

## Computational study of chalcogenide based solar energy materials

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## Declaration

I declare that this thesis is my own unaided work. It is being submitted for the award of the Doctor of Philosophy in Physics at the University of Witwatersrand, Johannesburg. It contains the outcome of research under the supervision of Prof. Daniel P. Joubert. No part of this thesis has been or is being submitted for any degree at any other University.



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May 23, 2016

## Dedication

To my late father and my late sister.

### Abstract

Amongst the major technological challenges of the twenty first century is the harvesting of renewable energy sources. We studied the solar cell performance of the ternary compounds  $AgAIX_2$ (X = S, Se and Te) and AgInS<sub>2</sub> as promising materials for meeting this challenge. Structural, electronic and optical properties of the compounds were investigated by means of the density functional theory and many body perturbation theory. Using cohesive energy and enthalpy, we found that among six potential phases of  $AgAIX_2$  and  $AgInS_2$ , the chalcopyrite and the orthorhombic structures were very competitive as zero pressure phases. We predicted a low pressure-induced phase transition from the chalcopyrite phase to a rhombohedral phase. For the chalcopyrite phase, we found that the tetragonal distortion and anion displacement were the cause of the crystal field splitting. The bandgaps from the general gradient approximation PBEsol were underestimated when compared to experiment and accurate bandgaps were obtained from the hybrid functioanl HSE06, the meta-general gradient approximation MBJ and GW approximation. Optical absorption from the Bethe-Selpeter equation indicated the presence of bound exciton in AgAIX $_2$ . We estimated the solar cell performance of the compounds using the Shockley and Queisser model and the spectroscopy limited maximum efficiency approach. We found that apart from AgAIS<sub>2</sub>, the estimated theoretical efficiency of the other compounds was greater that 13 %.

## **Publications**

- G.M. Dongho Nguimdo and Daniel P. Joubert, A density functional (PBE, PBEsol, HSE06) study of the structural, electronic and optical properties of AlAgX<sub>2</sub>(X = S, Se, Te) Eur. Phys. J. B 88 (2015). Ref [1]
- G.M. Dongho Nguimdo, George S. Manyali, Mahmud Abdusalam, Daniel P. Joubert, Structural stability and electronic properties of AgInS<sub>2</sub> under pressure, Eur. Phys. J. B. 89 Ref. [2]
- G.M. Dongho Nguimdo and Daniel P. Joubert, First principle study of structural, thermal and electronic properties of the chalcopyrites AlAgX<sub>2</sub> (X = S, Se, Te) SAIP2014 pp. 602–607. ISBN: 978-0-620-65391-6 (2015). Ref. [3]
- 4. **G.M. Dongho Nguimdo**, Mahmud Abdusalam, Daniel P. Joubert. *Exciton energies of chalcopyrites AgAlX*<sub>2</sub> (X = S, *Se*, *Te*) from GW and BSE calculations, Under review at SAIP2015.
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"A single palm is not sufficent for clapping ,

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## 1. Introduction

#### **1.1** Solar cells: the current status

The harvesting of solar energy has been the fastest growing renewable technique over the last decades. According to the US Department of Energy, the solar energy industry is growing by 2.5% per year [4]. However, it is predicted that fossil fuels will still supply more than 80 % of the world demand in energy by 2040 despite being the most environmental unfriendly way of producing energy [4,5]. Sunlight is an enormous underexploited source of renewable energy. The amount of sunlight received on earth within an hour would be enough to supply the entire world demand of electricity for a year [6]. Unfortunately the energy produced from photovoltaic (PV) solar panel represents less than 5% of the world's consumption. Why is it that a free, clean and an inexhaustible source of energy as such is still not exploited? What is holding back the growth of solar energy? The cost of production and the efficiency are the main factors that have prevented the development of the solar industry. The first generation of PV solar based on silicon wafers has an efficiency between (15-20) %, but the cost of production is very high. The second generation also known as thin film solar cells, are based on amorphous and polycrystalline materials, unlike the first generation. Hence it is more cost effective compared to the fist generation, but is not as efficient as the former with a typical performance of (10-15) %.

Fossil fuel lobbyists sometimes argue that solar PV is way worse for land use than any other form of energy harvesting [7,8]. However, it has been shown recently that more land has been lost due to oil and gas well pads, storage tanks and associated roads developed in North America since the year 2000 [8,9]. It is predicted that by using PV with performance of about 20 %, only 5.5 % of the land area of the uninhabited part of Sahara desert covered with PV would power the whole world [10]. Moreover, if we look at the impact of each of the energy sources, fossil fuels put the global ecosystem in danger. The carbon dioxide released from the combustion of fossil energy

leads to global warming of the planet unlike renewable energy. It is true that solar technology requires very huge initial investment, but it is profitable in the long term. It is now a global concern to reduce the use of fossil energy and develop alternative sources of energy based on renewable energy. Leaders around the world specially in developing countries such as China and India have started making considerable investment in solar energy. In the first quarter of 2015 for example, China added the equivalent of the total French solar capacity to its grid [11]. More than 3.5 million solar home systems have recently been installed in Bangladesh [11]. In the last six years, solar panels have dropped from \$1.90 to less than \$1 per watt today [12,13]. However, in order to reach an affordable solar technology production, there is a need for alternative materials which could meet both the challenges of good efficiency and cost effectiveness. These materials form the third generation of the PV solar cells.

## 1.2 Ternary compounds based on transition metal chalcogenides

Ternary compounds based on transition metal chalcogenides (TMCs) are some of the promising materials which have been explored as potential candidates for the third generation of solar cells. They are a combination of some elements from group I, III, IV and VI. Their general formula is  $A_x B_y X_z$  with A = (Cu, Ag, Au); B = (AI, Ga, In); X = (S, Se, Te) and x, y and  $z \in \mathbb{N}^*$ . They crystallise in different structures and the most common ones are the ABX<sub>2</sub> in tetragonal, or-thorhombic, hexagonal and rhombehodral structures [1,14–19] and AB<sub>5</sub>X<sub>8</sub> with the space group  $F\bar{4}3m$  and  $P\bar{4}2ma$  in cubic and tetragonal system respectively [20–22]. The ABX<sub>2</sub> chalcopyrites for example have been subjected to numerous studies due to their potential technological applications for the harvesting of the solar energy and electronic components [14, 23–31]. Because of their anisotropy, they are also birefringent materials and can also find applications in non linear

optics process including second harmonic generation [32, 33]. In solar cell applications, ternary TMCs are predicted to have a life-time in outer space fifty times longer than that of Si-based solar cells [1, 34]. Moreover, with their high flexibility and low weight, they could make a good alternative to Si-based materials in the electronics industry [35]. Wide bandgap chalcopyrites such as AgAIX<sub>2</sub> (X = S, Se, Te) are difficult to use as single junction solar cells. However, it has been shown recently that the efficiency of a solar cell could be increased by making a tandem (multi-junction) solar cell [36]. It consists of an association of single junction solar cells of different bandgaps which allow capturing light with different wavelengths and thus increasing the efficiency. Their electronic and optical properties can also be tuned easily by doping or by stress [17, 37–41]. The AgInX<sub>2</sub> is also very attractive group of ternary TMCs and could be used as visible light absorber layers and outer shell sensitizers of multi junction solar cells because of its high absorption coefficients [42, 43].

#### **1.3** Objectives of the thesis

Motivated by their potential applications in the solar cell industry, a systematic theoretical and computational study of the structural, electronic and optical properties of the ternary compound based on TMCs as possible component of solar-energy harvests need to be done. We are specifically interested in the AlAgX<sub>2</sub> and AgInS<sub>2</sub> families. Very few studies on these groups have been performed so far contrary to their analogues copper indium Gallium selenide (GIGS) and copper zinc tin sulfide (CZTS) despite the similarities. The Density Functional Theory (DFT) and Many Body Perturbation Theory (MBPT) will be used as the main tools of the study. In the first stage, we will perform a structural phase stability of different potential phases of AlAgX<sub>2</sub> and AgInS<sub>2</sub>. From the energetic, dynamical, mechanical and elastic stability studies, the most stable phases will be identified. Further studies including electronic and optical properties will be carried out. Finally, we will estimate the solar cell performance of those phases.

#### 1.4 Thesis outline

This thesis is organised as follows: In Chapter 1, we give an idea of the current status of the solar energy and motivation for our study. An overview of the Density Functional Theory (DFT) approach is presented in Chapter 2. Chapters 3 and 4 provide some background information about the different DFT exchange-correlation approximations and MBPT. More details about the calculation methods are given in Chapter 5. Chapter 6 provides a description of the structure under investigation. Then, Chapters 7 and 8 are dedicated to the structural, electronic and optical properties of AgAlX<sub>2</sub> and AgInS<sub>2</sub>, respectively. Based on results from the preceding chapters, estimation of the solar cells performance of the compounds using different approximations is presented in Chapter 9. Finally, we summarise the results of our work and give the direction for future works in Chapter 10. Detailed information on some useful aspects of the work is given in Appendices.

## Part I

# Theoretical methods and outline of the calculations

## 2. The many-body problem: density functional theory approach

The prediction of the collective behaviour of a large number of interacting particles constituting the matter is still a cumbersome task for the scientific community. The complexity of such problem can be circumvented by decoupling the movement of the more massive nuclei from that of electron. Each of the two sets of particles, is by itself a many body problem. Solving the many electron problem is referred to as the electronic structure study and it can help predict the properties (structural, mechanical, dynamical, thermodynamic, electronic and optical) of a material. Density Functional Theory (DFT) turns out to be, if not only, the most popular and most successful quantum mechanical approach to solve such problem. Before introducing DFT, let us recall the many-body problem and DFT predecessor methods.

#### 2.1 Many-body problem

The many-body problem refers to the problem of solving the Schrödinger equation for a system of atoms and electrons. The energy of such a system is given by the stationary Schrödinger equation:

$$H\psi\left(\mathbf{R}_{1}\ldots,\mathbf{R}_{N},\mathbf{r}_{1},\ldots,\mathbf{r}_{n}\right)=E\psi\left(\mathbf{R}_{1},\ldots,\mathbf{R}_{N},\mathbf{r}_{1},\ldots,\mathbf{r}_{n}\right),$$
(2.1.1)

where  $\mathbf{R}_i$  is the position of the nucleus *i*,  $\mathbf{r}_i$  the position of the electron *i*, N and n are the

numbers of nuclei and electrons of the system respectively and

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2M_i} \nabla_{\mathbf{R}_i}^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1\\i \neq j}}^{N} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} - \sum_{i=1}^{n} \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{i=1}^{n} \sum_{\substack{j=1\\i \neq j}}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|^2} - \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} = T_n + V_{nn} + T_e + V_{ee} + V_{en}.$$
(2.1.2)

 $T_n$  and  $V_{nn}$  are respectively, the kinetic energy and the potential energy of the nuclei.  $T_e$  and  $V_{ee}$  are referred to as the kinetic energy and potential energy of the electrons respectively. The last term  $V_{en}$  is the nuclei-electron interaction. Equation 2.1.1 is very complicated to solve exactly due numerous interactions between particles and it is most often approximated. The most important approximation used is the Born-Oppenheimer approximation [44]. This approximation uses the fact that the nucleus is about 2000 times heavier than the electron and the time scales of their motions are very different. Hence, the wave-function of Equation 2.1.1 can be approximated as a product of two wave-functions:

$$\psi\left(\mathbf{r}_{i},\mathbf{R}_{j}\right)=\psi_{e}\left(\mathbf{r}_{i},\mathbf{R}_{j}\right)\psi_{n}\left(\mathbf{R}_{j}\right),$$
(2.1.3)

where  $\psi_e(\mathbf{r}_i, \mathbf{R}_j)$  is the electron wave-function and  $\psi_n(\mathbf{R}_j)$  the nucleus wave-function. Substituting (2.1.3) into (2.1.1) yields the set of two equations:

$$H_e \psi_e \left( \mathbf{r}_i; \mathbf{R}_j \right) = \left( T_e + V_{ee} + V_{en} \right) \psi_e \left( \mathbf{r}_i; \mathbf{R}_j \right)$$

$$= E_e \psi_e \left( \mathbf{r}_i; \mathbf{R}_j \right),$$

$$H_n \psi_n \left( \mathbf{R}_j \right) = \left( T_n + V_{nn} + E_e \right) \psi_n \left( \mathbf{R}_j \right)$$

$$= E \psi_n \left( \mathbf{R}_j \right).$$
(2.1.4a)
(2.1.4b)

Equation 2.1.4a describes the quantum mechanical behaviour of electrons in solids with  $V_{en}$  the interaction between electrons and nuclei. We can consider it as an external field  $V_{ext}$  of a fixed

nuclei in which the electrons (quantum particles) are moving.

$$H_e = T_e + V_{ee} + V_{ext}.$$
 (2.1.5)

Up to this point, the many electron problem is still difficult to solve because the wave-function describing a particle does not only depend on the particle itself, but also on what an electron is doing with each of the other electrons and nuclei in the system. Over the years, the challenge of the study of electronic structure has been to solve this problem exactly. Many approaches have been developed such as: Hartree-Fock approach, Thomas-Fermi approach and DFT. An overview of these approaches will be discussed in the next section.

#### 2.2 The Hartree-Fock approach

In the Hartree approximation, electrons are treated as a fictitious non-interacting particles. The Hamiltonian can be rewritten as:

$$H = \sum_{\alpha}^{N} h_{\alpha} \tag{2.2.1}$$

where  $h_{\alpha}$  is the sum of the kinetic energy and potential energy of a single electron. The wavefunction associated to this new Hamiltionian is the product of the wave-functions of a single electron also known as a Hartree product [45]

$$\phi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, ..., \mathbf{x}_N) = \psi_1(\mathbf{x}_1) \cdot \psi_2(\mathbf{x}_2) \cdot \psi_3(\mathbf{x}_3) \dots \cdot \psi_N(\mathbf{x}_N)$$
(2.2.2)

where  $\mathbf{x}_i$  is a generalized coordinate that includes spatial as well as spin degrees of freedom  $(\psi(\mathbf{x}) = \psi(\mathbf{r}) | \sigma \rangle)$ . Hence, the energy of a single electron at the spin orbital j is given by

$$h_j \psi_j(\mathbf{x}_i) = \varepsilon_j \psi_j(\mathbf{x}_i). \tag{2.2.3}$$

Thus, the total energy of the non-interacting electron system is the sum of the energies of the N non-interaction electron:

$$\langle \phi \left( \mathbf{x}_{1}, \mathbf{x}_{2}, \mathbf{x}_{3}, \dots, \mathbf{x}_{N} \right) \mid H \mid \phi \left( \mathbf{x}_{1}, \mathbf{x}_{2}, \mathbf{x}_{3}, \dots, \mathbf{x}_{N} \right) \rangle = \sum_{ij}^{N} \langle \phi \left( \mathbf{x}_{1}, \mathbf{x}_{2}, \mathbf{x}_{3}, \dots, \mathbf{x}_{N} \right) \mid h_{j_{k}} \mid \phi \left( \mathbf{x}_{1}, \mathbf{x}_{2}, \mathbf{x}_{3}, \dots, \mathbf{x}_{N} \right) \rangle$$

$$= \varepsilon_{1} + \varepsilon_{2} + \varepsilon_{3} + \dots + \varepsilon_{N}$$

$$= E.$$

$$(2.2.4)$$

Unfortunately, this Hartree model fails because it does not account for the Pauli exclusion principle according to which the true wave-function of any fermionic system has to be antisymmetric with respect to particle exchange i.e.

$$\phi\left(\mathbf{x}_{1},\mathbf{x}_{2},\mathbf{x}_{3},\cdots,\mathbf{x}_{k},\cdots,\mathbf{x}_{p},\cdots,\mathbf{x}_{N}\right) = -\phi\left(\mathbf{x}_{N},\mathbf{x}_{2},\mathbf{x}_{3},\cdots,\mathbf{x}_{k},\cdots,\mathbf{x}_{p},\cdots,\mathbf{x}_{1}\right) = (2.2.5)$$

The Slater determinant is an antisymmetric wave-function [46, 47] and therefore can be used for describing such a system. For an N electron system, it is the determinant of an N x N matrix of the single electron wave-function:

$$\phi(\mathbf{x}_{1}, \mathbf{x}_{2}, \dots, \mathbf{x}_{N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{1}(\mathbf{x}_{1}) & \psi_{2}(\mathbf{x}_{1}) & \cdots & \psi_{N}(\mathbf{x}_{1}) \\ \psi_{1}(\mathbf{x}_{2}) & \psi_{2}(\mathbf{x}_{2}) & \cdots & \psi_{N}(\mathbf{x}_{2}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{1}(\mathbf{x}_{N}) & \psi_{2}(\mathbf{x}_{N}) & \cdots & \psi_{N}(\mathbf{x}_{N}) \end{vmatrix}.$$
(2.2.6)

ī.

For illustration, consider the two electron system, Equation 2.2.6 then becomes

$$\phi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \left[ \psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2) - \psi_1(\mathbf{x}_2) \psi_2(\mathbf{x}_1) \right].$$
(2.2.7)

By exchanging the two electrons, the new wave-function is

$$\phi(\mathbf{x}_{2}, \mathbf{x}_{1}) = \frac{1}{\sqrt{2}} [\psi_{1}(\mathbf{x}_{2})\psi_{2}(\mathbf{x}_{1}) - \psi_{1}(\mathbf{x}_{1})\psi_{2}(\mathbf{x}_{2})]$$

$$= -\phi(\mathbf{x}_{1}, \mathbf{x}_{2}).$$
(2.2.8)

If we force two electrons to be on the same state, this yield

$$\phi(\mathbf{x}_{1}, \mathbf{x}_{1}) = \frac{1}{\sqrt{2}} [\psi_{1}(\mathbf{x}_{1})\psi_{2}(\mathbf{x}_{1}) - \psi_{1}(\mathbf{x}_{1})\psi_{2}(\mathbf{x}_{1})]$$

$$= 0.$$
(2.2.9)

The Slater determinant is then an exact wave-function of N, non interacting, single particles moving in the field of the effective potential  $V_{HF}$  which is the average repulsive potential experienced by an electron due to the (N - 1) other electrons and the nuclei. The Hartree-Fock (HF) equation is given by [48]

$$\begin{bmatrix} -\frac{1}{2}\nabla_i^2 + \sum_K^n \frac{1}{|\mathbf{R}_K - \mathbf{r}_i|} \end{bmatrix} \psi_{\alpha}(\mathbf{r}_i) + \begin{bmatrix} \sum_{\beta}^{occ} \int d\mathbf{r}_j \psi_{\beta}^*(\mathbf{r}_j) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \psi_{\beta}(\mathbf{r}_j) \end{bmatrix} \psi_{\alpha}(\mathbf{r}_i) \\ - \begin{bmatrix} \sum_{\beta}^{occ} \int d\mathbf{r}_j \psi_{\beta}^*(\mathbf{r}_j) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \psi_{\alpha}(\mathbf{r}_j) \end{bmatrix} \psi_{\beta}(\mathbf{r}_i) = E_i \psi_{\alpha}(\mathbf{r}_i).$$
(2.2.10)

The first term defines the kinetic energy and the potential due to the interaction between a single electron and the collection of atomic nuclei. The second term is the Coulomb electron-electron interaction also called the Hartree potential  $V_H$ , and the last term is the Fock or exchange term  $V_x$  due to the Pauli principle through the anti-symmetric nature of the wave-function. It is a non-local term and is very important because it cancels out the self interaction introduced by the second term. The best Slater determinant for approximating the energy is the one which minimises the expectation value of the HF Hamiltonian through the variational principle.

$$E_{HF} = \min_{\psi} \Big[ \langle \psi | T + V_H + V_x + V_{ext} | \psi \rangle \Big].$$
(2.2.11)

However, the HF method usually fails to fully describe the many electron system because it does not included the correlation effects [49]. The energy obtained from the HF method is higher than the exact ground-state energy of the system. The difference between the two energies is termed as correlation energy  $E_c$ . In the HF approach, each electron feels the average electrostatic repulsion of the others. This electric field does not included the screening effect [49] which exists in real system. Instead, it is the direct unscreened bare coulomb interaction. The screening effect comes from the fact that the interaction between two electron is weaken by the presence of other electrons in the system. The average electrostatic repulsion tends to make the electrons more closer than they should be in the real electron system and thus leads to the overestimation of the electron-electron repulsion. This is known as dynamical correlation. One could understand why the HF methods works better for atoms and small molecules where the screening effect is not as large as it is in solids [50].

Another limitation of the HF approach is the static correlation effect. A single Slater determinant is not always a suitable way for describing the many-body wave-function. There are other possible antisymmetric wave-functions which are not necessary written as Slater determinant. Hence, the Slater determinant constitutes only a subset of all the possible antisymmetric wave-functions that can be use for describing the many electron system. The HF approach can be improved by using a combination of several Slater determinants, but the search for the complete basis set of such wave-functions is a very demanding task. An alternative way of describing the behaviour of electron system is therefore necessary.

#### 2.3 The density functional theory

''...density functional theory is evident by the fact that one equation for the density is remarkably simpler than the full many-body Schrödinger equation that involves 3N degrees of freedom for N electron.''

Richard Martin [51].

Since the conception and the proof of the fundamental Density Functional Theory (DFT) theorems by Hohenberg and Kohn, a huge effort has been made to fully elaborated the theory of DFT such

that it cannot be covered in details in a thesis. Thus, the discussion in this section is just an overview of DFT. For more details, the readers are referred to the references [45–54] an references therein. We will start by introducing the notion of electronic density which is the cornerstone of DFT.

#### 2.3.1 The Notion of electronic density and the Thomas–Fermi model

The wave-function describing the state of one electron within a many-body system of interacting particles is coupled with that of others and the many-body wave-function of the N particles is explicitly written as:

$$\phi(\mathbf{r}\sigma) = \phi\left(\mathbf{r}_{1}\sigma_{1}, \mathbf{r}_{2}\sigma_{2}, \mathbf{r}_{3}\sigma_{3}, \dots, \mathbf{r}_{N}\sigma_{N}\right)$$
(2.3.1)

with  $\mathbf{r}_i$  and  $\sigma_i$  the space and the spin coordinates of the  $i^{th}$  particle. The number of electron with spin  $\sigma$  within the region  $d\mathbf{r}$  around the point  $\mathbf{r}$  is defined by  $n(\mathbf{r}, \sigma)d\mathbf{r}$  and the probability of finding electrons in that region is a multiple integral over spin and space coordinates defined as:

$$n(\mathbf{r},\sigma) = N \sum_{\sigma_2,\sigma_3,\dots,\sigma_N} \int d\mathbf{r}_2 \int d\mathbf{r}_3 \dots \int d\mathbf{r}_N |\phi(\mathbf{r}\sigma,\mathbf{r}_2\sigma_2,\mathbf{r}_3\sigma_3,\dots,\mathbf{r}_N\sigma_N)|^2$$
(2.3.2)

with

$$\widehat{n}(\mathbf{r},\sigma) = \sum_{k=1}^{N} \delta(\mathbf{r}_{k} - \mathbf{r}) \delta(\sigma_{k} - \sigma)$$
(2.3.3)

as the density operator and

$$N = \sum_{\sigma} \int d\mathbf{r} \ n(\mathbf{r}, \sigma)$$
(2.3.4)

as the total number of electron. Hence, the state of an electron is completely defined by one parameter instead of the multi variable wave-function. The density contained exactly the same

information as the wave-function with the advantage of been easy to manipulate. Thomas and Fermi were the first to use this notion to estimate the energy of the many electron system. In their approximation, the system is considered as a homogeneous electron gas with uniform density at each point of the space. The electron-electron interaction is taken as the classical bare Coulomb repulsion only. The exchange and the correlation are neglected. Thus, the energy of such a system is written as [51]

$$E_{TF}[n(\mathbf{r})] = T_{TF}[n(\mathbf{r})] + \frac{1}{2} \int d\mathbf{r}' d\mathbf{r} \quad \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} + \int d\mathbf{r} \ n(\mathbf{r})V_{ext}(\mathbf{r}).$$
(2.3.5)

With the assumption of the classical particles and uniform density, the kinetic energy can be written as [55]

$$T = \int t(\mathbf{r}) d\mathbf{r},$$

where  $t(\mathbf{r})$  is the kinetic energy density. The number of electron with momentum between p and p + dp is

$$dN = \frac{2V}{h^3} 4\pi p^2 dp \quad \text{and} \quad t = \frac{T_{TF}}{V} = \frac{1}{V} \int_{p \le p_F} \frac{p}{2m} dN = n(\mathbf{r})^{5/3} C_F$$
(2.3.6)

with  $C_F = \frac{3h^2}{10m} \left(\frac{3}{8\pi}\right)^{2/3}$ . Substituting (2.3.6) into (2.3.5), the Thomas-Fermi energy can be rewritten as

$$E_{TF}[n(\mathbf{r})] = C_F \int d\mathbf{r} \ n(\mathbf{r})^{5/3} + \frac{1}{2} \int d\mathbf{r}' d\mathbf{r} \ \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} + \int d\mathbf{r} \ n(\mathbf{r})V_{ext}(\mathbf{r}).$$
(2.3.7)

Albeit the TF method is a very simplistic approach, it is found in most cases to be in poor agreement with the HF approach [56–58]. Moreover, it yields an atomic charge density which is divergent at the nucleus and does not allow atoms to bind in order to form molecules [57, 59]. Over the years, this model has been subject to improvement in order to reflect the real electron system. The first attempt was made by Paul Dirac(1930) [51, 56, 60] by adding the exchange contribution  $(C_x \int d\mathbf{r} \ n(\mathbf{r})^{4/3})$  which was initially neglected by Thomas and Fermi. Later in 1935, Weizsäcker [51, 56] introduced inhomogeneity effect to the electron gas by including a correction to the kinetic energy in term of gradient of the charge density. Despite all the efforts for improvement, this approach did not lead to a complete description of the real inhomogeneous and interacting system of electrons. Nonetheless, it constitutes a milestone to the exact solution of the many electrons problem via the use of the electron density. In 1964, Hohenberg and Kohn [52] used the electron density as a cornerstone for a new theory of many electrons system which is now known as the density functional theory (DFT). The field of DFT is based on the Hohenberg–Kohn theorems and the Kohn–Sham equation.

