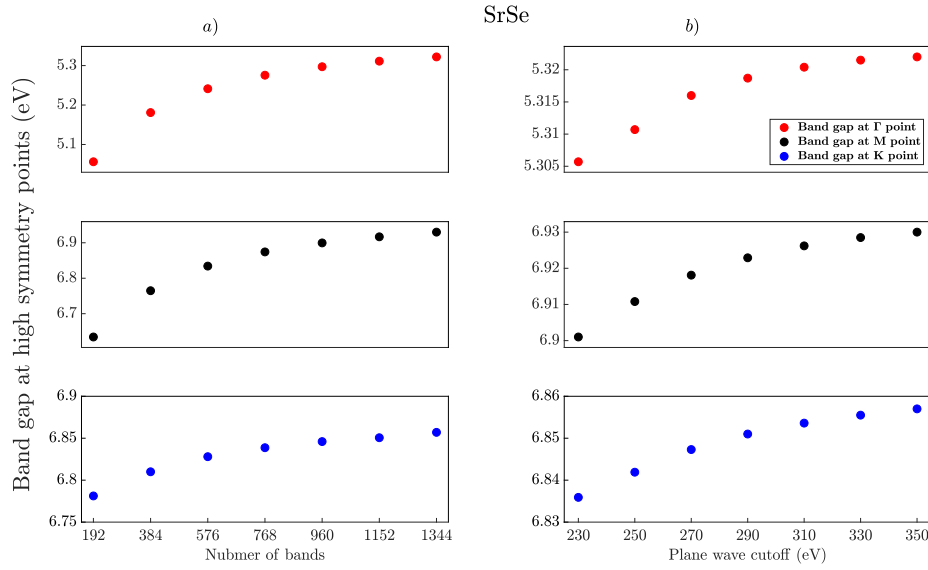


Figure A.8: Convergence of the quasiparticle band gap for SrSe with respect to a) number of bands and b) the screened cutoff ($2/3$ of the plane wave cutoff).

Appendix B

Phonon Dispersion of AA_{II} Structure

As it is mentioned in chapter 4 neglected AA_{II}, because it possess many imaginary frequencies. The phonon dispersion curves of is shown in Figure B.1.

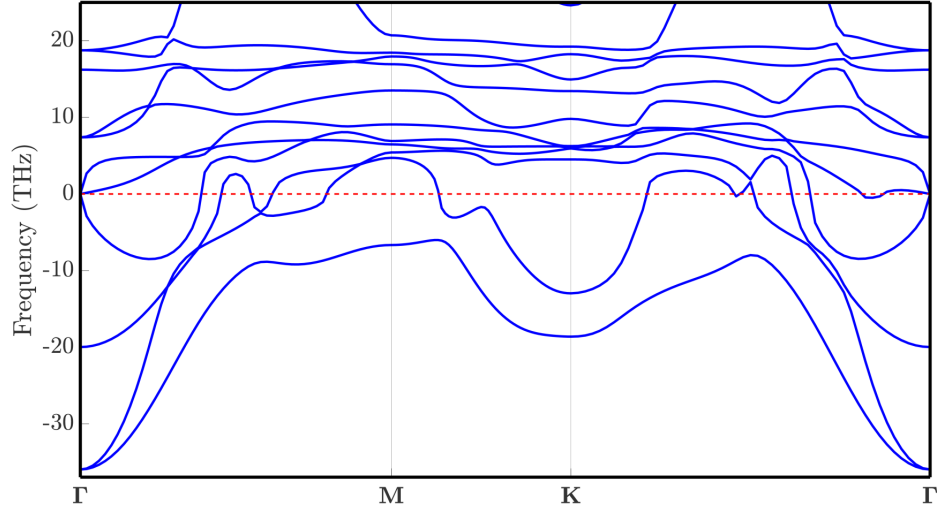


Figure B.1: Phonon dispersion curves of AA_{II} structure.