#### 2.3.2 Hohenberg–Kohn theorems

DFT is based on the original idea of Thomas and Fermi [61, 62] which consists of replacing the complex N-electron wave-function  $\phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$  in the corresponding Schödinger equation with the much simpler electronic density  $\mathbf{n}(\mathbf{r})$  as mentioned above. In 1964, Hohenberg and Kohn [52] came out with an original idea and showed that the many electron problem as described in the Thomas-Fermi-Dirac model could be seen as an approximation to an exact theory; the density functional theory. According to Hohenberg and Kohn, the DFT can be explained(summarised) in two fundamental theorems also known as Hohenberg and Kohn theorems. **Theorem I:** The first theorem shows that the ground-state density is the basic variable for determining the ground-state of any interacting system. It states that: *The external potential*  $V_{ext}(\mathbf{r})$  *is (to within a constant) a unique functional of the ground-state density* [52].

This theorem can be proved by considering a set  $\mathcal{V}$  of external potentials which differ by more than a constant ( $v_{ext}(\mathbf{r}) \neq v_{ext}(\mathbf{r}) + const$ ) and leads to a set  $\Psi$  of non-degenerate groundstate wave-functions.  $\mathcal{N}$  a set of the ground-state density  $n_0(\mathbf{r})$  as defined by (2.3.2) where the wave-functions are  $\in \Psi$ . A a map from  $\mathcal{V}$  to  $\Psi$  and  $\mathbb{B}$  from  $\Psi$  to  $\mathcal{N}$ :

$$\mathbb{A}: \mathcal{V} \longrightarrow \Psi, \qquad \qquad \mathbb{B}: \Psi \longrightarrow \mathcal{N}.$$

Since the ground-state wave-functions are not degenerated, every external potential  $v({f r})\in {\cal V}$ 

uniquely determined the ground-state wave-function [63]. The case of the degenerated groundstates will be tackled in the Section (2.3.3). The one-to-one maps can be proven by *reductio ad absurdum* [63, 64]. For the map  $\mathbb{A}$ , if  $|\psi_0\rangle$  is simultaneously the ground-state wave-function for two different potentials  $\in \mathcal{V}$ , the corresponding Hamiltonians H and H' satisfy the following Schrödinger equations:

$$H|\psi_0\rangle = (T + V_{ee} + V_{ext})|\psi_0\rangle = E_0|\psi_0\rangle$$
(2.3.8)

$$H'|\psi_0\rangle = (T + V_{ee} + V'_{ext})|\psi_0\rangle = E'_0|\psi_0\rangle.$$
(2.3.9)

Subtracting (2.3.8) and (2.3.9) and calculate the expectation value yields

$$\langle \psi_0 | (V_{ext} - V'_{ext}) | \psi_0 \rangle = (E_0 - E'_0)$$
(2.3.10)

Recall that

$$V_{ext} = \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}, \sigma)$$
(2.3.11)

with the density operator given by (2.3.3). For all the position where  $|\psi_0\rangle$  does not vanish, (2.3.10) leads to

$$\sum_{i}^{N} \left[ (v_{ext}(\mathbf{r}) - v'_{ext}(\mathbf{r})) \right] = (E_0 - E'_0).$$
(2.3.12)

The right hand side of (2.3.12) is constant but the left hand side is not if we keep N-1 coordinate position fix and leave the remaining vary. More details about this argument can be found in [65]. Hence two potentials  $\in \mathcal{V}$  will always yield to two ground-state wave-functions  $\in \Psi$ . In the case of the map  $\mathbb{B}$ , if we assume  $n_0(\mathbf{r}) \in \mathcal{N}$  the ground-state density leads simultaneously by  $|\psi_1\rangle, |\psi_2\rangle \in \Psi$  and  $H_1, H_2$  two Hamiltonians which differ by the external potential. By means of the variation principle,

$$\langle \psi_{1} | H_{1} | \psi_{1} \rangle \leq \langle \psi_{2} | H_{1} | \psi_{2} \rangle$$

$$E_{1} \leq \langle \psi_{2} | T + V_{ee} + V_{ext}^{1} | \psi_{2} \rangle$$

$$\leq \langle \psi_{2} | T + V_{ee} + V_{ext}^{2} + V_{ext}^{1} - V_{ext}^{2} | \psi_{2} \rangle$$

$$\leq \langle \psi_{2} | T + V_{ee} + V_{ext}^{2} | \psi_{2} \rangle + \langle \psi_{2} | V_{ext}^{1} - V_{ext}^{2} | \psi_{2} \rangle$$

$$\leq \langle \psi_{2} | H_{2} | \psi_{2} \rangle + \langle \psi_{2} | V_{ext}^{1} - V_{ext}^{2} | \psi_{2} \rangle$$

$$E_{1} \leq E_{2} + \int n_{0}(\mathbf{r}) \left( v_{ext}^{1}(\mathbf{r}) - v_{ext}^{2}(\mathbf{r}) \right) d\mathbf{r}.$$

$$(2.3.13)$$

Since  $|\psi_1\rangle$  and  $|\psi_2\rangle$  lead to the same  $n_0(\mathbf{r})$  by interchanging the two quantities, it follows that

$$\langle \psi_2 \mid H_2 \mid \psi_2 \rangle \leq \langle \psi_1 \mid H_2 \mid \psi_1 \rangle$$

$$E_2 \leq \langle \psi_1 \mid T + V_{ee} + V_{ext}^2 \mid \psi_1 \rangle$$

$$\leq \langle \psi_1 \mid T + V_{ee} + V_{ext}^1 + V_{ext}^2 - V_{ext}^1 \mid \psi_1 \rangle$$

$$E_2 \leq E_1 - \int n_0(\mathbf{r}) \left( v_{ext}^1(\mathbf{r}) - v_{ext}^2(\mathbf{r}) \right) d\mathbf{r}.$$

$$(2.3.14)$$

By adding Equation 2.3.13 and Equation 2.3.14, we arrive at  $E_1 + E_2 < E_1 + E_2$  which is contradictory. This means that two wave-functions  $\in \Psi$  cannot yield the same ground state density  $\in \mathcal{N}$ . Therefore the maps  $\mathbb{A}$  and  $\mathbb{B}$  are unique and thus, there is a one-to-one map between the external potential and the ground-state wave-function in one hand and between the ground-state wave-function and the ground-state density in the other hand.

**Corollary I:** Since the ground-state energy of the Hamiltonian is an unique functional of the electron density  $n_0(\mathbf{r})$ , it follows that all ground-state and excited state properties of a system are in principle completely determined [51, 60].

**Theorem II:** The first theorem proves the existence of a one-to-one mapping between the density and the external potential, but it says nothing about the way that the functional energy is obtained. According to the second theorem, an universal functional for the energy E[n] in term

of density  $n(\mathbf{r})$  can be defined, valid for any given external potential  $V_{ext}(\mathbf{r})$ . Hence, the density which minimises the total energy E[n] is the exact ground-state density [45, 51]. E[n] can be written as a functional of the density as follow:

$$E[n] = F[n] + V_{ext}[n]$$
(2.3.15)

with

$$F[n] = T[n] + V_{ee}[n].$$
(2.3.16)

F[n] is an universal functional and it is valid for all the system regardless of the number of particles.

**Corollary II:** The functional for the energy E[n] is alone sufficient to determine the exact groundstate energy and density. In general, excited states of the electrons must be determined by other means. According to the variational principle, if  $F[\tilde{n}]$  is the universal functional associated to the trial density  $\tilde{n}(\mathbf{r})$ ,

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

$$\geq E[n_{0}]$$
(2.3.17)

with  $E[n_0]$  the exact ground-state energy.

To be eligible as a potential ground-state density, a given density  $n(\mathbf{r})$  must satisfy the following condition [55]:

- Positve i.e.  $n(\mathbf{r}) \ge 0$
- Normalisable i.e  $\int n(\mathbf{r})d\mathbf{r} = N$
- Vanishes at infinity i.e.  $n(\textbf{r}\longrightarrow\infty)=0$

#### 2.3.3 Levy constrained—search formulation

The Hohenberg-Kohn (HK) theorem as presented above required the ground-state wave-function to be non-degenerated. What happened in the case of degenerated ground-state? With a degenerated ground-state, there is a possibility of getting a subset  $\varphi \subseteq \Psi$  of ground-state wavefunctions which all originated from the same external potential  $v \in \mathcal{V}$ . In that case the expectation value of  $v(\mathbf{r})$  of two elements  $\psi$  and  $\psi' \in \varphi$  is the same.

$$\langle \psi | V_{ext} | \psi \rangle = \langle \psi' | V_{ext} | \psi' \rangle. \tag{2.3.18}$$

Considering  $|\psi\rangle$  as the exact ground-state and making use of the variational principle, it turns out that

$$\langle \psi' | H | \psi' \rangle \geq \langle \psi | H | \psi \rangle$$

$$\langle \psi' | T + V_{ee} + V_{ext} | \psi' \rangle \geq \langle \psi | T + V_{ee} + V_{ext} | \psi \rangle$$

$$\langle \psi' | T + V_{ee} | \psi' \rangle + \langle \psi' | V_{ext} | \psi' \rangle \geq \langle \psi | T + V_{ee} | \psi \rangle + \langle \psi | V_{ext} | \psi \rangle$$

$$(2.3.19)$$

Substituting (2.3.18) into (2.3.19), it follows that

$$\langle \psi' | T + V_{ee} | \psi' \rangle \ge \langle \psi | T + V_{ee} | \psi \rangle$$
  
 
$$\ge F_{HK}[n]$$
 (2.3.20)

with  $F_{HK}[n]$  the Hohenberg and Kohn universal functional. Thus, the Hohenberg-Kohn theorem does not stand any longer for the degenerated states.

The Levy minimizaton approach [55,63,64] consists of bypassing the *v*-representability condition impose by Hohenberg and Kohn and account for all the possible antisymmetric wave-functions resulting from the same  $v_{ext}(\mathbf{r})$ . Hence, a new one-to-one map is established between the  $v_{ext}(\mathbf{r}) \in$  $\mathcal{V}$  and all the possible wave-functions  $|\psi\rangle \in \varphi$  with  $\varphi \subseteq \Psi$ . Thus, the search for the ground-state energy E<sub>0</sub> can be achieved in two steps; firstly by considering all the wave-functions whose the
density is equal to the ground-state density  $n_0(\mathbf{r})$  and secondly by finding the one that minimises the universal functional F[n]

$$F[n] = \min_{\psi \to n} \langle \psi | T + V_{ee} | \psi \rangle$$
  
=  $\langle \psi_n^{min} | T + V_{ee} | \psi_n^{min} \rangle.$  (2.3.21)

It follows that the ground-state energy is

$$E_0[n] = \min_{\psi \to n} F[n] + \langle \psi | V_{ext} | \psi \rangle = \left[ \langle \psi_n^{min} | T + V_{ee} | \psi_n^{min} \rangle + \int n(r) V_{ext}(r) dr \right], \quad (2.3.22)$$

hence, with this new approach, the constraint on the non-degenerate ground-state is waived.

#### 2.3.4 Kohn–Sham equation

The definition of the universal functional F[n] from the HK theorem and the Levy constraint are not sufficient for solving the many-electron problem since it does not suggest any framework which can be used to get F[n] explicitly. In 1965, Kohn and Sham proposed a practical ansatz based on a fictitious *non-interacting electron system* [53]. The idea is to replace the original system of interacting electron by an imaginary system of non-interaction electron. The auxiliary system is required to have the same ground-state density as the exact system. The *Kohn–Sham electrons* feel an effective potential  $V_{KS}$  and satisfied the following Hamiltonian

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}\right]\varphi_i(\mathbf{r}) = E_i\varphi_i(\mathbf{r})$$
(2.3.23)

where  $\varphi_i(\mathbf{r})$  is the Slater determinant because of the non-interacting character of the system and  $-\frac{1}{2}\nabla^2$  its kinetic energy operator. Point to note here is that the kinetic energy of the Kohn–Sham (KS) system is different from the one of the real system since  $\varphi_i(\mathbf{r})$  is not the ground-state wave-function of the real system. In order to evaluate  $V_{KS}$ , let  $|\psi\rangle$  and  $|\psi'\rangle$  be the wave-function associated to the interacting and the non-interacting system respectively. It follows that

$$\sum_{i}^{N} |\psi|^{2} = \sum_{i}^{N} |\psi'|^{2}$$
(2.3.24)

since the two system have equal ground-state density. Their universal functionals are respectively

$$F[n] = \langle \psi | T + V_{ee} | \psi \rangle$$
  
=  $T[n] + \langle \psi | V_{ee} | \psi \rangle.$  (2.3.25)

and

$$F_{KS}[n] = \langle \psi' | T + V_{ee} | \psi' \rangle$$
  
=  $\langle \psi' | T | \psi' \rangle + \langle \psi' | V_{ee} | \psi' \rangle$  (2.3.26)  
=  $T_s[n] + \langle \psi' | V_{ee} | \psi' \rangle$ .

Following the HF scheme, the second term of Equation 2.3.26 can be rewritten as a sum of the classical electrostatic, U[n], repulsion energy and exchange energy,  $E_x[n]$ ,

$$\langle \psi' | V_{ee} | \psi' \rangle = U[n] + E_x[n].$$
 (2.3.27)

Because of the energy difference between the two systems, a correlation energy,  $E_c[n]$ , is defined as the remaining part of the energy, E[n], which is not captured in the Kohn-Sham energy  $E_{KS}[n]$ :

$$E_{c}[n] = E[n] - E_{KS}[n]$$

$$= \langle \psi | T + V_{ee} + V_{ext} | \psi \rangle - \langle \psi' | T + V_{ee} + V_{ext} | \psi' \rangle$$

$$= \langle \psi | T + V_{ee} | \psi \rangle - \langle \psi' | T + V_{ee} | \psi' \rangle$$

$$= F[n] - F_{KS}[n].$$
(2.3.28)

Therefore,  $E_c[n]$  is not only the residual potential energy, but also comes from the kinetic energy. From Equations 2.3.26, 2.3.27 and 2.3.28, F[n] can be rewritten as

$$F[n] = \langle \psi'|T + V_{ee}|\psi'\rangle + [\langle \psi|T + V_{ee}|\psi\rangle - \langle \psi'|T + V_{ee}|\psi'\rangle]$$
  

$$= \langle \psi'|T|\psi'\rangle + \langle \psi'|V_{ee}|\psi'\rangle + E_c[n]$$
  

$$= T_s[n] + \langle \psi'|V_{ee}|\psi'\rangle + E_c[n]$$
  

$$= T_s[n] + U[n] + E_x[n] + E_c[n].$$
  
(2.3.29)

 $E_c[n]$  and  $E_x[n]$  are very small portion of energy compare to the other contributions of the total energy. Usually they are written as a unique term  $E_{xc} = E_x[n] + E_c[n]$  called as the exchangecorrelation energy. The ground-state can be obtained through the minimization of the total energy E[n]. We can make use of the Lagrange Multiplier  $\mu$ , with the constraint that the total number of particle N of the system is conserved. This leads to

$$\delta \Big\{ E[n] - \mu (\int n(\mathbf{r}) d\mathbf{r} - N) \Big\}$$
(2.3.30)

which can be rewritten in form of Euler equation as

$$\frac{\delta E[n]}{\delta n} - \mu = 0. \tag{2.3.31}$$

Using F[n] from Equation 2.3.29, it follows that

$$\frac{\delta E[n]}{\delta n} - \mu = \frac{\delta F[n]}{\delta n} + v_{ext} - \mu$$
$$= \frac{\delta T_s[n]}{\delta n} + \frac{\delta U[n]}{\delta n} + \frac{\delta E_{xc}}{\delta n} + v_{ext} - \mu$$
(2.3.32)

which leads to

$$\frac{\delta T_s[n]}{\delta n} + V_{KS} = \mu. \tag{2.3.33}$$

 $V_{KS}$  is the so-called Kohn–Sham potential equals to

$$V_{KS} = \frac{\delta U[n]}{\delta n} + \frac{\delta E_{xc}[n]}{\delta n} + V_{ext}[n]$$
  
=  $V_H[n] + V_{xc}[n] + V_{ext}[n],$  (2.3.34)

where  $V_{xc}[n]$  is the exchange-correlation potential and  $V_H$  the Hartree potential defined as

$$V_H = \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}.$$
(2.3.35)

From the expression of the potential  $V_{KS}$ , it can be seen that any change on the density/orbital will automatically imply a change on the potential itself. Hence, the Kohn–Sham Equation 2.3.23 can only be solved self-consistently. It is also worth to note that contrary to previous approaches such as the Thomas-Fermi model, the kinetic energy can be obtained exactly here since the wave-function associated to the non-interacting system is a Slater determinant. Therefore, from this point forward, the only unknown part of  $V_{KS}$  is the exchange-correlation potential. Luckily, the exchange-correlation energy accounts for a very small contribution to the total energy [53]. However, it has been shown that some important properties such as the binding energy, the bandgap, the optical absorption are very dependant on the exchange-correlation energy [47, 49, 55, 66]. Hence, it cannot be neglected and finding the exact or the best approximation for the exchange-correlation has became one of the major challenge in DFT. A discussion about the different approximations will be the subject of the next chapter.

## 3. Exchange–correlation functionals: "Jacob's ladder" of density functional approximations

''Exchange-correlation potential is the 'bin' of DFT ...'' [67]

The construction of an exchange-correlation functional is one of the most challenging problem in DFT. Its complexity lies on the fact that it contains all unknow parts of the total energy which are not captured by the kinetic, the Hartree and the external energy in the KS scheme. These residuels of the real energy included [67]:

- Fermi correlation for electrons of the same spin
- Coulomb effect between electrons of opposite spin
- self-interaction correction
- difference of kinetic energy between virtual and real system ...

Over the year, attempts for improving the DFT accuracy results have led to a complete hierarchy of exchange-correlation functionals. Perdew refers to this hierarchy as the "Jacob's ladder" <sup>1</sup> starting from the "Hartree world" to the "Heaven of chemical accurary" [60,68]. An overview of some of these exchange-correlation functionals will be given in the next sections.

<sup>&</sup>lt;sup>1</sup> The phrase "Jacob's ladder of density functional approximation" does not have any religious connotation. Any resemblance to the Babel's Tower is purely coincidental.

#### 3.1 The local density approximation

The first attempt for constructing an exchange-correlation was done by Kohn and Sham (1965) [53] based on the Thomas-Fermi-Dirac theory. The local density approximation (LDA) is considered as the mother of all the approximations of the exchange-correlation. The main idea is to mimic the inhomogeneous electronic system by an homogeneous electron gas with uniform density. The advantage is that the exchange-correlation hole corresponding to the electron gas can be calculated with excellent accuracy because of its local character. With that assumption, the LDA exchange-correlation energy is

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) \varepsilon_{xc}^{hom}(n(\mathbf{r})) d\mathbf{r}$$
(3.1.1)

where  $\varepsilon_{xc}^{hom}(n(\mathbf{r}))$  is the homogeneous electron density per atom. In practice, the  $\varepsilon_{xc}^{hom}(n(\mathbf{r}))$  is decomposed into exchange and correlation terms as

$$\varepsilon_{xc} = \varepsilon_x + \varepsilon_c.$$
 (3.1.2)

The exchange term  $\varepsilon_x$  is given analytical by the Dirac's expression [69, 70]

$$\varepsilon_x^D[n] = -\frac{3}{4} (\frac{\pi}{3})^{1/3} n(\mathbf{r})^{1/3} = -\frac{0.458}{r_s} \text{ atomic units}$$
(3.1.3)

where  $r_s=\frac{3}{4}\pi n({\bf r})^{1/3}$  is the mean interatomic distance.

The analytic expression for the correlation is not straightforward. Several approaches have been developed including the Perdew and Zunger parametrisation [70, 71]

$$E_{c}^{PZ}[n] = f(x) = \begin{cases} A \ln r_{s} + B + Cr_{s} \ln r_{s} + Dr_{s} & :r_{s} \le 1\\ \gamma/(1 + \beta\sqrt{r_{s}} + \beta r_{s}) & :r_{s} \ge 1. \end{cases}$$
(3.1.4)

The most accurate values of  $E_c[n]$  have been obtained from the quantum Monte Carlo simulations of Cerpeley and Alder [72]. In reality the exchange-correlation

$$\varepsilon_{xc}[n] = \frac{1}{2} \int \frac{n_{xc}(\mathbf{r}, \mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'}$$
(3.1.5)

is non local, but in this approximation, that aspect is not explicitly taking into account. Contrary to what one would have expected, LDA works quite well for many inhomogeneous system. However, a general trends has been observed that it underestimates the lattice parameter. The bandgap of semiconductors and insulators is dramatically underestimated. Moreover, van der Waals interactions present layer in materials, hydrogen bonds crucial in water and biological system are poorly reproduce within LDA [49]. This shows that there is still room for improvement in order to account for the inhomogeneity.

#### 3.2 The generalised gradient approximations

As mentioned in section 3.1, one of the major reason for the failure of the LDA come from the homogeneous electron gas approximation. A natural way of improving it will be to incorporate some inhomogeneity in the system by considering higher order terms of derivative of the density. This is also know as the gradient expansion approximation (GEA). However, it was shown that taking into consideration higher term of the GEA does not necessary improve the exchange-correlation functional [53, 60, 73]. Contrary, some important properties already included in the LDA such that the sum rules were no longer captured in the GEA [51, 73]. Notwithstanding, the lower terms of the GEA tends to preserve and to some extent improve the desired properties. The generalised gradient approximation (GGA) include the gradient of the density to description of the exchange-correlation functional. It can be written in the following form [49]

$$E_{xc}^{GGA}[n] = \int n(\mathbf{r})\varepsilon_{xc}^{hom}(n(\mathbf{r}))F_{xc}\Big(n(\mathbf{r}), \nabla n(\mathbf{r})\Big)d\mathbf{r}$$
(3.2.1)

where  $\epsilon_x^{hom} [n(\mathbf{r})]$  is the exchange energy per atom of the unpolarised gas and  $F_{xc}$  a dimensionless parameter also know as the *enhancement factor*. It is generally written in term of the Seitz radius  $r_s$  and the dimensionless reduced density gradient s(r). The consideration of the gradient of the density  $(\nabla n(\mathbf{r}))$  introduces some non locality in the model though it is hardly capture at longer ranges [49]. Numerous GGA flavours have been proposed with the analytic forms of  $F_{xc}$  making the major the difference. These flavours include but is not limited to:

- the FT97 functional of Filatov and Thiel [74].
- the B88 functional of Becke [75].
- the PW91 exchange functional of Perdew and Wang [76].
- the LYP correlation functional due to Lee, Yang and Parr [77].
- the PBE functional of Perdew, Burke and Ernzerhof [78].
- the AM05 of Armiento and Mattssonn [79],
- the PBEsol functional of Perdew and co workers [80]

However, common GGAs do not describe long-range electron correlations that are responsible for van der Waals interaction. F. Ricci and G. Profeta [81] demonstrated that the inclusion of van der Waals dispersive interaction sensibly improves the prediction of the structural properties of chalcogenides. Suggestions have been made to account for these interactions. As example,

- \* the DFT-D2 method of Grimme [82] where a semi-empirical dispersion potential is adding to the conventional Kohn-Sham DFT energy.
- \* the vdW-DF2 functional of Langreth and Lundqvist et al [83] first proposed by Dion et al. [84] which used a more accurate semi-local exchange functional and a large-N asymptote gradient correction in determining the vdW kernel.

It is also important to point out that it is not the physics behind those functionals but the results obtained from them which guide the choice of the mathematical constructs.

While comparing GGA to LDA, the former tends to slightly improve on the binding energy, the atomisation energy, the bond lengths, the angles and the structural energy differences [49,78,79]. Nonetheless, some important properties such that the bandgap and the accurate description of d and f orbitals of the transition metals are still misleading.

#### 3.3 The hybrid functionals

Hybrid functionals is an active line of research which goes beyond GGA. The KS approach has the advantage that it is easy to manipulate because of its dependency on one parameter only namely, the electron density. It is also computational cost effective. Unfortunately the exchangecorrelation within the KS scheme leads to a poor description of the bonding character of molecules and intermolecular interaction [85, 86]. On the other hand and contrary to DFT, the exact exchange can be treated with good accuracy in the HF approach. Hybrid functionals consist of constructing an exchange-correlation which mixes a portion of the exact exchange from the HF theory with local or semilocal exchange-correlation based on the KS scheme of DFT. Here, the idea is to exploit the strengths of each of the two methods. This coupling was found very successful specially on the description of the molecular properties [86]. Moreover, the hybrid methods require a moderate computational effort to deliver results of an accuracy comparable to that of very computational demanding methods especially for energetic and electronic properties [87]. Becke was one of the pioneers to adopt this approach. He gave a theoretical proof of this mixing by using the adiabatic connection formula [85, 86, 88]

$$E_{xc} = \int_0^1 U_{xc}^{\lambda} d\lambda \tag{3.3.1}$$

where  $\lambda$  is an interelectronic coupling strength parameter that controls the strength of the Coulomb interaction between electron and  $U_{xc}^{\lambda}$  the exchange-correlation potential at a given  $\lambda$ . Hence, the non-interacting KS system ( $\lambda$ =0) is connected to the real interacting system

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 $(\lambda=1)$  through a continuum of partial interacting system  $(0 \le \lambda \le 1)$ . The constraint is that the partial interacting system must have the same density as the fictitious/non interaction system. Becke used the simple linear interpolation of  $U_{xc}^{\lambda}$  for  $\lambda = 0$  and  $\lambda = 1$  to come out with the first hybrid functional, namely, the half-and-half functional expressed as [85, 86, 88]

$$E_{xc} = \frac{1}{2}U_{xc}^{0} + \frac{1}{2}U_{xc}^{1}$$
(3.3.2)

where  $U_{xc}^0$  is the exchange-correlation of the KS non-interacting system and  $U_{xc}^1$  that of the real system. In spite of the empirical character of this functional, it improves significantly on the atomisation energy and ionisation energy of many molecular system [86]. Another empirical and successful hybrid functional is the B3LYP functional

$$E_{xc}^{B3LYP} = 0.8E_x^{LDA} + 0.2E_x^{HF} + 0.72\Delta E_x^{B88} + 0.19E_c^{VWN3} + 0.81E_c^{LYP}$$
(3.3.3)

of Stephens et al [89] where  $E_x^{B88}$  Becke's gradiant,  $E_c^{VWN3}$  the Lee-Yang-Parr correlation energy [77] and  $E_c^{LYP}$  the Vosko-Wilk-Nusair correlation functional III [90].

Efforts have also been made to develop parameter-free hybrid functional. As example the PBE0 hybrid functional

$$E_{xc}^{PBE0} = aE_x^{HF} + (1-a)E_x^{PBE} + E_c^{PBE}.$$
(3.3.4)

Here the mixing coefficient of the exchange functional was found to be equalled to  $\frac{1}{4}$  using the perturbation theory [88, 91]. However, this functional has been found to be computational demanding because of the slow decay of the exchange at long-range distance [88]. Thus, Heyd et al [91] suggested to use the error function erf to split the Coulomb operator into short-range (SR) and long-range (LR) components:

$$\frac{1}{r} = \underbrace{\frac{1 - erf(\omega r)}{r}}_{SR} + \underbrace{\frac{erf(\omega r)}{r}}_{LR}$$
(3.3.5)

where  $\omega$  is an adjustable parameter which governs the extent the SR interaction. Subsequently, this led to the well-known HSE functionals [88, 91]

$$E_{xc}^{HSE} = a E_x^{HF,SR}(\omega) + (1-a) E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE}$$
(3.3.6)

In practice, the HSE functionals yield satisfactory results for solids [1]. We will be using it widely in Chapter 7 to calculate the bandgap and optical properties of the chalcopyrites  $AgAIX_2$  (X = S, Se, Te)

## 3.4 The meta GGAs : the modified Becke Johnson potential

The idea beyond meta GGA is to develop new functional that could incorporated additional non local information. Here the kinetic energy density (Laplacian of the density) is included in the expression of the exchange-correlation. As example of those functionals, we have:

- the TPSS and the RTPSS developed by Sun et al. [92].
- the M06L of Zhao and Truhlar [93].
- the new modified Becke Jonhson (MBJ) potential recently implemented by Tran and Blaha [94].

We are going to stress on the MBJ since it will be widely used in our work. The MBj was developed by Tran and Blaha [94] for the aims of getting a functional which could be more accurate than the GGAs, but computationally less demanding than HSE. The MBJ potential is defined as:

$$v_{x,\sigma}^{\mathsf{MBJ}}(\mathbf{r}) = c v_{x,\sigma}^{\mathsf{BR}}(\mathbf{r}) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_{\sigma}(\mathbf{r})}{\rho_{\sigma}(\mathbf{r})}},$$
(3.4.1)

where  $v_{x,\sigma}^{BR}(\mathbf{r})$  is the Becke-Roussel potential,  $\rho_{\sigma}(\mathbf{r})$  and  $t_{\sigma}(\mathbf{r})$  are the electron and the kinetic energy densities. The *c* parameter depends on the unit cell volume and some free parameters whose values are obtained according to a fit to experimental data. In general MBJ is very accurate for the electronic structure calculations of most semiconductors and insulators. Unfortunately, it looses some fundamental properties of an exchange-correlation although they usually give accurate bandgap. In fact, in the construction of the exchange-correlation, the energy functional is approximated and the potential is then determined as a functional derivative of the energy functional,  $V_{xc} = \left(\frac{\delta E_{xc}[n]}{\delta n}\right)$ . The MBJ potential was originally constructed as an approximate potential itself [94]. In such cases, it is suggested to use the van Leeuwen-Baerends line integral [95] or the Levy-Perdew virial relation [96] to obtain the energy. Recently, Gaiduk *et al.* showed that the Becke Jonshon potential doest not satisfy those conditions and therefore is not a functional derivative [97].

#### 3.5 Can DFT do everything?

As establish by Hohenberg, Kohn and Sham, DFT is an exact theory for the ground-state properties. DFT has been very successful for describing ground-state properties such as lattice parameters, equilibrium volume, cohesive/formation energy, bulk modulus, elastic constants,...etc. However, system with d and f orbitals are usually well described within the DFT+U [98], but the determination of the U parameter is not straightforward. Most often, it is fixed with respect to the experimental results and therefore cannot be used for hypothetical systems. When it comes to excited state properties, DFT rarely gives reliable results. As illustrate in Figure 3.1, there is a large discrepancy between the experimental and the calculated the bandgaps of semiconductors and insulators. Accurate optical properties are also not directly accessible from DFT calculation. For example, the onset of the absorption of silicon from random phase approximation (RPA) [101] is underestimated as shown in Figure 3.2. Moreover, the amplitudes and the positions of the peaks



Figure 3.1 Experimental versus calculated LDA bandgaps for some *sp* compounds [99, 100].

are misleading.

Most of these shortcomings with DFT are related to the innacuracy of the KS formalism for describing the bandgap. Let us recall the notion of fundamental gap. Strictly speaking, the fundamental gap is the difference between the lowest conduction band energy and the highest valence band energy of a system [63]. Experimentally, one can get access the fundamental gap from photoemission and inverse photoemission measurements. Here, the fundamental gap is defined as the difference between the energy for adding and subtracting an electron from the neutral N-particles ground-state [51, 63].

$$E_g = (E_{N+1} - E_N) - (E_N - E_{N-1}).$$
(3.5.1)

Typically, the energy required to remove an electron from a neutral system is the ionisation energy  $I = (E_{N-1} - E_N)$  and that for adding an electron is the electron affinity  $A = (E_N - E_{N+1})$ .



**Figure 3.2** Optical absorption of silicon from the experimental measurement (EXP) and the DFT-LDA calculations within the random phase approximation (RPA). The image from taking from Ref. [99,100]

The fundamental gap can therefore be rewritten as

$$E_g = I - A. \tag{3.5.2}$$

These energies also correspond to the lowest unoccupied molecular orbitals (LUMO) and the highest occupied molecular orbitals (HOMO). It follows that the fundamental gap is the energy difference between the (N+1)<sup>th</sup> KS orbital of a (N+1)-particles system  $\left(\varepsilon_{N+1}^{KS}(N+1)\right)$  and the N<sup>th</sup> KS orbital of a N-particles system  $\left(\varepsilon_{N}^{KS}(N)\right)$  [46,63]:

$$E_g = \varepsilon_{N+1}^{KS}(N+1) - \varepsilon_N^{KS}(N).$$
(3.5.3)

This expression is based on the fact that the electron affinity of the N-electron system is equal to the first ionisation energy of an (N+1)-particles system ( $A_N = I_{N+1}$ ). For the KS system of

N non interacting particles, the bandgap is defined as

$$E_g^{KS} = \varepsilon_{N+1}^{KS}(N) - \varepsilon_N^{KS}(N)$$
(3.5.4)

where  $\varepsilon_{N+1}^{KS}(N)$  is the (N+1)<sup>th</sup> orbital of the N-particles system. Combining equation (3.5.3) and equation (3.5.4), the fundamental gap is related to of KS gap through

$$E_g = \left[\varepsilon_{N+1}^{KS}(N) - \varepsilon_N^{KS}(N)\right] + \varepsilon_{N+1}^{KS}(N+1) - \varepsilon_N^{KS}(N) = E_g^{KS} + \Delta_{xc}.$$
 (3.5.5)

 $\Delta_{xc}$  is the missing quantity in the KS approach. One would say that the KS energy undergoes a jump by a constant when crossing integer particle numbers (from N to N + 1). This was shown by Perdew et *al.* and it is known as the derivative discontinuity of the exchangecorrelation functional [102–104]. Thus, the KS eigenvalues are different from the excitation energies. The fundamental gap can be obtained in this formalism through the knowledge of the exact exchange-correlation energy and potential. The search of the exchange-correlation functional has led to the *Jacob's ladder* as mentioned previously. Each of these functionals have its strength and weakness especially when it comes to excited properties. Even the HSE functionals, very powerful for calculations of the bandgaps, fails to predict the electronic properties of small gap transition metal oxides such as VO<sub>2</sub> [105]. Hence, there is a need to go beyond DFT for the description of the excited state properties. Time-dependant DFT and many-body perturbation theory (MBPT) are two of the alternative approaches to overcome these limitations. In our work, we adopt the MBPT and it will be the subject of the next chapter.

### 4. The Many-body pertubation theory

''Perturbation theory starts from what is known to evaluate what is not known, hoping that the difference is small ...'' [106]

The ground-state total energy is sufficient for the study of structural properties, but we cannot rely on it for the determination of the excited state properties. This is due to two main reasons:

- the KS DFT scheme usually underestimate the fundamental bandgaps.
- the Fermi's golden rule [99] in the independent particle picture is not reliable for calculating the absorption spectra as illustrated in Figure 3.1.

It is therefore necessary to go beyond DFT to get access to an accurate description of excited properties. A successful method to achieve it is the many-body pertubation theory (MBPT) based on Green's function and quasiparticle concepts. Accurate fundamental bandgaps are usually obtained at the GW level [107–110] while for optical absorption, it is necessary to take into account electron-hole interactions which can be done by solving the Bethe Selpeter Equation (BSE) [111,112]. The focus in this chapter is to describe the notion of the Green's function, the concept of the self energy and GW approximation, then end up by giving an overview of the BSE.

# 4.1 The Green's function and perturbation theory: the self-energy

The Green's function is a mathematical tool to solve partial differential equations. In quantum physics, the Green's function can be used to solve Schrödinger-like equation

$$[H(\mathbf{r}) - E]\varphi(\mathbf{r}) = 0, \qquad (4.1.1)$$

where  $H(\mathbf{r})$  is a Hermitian operator. The Green's function is defined as the solution of the equation [113]

$$[H(\mathbf{r}) - E]G_0(\mathbf{r}, \mathbf{r'}, E) = -\delta(\mathbf{r} - \mathbf{r'}), \qquad (4.1.2)$$

with  $\delta(\mathbf{r} - \mathbf{r'})$  the Dirac's delta function. The Green's function  $G_0(\mathbf{r}, \mathbf{r'}, E)^1$  satisfies exactly the same boundary conditions as the wave-function in Equation 4.1.1. For an N electron system, the one particle Green's function is defined as [46]:

$$G(\mathbf{x}t, \mathbf{x}'t') = -i\langle N | T\varphi(\mathbf{x}t)\varphi^{\dagger}(\mathbf{x}'t') | N \rangle$$
(4.1.3)

where T is the time-ordering operator,  $|N\rangle$  is the N-electron ground-state and  $\varphi(\mathbf{x}t)$  and  $\varphi^{\dagger}(\mathbf{x}'t')$ , the annihilation and creation field operators respectively.  $\mathbf{x}$  stands for the spatial  $\mathbf{r}$  and spin  $\sigma$ coordinates ( $\mathbf{x} = (\mathbf{r}, \sigma)$ ).  $G(\mathbf{x}t, \mathbf{x}'t')$  can be interpreted as the probability amplitude for the propagation of an additional electron from ( $\mathbf{x}', \mathbf{t}'$ ) to ( $\mathbf{x}, \mathbf{t}$ ) in a many-body electron system. In reality, the real wave-function describing a many-body system contains much more information than the Green's function itself. But, the Green's function has the advantage that it can easily provide useful information directly measured in experiments, such as the inverse photoemission and the direct photoemission experiments [110]. The information about single particle spectra is

<sup>&</sup>lt;sup>1</sup>The notation  $G_0$  referring to an unperturbed system by apposition to a perturbed system which will be introduced later.

contained in the one electron Green's function, whereas the electron-hole properties are described by the two-electrons Green's function [46]. The single particle Green's function can be written in spectral representation in terms of occupation numbers and excitation energies

$$f_n(\mathbf{x}) = \langle N | \varphi(\mathbf{x}) | N+1, n \rangle, \epsilon_n = E_{N+1}^{(n)} - E_N^{(0)} \text{ if } \epsilon_n > \mu$$
(4.1.4)

$$f_n(\mathbf{x}) = \langle N - 1, n | \varphi(\mathbf{x}) | N \rangle, \epsilon_n = E_N^{(0)} - E_{N-1}^{(n)} \text{ if } \epsilon_n < \mu$$
(4.1.5)

as:

$$G(\mathbf{x}, \mathbf{x}', \omega) = \sum_{n} \frac{f_n(\mathbf{x}) f_n^{\star}(\mathbf{x}')}{\omega - \epsilon_n - i\eta \, \operatorname{sgn}(\mu - \epsilon_n)}$$
(4.1.6)

with  $\mu$  the Fermi energy and  $\eta$  is a positive infinitesimal. The Green's function is then well defined by Equation 4.1.3 and 4.1.4, but it is still not straightforward to be obtained since the N-electron interacting ground-state  $|N\rangle$  is in principle not known. Let us assuming h<sub>0</sub> the Hamiltonian of a non interacting electron system and G<sub>0</sub> the Green's function associated to it. The equation of motion and the spectral function are respectively

$$\left[i\frac{\partial}{\partial t_i} - h_0(\mathbf{x}_1)\right] G_0(\mathbf{x}_1, t_1, \mathbf{x}_2, t_2) = \delta(\mathbf{x}_1 - \mathbf{x}_2)\delta(t_1 - t_2)$$
(4.1.7)

and

$$A(\mathbf{x}_1, \mathbf{x}_2, \omega) = \sum_i \phi(\mathbf{x}_1) \phi^{\dagger}(\mathbf{x}_2) \delta(\omega - \epsilon_i)$$
(4.1.8)

where  $\phi$  is the independent particle eigenstate and  $\epsilon_i$  the eigenvalue. For the interacting system, the equation of the motion

$$\left[i\frac{\partial}{\partial t_i} - h_0(\mathbf{x}_1)\right]G(1,2) = \delta(1,2) - i\int d_3v(1,3)G_2(1,3,2,3^+)$$
(4.1.9)

depends on the two particles Green's function  $G_2$  which involves a four field operators

$$G_2(1,2,3,4) = (-i)^2 \langle N | T \left[ \varphi(1)\varphi(2)\varphi^{\dagger}(4)\varphi^{\dagger}(3) \right] | N \rangle$$
(4.1.10)

with  $1 = (\mathbf{x}_1, t_1)$  and  $1^+ = (\mathbf{x}_1, t_1 + \delta)$  where  $\delta$  a positive infinitesimal number added to the time variation. The two particle Green's function  $G_2$  itself depends on a three particle Green's function  $G_3$  and  $G_3$  will also depend on  $G_4$ , hence forming a hierarchy of equations involving Green's functions of increasing order:  $G_2$ ,  $G_3$ ,  $G_4$ , .... However, this reformulation in terms of Green's functions does not provide a straightforward answer to the many-body interacting problem. One common practice in Quantum Mechanic is to evaluate such operator using the perturbation theory. Here, the Green's function G associated to the interaction system is obtained by successive approximation as [113]

$$G(\mathbf{r}, \mathbf{r}', E) = G_0(\mathbf{r}, \mathbf{r}', E) + \int G_0(\mathbf{r}, \mathbf{r}'' E) V(\mathbf{r}'') G_0(\mathbf{r}'', \mathbf{r}', E) d\mathbf{r}'' + \int G_0(\mathbf{r}, \mathbf{r}'', E) V(\mathbf{r}'') G_0(\mathbf{r}'', \mathbf{r}'', E) V(\mathbf{r}'') G_0(\mathbf{r}''', \mathbf{r}', E) d\mathbf{r}'' d\mathbf{r}'' + \dots$$
(4.1.11)

generally termed as Dyson equation [46, 49, 60, 110, 113, 114] where  $G_0$  refers to the Green's function of the unperturbed system. It can also be written in its simplest form as

$$G = G_0 + G_0 V G. (4.1.12)$$

It is worthy to point out that in order to use the perturbation theory, the perturbative term V must be very small as compared to other terms of the Hamiltonian. Looking at this definition, one question that one might ask is, can this approach be used for solving the many electron problem where the electron-electron interaction is considered as the perturbative term? Unfortunately, it is known that the bare Coulomb interaction is very strong especially in the region close to the nuclei. Hence, the perturbative approach cannot be satisfactory in describing the problem as defined. However, it is also known that systems of interacting particles can be described in term of *quasiparticles* [114]. The quasiparticle (QP) arises from the fact that when an electron (*bare* particle) is moving through the system, it repels other electrons is then screened by the correlation motions of other electrons. The association of the screening cloud and the screened electron form the quasiparticle (*dressed* particle) as shown in Figure 4.1. Hence, the bare Coulomb

interaction V between electrons (Figure 4.2a) is replaced by a weak screened Coulomb interaction W between quasiparticle (Figure 4.2b). The energy possesses by the quasiparticle is termed *self-energy* ( $\Sigma$ ) [114, 115] and it can be seen as the residual energy between the bare electron and the dressed electron. Following the definition above, the one electron Green's function and the perturbation theory become suitable for describing the many electron interaction system. The non interacting KS system could be taken as unperturbed (reference) system associated with G<sub>0</sub> and the  $\Sigma$  as the perturbative term. Thus, the Green's function solution of the interaction problem is given by the Dyson equation

$$G = G_0 + G_0 \Sigma G. (4.1.13)$$

The  $\Sigma$  is a non-local, non-Hermitian and frequency dependent operator [114]. It contains all the exchange and correlation effects which were not captured in the reference KS system.



Figure 4.1 Creation of a quasiparticle via interaction between an electron an its polarisation could.

The motion of the quasiparticles is governed by the equation [46]:

$$h_0(\mathbf{r})\varphi_i^{\mathsf{QP}}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E_i^{\mathsf{QP}})\varphi_i^{\mathsf{QP}}(\mathbf{r}) = E_i^{\mathsf{QP}}(\mathbf{r})\varphi_i^{\mathsf{QP}}(\mathbf{r}), \qquad (4.1.14)$$

where  $\varphi_i^{\rm QP}$  are the QP states and  $E_i^{\rm QP}$  are the complex energies. This equation is known as



**Figure 4.2 a**-Strong bare Coulomb interaction between electrons, **b**-weak screened Coulomb interaction between quasiparticles.

quasiparticle equation. At a first glance, it is similar to the KS equation

$$h_0(\mathbf{r})\varphi_i^{\mathsf{KS}}(\mathbf{r}) + V_{xc}\varphi_i^{\mathsf{KS}}(\mathbf{r}) = \epsilon_i^{\mathsf{KS}}\varphi_i^{\mathsf{KS}}(\mathbf{r}), \qquad (4.1.15)$$

where the exchange-correlation  $V_{xc}$  is replaced by the self-energy  $\Sigma$ . But the two quantities are actually far away to be the same.  $\Sigma$  is a non-Hermitian, non-local and frequency dependent operator while  $V_{xc}$  is a local and static operator. Moreover,  $V_{xc}$  is covered in the KS noninteracting system. Important physical quantities can be extracted from this Equation 4.1.14: The lifetime of the QP can be obtained from the inverse of the imaginary part of the complex energy  $E_i^{QP}$ . Many important properties of a system such transport and thermalisation can then be determined from the QP lifetime [116]. The real part of  $E_i^{QP}$  corresponds to the QP energy, thus, it can provide the bandgap and bandstructure of the system. However, the challenge here is how to calculate  $\Sigma$  accurately. Details about the method for obtaining  $\Sigma$  will be discussed in the next section.

#### 4.2 The GW Approximation

Section 4.1 gives a new insight into the many electron problem in terms of the QP following the quasiparticle equation

$$h_0(\mathbf{r})\varphi_i^{QP}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', E_i^{QP})\varphi_i^{QP}(\mathbf{r}) = E_i^{QP}\varphi_i^{QP}(\mathbf{r}), \qquad (4.2.1)$$

where  $h_0(\mathbf{r})$  defines the unperturbed system and  $\Sigma$  the perturbation term. It is common to use the non-interacting KS system as the unperturbed system. The idea is that the exchangecorrelation potential already includes some of the exchange and correlation effects in the actual system. Regarding  $\Sigma$ , since the interaction between the QP is described by the dynamically screened Coulomb interaction W, Hedin [107] proposed that it can be expressed as perturbation series in terms of W as

$$\Sigma = iGW - GWGWG + \dots \qquad (4.2.2)$$

G and W are obtained using a self-consistent procedure from a set of Dyson-like equation also known as Hedin's equations [46, 114]:

$$P(12) = -i \int d(34)G(13)G(41^{+})\Gamma(34,2)$$
(4.2.3)

$$W(12) = V(12) + \int d(34)W(13)P(34)V(42)$$
(4.2.4)

$$\Sigma(12) = i \int d(34)G(14^+)W(13)\Gamma(42,3)$$
(4.2.5)

$$G(12) = G_0(12) + \int d(34)G_0(13) \left[\Sigma(34) - \delta(34)V_{xc}(4)\right] G(42)$$
(4.2.6)

$$\Gamma(12,3) = \delta(12)\delta(13) + \int d(4567)\frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(67,3), \qquad (4.2.7)$$

where  $\Gamma$  the vertex function is given by the variation of the inverse of G with respect to the potential change, P the polarisation function, V the bare coulomb potential and G<sub>0</sub> the Green's function of the unperturbed system. These equations are very difficult to be solve exactly. By

truncating the series expansion from Equation 4.2.2 at the first term, we obtain the so-called GW approximation. At this level of the approximation, the second term of Equation 4.2.7 is neglected, i.e.  $\Gamma = \delta$ , hence,

$$P(12) = -iG(12)G(21) \tag{4.2.8}$$

which corresponds to the random phase approximation (RPA) for the screened Coulomb interaction W. Hence,  $\Sigma$  becomes a direct product of G and W. Details about the practical aspect of GW will be given in the chapter. The GW method is very efficient for calculating the fundamental bandgap of a broad range of materials. It will be used for calculating the electronic properties of some of the materials investigated in this work. Single particle Green's function only provides information on non-particle conserving excitations such as photoemission and photoabsorption. Neutral excitations such as the excitonic effect can only be captured by two particle Green's function. The next section will give insight to this notion.

# 4.3 The two-particle Green's functions: the Bethe Salpeter equation

In the MBPT, charged excitations corresponding to the addition or removal of electrons from a material are well described by using of the one particle Green's function by means of the Hedin's equations at the GW level of the approximation. But, neutral excitations such as optical and energy-loss spectra cannot be treated in the same framework since it they require the use of a two particles Green's function. The Bethe Sepeter Equation (BSE) has been a very successful tool for calculating these properties. It makes use of a two particles Green's function (Equation 4.1.10) to describe the propagation of the electron-hole pair. Moreover, in the construction of the polarisation P, the vertex correction has to be considered. In this regard, one has to go through the second iteration of Hedin's equation but now considering  $\Sigma = iGW$  in Equation 4.2.7. This

yields [117]

$$\Gamma(12,3) = \delta(12)\delta(13) + iW(1^{+}2) \int d(67)G(16)G(72)\Gamma(67,3)$$
(4.3.1)

with the assumption that

$$\frac{\delta \Sigma}{\delta G} \approx iW,\tag{4.3.2}$$

where W is the screened Coulomb potential based on the RPA polarisation (Equation 4.2.8) and the change in screening due to the excitation  $\left(\frac{\delta W}{\delta G}\right)$  is negligible. Equation 4.3.1 can be transformed to an integral equation for polarisation by multiplying with iG(41)G(25) on the left and integrating over d(12):

$$P(345) = iG(43)G(35) + i \int d(12)P(312)W_0(1^+2)G(41)G(25)$$
(4.3.3)

The kernel GGW of the integral in (4.3.3) can be seen as a four-point function, thus, we can also define a four-point screened Coulom interaction as

$$W(1234) = W(12)\delta(13)\delta(24). \tag{4.3.4}$$

Subsequently, Equation 4.3.3 will be transformed to a four-point integral equation [110, 118]

$$P(1234) = P_0(1234) - \int d(5678)P(1234)W(5678)P_0(7834).$$
(4.3.5)

Following the description of Onida et al. in Ref [117], we define a new polarisation

$$\bar{P} = P + P\bar{v}P,\tag{4.3.6}$$

where  $\bar{v}$  is the Coulomb potential without long range term in reciprocal space reads

$$\bar{v}_{\mathbf{G}} = \begin{cases} 0, & \mathbf{G}(\mathbf{q}) = 0\\ \bar{v}_{\mathbf{G}}(\mathbf{q}) & \mathbf{G} \neq 0. \end{cases}$$
(4.3.7)

Inserting Equation 4.3.3 in Equation 4.3.6, we arrive at the so-called Bethe Selpeter equation:

$$\bar{P} = P_0 + P_0 K \bar{P}, \tag{4.3.8}$$

where K the kernel of the BSE given by

$$K(1234) = -i\delta(12)\delta(34)\bar{v}(13) - i\delta(13)\delta(24)W(12).$$
(4.3.9)

 $P_0$  the polarisation function of independent quasiparticle defined as

$$P_0(12, 1'2') = G(1'2)G(21'). \tag{4.3.10}$$

The macroscopic dielectric function  $\epsilon_M(\omega)$  is yielded by

$$\epsilon_M(\omega) = 1 - \lim_{\mathbf{q} \to 0} v(\mathbf{q}) \hat{\chi}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q};\omega)$$
(4.3.11)

where  $\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) = -iP(\mathbf{r}, \mathbf{r}, \mathbf{r}', \mathbf{r}'; \omega)$ . In partice, Equation 4.3.8 is written in the form of eigenvalues equation as [119]

$$(E_{c,\mathbf{k}+\mathbf{Q}} - E_{vc\mathbf{k}})A_{vc\mathbf{k}}^{S} + \sum_{v',c',\mathbf{k}'} \langle vc\mathbf{k}|K^{eh}|v'c'\mathbf{k}'\rangle A_{v'c'\mathbf{k}'}^{S} = \Omega_{S}A_{vc\mathbf{k}}^{S}$$
(4.3.12)

where  $E_{c\mathbf{k}}$  and  $E_{v\mathbf{k}}$  are the single particle QP energies of the conduction and valence band at a specific **k**-point,  $A_{vc\mathbf{k}}^S$  the electron-hole amplitude and  $\Omega_S$  the corresponding excitation energies. Details about the practical aspect of GW/BSE as well as other properties will be given in the next chapter.

## 5. Calculation Methods

The aim of this chapter is to outline the procedure used in calculations in this thesis. Some of the aspects including, practical solution of the KS equation, geometry optimisation, thermodynamic stability are in Appendixes A, B and C.

#### 5.1 Electronic bandstructure and density of states

Electrons in an atom occupy a set of orbitals. Within a molecule/solid, these orbitals overlap and form a energy band known as the fully occupied valence band and the unoccupied conduction band. However, depending on how they overlap, some of the energy levels may be left empty. Such forbidden regions are what are known as bandgaps. Materials are classified insulators, semi-conductors or metal according to the size of the bandgap. For the insulators and semiconductors, the valence band is completely filled while the conduction is empty. The insulators have bandgap larger than 3 eV while that of the semiconductors is usually smaller. In semiconductors, some of the valence electrons can actually move to the conductor band by small excitations. GaAs is a typical semiconductor with a bandgap of 1.43 eV. Metals do not have a bandgap and their conduction band is partially filled.

Bandstructure corresponds to the plot of electron energy  $E_{\mathbf{k}}$ , solution to Equation A.3.2, at different  $\mathbf{k}$  vector ( $\mathbf{k} \in$  reciprocal space). Because of the translational symmetry of the crystal, it is advisable to plot  $E_{\mathbf{k}}$  along the high symmetry point in the BZ. The number of high symmetry  $\mathbf{k}$ -points as well as the integration path along BZ depends on the Bravais lattices. All the  $\mathbf{k}$ -point paths used in our calculations were automatically generated from the AFLOW software [120]. The density of states (DOS) represent the number of states which can be occupied at each energy level. In the energy range [E, E + dE], the DOS per unit volume  $\Omega$  is given as [51]

$$N(E) = \frac{\Omega}{2\pi^3} \int_{BZ} d\mathbf{k} \ \delta(E_{i,\mathbf{k}} - E).$$
(5.1.1)

In the case of complex solids with different atomic species, the contribution of a given atom to the total DOS is obtained through the projected density of states.

#### 5.2 Optical properties: the dielectric function

The complex dielectric function  $\varepsilon(\omega)$  is the fundamental quantity used to determine optical properties of a material. It describes the response of the material to electromagnetic radiation. When an external electric field  $E_{ext}$  is applied to an electronic system, it creates an induced electric field  $E_{ind}$  within the system in such a way that the total electric field acting on the system is

$$E_{tot} = E_{ext} + E_{ind}.$$
(5.2.1)

The dielectric tensor  $\varepsilon^{-1}$  relates the total electric field to the external field:

$$E_{tot} = \varepsilon^{-1} E_{ext}.$$
 (5.2.2)

Subsequently, the total potential and external potential are related similarly:

$$V_{tot} = \varepsilon^{-1} V_{ext}.$$
 (5.2.3)

The dielectric function and its inverse can also be expressed in terms of reducible polarisation  $\chi$  and irreducible polarisation P as:

$$\varepsilon = \frac{\delta V_{ext}}{\delta V_{tot}} = 1 - \nu \frac{\delta \rho}{\delta V_{tot}} = 1 - \nu P$$
 (5.2.4)

$$\varepsilon^{-1} = \frac{\delta V_{tot}}{\delta V_{ext}} = 1 + \nu \frac{\delta \rho}{\delta V_{ext}} = 1 + \nu \chi$$
(5.2.5)

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where P and  $\chi$  are the functional derivatives of the electronic density with respect to the total potential and the external potential respectively.  $\nu$  is the bare Coulomb kernel:  $\nu = \frac{4\pi e^2}{\mathbf{q}^2}$ . The product of the two polarisations leads to a Dyson-like equation

$$\chi = P + P\nu\chi. \tag{5.2.6}$$

The response function as described above is macroscopic since it depends on the external and the total potential which are macroscopic<sup>1</sup> quantities. At the atomic level, the total electric field  $\mathbf{e}(\mathbf{r},\omega)$ 

$$\mathbf{e}(\mathbf{r},\omega) = \int d\mathbf{r}' \varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) E_{ext}(\mathbf{r}',\omega)$$
(5.2.7)

is microscopic. We then need to find a connection between the macroscopic quantities (experimentally measurable<sup>2</sup>) and the microscopic ones (obtained from ab-initio calculations). In momentum space, the macroscopic electric field is

$$E_{tot}(\mathbf{q},\omega) = \varepsilon_{macro}^{-1} E_{ext}(\mathbf{q},\omega).$$
(5.2.8)

Since the microscopic electric field oscillates in the scale of the unit cell in a periodic system, the microscopic dielectric function is invariant by a translation of lattice vector  $\mathbf{R}$ :

$$\varepsilon(\mathbf{r}, \mathbf{r}', \omega) = \varepsilon(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}, \omega).$$
(5.2.9)

In general, the Fourier transform of a function  $g(\mathbf{r}, \mathbf{r}', \omega)$  can be written as:

$$g(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) = \int d\mathbf{r} d\mathbf{r}' e^{-i(\mathbf{q} + \mathbf{G})\mathbf{r}} g(\mathbf{r}, \mathbf{r}', \omega) e^{+i(\mathbf{q} + \mathbf{G}')\mathbf{r}'}.$$
 (5.2.10)

Therefore, in momentum space, Equation 5.2.7 becomes:

$$e(\mathbf{q} + \mathbf{G}, \omega) = \sum_{\mathbf{G}'} \varepsilon_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega) E_{ext}(\mathbf{q} + \mathbf{G}', \omega)$$
(5.2.11)

<sup>&</sup>lt;sup>1</sup> The total macroscopic electric field follows the periodicity of the external perturbation.

<sup>&</sup>lt;sup>2</sup>The macroscopic quantities directly measured in spectroscopy experiments included the electron energy Loss spectrum(EELS), the absorption, etc

where **G** and **G**' are the reciprocal lattice vectors. The Fourier transform of  $e(\mathbf{r}, \omega)$  and  $E_{tot}(\mathbf{r}, \omega)$ are respectively

$$e(\mathbf{r},\omega) = \sum_{\mathbf{G}} \int_{BZ} \frac{d\mathbf{q}^3}{(2\pi)^3} e(\mathbf{q} + \mathbf{G},\omega) e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}$$
(5.2.12)

$$E_{tot}(\mathbf{R},\omega) = \sum_{\mathbf{G}} \int_{BZ} \frac{d\mathbf{q}^3}{(2\pi)^3} E(\mathbf{q} + \mathbf{G},\omega) e^{i(\mathbf{q}+\mathbf{G})\mathbf{R}}.$$
 (5.2.13)

 $E_{tot}(\mathbf{R},\omega)$  can be evaluated using  $e(\mathbf{r},\omega)$  by integrating over unit cell around the position  $\mathbf{R}$ :

$$E_{tot}(\mathbf{R},\omega) = \frac{1}{V} \int_{V(\mathbf{R})} e(\mathbf{r},\omega) d\mathbf{r}.$$
(5.2.14)

Assuming  $(\mathbf{G}\gg\mathbf{q})^{\mathbf{3}}$ ,

$$E_{tot}(\mathbf{R},\omega) = \int_{BZ} \frac{d\mathbf{q}^3}{(2\pi)^3} e(\mathbf{q},\omega) e^{i\mathbf{q}\mathbf{R}}.$$
(5.2.15)

Comparing Equation 5.2.13 and Equation 5.2.15, it follows that the macroscopic averaged field corresponds to the  $\mathbf{G} = 0$  component of the corresponding microscopic field [121]:

$$E_{tot}(\mathbf{q} + \mathbf{G}, \omega) = e(\mathbf{q}, \omega)\delta_{\mathbf{G}, 0}.$$
(5.2.16)

The external field can also be written as

$$E_{ext}(\mathbf{q} + \mathbf{G}, \omega) = E_{ext}(\mathbf{q}, \omega)\delta_{\mathbf{G}, 0}.$$
(5.2.17)

Hence,

$$E_{tot}(\mathbf{q},\omega) = e(\mathbf{q},\omega) = \sum_{\mathbf{G}'} \varepsilon_{0\mathbf{G}'}^{-1}(\mathbf{q},\omega) E_{ext}(\mathbf{q},\omega) \delta_{\mathbf{G}'0}$$
$$= \varepsilon_{00}^{-1}(\mathbf{q},\omega) E_{ext}(\mathbf{q},\omega).$$
(5.2.18)

<sup>3</sup>The assumption stands from the fact that the macroscopic field varies on a larger scale that the atomic distance.

Equating Equation 5.2.8 and Equation 5.2.18 leads to the connection between the macroscopic and the microscopic dielectric function

$$\varepsilon_{macro}(\mathbf{q},\omega) = \frac{1}{\varepsilon_{\mathbf{g}=0,\mathbf{g}'=0}^{-1}(\mathbf{q},\omega)}.$$
(5.2.19)

For homogeneous system,  $\varepsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q},\omega)$  is diagonal and

$$\varepsilon_{macro}(\mathbf{q},\omega) = \varepsilon_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega).$$
(5.2.20)

However, in a real solid, the microscopic electric field often varies rapidly over the unit cell compared to the external field. This is known as the local field effect [122]. As a consequence, the off-diagonal elements of the tensor  $\varepsilon_{\mathbf{GG}'}^{-1}(\mathbf{q},\omega)$  are no longer equal to zero. In practice,  $\varepsilon_{macro}(\mathbf{q},\omega)$  is obtained as follow :

- invert  $\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega):\to \varepsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q},\omega)$ ,
- construct  $\varepsilon_{{\bf G}=0,{\bf G}'=0}^{-1}({\bf q},\omega)$  by taking the diagonal element of  $\varepsilon_{{\bf G}{\bf G}'}^{-1}({\bf q},\omega)$ ,
- invert  $\varepsilon_{\mathbf{G}=0,\mathbf{G}'=0}^{-1}(\mathbf{q},\omega) \rightarrow \varepsilon_{macro}^{-1}(\mathbf{q},\omega).$

Once the  $\varepsilon_{macro}$  is known, the absorption (Abs) and the electron energy loss spectrum (ELLS) are obtained as

$$\mathsf{Abs}(\omega) = \lim_{\mathbf{q}\to 0} \Im m[\varepsilon_{macro}(\mathbf{q},\omega)] = \lim_{\mathbf{q}\to 0} \Im m\left[\frac{1}{\varepsilon_{\mathbf{g}=0,\mathbf{g}'=0}^{-1}(\mathbf{q},\omega)}\right]$$
(5.2.21)

and

$$\mathsf{EELS}(\omega) = -\lim_{\mathbf{q}\to 0} \Im m [\varepsilon_{macro}(\mathbf{q},\omega)]^{-1} = -\lim_{\mathbf{q}\to 0} \Im m \left[ \varepsilon_{\mathbf{G}=0,\mathbf{G}'=0}^{-1}(\mathbf{q},\omega) \right].$$
(5.2.22)

Using (5.2.4) and (5.2.5),  $\varepsilon_{\mathbf{GG}'}(\mathbf{q},\omega)$  and  $\varepsilon_{\mathbf{GG}'}^{-1}(\mathbf{q},\omega)$  become:

$$\varepsilon_{\mathbf{GG}'}(\mathbf{q},\omega) = \delta_{\mathbf{GG}'} - \nu_{\mathbf{GG}'} P_{\mathbf{GG}'}(\mathbf{q},\omega), \qquad (5.2.23)$$

$$\varepsilon_{\mathbf{GG}'}^{-1}(\mathbf{q},\omega) = \delta_{\mathbf{GG}'} + \nu_{\mathbf{GG}'}\chi_{\mathbf{GG}'}(\mathbf{q},\omega).$$
(5.2.24)

Either P or  $\chi$  has to be approximated in order to get  $\varepsilon_{macro}$ . The polarisation P can be calculated in the KS scheme as

$$P = \chi^{KS} + \chi^{KS} f_{xc} P \tag{5.2.25}$$

where  $f_{xc}$  is the exchange-correlation kernel which expressed the change (functional derivative) of the exchange-correlation potential with respect to the change of the density n:

$$f_{xc} = \frac{\delta v_{xc}}{\delta n}.$$
(5.2.26)

By neglected  $f_{xc}$ ,  $P_{\mathbf{GG'}} = \chi^{KS}_{\mathbf{GG'}}$  and Equation 5.2.23 becomes:

$$\varepsilon_{\mathbf{GG}'}(\mathbf{q},\omega) = \delta_{\mathbf{GG}'} - \nu_{\mathbf{GG}'} \chi_{\mathbf{GG}'}^{KS}(\mathbf{q},\omega).$$
(5.2.27)

This approximation is known as random phase approximation (RPA). Some of our calculations will be done at this level of the approximation.

#### 5.3 The GW routine

The GW approximation consist of solving the Hedin's equations (4.2). Practical implementation of such equations is very cumbersome and approximations need to be made. There are quite different levels of approximation starting from a non self-consistent to a fully self-consistent calculation of the self-energy. The non self-consistent method is also known as the single shot GW ( $G_0W_0$ ). At this level of approximation, the Green's function  $G_0$  is constructed from eigenvalues  $E_i$  and orbitals  $\varphi$  of a reference system and the dynamically screened Coulomb potential  $W_0$  within the RPA:

$$G_0(\mathbf{r}', \mathbf{r}; E) = \sum_i \frac{\varphi(\mathbf{r})\varphi^*(\mathbf{r}')}{E - E_i + i\eta sng(E_i - \mu)},$$
(5.3.1)

$$W_0(\mathbf{r}, \mathbf{r}', E) = \int \varepsilon^{-1}(\mathbf{r}, \mathbf{r}_1, E) v(\mathbf{r}, \mathbf{r}') d\mathbf{r}_1$$
(5.3.2)

where  $v(\mathbf{r}, \mathbf{r}')$  is the bare Coulomb potential and  $\varepsilon^{-1}$  the dielectric function as presented in Equation 5.2.27 in momentum space. Most often, the HF and the KS system are chosen as a reference. In our study, we employed the KS reference at the GGA-PBEsol level. In a first-order perturbation scheme, the eigenvalues are simply obtained thanks to the evaluation of the diagonal matrix elements [123]:

$$E_{i,\mathbf{k}}^{GW} = E_{i,\mathbf{k}}^{KS} + \langle \varphi_{i,\mathbf{k}}^{KS} \mid \Sigma(E_{i,\mathbf{k}}^{GW}) - V_{xc}^{KS} \mid \varphi_{i,\mathbf{k}}^{KS} \rangle.$$
(5.3.3)

In the vicinity of the KS eigenvalues, the  $\Sigma(E_{i,\mathbf{k}}^{GW})$  is expanded at the first order of a Taylor series as

$$\Sigma(E_{i,\mathbf{k}}^{GW}) = \Sigma(E_{i,\mathbf{k}}^{KS}) + \left(E_{i,\mathbf{k}}^{GW} - E_{i,\mathbf{k}}^{KS}\right) \frac{\partial \Sigma}{\partial E}\Big|_{E_{i,\mathbf{k}}^{KS}}.$$
(5.3.4)

Inserting this expansion in Equation 5.3.3, the QP energies are obtained as

$$E_{i,\mathbf{k}}^{GW} = E_{i,\mathbf{k}}^{KS} + Z \langle \varphi_{i,\mathbf{k}}^{KS} \mid \Sigma(E_{i,\mathbf{k}}^{KS}) - V_{xc}^{KS} \mid \varphi_{i,\mathbf{k}}^{KS} \rangle$$
(5.3.5)

where

$$Z = \frac{1}{1 - \frac{\partial \Sigma}{\partial E} \Big|_{E_{i,\mathbf{k}}^{KS}}}.$$
(5.3.6)

The  $G_0W_0$  method works quite well for semiconductors and insulators [124], but in some cases, one has to go beyond this level of approximation. Different approaches can be employed here:

- use a different starting point for the  $G_0W_0$  calculations such as
  - choosing another approximation for exchange-correlation : LDA, GGA, .....
  - LDA/GGA+U
  - hybrid functionals

for a good approximation of the QP eigenvalues and states.

- use a semi self-consistent GW (GW<sub>0</sub>) where the Green's function is updated from a G<sub>0</sub>W<sub>0</sub> calculation
- use the self-consistent Coulomb hole plus screened exchange (scCOHSEX) scheme and build the single-shot GW on top of it (scCOHSEX+G<sub>0</sub>W<sub>0</sub>) [123].

The fully self-consistent GW is used rarely because of its computational cost and it does not necessary lead to improvement. Generally, GW approaches lead to the improvement on the bandgaps but not for the response function. This is due to the fact that the polarisation  $P = GG\Gamma$  ( $\Gamma = 1$ ) entering in the calculation of the dielectric function at this level of the approximation does not incorporate the vertex correction. One has to go beyond the RPA by finding the solution of the BSE where the electron-hole interaction is included in the polarisation through a second iteration of Hedin's equations.

The key quantity extracted from the BSE calculation is the macroscopic dielectric function that reads [117, 119, 125]

$$\varepsilon_{M}(\omega) = 1 - \lim_{\mathbf{q} \to 0} v_{\mathbf{G}=0}(\mathbf{q}) \sum_{\lambda} \frac{\left| \sum_{(vc\mathbf{k})} \langle v, \mathbf{k} | e^{-i\mathbf{q} \cdot \mathbf{r}} | c, \mathbf{k} \rangle A_{\lambda}^{(vc\mathbf{k})} \right|^{2}}{\Omega_{\lambda}^{exc} - \omega - i\eta},$$
(5.3.7)

where  $A_{\lambda}$  and  $\Omega_{\lambda}^{exc}$  are the exciton eigenstates and eigenvalues obtained by diagonalising the resonant part of the two particle Hamiltonian<sup>4</sup>

$$H^{exc,res}_{(v,c;\mathbf{k})(v',c';\mathbf{k}')}A^{(v',c';\mathbf{k}')}_{\lambda} = \Omega^{exc}_{\lambda}A^{(v',c';\mathbf{k}')}_{\lambda}.$$
(5.3.8)

<sup>&</sup>lt;sup>4</sup>Neglecting the coupling part of the two particle Hamiltonian is called the Tamm-Dancoff approximation [117]

In the reciprocal space,  $H^{exc,res}$  written [126]

$$H_{(v,c;\mathbf{k})(v',c';\mathbf{k}')}^{exc,res} = \left(E_{c\mathbf{k}}^{QP} - E_{v\mathbf{k}}^{QP}\right)\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k},\mathbf{k}'} + \frac{4\pi}{V}\sum_{\mathbf{G},\mathbf{G}'}\left[2\frac{\delta_{\mathbf{G},\mathbf{G}'}(1-\delta_{\mathbf{G},0})}{|\mathbf{G}|^2}B_{cv}^{\mathbf{k},\mathbf{k}}(\mathbf{G})B_{c'v'}^{\mathbf{k}',\mathbf{k}'*}(\mathbf{G}) - \frac{\varepsilon^{-1}(\mathbf{k}-\mathbf{k}'+\mathbf{G},\mathbf{k}-\mathbf{k}'+\mathbf{G}',\omega=0)}{|\mathbf{k}-\mathbf{k}'-\mathbf{G}|^2}B_{cc'}^{\mathbf{k},\mathbf{k}'}(\mathbf{G})B_{vv'}^{\mathbf{k},\mathbf{k}'*}(\mathbf{G}')\right]$$
(5.3.9)

$$=H^{diag,res} + H^{exc,res} + H^{Coul,res}$$
(5.3.10)

where

$$B^{\mathbf{k},\mathbf{k}'}_{n\ n'}(\mathbf{G}) = \frac{1}{V}\int u_{n\mathbf{k}}(\mathbf{r})u_{n'\mathbf{k}'}(\mathbf{r})e^{i\mathbf{G}\mathbf{r}}d\mathbf{r}$$

with u the periodic part of the Bloch wave-functions and V the unit cell volume.  $H^{diag,res}$  is the diagonal term,  $H^{exc,res}$  the unscreened short-range exchange term and  $H^{Coul,res}$  the Coulomb term. From BSE calculations, excitonic effects in the optical absorption spectra of semiconductors and insulators can be quantified. In absorption spectra, the presence of absorption peaks appearing below the bandgap are an indication of bond excitons. In direct bandgap materials, the binding energy of the exciton can easily be estimated as the energy difference between the position of the exciton peaks and the fundamental bandgap estimated from GW calculations. The notions mentioned in this chapter will be used in the Part II where we will present our results.

## Part II

## **Results and Discussions**

### 6. Crystal structure description

Before going into details of the calculations, we start by giving a short crystallography description of the structures under investigation. Chalcopyrite I-III-VI<sub>2</sub> compounds (also termed ABC<sub>2</sub> materials) are ternary analogues of binary II-IV zincblende materials where the group II cation in the zincblende structure is replaced by two cations, A and B, from different groups of the periodic table, see Figure 6.1. The presence of the two cations, A and B, induces important changes in the properties of chalcopyrites, despite the structural similarity with the binary analogues. Many of these differences are important in this study. In terms of structural properties, the symmetry changes from cubic to tetragonal and the ratio  $\eta = c/2a$  of the lattice parameters c and a changes from unity. This is known as tetragonal distortion [127]. Moreover, the new atomic environment constrains the anions to adopt equilibrium positions which tend be at unequal distances from the cations. Jaffe et *al.* refer to it as bond alternation and it can be measured by the anion displacement [127].

$$u = \frac{1}{4} + \frac{\left(R_{CA}^2 - R_{CB}^2\right)}{a^2},\tag{6.0.1}$$

with  $R_{CA} \neq R_{CB}$  where  $R_{CA}$  and  $R_{CB}$  are the distances from the anion C to each of the cations A and B respectively.

In addition to the structural changes, the bandgaps of the chalcopyrites tend to be smaller than that of their corresponding binaries. Many authors have predicted such behaviour as a result of crystal field splitting at the upper most valence band and hybridisation between the *d*-orbital of the A cation and *p*-orbital from the C anion [24, 127–130]. These important changes will be explored in our study.


**Figure 6.1** Chalcopyrite I-III-VI<sub>2</sub> crystal structure. A(blue), B(violet) and C(grey) represent the cations I, III and the anion VI respectively.

The crystallographic description including the space group and the space group number as well as the prototype structure, and the identification numbers of the other structures is summarised in Table 6.1. It is important to point out here that the choice of the phases to investigate is based on the fact that they were previously observed in other ternary chalcogenide materials.

**Table 6.1** Crystallographic description of the chalcopyrite structures and some other phases of ABC<sub>2</sub> materials investigated. The space group and the space group number are in square brackets while the prototype structures are given as an example of the structures under investigation. Details about the structures can be found using the identification numbers (IDs) from the Materials Project (MP) [131] or the Inorganic Crystal Structure Database (ICSD) [132].

Phase	Space Group	MP or	Prototype
		ICDS IDs	
chalcopyrite(CH-)	l42d[122]	mp-19833	$CuFeS_2$
		icds-52577	
orthorhombic(OR-)	$Pna2_1[33]$	mp-21459	$\beta\text{-}NaFeO_2$
		icds-51618	
rhombohedral(RH-)	R3̄m[166]	mp-20162	$\alpha\text{-NaFeO}_2$
		icds-32655	
monoclinic	C2/m[12]	mp-634855	$NaNiO_2$
		icds-853177	
hexagonal	P3m1[156]	mp-7885	$LiMnSe_2$
		icds-25356	
rocksalt	Fm3m[225]	icds-165739	$CuAlS_2$

# 7. Chalcopyrites AgAlX<sub>2</sub>(X= S,Se,Te)

The focus of this chapter is to investigate the structural properties of  $AgAIX_2(X = S, Se, Te)$ . We shall explore the implications of tetragonal distortion and anion displacement. We also perform a detailed study of the pressure-induced phase transition and structural stability of these compounds. Furthermore, we explore the ability of different approximations, namely, the GGA functionals (PBE and PBEsol), the hybrid functional HSE06, the new modified Becke-Jonshon meta-GGA functional and the GW approximations to describe the electronic and optical properties. Because of the presence of heavy metals such as Se and Te in the structure of these materials, spin-orbit coupling (SOC) can have an effect on the bandgap by splitting the energy levels around the Fermi level. Thus, the impact of the SOC on the electronic properties is also investigated as well as the effect of anionic displacement on the optical properties.

We employed the Projector Augmented Wave method (PAW) [133] as implemented in the Vienna Ab Initio Package [134] for the calculations. The exchange-correlation was approximated by the GGAs PBE [78] and PBEsol [80], the modified Becke-Jonshon (MBJ) meta-GGA functional [94] and the hybrid functional HSE06 with the Hartree-Fock screening parameter  $\mu$  was set at 0.2 Å<sup>-1</sup> [91]. We used a Monkhorst-Pack **k**-point mesh for sampling the Brillouin zone [135]. A  $\Gamma$ - centered grid of 7x7x7 was chosen and leads to a total energy per atom converged to within 0.1 meV. After a series of convergence tests for the plane wave cut-off energy, 520 eV was found to be sufficient for our calculations. The high symmetry points for plotting the band structure and the phonon dispersion curves were generated using the online version of the AFLOW software [120]. Structural optimisation can be performed efficiently with GGAs and therefore the structural optimisation in this study was done by employing the GGAs only. To obtain the equilibrium structural parameters, the volume and the ion positions of the crystal were fully relaxed using the PBE and PBEsol approximations. Stability studies were performed by comparing the cohesive energy of the chalcopyrite phase relative to five other potential structural phases of AgAlX<sub>2</sub>; the monoclinic phase with space group C2/m (No. 12), the orthorhombic phase with space group  $P2_1nb$  (No 33), the trigonal phase in the hexagonal lattice system with space group P3m1 (No. 156), the trigonal phase in the rhombohedral lattice system with space group R3m (No. 166) and the cubic phase with space group  $Fm\overline{3}m$  (No. 225). More details about atomic position are given in Table 6.1. To the best of our knowledge these phases have not yet been explored as potential stable phases in the AgAIX<sub>2</sub> family, although other ternary chalcogenides such as AgInX<sub>2</sub>, CuAlX<sub>2</sub>, CuGaSe<sub>2</sub> and CuInSe<sub>2</sub> have been predicted to exist in these structures [136–140]. Recall that the chalcopyrite phase crystallises in a tetragonal structure with space group I42d (No. 122). The linear response method within the density function perturbation theory (DFPT) [141, 142] as implemented in VASP was used for the calculation of phonon and thermal properties. The PHONOPY package [143] was used to extract information from the DFPT calculations. The effect of the excitons on the optical absorption was studied by means of the many body perturbation theory at the BSE level. The quasiparticle energies entered into the BSE equation were obtained from single shot  $G_0W_0$  and the semi self consistent  $GW_0$ calculations. 264 conduction bands were used to determine the HSE06 and PBEsol dielectric function while about 969 bands were needed in GW calculations..

# 7.1 Structural properties

#### 7.1.1 Structural optimisation

Relaxed structures were obtained after performing a relaxation of the cell volume and ionic positions until the forces were less than 0.1 eV/Å. To study the equation of state, further calculations of the total energy at different cell volumes were carried out and the results were fitted by the third order Birch-Murnaghan equation of state [146]. The resulting equilibrium parameters are summarised in Table 7.1. The lattice parameter a, the tetragonal distortion  $\eta$ , the anion disMaterial

 $AgAlS_2$ 

 $AgAlSe_2$ 

 $AgAITe_2$ 

"CTB

"CTB rule"

PBE

PBEsol

Exp.

LDA

"CTB rule"

6.40

6.31

6.29

6.22

	-					
Method	a(Å)	$\eta$	u	$V_0(Å^3)$	$B_0(GPa)$	Ref.
PBE	5.75	0.911	0.293	21.63	63.81	PW
PBEsol	5.66	0.911	0.288	20.69	73.78	PW
Exp.	5.72	0.885	0.290	20.86	-	[144]
LDA	5.48	0.994	0.265	-	-	[145]
CTB rule"*			0.288			[127]
PBE	6.04	0.919	0.285	25.28	52.94	PW
PBEsol	5.91	0.933	0.281	24.00	61.23	PW
Exp.	5.95	0.903	0.270	23.83	-	[144]
LDA	5.78	0.996	0.263	-		[145]

0.287

0.270

0.265

0.260

0.261

0.285

31.44

29.91

29.31

0.955

0.953

0.940

0.987

[127]

ΡW

PW

[144]

[145]

[127]

42.21

49.83

\_

**Table 7.1** Obtained structural parameters of  $AgAIX_2(X = S, Se, Te)$  compared to the available experimental and theoretical data, PW = Present Work. \*CTB stands for Conservation of Tetrahedral Bonds. For more detail about the method, readers are referred to Ref. [127] and references therein.

placement u and the equilibrium volumes per atom, V<sub>0</sub>, for both PBE and PBEsol show good agreement with experimental data. For example, the PBEsol volume of 24.00Å $^3$  of AgAlSe $_2$  is closer to the experimental volume of 23.83Å<sup>3</sup> than the PBE volume of 25.28Å<sup>3</sup>. This accuracy could be attributed to the fact that PBEsol was specially designed to correct the PBE underbonding for solids [80]. It is also worth noting here (see Table 7.1) that the equilibrium volume per atom of AgAITe<sub>2</sub> is larger than that of AgAISe<sub>2</sub> which in turn is larger than the volume per atom of AgAIS<sub>2</sub>. This can be explained by the following: In the same group of the periodic table, the atomic radius increases with increasing atomic number. S, Se and Te belong to the same group; the atomic radius of Te is larger than that of Se which in turn has a larger atomic radius than S.

The bond lengths of the chalcogenide atoms with the transition metal atoms tend to increase with atomic radius and hence, the volume per atom of AgAlTe<sub>2</sub> is the largest of the series. Using the bond lengths from the relaxed structures, we estimate the anion displacement from Equation 6.0.1. u decreases as the lattice bond lengths increase for both GGAs. The results are consistent with the experimental data with PBEsol giving more accurate values when compared to experiment. Jaffe and Zunger [127] used the "CTB plus  $\eta = \eta_{tet}$  rule" to calculate u as seen in Table 7.1. A fairly good agreement is found for AlAgS<sub>2</sub> while their prediction seems to overestimate the experimental data for AlAgSe<sub>2</sub> and AlAgTe<sub>2</sub>. The tetragonal distortion increases with increment of the bond lengths.

The bulk modulus  $B_0$  is defined as the resistance of a material to a uniform compression. Our calculated results show AgAlS<sub>2</sub> has the largest  $B_0$  of the series. Overall, the PBEsol is inclined to increase the moduli compared to PBE. This trend is consistent with the decrease in lattice parameters and atomic volumes when PBE and PBEsol results are compared, as mentioned earlier. We could not find any experimental or theoretical bulk moduli for the AgAlX<sub>2</sub> (X=S,Se,Te) family of compounds. However, our results are in the same range as the values calculated in Ref. [147,148] for the chalcopyrites AlCuX<sub>2</sub>. From this point forward, PBEsol results will be used as the GGA functional in the rest of this study.

#### 7.1.2 Phase stability

Stability can be examined in terms of the cohesive energy  $E_{coh}$ , defined as the energy required to separate atoms infinitely far apart from a solids by breaking the atomic bonds. Defined as in Equation C.1.1, the more negative the cohesive energy, the more stable the phase. We show in Figures 7.1a–7.1c the cohesive energy per atom versus volume per atom for the chalcopyrite and

the other potential phases of  $AgAlX_2$  considered in this study. The chalcopyrite structure has the lowest cohesive energy among the six phases indicating that it is the energetically favoured structure at equilibrium. Moreover, a stable phase at a given pressure is the one with the smallest enthalpy. Figures 7.1d–7.1f depict the enthalpy at different pressures. One can note that the chalcopyrite phase is the most stable relative to the others at zero pressure.

The transition pressure  $P_T$  is the pressure at which a structural phase transition is predicted to occur. It corresponds to the crossing point between two phases when the enthalpy versus pressure curves cross. From Figures 7.1d–7.1f we note that each of the AgAIX<sub>2</sub> systems considered are predicted to undergo a pressure phase transition. The values of  $P_T$  are summarised in Table 7.2 and it can be seen that the chalcopyrite structure transforms to the trigonal R $\bar{3}$ m structure with increase in pressure. **Table 7.2** Cohesive energy  $E_{coh}$  (eV) and transition pressure  $P_T$  (Gpa) for various phases AgAlX<sub>2</sub>(X=S,Se,Te). I $\bar{4}$ 2d, R $\bar{3}$ m and C2/m refer to the chalcopyrite, the trigonal and the monoclinic phase respectively.

	Space group	$E_{coh}$	Transition	$P_T$
	$Fm\bar{3}m$	-3.41		
	$P2_1nb$	-3.81		
$AgAlS_2$	P3m1	-3.77		
	$I\bar{4}2d$	-4.16		
	R3m	-4.09	$I\bar{4}2d\toR\bar{3}m$	2.79
	C2/m	-4.06		
	$Fm\bar{3}m$	-3.18		
	$P2_1nb$	-3.43		
$AgAlSe_2$	P3m1d	-3.48		
	$I\bar{4}2d$	-4.16		
	R3m	-3.72	$I\bar{4}2d\toR\bar{3}m$	2.46
	C2/m	-3.70		
	$Fm\bar{3}m$	-2.95		
	$P2_1nb$	-3.06		
$AgAlTe_2$	P3m1	-3.18		
	$I\bar{4}2d$	-4.16		
	R3m	-3.34	$I\bar{4}2d\toR\bar{3}m$	2.30
	C2/m	-3.29		



**Figure 7.1** Cohesive energy versus volume (a-c) and enthalpy versus pressure (d-f) for the chalcopyrite (I $\bar{4}2d$ ), the monoclinic C2/m, the orthorhombic  $P2_1nb$ , the trigonal P3m1, the trigonal  $R\bar{3}m$  and the cubic  $Fm\bar{3}m$ .

# 7.2 Dynamical stability and thermodynamic properties

A supercell of 64 atoms generated from the optimized unit cell (8 atoms) was used for the calculations of the force constants. The dynamical matrix is then obtained as the Fourier transform of the force constant matrix:

$$D_{\alpha\beta}^{kk'}(\mathbf{q}) = \frac{1}{\sqrt{M_k M_{k'}}} \sum_{l'} \Phi_{\alpha\beta}(0k, l'k') e^{i\mathbf{q}[\mathbf{r}(l'k') - \mathbf{r}(0k)]}$$
(7.2.1)

where  $M_k$  are the atomic masses. Subsequently, the normal phonon modes are computed from the dynamical matrix by solving the eigenvalues problem [141, 143]

$$\sum_{\beta k'} D^{kk'}_{\alpha\beta}(\mathbf{q}) e^{\beta k'}_{\mathbf{q}j} = \omega^2_{\mathbf{q}j} e^{\alpha k}_{\mathbf{q}j}$$
(7.2.2)



**Figure 7.2** The phonon-dispersion curves of AgAIX<sub>2</sub>.

where **q** and *j* are the wavevector and the band index respectively. Some details about the calculation of the force constant within DFPT can be found in Appendix C.3. Keeping in mind that the word "supercell" mentioned above does not have anything to do with the supercell method or direct method [149], an alternative approach to the linear response method that we used throughout our study for the phonon calculations. The implementation of the the linear response method (DFPT) in VASP only allows the calculation of the force constants at the  $\Gamma$  point contrary to other DFT codes. PHONOPY then advised to use a supercell in order to compensate for the DFT implementation in VASP.

A structure is predicted to be stable with respect to dynamical stability when no vibration modes have imaginary frequencies. The phonon spectrum along the high symmetry points is depicted in Figure 7.2. A careful observation shows that apart from the acoustic modes going to zero frequencies around the  $\Gamma$  point, all the phonon-dispersion curves remain positive throughout the BZ attesting to the stability of the structures. Moreover, there is not a clear limit between the acoustic and the optical modes for all the three spectra with AgAlS<sub>2</sub> having the highest optical modes. Phonons contribute to a range of thermodynamic properties including Helmholtz free energy F, entropy S and heat capacity at constant volume  $C_v$ . They can be calculated as function of the temperature using the following equations [143, 150]:

$$F = \frac{1}{2} \sum_{\mathbf{q}_j} \hbar \omega_{\mathbf{q}_j} + k_B T \sum_{\mathbf{q}_j} ln \left[ 1 - \exp\left(\frac{-\hbar \omega_{\mathbf{q}_j}}{k_B T}\right) \right],$$
(7.2.3)

$$S = -k_b \sum_{\mathbf{q}_j} ln \left[ 1 - \exp\left(\frac{-\hbar\omega_{\mathbf{q}_j}}{k_B T}\right) \right] - \frac{1}{T} \sum_{\mathbf{q}_j} \left[ \frac{\hbar\omega_{\mathbf{q}_j}}{\exp\left(\frac{-\hbar\omega_{\mathbf{q}_j}}{k_B T}\right) - 1} \right]$$
(7.2.4)

and

$$C_{v} = k_{b} \sum_{\mathbf{q}_{j}} \left(\frac{\hbar\omega_{\mathbf{q}_{j}}}{k_{B}T}\right)^{2} \frac{\exp\left(\frac{\hbar\omega_{\mathbf{q}_{j}}}{k_{B}T}\right)}{\left[\exp\left(\frac{\hbar\omega_{\mathbf{q}_{j}}}{k_{B}T}\right) - 1\right]^{2}},$$
(7.2.5)

where  $\omega_{\mathbf{q}_j}$  is the phonon frequency at the wavevector  $\mathbf{q}$  and band index j.  $k_B, \hbar$  and T are respectively the Boltzmann constant, the Planck's constant and the temperature. F(T) and  $C_v(T)$  are displayed in Figure 7.3 up to 500K. Inharmonic interactions are still not significant in the range of temperature.

Many factors contribute to the heat capacity and are of varying importance. For insulators and semiconductors, the principal contribution comes from lattice vibrations at low temperature. By increasing the temperature, electrons get excited and their contribution cannot be neglected. The population of electrons in the conduction band starts increasing when the thermal energy  $K_BT$  ( $K_B$ , the Boltzmann constant) approaches the energy gap ( $K_BT \sim E_g$ ). The maximum temperature in our study was set at 500K which leads to a thermal energy of 0.042 eV. This value is lower than all the calculated bandgaps (see in section 7.3). We can conclude that up to 500K, the phonon contribution to  $C_v$  is still the most important for the compounds under investigation.

The Helmholtz free energy is defined as F = U - TS with the internal energy U. Since the entropy S is an increasing function of the temperature, F should decrease with increasing of



Figure 7.3 Free energy and Heat capacity of AgAIX<sub>2</sub>.

temperature. All the three compounds satisfy that condition. F(T) does not go to zero at 0K indicating a zero point motion in the systems.  $C_v(T)$  increases rapidly at lower energy [0 - 200K] as predicted in the Debye model [151]. From the room temperature  $\sim 300$  K, it converges to a limit close to 200 J/K.mol . This asymptotic behaviour is in agreement with the Dulong-Petit law which states that  $C_v(T)$  should tend to 3Rn at high temperature with R = 8.31 J/K.mol the gas constant and n the number of atoms in the unit cell [151]. Each of our unit cells has n = 8 atoms and leads to  $C_v(T) \simeq 199,44$  J/K.mol which corresponds to the limit obtained in Figure 7.3b.

## 7.3 Electronic properties

Using the PBEsol optimised structural parameters, a systematic study of the density of states (DOS) and bandstructures were carried out using the PBEsol and hybrid functional HSE06. To address the issue of band splitting as mentioned in the introduction, we also perform a spin-orbit coupling calculation with PBEsol. PBEsol yields direct bandgaps at the  $\Gamma$  point of 1.83 eV, 1.11 eV and 1.03 eV for AgAlS<sub>2</sub>, AgAlSe<sub>2</sub> and AgAlTe<sub>2</sub> respectively. One can note that when both  $\eta$  and u decrease, the bandgap decreases as we go from S to Te. With inclusion of SOC, the bandgaps decrease by 0.01 eV, 0.07 eV and 0.11 eV respectively for AgAlS<sub>2</sub>, AgAlSe<sub>2</sub> and AgAlTe<sub>2</sub> as seen in Table 7.3. The bandgaps are in the same range as the previous theoretical results [145], but underestimate the experimental bandgaps as expected. This is a well known problem when using local and semi-local functionals. Such discrepancies come from the discontinuity of the functional derivative of the exchange correlation in the Kohn-Sham DFT formalism [66] as discussed in Chapter 3.

Representative graphs of both the bandstructure with and without SOC and the projected density of states (PDOS) are shown in Figure 7.5 with the Fermi level shifted to the zero. The bandstructures are calculated along the high symmetry points in the Brillouin zone. The AgAlX<sub>2</sub> family have different bandgaps, but the PDOS analysis shows common features. The PDOS of AgAlTe<sub>2</sub> is displayed in Figure 7.5c. The Ag(s), X(p), Al(s) and Al(p) orbitals dominate the conduction band. The valence band is divided into sub-bands of different width. The major contribution to the lowest sub-band comes from the chalcogenide s orbitals. For AgAlTe<sub>2</sub>, which is representative of the series, the region within the energy range  $\sim -6.45$  to  $\sim -4.99$  eV consists essentially of the Al(s) orbitals. The upper valance sub-band situated in the range of  $\sim -4.99$  to  $\sim 0$  eV is mainly due to Ag(d) and Te(p) with a strong hybridisation between the two orbitals. Hybridisation plays an important role in the bandgap reduction. In fact, the Ag(d) and Te(p) states which form the upper most valence band repel each other. This repulsion between the two orbitals pushes the valence band up and therefore reduces the bandgap [127]. The higher the repulsion, the smaller the bandgap. This hypothesis has been verified in most chalcopyrites [127, 130, 152]. A point to note here is that in the PAW method we used to perform our study, the Ag(d) orbitals are taken as non-core states.

To evaluate the importance of hybridisation in these compounds, Mishra et al. [145] used a LDA TB-LMTO method to study their DOSs and the bandstructures. In their first assumption, they considered the Ag(d) states as core states. Secondly they included the Ag(d) contribution to the bandstructure. A significant reduction of the gap of about 50% was noted. Hence, they concluded the Ag(d) and X(p) hybridisation plays a crucial role in determining the electronic properties.

The bandstructure of AgAlTe<sub>2</sub> with and without SOC are shown in Figure 7.5*a* and 7.5*b*. In contrast to Figure 7.5*b*, the band splitting can be observed at the valence band around the  $\Gamma$  due to incorporation of SOC. It also contributes to the bandgap reduction as seen in Table 7.3. In the binary zincblende compounds,  $\Gamma_{15}$  is the upper most valence band and is triply degenerate. In chalcopyrite compounds,  $\Gamma_{15}$  is split into a non-degenerate  $\Gamma_4$  and doubly degenerate  $\Gamma_5$  band due to the crystal field. The doubly degenerate  $\Gamma_5$  band is split into  $\Gamma_6$  and  $\Gamma_7$  when the SOC is taken into account as illustrated in Figure 7.6. The bandgap is reduced as a consequence of these band splittings.

Crystal field effects can be evaluated when the SOC is turned off and it corresponds to the energy difference between  $\Gamma_5$  and  $\Gamma_4$ ,  $\Delta_{cf} = \Gamma_5 - \Gamma_4$ , as shown in Figure 7.6. Spin-orbit splitting,  $\Delta_{so}$ , can be obtained from SOC calculation using the quasi-cubic model as reformulated by Rowe et *al.* [153] for the case of ternary chalcopyrite crystals:

$$E_{1,2} = \frac{1}{2} \left( \Delta_{so} + \Delta_{cf} \right) \pm \sqrt{\left[ \left( \Delta_{so} + \Delta_{cf} \right)^2 - \frac{8}{3} \Delta_{so} \Delta_{cf} \right]}$$
(7.3.1)

where  $E_{1,2}$  are the energies of the  $\Gamma_7$  levels relative to the  $\Gamma_6$  levels. The calculated values of  $\Delta_{so}$ and  $\Delta_{cf}$  for the three compounds are summarised in Table 7.3. We found that all the AgAIX<sub>2</sub> have a negative  $\Delta_{cf}$ . It as been shown that for chalcopyrites, when  $\eta < 1$ ,  $\Gamma_4$  is above  $\Gamma_5$ and  $\Delta_{cf}$  is negative. Moreover,  $\Delta_{cf}$  increases with increasing tetragonal distortion and anion displacement. Previous studies have shown that  $\Delta_{cf}$  changes with respect to the amplitude of the tetragonal distortion following the linear relation  $\Delta_{cf} = \frac{3}{2}b(2 - c/a)$  where c/a is the ratio between the lattice parameters and b, the deformation potential [154]. Using experimental data, Shay and Wernick [155] predicted  $b \simeq -1.0$  eV for I-III-VI<sub>2</sub> compounds. Calculated values of  $\Delta_{cf}$  using the latter relation are given in brackets in Table 7.3. They are slightly smaller than the previous values, but follow the same trend. Experimental values are not available for comparison.

As for  $\Delta_{so}$ , all three compounds have positive values and increase with increasing atomic number of the chalcogenide atom. Thus, the bandgap reduction is more pronounced in AgAlTe<sub>2</sub>. As in the case of the crystal field, we could not find experimental or calculated results in the literature. However, results for other I-III-VI<sub>2</sub> compounds also show an increase in the magnitude of  $\Delta_{so}$  as we go from S to Te [129, 130]. **Table 7.3** Calculated bandgap  $E_g$  (eV), crystal field splitting  $\Delta_{cf}$  (eV) and spin-orbit splitting  $\Delta_{so}$  (eV) of AgAlX<sub>2</sub> compared to the available experimental and theoretical data. The calculations in Ref. [145] were performed using the tight-bonding linear muffin-tin orbital (TB-LTMO) method within LDA. The values of  $\Delta_{cf}$  in brackets are calculated using the relation  $\Delta_{cf} = \frac{3}{2}b(2 - c/a)$ . PBEsol+soc refers to the PBEsol functional with inclusion of spin orbit coupling.

Compounds	Method	Eg	$\Delta_{cf}$	$\Delta_{so}$	Reference
	PBEsol	1.83	-0.273(-0.267)		PW
	$PBEsol{+}\mathrm{SOC}$	1.82		0.042	PW
$AgAIS_2$	HSE06	3.14			PW
	others	1.98			[145]
	Exp.	3.13			[145]
$AgAlSe_2$	PBEsol	1.11	-0.245(-0.201)		PW
	$PBEsol{+}\mathrm{SOC}$	1.04		0.204	PW
	HSE06	2.7			PW
	others	1.59			[145]
	Exp.	2.55			[145]
	PBEsol	1.03	-0.159(-0.141)		PW
$AgAITe_2$	$PBEsol{+}\mathrm{SOC}$	0.92		0.645	PW
	HSE06	2.34			PW
	others	1.36			[145]
	Exp.	2.27			[145]

An approach for finding a more accurate prediction of the bandgap is to carry out a hybrid functional HSE06 calculation which is well known for its performance when it comes to nonmetallic systems [91]. A comparative analysis of the HSE06 bandgap with experimental and other calculated results is presented in Table 7.3. HSE06 slightly overestimates the experimental results by about 5%, and is a considerable improvement over the dramatic underestimation of PBEsol. To understand the influence of the chalcogenide atoms on the bandgap of these chalcopyrite compounds, we plot in Figure 7.4 the bandgap Eg against the equilibrium volume per atom  $V_0$ .



**Figure 7.4** AgAIX<sub>2</sub> bandgap Eg against equilibrium volume per atom V<sub>0</sub>. The experimental data (Exp.) can be found in Refs. [145, 156]

From Table 7.3, one can note that AgAlTe<sub>2</sub> has the smallest gap irrespective of the functional used. Moreover, it is known that the atomic volume increases down each group of the periodic table. Meaning that as the volume of the chalcogenide atom increases, V<sub>0</sub> increases. We can then conclude that for the AgAlX<sub>2</sub> compounds, the bandgap decreases with increasing volume of the chalcogenide atom which allows a degree of bandgap tuning. In Figure 7.7 where we present the total density of states (DOS) of the three compounds, it can be seen that HSE06 opens the bandgap. Such modification could be attributed to the changes that occur on the orbitals around the bandgap while going from PBEsol to HSE06. With LDA and GGA-type of functionals, the orbitals are sometimes too delocalised and hence contribute to the narrowing of the bandgap. This is known as delocalisation error [157]. In Cu-based and Ag-based chalcopyrites, the *d* states are more localised than the *p* states [158]. Thus, HSE06 most likely corrects the delocalisation of the Ag(*d*) states and therefore opens the gap. Hartree-Fock (HF) type of functionals are known to localise electrons while GGA-type of functionals delocalise the electrons. By using the



**Figure 7.5** Bandstructure with (a) and without (b) SOC and PDOS (c) of AgAITe<sub>2</sub> using the PBEsol functional. The direct bandgap is located at the  $\Gamma$  point. With exception of the top valence band, AgAIS<sub>2</sub> and AgAISe<sub>2</sub> show almost identical features.

hybrid HSE06 functional which contains both GGAs and HF flavour, delocalisation and localisation can cancel out and lead to an accurate description of orbitals as pointed out in previous works [157, 159–161].

However, it is known that in first principles calculations, a balance should be found between accuracy of the result and computational time. As we noted above, HSE overcomes the issue the underestimation of the bandgap, but if we compare its computational cost to that of the GGA PBEsol, it turns out that it is very expensive. Bandgaps were then calculated with the MBJ which is known to be as less demanding as GGA PBEsol and as accurate is HSE. When comparing the bandgaps from MBJ with those HSE06 calculations (see Table 7.4), it can be seen that MBJ slightly underestimated the gap of AgAlSe<sub>2</sub> and AgAlTe<sub>2</sub> while HSE slightly overestimated the



**Figure 7.6** Manified bandstructure of AgAlX<sub>2</sub> around the  $\Gamma$  point when SOC is included (black) and excluded (red). Regarding the indexation of the bands we refer to the notation for chalcopyrites used in Ref. [24, 162, 163].

bandgaps.  $AgAIS_2$  gaps from the two functionals are in a very good agreement with those from the experiments. Figure 7.8 shows that the bandstructures from the two functionals are very similar. As for PBEsol, the direct bandgap observed experimentally is also predicted by these functionals.



Figure 7.7 TDOS of  $AgAIX_2$  with PBEsol and HSE06: (a)  $AgAIS_2$ ; (b)  $AgAISe_2$ ; (c)  $AgAITe_2$ .

**Table 7.4** Comparison of the MBJ bandgaps  $E_g$  (eV) with those from HSE06 and experimental (Exp.) data. method.

	$AgAIS_2$	$AgAlSe_2$	$AgAITe_2$
MBJ	3.15	2.38	2.14
HSE	3.14	2.7	2.34
Exp*.	3.13	2.55	2.27

\* = Ref. [145]



Figure 7.8 Bandstructures of  $\mathsf{AgAIS}_2$  from the MBJ (a) and HSE06 (b) approximations

# 7.4 Optical properties

#### 7.4.1 Dielectric function within the independent particle picture

We calculated the frequency dependant dielectric function within the independent particle picture with local field effects [101]. In an anisotropic crystal, the susceptibility  $\chi$  varies according to the polarisation and propagation direction of light. It usually leads to the phenomenon of birefringence [164]. Hence, due to the tetragonal structure of chalcopyrite crystals, we compute the dielectric function in the xy plane ( $\varepsilon^{\perp} = (\varepsilon_x + \varepsilon_y)/2$ ) and along the z axis ( $\varepsilon^{\parallel} = \varepsilon_z$ ) as shown in figure 6.1. Figure 7.9 depicts the real and imaginary parts of the frequency dependent dielectric function from 0 to 5 eV. The optical region ~(1.65 eV - 3.1 eV) is shaded in all the sub-figures. At first glance, one may note a similarity between Figure 7.9a, 7.9c and 7.9e which show the real parts for the three compounds, and Figure 7.9b, 7.9d and 7.9f which display the corresponding imaginary parts.

The spectra show that the static dielectric function  $\varepsilon_1(0)$ , increases from AgAIS<sub>2</sub> to AgAITe<sub>2</sub> as reported in Table 7.5. This could be linked to the size of their respective bandgaps. In fact, optical properties and electric properties are strongly related via the dielectric constant. The polarisation measures the strength of the interaction between the electronic states of the valence and the conduction bands in the presence of an external electric field. For large bandgap materials, this interaction is limited and hence leads to a small polarisation and therefore small dielectric constant. The smaller the band gap, the larger the dielectric constant. A careful examination of these spectra show an upwards trend from the infrared ( $\leq 1.65 \text{ eV}$ ) to the ultraviolet region ( $\geq 3.1 \text{eV}$ ). With the exception of AgAITe<sub>2</sub>, the main peaks are reached either at the edge of the optical region or in the ultraviolet region for both approximations. It can be observed on the  $\varepsilon_2$ spectra that the fundamental transitions vary from one system to another and depend on their respective bandgaps. These transitions are dominated by the Ag(s), Al(s/p) and X(p) states of

	$AgAIS_2$		AgAlSe	2	$AgAITe_2$		
	PBEsol	HSE06	PBEsol	HSE06	PBEsol	HSE06	
$\varepsilon_1^{\perp}(0)$	6.22	4.90	7.41	5.58	9.22	6.88	
$\varepsilon_1^{\parallel}(0)$	6.10	4.82	7.31	5.51	9.20	6.85	
<i>n</i> (0)	2.48 $(1.806)^a$	2.21	$2.72 (1.971)^a$	2.35	3.03 (2.168) <sup>a</sup>	2.62	

 Table 7.5 Static dielectric constant and refractive index.

a = Ref. [156]

the conduction band and the Ag(d) and X(p) states of the valence band.

A reduction of the intensity of the peaks and a blue-shift are also observed in the HSE06 compared to PBEsol. This seems to be a general trend when it comes to the calculated  $\varepsilon(\omega)$  using hybrid functionals. We could not find in the literature any previous study carried out for the AgAlX<sub>2</sub> (X=S,Se,Te) family of compounds using GGAs or beyond GGA methods. However, calculations and experiments done on other chalcopyrites and quaternary compounds based on chalcogenides suggest that the dielectric function peaks obtained with hybrid functionals match the experimental results better than those from GGA functionals [25, 165, 166].

One can also note that the main peaks of  $\varepsilon_1(\omega)$  increase in intensity, and shift towards lower energies as we go from AgAlS<sub>2</sub> to AgAlTe<sub>2</sub> independent of the functional used. Jayalakshmi et al. [156] studied the optical properties of these compounds using LDA and reported different values of  $\varepsilon_1(0)$ , but with the same trend from AgAlS<sub>2</sub> to AgAlTe<sub>2</sub>. We attribute the difference to the functional used. In spite of having the smallest  $\varepsilon_2$  onset, AgAlTe<sub>2</sub> has the highest peaks with the PBEsol one occurring in the optical range.

A number of quantities which also reflect the interaction of a material with electromagnetic radiation can be extracted from the dielectric function. We calculated the absorption coefficient  $\alpha(\omega)$  and the refractive index  $n(\omega)$  for the three compounds. The absorption coefficient  $\alpha$  is the measure of the amount of light which can be absorbed by a given medium [164]. As depicted in



**Figure 7.9** Real  $(\varepsilon_1)$  and imaginary  $(\varepsilon_2)$  part of the dielectric function. The dash-line represents the z component  $(\varepsilon^{\perp})$  and the solid line represents the average function along x and y  $(\varepsilon^{\parallel} = (\varepsilon_x + \varepsilon_y)/2)$ .  $\varepsilon_1$  and  $\varepsilon_2$  are dimensionless quantities. Throughout the spectra, the peaks in HSE06 are higher than those for PBEsol.



Figure 7.10 Absorption coefficient ( $\alpha$ ) and refractive index (n). Because of the small difference between  $\varepsilon^{\perp}$  and  $\varepsilon^{\parallel}$ , only the average  $\alpha$  and n are depicted here.

Figure 7.10, HSE06 calculations predict that these materials start absorbing in the visible range, but only a very small quantity of energy. From the PBEsol calculations, the absorption is still moderate for AgAlS<sub>2</sub> in the optical range while AgAlSe<sub>2</sub> and AgAlTe<sub>2</sub> show increasing absorbtion in the visible range. In summary the absorption is mainly in the ultraviolet range irrespective of the functional used.

The calculated refractive index showed peaks at 3.36 eV , 3.49 eV and 3.91 eV for PBEsol and 3.06 eV, 3.19 eV and 3.59 eV for HSE06 studies of  $AgAIX_2(X = S,Se,Te)$  respectively. Their static values n(0) are also reported in Table 7.5. Experimentally, these properties have not been determined yet, however our results are slightly larger than of those of their well known chalcopyrite analogues Cu-III-VI<sub>2</sub> which are used in optoelectronics devices [167, 168]. The aforementioned features are bandgap dependent, it is noted that the absorption threshold increases as the bandgap increases while the zero frequency refractive index increases when the bandgap decreases. This is consistent with observed and calculated relationships between the bandgap and refractive index of semiconductors [169].

#### 7.4.2 Exciton effect on the absorption

During the absorption of photons by the interband transitions, an electron and a hole are usually created in the conduction and valence bands respectively. The Coulomb interaction between the two particles leads to the formation of a new excitation in the crystal also know as exciton. It has been proved that these excitons can considerably impacted the optical properties of semiconductor materials and therefore are very important for opto-electronic applications [164, 170]. The determination of the exciton energy has been a cumbersome task for the scientific community. From theoretical point of view, accurate optical properties are not always directly accessible from first-principle DFT calculations. For example the eigenvalue energies  $\epsilon_{v\mathbf{k}}$  and  $\epsilon_{c\mathbf{k}}$  found in Equation D.0.1 for calculating the absorption spectra correspond to the Kohn-Sham (KS) highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) respectively. The energy difference between the HOMO and LUMO yields the KS bandgap. However, as we pointed out early it is now well established that the KS bandgap is underestimated by more than 50% compared to the experimental measurement. As such, there is a need to go beyond the standard DFT in order to accurately predict the bandgap and the optical spectra. As we saw in section 7.3, HSE06 or MBJ can reproduce the correct bandgap, but still do not take the electron-hole interaction into account. In most chalcopyrite materials, electron-hole interactions have not received much attention in contrast to the massive effort put into the investigation of bandgap and electronic properties. Most of the previous works have been limited to the calculation of the dielectric response function in the independent particle picture with and/or without local field effect [1,171,172]. This is because of the difficulty of including that interaction in the calculations.

Excitonic effect can be captured by solving the Bethe-Selpeter Equation (BSE) [111, 112]. BSE relies on the quasiparticle (QP) energies calculated from the GW approach [109]. The QP energies are obtained by solving the QP equation (see Equation 4.1.14). Recall that the self-energy

$$\Sigma = iGW. \tag{7.4.1}$$

contained all the exchange and correlations effects among the electrons. At the first order of the approximation (single shot  $G_0W_0$ ), the Greens function G is built from the Kohn-Sham (KS) orbitals and eigenvalue energies as given by Equations 5.3.1 and 5.3.2 respectively; and  $\Sigma$  by Equation 5.3.5. For the BSE calculations, a more dense Monkhorst-Pack meshes **k**-points of 9x9x9 and a cut off energy of 520 eV were used for sampling the Brillouin zones. Ten highest valence bands and ten lowest conduction bands were found to be sufficient to converge the positions of the absorption peaks.

Our results in Table 7.6 show an underestimation of the fundamental bandgap despite the large number of empty bands included in the calculations. Similar results were found by Aguilera et

al. [166] while studying the bandstructure and optical properties of CuGaS<sub>2</sub>. They attributed the underestimation to the fact that an important contribution of the Cu-d electrons at the upper most valence band leads to a strong hybridasation with the Ga-p orbitals. G<sub>0</sub>W<sub>0</sub> is then not capable of reproducing these behaviours. In section 7.3, we also found from the PDOS of AgAIX<sub>2</sub> that the d and p orbitals from the Ag and chalcogenide atoms respectively were also hybridised at the top of the valence band. Since both  $AgAIX_2$  and  $CuGaS_2$  are all chalcopyrite compounds, the underestimation of the bandgap by  $G_0W_0$  should also originated from its inability to capture the pd hybridisation. We therefore proceed by doing a semi self-consistent GW calculation (GW $_0$ ) where screened Coulomb interaction  $W_0$  remains at the RPA level and the Green's function updated by using the quasiparticle energy from the single shot calculation. The bandgaps obtained from this approach are also summarised in Table 7.6. An agreement within 4% is found with the experimental results. Note here that similar results on chalcopyrite materials including  $CuGaS_2$ were obtained using the self-consistent Coulomb Hole Screened Exchange followed by G<sub>0</sub>W<sub>0</sub> (sc-COHSEX+ $G_0W_0$ ) [173]. Moreovever, accurate QP energies are sometime obtained at the  $G_0W_0$ if the HSE06 was used as the reference system These procedures have successfully been used by some authors [166, 173–176], but we find them too demanding in terms of computational resources for the cases of the systems of interest.

We present in Figure 7.11 the bandstructure from PBEsol and  $GW_0$  of AgAlS<sub>2</sub>. The two other structures (not shown here) have similar bandstructures.  $GW_0$  approximation shows a direct bandgap at the  $\Gamma$  in accordance with PBEsol, HSE06, MBJ and the experimental data [145]. The main difference between the bandstructure is the shift from 1.83 eV to 3.22 eV at the  $\Gamma$ .

**Table 7.6** Bandgap from different methods, position of the exciton peak from BSE calculations and binding energies of AgAIX<sub>2</sub>. All the quantities are gievn en eV. k and l refer to Ref. [1] Ref. [145] respectively.

	$AgAlS_2$	$AgAlSe_2$	$AgAITe_2$
$PBEsol^k$	1.83	1.11	1.03
$G_0W_0$	2.67	2.12	2.08
$GW_0$	3.30	2.46	2.22
EXP. <sup>k,l</sup>	3.13	2.55	2.27
First BSE peak	3.09	2.26	2.07
Binding energy	0.21	0.20	0.15



Figure 7.11 Representative bandstrcture of  $AgAIX_2$  from PBEsol and  $GW_0$  calculation: Case of  $AgAIS_2$ .



Figure 7.12 AlAgS<sub>2</sub> imaginary part of the dielectric function  $\varepsilon_2$  from GW and BSE calculations.

The neutral electron-hole interaction was included in the calculation of optical absorption by solving the BSE equation numerically . We presented in Figure 7.12 the imaginary part of the dielectric  $\varepsilon_2$  from GW and BSE of AlAgS<sub>2</sub>. Experimental data are not available for comparison. The onset of from GW lies at 3.19 eV, 2.44 eV, and 2.10 eV for AgAlS<sub>2</sub>, AgAlSe<sub>2</sub> and AgAlTe<sub>2</sub> respectively. The values are in the range their respective bandgaps as seen in Table 7.6. In Figure 7.12 we observe that the electron-hole interaction leads a reduction in the onset of the absorption with a peak appearing in the bandgap attesting to the presence of bound excitons in these materials. In direct bandgap materials, the binding energy of the exciton can easily be estimated. Here, electrons and holes have the same group velocity ( $v_{ge} = v_{gh} = \frac{1}{\hbar} \frac{\partial E}{\partial k}$ ) since they appear at the same k vector [164]. Under these conditions, the exciton energy can be estimated as the difference between the bandgap from GW and the position of the first excitonic peak from BSE [177]. As summarised in Table 7.6, the excitonic binding energies range from 0.15 eV for AgAlTe<sub>2</sub> to 0.21 eV for AgAlS<sub>2</sub>. Comparing the bandgaps and the excitonic binding energies, it we can note that the bigger the bandgap, the bigger the excitonic binding energy. Hence, the excitonic binding energy should be related to the nature of the chalcogenide atom present in the

chalcopyrites.

# 7.5 Summary

The aim of this chapter was to provided a detailed study of the structural, electronic and optical properties of ternary compounds AgAlX<sub>2</sub> (X=S,Se,Te). Thermodynamic and phase stability studies revel that the chalcopyrite structure is the favoured phase of these materials at zero pressure and temperature. The GGA-PBEsol functional gives structural properties closer to the experimental values when compared to the results of PBE. Tetragonal distortion and anion displacement were calculated and we found them to be the cause of the crystal field splitting. Reduction of the bandgap and band splitting around the  $\Gamma$  in the Brillouin zone was noted when spin-orbit coupling was included in our study especially in the case of AgAlTe<sub>2</sub>. The HSE06, MBJ and GW<sub>0</sub> bandgaps were in agreement with experimental results. Optical absorption spectra and optical gaps were determined from the solution of the Bethe-Selpeter Equation (BSE) in the Tamm-Damcoff approximation. It predicted the existence of bound excitons in these compounds and the exciton bounding energies were also estimated.

# 8. Structural stability and elastic, mechanical, electronic and optical properties of AgInS<sub>2</sub> under pressure

In this chapter, we are interested in the effect of pressure on different properties of  $AgInS_2$ materials. Initially, our intentions was to study the chalcopytite phase only. Motivated by the stability study on AlAgX $_2$  where we found that apart from the chalcopyrite phases, there were other low pressure potential phases which might also have interesting properties. We therefore decided to carry out a detailed study on other phases of AgInS2.All the phases listed in Table 6.1 are considered in the study looking for the most favoured phase at a given pressure. As we mentioned in Chapter 7, the choice of these structures is based on previous investigations on other families of ternary chalcogenides. The chalcopyrite, the orthorhombic and the rhombohedral-type structures have been observed experientially while the others are hypothetical structure. We used the GGA-PBEsol generalised gradient approximation (GGA), the hybrid functional HSE06 and the modified Becke-Johnson potential (MBJ) as exchange-correlation interaction. The GW method [109] at the  $G_0W_0$  and  $GW_0$  level was also used to evaluate the bandgaps. From the previous chapter, we found that GGA-PBEsol is very accurate for describing the structural properties. Hence, we also used it here for the same purposes. Plane waves with kinetic energy up to 550 eV were considered in the calculations. For the sampling of the Brillouin Zone (BZ), Monkhorst-Pack [135] **k**-point meshes with grids of  $7 \times 7 \times 7$  were used for the tetragonal and the rocksalt phase while 6x6x6 and 4x9x8 were used for the orthorhombic and the monoclinic and the phases respectively. For the hexagonal and the rhombohedral cells which require the inclusion of the  $\Gamma$  point in order to avoid broken symmetry, the Gamma centered **k**-point grids centered  $7 \times 7 \times 7$  and  $8 \times 8 \times 6$  were used. These parameters were found to be sufficient for energy convergence to within 0.1 meV per atom. Full ionic relaxation of all the structures were performed until the total energy was converged to within 0.1 meV. To remain in the harmonic approximation, small distortions of  $\pm 0.01$ Å were allowed for the elastic constant calculations. Force constants were calculated using density functional perturbation theory (DFPT) [142] as implemented in the VASP code. Phonon dispersion relations were obtained from the force constants by means of the PHONOPY code [143, 178].

### 8.1 Structural and energetic properties

We started by performing full relaxation calculations of volume, shape and atomic positions for all the structures while keeping the lattice type constant. Then a set of self-consistent calculations at different volumes spanning each predicted equilibrium volume V<sub>0</sub> were carried out and a third order Birch-Murnaghan [146] equation of state (EOS) was fitted to the obtained energies as depicted in Figure 8.1. Information extracted from the EOS fits are summarized in Table 8.1. Comparison to other calculated and experimental results shows that the lattice parameters and equilibrium volume are in general agreement with our results. As we pointed out in Chaper 6, being ternary analogues of the binary zincblende structures, chalcopyrite structures are defined by two extra parameters in addition to the lattice parameters, known as tetragonal distortion  $\eta = c/2a$  and anion displacement u [24]. We obtained  $\eta = 0.97$  and u = 0.25 which are in agreement with experimental data (  $\eta=0.96$  and u=0.25) [24]. The equilibrium volume V $_0$  of the orthorhombic (OR-AgInS $_2$ ) structure is slightly larger than that of the tetragonal chalcopyrite phase (CH-AgInS<sub>2</sub>). This trend is confirmed by the experimental results. From Table 8.1, it can also be seen that at zero pressure and zero temperature, the bulk modulus for the OR-AglnS $_2$ structure is the smallest while the rocksalt structure has the largest bulk modulus of the calculated values. The bulk modulus  $\mathsf{B}_0$  of CH-AgIn $\mathsf{S}_2$  (62 GPa) is in the range of the previously calculated  $B_0$  of 62 and 65 GPa [179]. We could not find any theoretical or experimental values for other

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#### phases for comparison.

**Figure 8.1** (Color online) Cohesive energy versus volume (a) and enthalpy versus pressure (b) for the chalcopyrite ( $\overline{142d}$ ), the monoclinic C2/m, the orthorhombic  $Pna2_1$ , the trigonal P3m1, the trigonal  $R\overline{3}m$  and the rocksalt  $Fm\overline{3}m$  structures.

At zero pressure and temperature we analyse the stability on the basis of the cohesive energy  $(E_{coh})$  and formation energy  $(E_f)$ . The  $E_f$  is the energy difference between the cohesive energy of a solid and that of the its constituents in solid form [183, 184]. Gerould et al. [185] noted that in addition to OR-AglnS<sub>2</sub>, the binary compounds Ag<sub>2</sub>S and In<sub>2</sub>S<sub>3</sub> could be present during the synthesis of CH-AglnS<sub>2</sub>. We investigated the possible decomposition of AglnS<sub>2</sub> into the stable binary compounds Ag<sub>2</sub>S [186] and In<sub>2</sub>S<sub>3</sub> [187, 188] according to the chemical reaction

$$\mathsf{AgInS}_2 \to \frac{1}{2}\mathsf{Ag}_2\mathsf{S} + \frac{1}{2}\mathsf{In}_2\mathsf{S}_3.$$

**Table 8.1** Lattice parameters a, b, c are given in Å, the volume per atom V<sub>0</sub> in Å<sup>3</sup>, the bulk modulus B<sub>0</sub> in GPa, the gravimetric density  $\rho$  in g.cm<sup>-3</sup> and the cohesive energy per atom E<sub>coh</sub> and the formation energy per atom E<sub>form</sub> in eV. All these parameters are from zero pressure and zero temperature calculations. The present results are compared to previous calculated (Calc.) and experimental data (Exp.) where available.

Phase	а	b	С	$V_0$	ρ	$B_0$	$E_{coh}$	$E_{for}$
tetragonal (CH)	5.80	5.80	11.33	23.86	4.99	62.40	-3.572	-0.126
	5.87 <sup><i>a</i></sup>	5.87 <sup>a</sup>	11.20 <sup><i>a</i></sup>	$24.17^{a}$				
	$5.81^{b}$	$5.81^{b}$	$11.21^{b}$					
	5.80 <sup>c</sup>	5.80 <sup>c</sup>	$11.35^{c}$			65 <sup><i>c</i></sup> ,62 <sup><i>c</i></sup>		
orthorhombic (OR)	6.69	6.98	8,18	23.87	4.98	61.43	-3.570	-0.124
	6.69 <sup><i>a</i></sup>	6.99 <sup>a</sup>	8.27 <sup><i>a</i></sup>	24.21 <sup><i>a</i></sup>				
	6.68 <sup>b</sup>	$6.99^{b}$	$8.25^{b}$					
	$6.81^d$	$7.14^{d}$	$8.33^{d}$					
rhombohedral (RH)	3.76	3.76	18.75	19.15	6.21	82.94	-3.521	-0.075
	3.76 <sup>e</sup>	3.76 <sup>e</sup>	19.35 <sup><i>e</i></sup>					
monoclinic	6.55	3,76	6.59	20.02	5.94	65.78	-3.481	-0.035
hexagonal	4.48	4.48	5.30	23.02	5.17	63.96	-3.378	+0.068
rocksalt	6.61	6.61	6.61	18.13	6.58	87.35	-3.058	+0.388
<sup>a</sup> Exp. [180]								
<sup>b</sup> Exp. [179]								
<sup>c</sup> Calc. [181]								
<sup>d</sup> Calc. [182]								

<sup>e</sup> Exp. [17]

Mathematically, the  $E_f$  is

$$E_{f}(\ln \mathsf{AgS}_{2}^{sol})) = E_{coh}(\mathsf{AgInS}_{2}^{sol}) - \frac{\left[\frac{1}{2}E_{coh}(\mathsf{Ag}_{2}\mathsf{S}^{sol}) + \frac{1}{2}E_{coh}(\mathsf{In}_{2}\mathsf{S}_{3}^{sol})\right]}{4}.$$
(8.1.1)

The lower the cohesive or the formation energy, the more stable the structure. As can be seen in Table 8.1, the cohesive energies are ordered as follows:  $E_{coh}(I\bar{4}2d) < E_{coh}(Pna2_1) < E_{coh}(R\bar{3}m) < E_{coh}(C2/m) < E_{coh}(P3m1) < E_{coh}(Fm\bar{3}m)$ , suggesting that CH-AgInS<sub>2</sub> is the most stable structural phase of the compounds at zero pressure and temperature. It is also worth noting that CH-AgInS<sub>2</sub> and OR-AgInS<sub>2</sub> are energetically competitive phases with a well converged energy difference of about 20 meV. This is an indication that care should be taken while synthesising any of the two phases. The formation energies show the same trend as the cohesive energies. The rocksalt and the hexagonal phases have positive formation energies which indicate that, should it be possible to synthesise these phases, they will at best be meta-stable and are likely to dissociate into their binary solids.

An appropriate method for analysing the pressure phase transition at zero temperature is to make use of the enthalpy-pressure relation:  $H = E_{coh}+PV$ . A pressure phase transition occurs between two phases when, at a given pressure  $P_t$ , the enthalpy-pressure curves cross. The stable phase is the one with the lowest enthalpy. Figure 8.1b depicts the enthalpy versus pressure curves for all the structures under investigation. The competition between CH-AgInS<sub>2</sub> and OR-AgInS<sub>2</sub> can be noted once again, but CH-AgInS<sub>2</sub> remains the zero pressure phase as previously predicted from the EOS. There is a transition from CH-AgInS<sub>2</sub> to the rhombohedral (RH-AgInS<sub>2</sub>) phase at around 1.78 GPa. In the early seventies, Range et al. [17] investigated high pressure transformations of ternary chalcogenides and observed a high pressure rhombohedral phase of AgInS<sub>2</sub> at 2 Gpa, but their study was limited to structural properties. To the best of our knowledge further studies on this phase have not been performed so far neither theoretically nor experimentally. The volume of the two phases as a function of pressure is shown in Figure 8.2. A volume collapse of about 19.30% is observed at this transition pressure. The relaxed lattice parameters of RH-AgInS<sub>2</sub>
at the transition pressure (1.78 GPa) are a = 3.74Å, c = 18.55Å which are within 5% relative error of the experimental values (a = 3.76Å, c = 19.35Å) obtained at 2 GPa [17]. A number of studies suggested the existence of a high pressure rocksalt phase in chalcopyrite CuAl $X_2$ (X = S,Se,Te) materials. Using an energy dispersion technique, Werner et *al.* [189] found that the chalcopyrites CuGaS<sub>2</sub> and AgGaS<sub>2</sub> undergo pressure-induced phase changes from chalcopyrite to a NaCl type structure at pressures near 15 GPa. DFT calculations by Addellaoui et *al.* [18] predicted a structural high pressure phase transition of CuAl $X_2$ (X = S,Se,Te) materials from the chalcopyrite phase to the rocksalt-type structure. We therefore extended our investigation up to 100 GPa to search for a possible high pressure rocksalt phase of AgInS<sub>2</sub>. We found that the rhombohedral phase has the lowest enthalpy between 1.78 GPa and 93.5 GPa where a structural phase transition from a rhombohedral to a rocksalt phase takes place, as seen in Figure 8.1b. Such a high transition pressure is practically difficult to achieve, therefore we focus on the low pressure (0 - 2.5GPa) phases, namely the chalcopyrite, the orthorhombic and the rhombohedral phases.

#### 8.2 Dynamical and mechanical stabilities

We study the dynamical stability by investigating phonon dispersions at different pressures. Accurate force constants and phonon dispersion relations were computed using 2x2x2 supercells<sup>1</sup> based on the optimised structures at a given pressure using the VASP DFPT interface to the PHONOPY code. A structure is dynamically stable when all the normal vibration modes have real and finite frequencies. Phonon dispersion curves along the high symmetry directions in the BZ are shown in Figure 8.3. The dispersion curves of CH-AglnS<sub>2</sub> and OR-AglnS<sub>2</sub> are above zero frequency as depicted in Figures 8.3a, 8.3d and 8.3f at 0, 1.78 and 2.5 GPa respectively.

 $<sup>^{1}</sup>$ As we mentioned early, supercell does not mean we employed the direct method. For more details, refer to Chapter 7 and Appendix C.3



**Figure 8.2** Variation of the relative volume with pressure.  $V_0$  is the equilibrium volume of the tetragonal phase at zero pressure and temperature.

Thus they are dynamically stable at these pressures. Figure 8.3g shows the phonon spectrum of RH-AglnS<sub>2</sub> at 0 GPa. Vibration modes with imaginary frequencies are seen near the  $\Gamma$  and the F points showing that RH-AglnS<sub>2</sub> at 0 GPa is dynamically unstable. Negligible imaginary modes are found at 1.78 GPa (seen in Figure 8.3h) while only positive frequencies are observed at 2.5 GPa as depicted in Figure 8.3i.



Figure 8.3 AgInS<sub>2</sub> phonon dispersion curves at different pressures. Negative frequencies observed around the  $\Gamma$  and the F points of the rhombohedral structure at zero pressure are an indication of instability.

Elastic constants were calculated to check for mechanical stability. Under stress, the total energy at volume  $V^*$ , in Voigt notation, is given by [191]:

$$E(\epsilon) = E(V^*, \epsilon = 0) + V^* \sum_i \sigma_i \epsilon_i + \frac{V^*}{2} \sum_{ij} C_{ij}(V^*) \varepsilon_i \epsilon_j + O(\epsilon^3).$$
(8.2.1)

Pres(GPa).	Phase	$C_{11}$	$C_{22}$	$C_{33}$	$C_{12}$	$C_{13}$	$C_{23}$	$C_{14}$	$C_{44}$	$C_{55}$	$C_{66}$	В	G	G/B	Е	ν
	$CH\operatorname{-AgInS}_2$	76		75	57	56			23		24	63	18	0.28	49	0.37
		79 <sup>c</sup> ,84 <sup>f</sup>		79°,97 <sup>f</sup>	64 <sup>c</sup> ,52 <sup>f</sup>	$64^c$ , $61^f$			$18^c$ , $23^f$		$22^c, 28^f$	69°,62°	13 <sup>c</sup>	0.19 <sup>c</sup>	36 <sup>c</sup>	0.41 <sup>c</sup>
0	$OR\text{-}AgInS_2$	97	79	84	46	46	53		13	14	15	61	16	0.26	44	0.38
	$RH\text{-}AgInS_2$	123		111	61	70		15	-20		-13					
1.78	$CH\text{-}AgInS_2$	82		80	67	64			20		23	70	16	0.22	45	0.39
	$OR\text{-}AgInS_2$	102	80	85	55	56	61		12	12	14	68	14	0.20	39	0.40
	$RH\text{-}AgInS_2$	124		124	73	78		9	-1		2					
	$CH\text{-}AgInS_2$	84		82	69	67			18		22	73	15	0.20	42	0.40
2.5	$OR\text{-}AgInS_2$	106	81	89	63	63	69		11	9	12	74	12	0.16	34	0.42
	$RH\text{-}AgInS_2$	135		124	70	73		8	5		34	91	21	0.23	58	0.39

**Table 8.2** Elastic constants  $C_{ij}$  (GPa), bulk moduli B(GPa), shear moduli G(GPa), Young's moduli E(GPa), Poisson's ratio  $\nu$  and G/B for CH-AgInS<sub>2</sub>, OR-AgInS<sub>2</sub> and RH-AgInS<sub>2</sub> at 0, 1.78 and 2.5 GPa.

<sup>c</sup> Calc. [181]

<sup>*f*</sup>Calc. [190]

where  $\sigma_i$  is the stress,  $\varepsilon_i$  is the strain and the  $C_{ij}$  are the elastic constants which correspond to the second derivative of the energy  $E(\epsilon)$  with respect to the applied stress evaluated at V<sup>\*</sup>:

$$C_{ij} = \frac{1}{V^*} \left( \frac{\partial^2 E(\epsilon)}{\partial \epsilon_i \partial \epsilon_j} \right)_{V^*}.$$
(8.2.2)

When the applied stress is hydrostatic, the Born stability criteria [192–194] must be applied to the coefficients [195, 196]

$$\tilde{C}_{\alpha\alpha} = C_{\alpha\alpha} - P; \qquad \alpha = 1, 2, \dots, 6; \quad \tilde{C}_{12} = C_{12} + P; 
\tilde{C}_{13} = C_{13} + P; \qquad \tilde{C}_{23} = C_{23} + P; \qquad \tilde{C}_{14} = C_{14}$$
(8.2.3)

Note that in absence of the pressure,  $\tilde{C}_{ij}$  and  $C_{ij}$  are equal. The stability conditions for a tetragonal system are [197]:

$$\tilde{C}_{11} - \tilde{C}_{12} > 0, \tilde{C}_{11} + \tilde{C}_{33} - 2\tilde{C}_{13} > 0$$
  
$$\tilde{C}_{ii} > 0, 2\tilde{C}_{11} + \tilde{C}_{33} + 2\tilde{C}_{12} + 4\tilde{C}_{13} > 0$$
(8.2.4)

According to Mouhat et al. [192] the necessary and sufficient mechanical stability conditions for an

orthorhombic system are:

$$\tilde{C}_{11}\tilde{C}_{22}\tilde{C}_{33} + 2\tilde{C}_{12}\tilde{C}_{13}\tilde{C}_{23} - \tilde{C}_{11}\tilde{C}_{23}^2 - \tilde{C}_{22}\tilde{C}_{13}^2 - \tilde{C}_{33}\tilde{C}_{12}^2 > 0$$
  
$$\tilde{C}_{ii} > 0, \tilde{C}_{11}\tilde{C}_{22} - \tilde{C}_{12}^2 > 0, \qquad (8.2.5)$$

while for a rhombohedral structure the following conditions have to be satisfied [192]

$$\tilde{C}_{11} - \tilde{C}_{12} > 0, \quad \left(\tilde{C}_{11} + \tilde{C}_{12}\right)\tilde{C}_{33} - 2\tilde{C}_{13}^2 > 0$$
  
$$\tilde{C}_{44} > 0, \quad \left(\tilde{C}_{11} - \tilde{C}_{12}\right)\tilde{C}_{44} - 2\tilde{C}_{14}^2 > 0.$$
(8.2.6)

Bulk and shear moduli can be expressed respectively as follows:

$$B_{V} = \frac{1}{9} \left[ (\tilde{C}_{11} + \tilde{C}_{22} + \tilde{C}_{33}) + 2(\tilde{C}_{12} + \tilde{C}_{13} + \tilde{C}_{23}) \right],$$
  

$$G_{V} = \frac{1}{15} \left[ (\tilde{C}_{11} + \tilde{C}_{22} + \tilde{C}_{33}) - (\tilde{C}_{12} + \tilde{C}_{13} + \tilde{C}_{23}) + 3\tilde{C}' \right]$$
  
with  $\tilde{C}' = (\tilde{C}_{44} + \tilde{C}_{55} + \tilde{C}_{66}).$   
(8.2.7)

Elastic constants and moduli are presented in Table 8.2. In order to confirm the reliability of our elastic constants calculations, we compared our results with other calculated results for CH-AgInS<sub>2</sub> at 0 GPa, the only results available. We are not aware of any experimental data. Fairly good agreement is found between our calculated elastic constants for CH-AgInS<sub>2</sub> and those reported by Verma et *al.* [190]. The notable differences could be attributed to the different calculation methods and pseudopotentials used.

The chalcopyrite structure satisfies the mechanical stability criteria as stated above at all three pressures at which calculations were performed. For the case OR-AgInS<sub>2</sub>, the stability criteria in Equation 8.2.5 are satisfied. Their elastic constants C<sub>11</sub>, C<sub>22</sub>, C<sub>33</sub>, C<sub>12</sub>, C<sub>13</sub> and C<sub>23</sub> increase with increasing pressure while C<sub>44</sub>, C<sub>55</sub> and C<sub>66</sub> decrease. For the rhombohedral structure, the two first conditions in Equation 8.2.6 are satisfied at all the pressures. At 0 GPa and 1.78 GPa, C<sub>44</sub> <0, hence  $\tilde{C}_{44} < 0$  and  $(\tilde{C}_{11} - \tilde{C}_{12})\tilde{C}_{44} - 2\tilde{C}_{14}^2 < 0$ . It follows that RH-AgInS<sub>2</sub> is mechanically unstable at 0 GPa and 1.78 GPa.

Bulk moduli are also calculated and listed in Table 8.2. However, because of the instability of RH-AgInS<sub>2</sub> at low pressure, the bulk moduli were only reported at 2.5 GPa. The bulk modulus of CH-AgInS<sub>2</sub> is consistent with previously calculated values. It can be noted that the bulk moduli increase with pressure

as expected. Poisson's ratio  $\nu$  is associated with the nature of the atomic bonding. For all three structures,  $\nu$  is greater than the critical value ( $\nu \ge 0.25$ ) predicting an ionic character of the atomic bonding [198]. The G/B ratio is commonly used as a measure of brittleness and ductility of materials. According to Pugh's criteria [199], a typical brittle material should have G/B $\ge$  0.5, otherwise the material is ductile. Overall, the structures have G/B< 0.5 indicating that the materials are ductile. The Young's moduli E are also reported in Table 8.2. At zero pressure, E(CH-AgInS<sub>2</sub>) > E(OR-AgInS<sub>2</sub>) suggesting that CH-AgInS<sub>2</sub> is stiffer than OR-AgInS<sub>2</sub>. It is also worth to note that E decreases under the effect of pressure and at 2.5 GPa, RH-AgInS<sub>2</sub> becomes the stiffest amongst the three structures.

### 8.3 Electronic and optical properties

We investigated the electronic properties by analysing the band structures and density of states (DOS). The GGA-PBEsol predicted a zero pressure bandgaps of 0.27 eV and 0.40 eV for CH- and OR-AgInS<sub>2</sub> respectively while RH-AgInS<sub>2</sub> has a metallic character. These values are very small when compared to the experimental values which are 1.86 eV and 1.98 eV respectively [200]. This is a well known problem in the DFT community as we mentioned previously in Chapter 3; employing a semilocal functional such as GGA-PBEsol can lead to the under-estimation of bandgaps. As in the case of AgAIX<sub>2</sub>, we then compute the bandgaps using other functionals (see Table 8.3). Contrary to our expectations, the HSE06, the single shot GW ( $G_0W_0$ ) and semi self consistent GW ( $GW_0$ ) all underestimated the bandgaps. Even a more dense **k**-points mesh and cut off energy lead to almost identical results. Similar shortcomings have previously been raised by Bruneval et *al.* while studying the bandgap of copper and indium based chalcopyrite materials [201–203]. They claimed it could be link to the inaccuracy of the GW for describing some of the orbitals of these atoms.

	$CH\text{-}AgInS_2$	$OR\text{-}AgInS_2$	$RH\text{-}AgInS_2$
Exp.	$1.87^{a}$	$1.98^b$	-
HSE06	0.98	1.30	0.72
$G_0W_0$	1.21	1.37	0.50
$GW_0$	1.24	1.40	0.55
MBJ	1.73	2.08	0.95

**Table 8.3** AgInS<sub>2</sub> bandgaps (eV) from different approximations. a = Ref. [200], b = Ref. [182]

The meta-GGA MBJ functional is also know for predicting accurately the bandgaps for a wide range of materials [204, 205]. It predicts bandgaps of 1.73 eV and 2.08 eV at 0 GPa for CH-AgInS<sub>2</sub> and OR-AgInS $_2$  respectively. These values are in the range of the experimental ones summarised in Table 8.3. RH-AgInS<sub>2</sub> changes from metal to semiconductor when the GGA-PBEsol exchange correlation potential is replaced by the MBJ approximation with a 2.5 GPa bandgap of about 0.95 eV. It is important pointing out that the meta-GGA MBJ combines accuracy and low computational cost which were missing in other functionals. As we mentioned before, some structural measurements were done on RH-AgInS $_2$ , but we are not aware of any previous experimental or theoretical work that determined its bandgap. We can note in Figure 8.4 that the bandgaps of CH-AgInS<sub>2</sub> and OR-AgInS<sub>2</sub> increase with increased pressure for both the GGA-PBEsol and MBJ potentials. Using GGA-PBEsol, RH-AgInS $_2$  is not sensitive to the effect of the pressure, remaining metallic at all pressures, but with MBJ a decrease of the bangap can be noted. The bandstructures and the density of states (DOS) are depicted in Figures 8.5, 8.6 and 8.7. The calculations were performed without inclusion of spin orbit coupling since it does not have a large impact on the electronic properties of sulfur based chalcopyrite materials [1, 206]. The bandstructures are plotted along the high symmetry directions in the Brillouin zone and show that these compounds are direct bandgap materials. The bandgaps of CH-AgInS $_2$  and OR-AgInS $_2$  occur at the  $\Gamma$  point and for RH-AgInS<sub>2</sub> it is at the F point. The spin polarized DOS's presented in Figures 8.5b, 8.6b and 8.7b show that the spin up and spin down DOS's are symmetric indicating that these compounds are nonmagnetic. Partial DOS show similar features for  $OR-AgInS_2$  and  $CH-AgInS_2$ , but that of  $RH-AgInS_2$ 



Figure 8.4 Pressure dependant bandgap of the CH-, OR- and RH-AgInS $_2$ 

looks different, despite the fact that all three compounds have the same atomic coordination. We predict from our calculations that the shortest distance between Ag and In is 4.05 Å and 3.98 Å for CH-AgInS<sub>2</sub> and OR-AgInS<sub>2</sub> respectively, but for RH-AgInS<sub>2</sub> it is more than twice as large at 9.22 Å. This difference in the atomic environment of RH-AgInS<sub>2</sub> could explain the contrast in the partial DOS. For all the structures, the uppermost valence band is dominated by the Ag(*d*) and S(*p*) orbitals. The minimum of the conduction band has mainly S(*s*), S(*p*) and In(*s*) character. These features are usually observed in chalcopyrite materials [1, 127, 166].



**Figure 8.5** Bandstructure, total and partial density of states of the CH-AgInS<sub>2</sub> structure at 0 GPa. Note that because of the small contribution to the bangap coming from the In atoms, the scale on the x-axis was changed.



Figure 8.6 Bandstructure, total and partial density of states of the OR-AgInS<sub>2</sub> structure at 0 GPa.

The absorption coefficient  $\alpha$  is a key property of a material since it measures the amount of electromagnetic radiation that can be absorbed by a given medium. It can be described by Beer's law [164]:

$$I(z) = I_0 e^{-\alpha z}$$
(8.3.1)

where  $I_0$  the initial light intensity. Theoretically, it can be obtained from the frequency dependent



Figure 8.7 Bandstructure, total and partial density of states of the RH-AgInS<sub>2</sub> structure at 2.5 GPa.



**Figure 8.8** Absorption coefficient of the chalcopyrite structure  $(I\bar{4}2d)$  and the orthorhombic structure $(Pna2_1)$  at 0 GPa and rhombohedral structure $(R\bar{3}m)$  at 2.5 GPa.

dielectric function using the relation

$$\alpha(\omega) = \sqrt{2}\omega \left[ \left( \varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) \right)^{\frac{1}{2}} - \varepsilon_1(\omega) \right]^{\frac{1}{2}}$$
(8.3.2)

where  $\varepsilon_1$  and  $\varepsilon_2$  are respectively the real and the imaginary part of the dielectric function. Calculations for the absorption coefficient were performed within the random phase approximation with local fields included using MBJ. In Figure 8.8 the absorption spectra of the three compounds are shown for  $\omega$  from 0 to 6 eV. The absorption threshold for CH-AgInS<sub>2</sub> and OR-AgInS<sub>2</sub> occurs at about 1.27 and 2.07 eV respectively. The maximum absorption for CH-AgInS<sub>2</sub> and OR-AgInS<sub>2</sub> are in the visible range at  $0.26 \times 10^5$  cm<sup>-1</sup> and  $0.22 \times 10^5$  cm<sup>-1</sup> respectively. RH-AgInS<sub>2</sub> starts absorbing light in the infra-red region at 0.95 eV. At the edge of the visible range (3.1 eV), it reaches an absorption of  $0.4 \times 10^5$  cm<sup>-1</sup> and a very sharp peak located around 5.13 eV can be observed in the spectrum. The high absorption in the visible range could make RH-AgInS<sub>2</sub> more suitable for solar application compared with the other structures.

#### 8.4 Conclusion

The presented studies confirmed that the chalcopyrite phase is the most energetically favoured stable structure at zero pressure and temperature although the energy difference with the orthorhombic phase was very small. It also showed that a pressure-induced phase transition from the chalcopyrite to the rhombohedral occurs around 1.78 GPa. A rocksalt phase occurs at 93.5 GPa contrary to the expectation from other ternary TMC family of compounds. The high pressure made this phase practically difficult to achieve. We also found a positive formation energy for the hexagonal and rocksalt phases which suggest that they are more likely to decompose into their elementary constituents. The chalcopyrite and the orthorhombic phases remained mechanically and dynamically stable at the selected pressure of our interest while the rhombohedral structure was only stable above the transition pressure. Accurate bandgaps could not be obtained from HSE06 and GW methods, but the meta-GGA MBJ functional predicts bandgaps which are in good agreement with available experimental values.

# 9. Efficiency limits for AgAIX<sub>2</sub> and AgInS<sub>2</sub> photovoltaic absorbers

The aim of this chapter is to estimate the ultimate solar efficiency of the compounds we have been investigated. The efficiency is calculated using two approaches namely, the Shockley-Queisser approach and the spectroscopy limited maximum efficiency approach.

#### 9.1 The Shockley-Queisser approach

In the seminal paper of Shockley and Queisser [207], the efficiency was estimated as the ratio of the maximum power delivered by the cell ( $P_{max}$ ) and the incident solar power impinging on the cell ( $P_{in}$ ):

$$\eta = \frac{P_{max}}{P_{in}}.\tag{9.1.1}$$

In the photovoltaic effect [208], photons with energy equal to or more than the bandgap of the material with which they interact are absorbed by the valence electrons. If the photon energy is greater than the bandgap, the excess energy is used by the valence electron to migrate the conduction band where they can move freely. In the Shockley and Queisser (SQ) model, it is assumed that each photon with energy above the bandgap of the absorber produces an electron-hole pair. The maximum output per unit area per unit time can be expressed as:

$$P_{max} = E_g N_{ph} \tag{9.1.2}$$

where  $E_g$  is the bandgap of the absorber and  $N_{ph}$  the number of incident photon per unit area per unit time with energy above  $E_g$ .  $N_{ph}$  is calculated using the Planck equation of a blackbody at the temperature of the sun [209]:

$$N_{ph} = \frac{2\pi}{h^3 c^2} \int_{E_g}^{\infty} \frac{E^2 dE}{\exp\left(E/k_B T_s\right) - 1}$$
(9.1.3)

where  $h, c, k_B, T_s$  are the Planck constant, the speed of light, the Boltzmann constant and the temperature of the sun ( $T_s \approx 6000$ K) respectively. Subsequently, the total incident energy from sun falling upon on the cell is

$$P_{in} = \frac{2\pi}{h^3 c^2} \int_0^\infty \frac{E^3 dE}{\exp\left(E/k_B T_s\right) - 1}$$
(9.1.4)

$$=\frac{2\pi^5 (k_B T_s)^4}{15h^3 c^2}.$$
(9.1.5)

The efficiency as function of the bandgap of the absorber is plotted in Figure 9.1. The maximum



Figure 9.1 Ultimate efficiency from blackbody at 6000 K.

efficiency is approximately 43.87% and occurs at 1.12 eV which corresponds to the bandgap of

silicon. For the AgAlX<sub>2</sub> compounds, this predicts a maximum performance of 23.89%, 17.27% and 11.02% for AgAlTe<sub>2</sub>, AgAlSe<sub>2</sub> and AgAlS<sub>2</sub> respectively.

However, this model is too simplistic and doest not capture some extrinsic factors. For instance, the solar spectral distributions vary with the atmospheric conditions of the site where the panels are mounted and the orientation of the panels with respect to the position of the sun (tilt angle). It is therefore necessary to have a reference solar spectral distribution which can serve as common basis for comparing solar cell models/prototypes. A common standard solar spectrum model is the AM1.5 spectrum [210]. In this distribution, the tilt and the zenith angle are 37° and 48.19° respectively, the temperature is 300 K and the air mass (AM) is equal to 1.5. The AM describes the relative path length taken by the sun's rays through the atmosphere before reaching the ground [211, 212]. Spectral irradiances from the two models are shown in Figure 9.2 where the non-homogeneity of the AM1.5 spectrum can be noted. Figure 9.3 shows that the AM1.5 efficiency is higher than that of the blackdody model for materials with bandgap smaller than 1.82 eV upwards, the number of photon absorbed by cell is smaller than that from the blackbody model.



Figure 9.2 Blackbody and AM1.5 solar spectral intensity.

In the above models, all photons with energy greater than the bandgap of the absorber are assumed to produce an electron-hole pair. However, various recombination processes have been inventoried including radiative and non radiative recombination. Hence, all the generated electrons are not always converted into current. If we take into take account the recombination processes, the net current will be the difference between the generated electrons and the recombined electrons:

$$J = J_{sc} - J' \left[ e^{(qV/k_B T_c)} - 1 \right].$$
(9.1.6)

The first term is the short circuit current [213]

$$J_{sc} = q \int a(E)S(E)dE\cos(\theta)d\theta d\Omega$$
(9.1.7)

with a(E) the probability of a photon with energy E will be absorbed (the absorptivity), S(E) is the normal solar radiation spectrum,  $\theta$  and  $\Omega$  are the solid and polar angles. The second term is



Figure 9.3 Comparaison between the blackbody at 6000 K and the AM1.5 efficiency.

the dark or diode current with V the voltage at the maximum power point tracking, q the charge carrier,  $T_c$  the cell temperature and J' the current recombination rate:

 $E_a(eV)$ 

$$J' = J_r + J_{nr} = J_r / f_r (9.1.8)$$

with  $f_r$  the fraction of the radiative electron-hole recombination current,  $J_r$  and  $J_{nr}$  are the radiative and non radiative recombination rate respectively.

$$J_r = q\pi \int_0^\infty \varepsilon(E) N_{ph}(E, T_c) dE$$
(9.1.9)

where  $N_{ph}(\mathsf{E},\mathsf{T}_c)$  is the a blackbody radiation at the cell temperature  $\mathsf{T}_c$  and  $\varepsilon(E)$  the emittance(probability of a photon to be emitted). Emittance and absorptivity are equal since the probability of an electron to be excited by a photon is equal to that of an electron to be spontaneously recombined and emitting a photon according to the principle of the detailed balance [214]. In the SQ approach, the absorptivity is taken as a step function [215]:

$$a(E) = \begin{cases} 1 \text{ for } E \ge E_g \\ 0 \text{ for } E < E_g. \end{cases}$$
(9.1.10)

and the radiative recombination is considered as the dominant recombination process according to the detailed balance principle where at equilibrium, everything which is absorbed as to be emitted [207, 216]. The implication of this assumption is that  $f_r$  in Equation 9.1.8 is equalled to one. Knowing that only the photon with energy greater that the bandgap  $E_g$  can be absorbed, the net current density in Equation 9.1.6 can be rewritten as

$$J = q \int_{Eg}^{\infty} AM15(E)dE - q\pi \left[ e^{(qV/k_B T_c)} - 1 \right] \int_{Eg}^{\infty} N_{ph}(E, T_c)dE.$$
(9.1.11)

Recall that the AM1.5 spectrum already includes the integration over  $\theta$  and  $\Omega$ . In order to get the maximum efficiency, Equation 9.1.11 has to be integrated numerically throughout the AM1.5 spectrum. The module operates at its maximum efficiency when it produces the maximum output power.



**Figure 9.4** J-V and P-V characteristics of silicum ( $E_g=1.12 \text{ eV}$ ).  $V_{OC}$  is the open circuit voltage  $J_{SC}$  the short circuit current density and MPP the maximum power point.

Figure 9.4 described the J-V characteristic of silicon. The area of the largest possible rectangle fitted under the J-V characteristic corresponds to the maximum output power. The current density ( $J_{MPP}$ ) and voltage ( $V_{MPP}$ ) at maximum power point (MPP) are 426 Am<sup>-2</sup> and 0.79 V respectively. Thus, the maximum power is 336.54 Wm<sup>-2</sup> and leads to an efficiency of 33.65 %. This value is lower than what was obtained from the previous approximations. The dependence of efficiency upon the bangdap depicted in Figure 9.5 is obtained by repeating this same procedure for all the  $E_g$  in AM1.5 spectrum. The general trend is that the efficiency is lowered when accounting for the losses by recombination. Details for calculating the Silicon efficiency can be found in Appendix E.



Figure 9.5 SQ efficiency against the bangdap.

## 9.2 The spectroscopy limited maximum efficiency

The idea of the spectroscopy limited maximum efficiency (SLME) was first introduced by Liping and Zunger [215]. They postulated that having a strong absorption and a direct bandgap is not a guarantee of a good solar cell material. Some materials with well positioned dipole forbidden (DF) direct transitions lower than dipole allowed (DA) direct transitions might have a good efficiency. Semiconductors can be classified in four optical types (OT) namely OT1, OT2, OT3 and OT4 [215, 217–219] as described in Figure 9.6. The main difference between the SQ efficiency (SQE) and the spectroscopy limited maximum efficiency lies in the way the fraction of the radiative electron-hole recombination current  $f_r$  and the absorptivity a(E) are taking into considerations.



**Figure 9.6** Illustration of the different optical types of transition. In optical type 1 (OT1) materials, a direct allowed (DA) direct transition  $(E_g^{da})$  is the lowest energy level followed by a dipole forbiden (DF) direct transition  $(E_g^{df})$  ie.  $E_g^{da} \leq E_g^{df}$ . In OT2, a DF direct transition is the lowest and a DA the second lowest. Accordingly, OT3 and OT4 are indirect gap materials where  $E_g^i < E_g^{da} \leq E_g^{df}$  and  $E_g^i < E_g^{df} < E_g^{da}$ , respectively. Source: Liping et *al.* Ref. [215].

Instead of the step function, the absorptivity is taken as

$$a(E) = 1 - e^{-2\alpha(E)L}$$
(9.2.1)

with  $\alpha(E)$  the absorption coefficient and L the thickness of the thin film.  $f_r$  is approximated by

$$f_r = e^{-\Delta/k_B T} \tag{9.2.2}$$

where  $\Delta = E_g^{da} - E_g$ . By considering these modifications, the total current in Equation 9.1.6 becomes:

$$J = q \int_{E_g}^{\infty} \left[ 1 - e^{-2\alpha(E)L} \right] AM_{15}(E) dE - \frac{q\pi}{f_r} \left[ e^{(qV/k_B T_c)} - 1 \right] \int_{E_g}^{\infty} \left[ 1 - e^{-2\alpha(E)L} \right] N_{ph}(E, T_c) dE$$
(9.2.3)

The SLME and the SQE of the materials we have been investigated throughout our study namely, CH-AgAIX<sub>2</sub>, CH-,OR-and RH-AgInS<sub>2</sub> are highlighted in Figure 9.7. From our SQ calculations, RH-AgInS<sub>2</sub> is the most efficient absorber with a a maximum efficiency of 31.42%. CH-AgInS<sub>2</sub>



**Figure 9.7** Efficiency vs bandgap of AgAIX<sub>2</sub>, CH-,OR-and RH-AgInS<sub>2</sub>. The SLME is limited to AgAIX<sub>2</sub>. The thickness of the thin film is L= $0.5\mu m$ .

and OR-AgInS $_2$  follow with efficiencies of 28.84% and 21.10% respectively. For the AgAIX $_2$ compounds, the SQ model predicts a maximum performance of 18.19 %, 13.36 % and 2.74 % for AgAITe<sub>2</sub>, AgAISe<sub>2</sub> and AgAIS<sub>2</sub> respectively. Studying the variation of the efficiency as a function of thickness of thin film of potential photovoltaic absorbers, Zunger et al. [215] showed that the efficiency does not change that much for thicknesses greater than 0.5  $\mu m$ . We choose to use a thickness of 0.5  $\mu m$  for our cases. From the spectroscopy limited maximum efficiency (SLME) model, we obtained 2.71%, 13.33% and 14.42% for AgAIS<sub>2</sub>, AgAISe<sub>2</sub> and AgAITe<sub>2</sub> respectively. Recall that the absorption  $\alpha(E)$  entering in the calculation of absorptivity  $\alpha(E)$  (Equation 9.2.1) is obtained at the BSE level of the approximation and the BSE was built on top of  $GW_0$ . Because we could not get reliable bandgaps of AgInS<sub>2</sub> materials from GW, we did not calculate their BSE absorptions. We therefore limited the calculations of their solar cell performance at the SQ level where the absorption coefficient is not included. Overall, the efficiency of the compounds of interest increases as the bandgap decreases for both SQE and SLME. For a given absorber, the SQEs are relatively higher than the SLME. This is due to the fact that the SQ model does not account for the non radiative recombination and the absorptivity is set to his maximum value (a(E) = 1). Contrary to AgAITe<sub>2</sub>, the SQE and the SLME of AgAISe<sub>2</sub> and AgAIS<sub>2</sub> are very close to each other. The reason being that  $AgAITe_2$  is OT2 material while  $AgAISe_2$  and  $AgAIS_2$  are OT1 according the classification from Ref. [220]. For OT1 materials,  $f_r = 1$  since  $E_g = E_g^{da}$  and  $\Delta = 0$ . The difference between the SQE and SLME of AgAITe $_2$  confirmed that the Shockley and Queisser well known selection condition for good absorbers is limited. It is only worked for OT1 materials. The very low efficiency of AgAIS<sub>2</sub> suggests that it cannot be used as single junction solar cell absorber. However, such large bandgap materials are indicated for multi junction solar cells. Multi junction or tandem solar cells are made of materials with different bandgaps. Here, the total number of absorbed photons is higher than that of a single junction solar cell since each material absorbs photons with energy higher or equal to its bandgap, and hence increasing the total cell performance.

9.3

# Conclusion

We estimated the efficiency of the compounds under our investigation using the SQE and the SLME models. We found that apart from  $AgAIS_2$ , the other compounds have an efficiency greater that 13 %.

# 10. Conclusion and future studies

## 10.1 Conclusion

The purpose of this work was to investigate various properties of ternary chalcogenide compounds  $AgAIX_2$  (X = S,Se,Te) and  $AgInS_2$  in order to provide useful information for their applications as solar cell materials. The investigation was done by means of different computational tools mostly based on density functional theory. Our results agree in most cases with the available experimental data. We hope that our predictions will be confirmed experimentally and/or theoretically in future. We arrived at the conclusions, written in the following subsections.

#### 10.1.1 AgAIX $_2$

We investigated the structural, electronic and optical properties of chalcopyrites AgAlX<sub>2</sub> and estimated their solar cells efficiency based on the Shockley-Queisser efficiency limit and the spectroscopy limited maximum efficiency. For the structural study, we found that the GGA-PBEsol was the most appropriate exchange correlation functional. Cohesive energy and enthalpy analyses predicted that the chalcopyrite phase is the most energetic favourable structure at equilibrium amongst the different phases of AgAlX<sub>2</sub>. A possibility of a pressure phase transition from the chalcopyrite to a trigonal phase was also observed. Using the linear response method, we studied the local stability with respect to lattice vibration. Because of the absence of negative phonon frequencies along the high symmetry **k**points in the BZ, we reached the conclusion that they were all dynamically stable at the ground state.

We calculated the electronic and optical properties at DFT and GW levels of the approximations. The bandstructures and PDOSs from GGA-PBEsol were very similar and the bandgap decreases from  $AgAIS_2$  to  $AgAITe_2$ . Tetragonal distortion and anion displacement originated from the presence of cations Ag and Al in their structures lead to a crystal field splitting at the upper most valence band contrary to their binary zincblende analogues. By including the spin-orbit coupling in our calculations, we found some additional splitting of the bands and a reduction of the bandgap for all the compounds. We attributed this splitting to the presence of heavy chalcogenide atoms in their structure. Using the quasi cubic model we determined the spin-orbit coupling and found that it is more pronounced in AgAITe $_2$ . Although PBEsol and PBEsol &spin orbit coupling succeeded in predicting the crystal field and the spin-orbit splitting, it fails to predict the bandgap, essential for solar cell applications. This limitation of the GGA-PBEsol was circumvented by the hybrid functional HSE06 which gave bandgaps in better agreement with experimental data. Our results predicted that the bandgaps strongly depend on the chalcogenide atom present in the chalcopyrite compounds. The dielectric response functions from HSE06 calculations have lower intensity and are shifted towards higher energy when compared to PBEsol values. The compounds start absorbing photon either at the edge or within the visible range and reach their absorption peaks in the ultraviolet range. The metta-GGA MBJ functional predicts bandgaps of 3.15 eV, 2.38 eV, and 2.14 eV for AgAIS<sub>2</sub>, AgAISe<sub>2</sub> and AgAITe<sub>2</sub>, respectively. These values are in good agreement with 3.14 eV, 2.55 eV and 2.27 eV respectively, obtained from experiments. Similar agreement was found when compared with 3.14 eV, 2.7 eV and 2.37 eV from HSE06, known to be computationally very expensive, whereas the computation time of MBJ scales as that of LDA and GGAs.

We also calculated the bandgap and optical spectra by means of the many body perturbation theory at GW and BSE level. The single shot  $G_0W_0$  method failed to predict the correct bandgaps. The semi self-consistent GW<sub>0</sub> gave bandgaps within 4% agreement with the experimental data. Quasiparticle energy from GW<sub>0</sub> was used for the BSE calculation. From the obtained absorption spectra, we predicted the existence of bound excitons in all the three compounds with exciton energies of 0.15 eV, 0.2 eV and 0.21 eV for AgAITe<sub>2</sub>, AgAISe<sub>2</sub> and AgAIS<sub>2</sub>, respectively. Knowing the bandgaps and the optical absorptions, we went further to calculate the solar cell efficiency limits. The Shockley-Queisser model predicted an efficiency of 18.19 %, 13.36 % and 2.74 % for AgAITe<sub>2</sub>, AgAISe<sub>2</sub> and AgAIS<sub>2</sub> respectively. With spectroscopy limited maximum efficiency (SLME) model, we obtained 14.42%, 13.33% and 2.71%, respectively. From the results, we concluded that SLME is a more effective theoretical technique for selecting potential solar cell absorbers. Contrary to AgAITe<sub>2</sub> and AgAISe<sub>2</sub>, AgAIS<sub>2</sub> cannot be used as single junction solar cell absorber because of its low efficiency. However, it might found applications in intermediate and/or multi junction solar cell absorbers technology.

#### 10.1.2 AgInS $_2$

The structural, mechanical, dynamical and electronic properties of different phases of  $AgInS_2$ were investigated using GGA-PBEsol and MBJ. The efficiency was also estimated using the SQ model. The effect of the pressure on the properties was carried out at selected pressure of 0, 1.78 and 2.5 GPa. The six phases investigated included the tetragonal (chalcopyrite  $CuFeS_2$ ), the rocksalt (CuAlS<sub>2</sub>), the orthorhombic ( $\beta$ -NaFeO<sub>2</sub>), the rhombohedral ( $\alpha$ -NaFeO<sub>2</sub>), the hexagonal (LiMnSe<sub>2</sub>) and the monoclinic (NaNiO<sub>2</sub>) phases. As for the case of AgAlX<sub>2</sub>, we found the chalcopyrite phase as the most energetically favoured stable structure at zero pressure and temperature although the energy difference with the orthorhombic phase remained very small. The variation of enthalpy with respect to pressure confirmed that the chalcopyrite is the most energetically favourable structure a zero pressure and zero temperature. A pressure-induced phase transition from the chalcopyrite to the rhombohedral occurs around 1.78 GPa. This prediction was in agreement with the experiment measured by Range et al. at 2 GPa. We also found transition from the rhombohedral phase to the rocksalt phase at about 93.5 Gpa, but this very high pressure would make it practically difficult to achieve. We also found a positive formation energy for the hexagonal and rocksalt phases which suggest that they are more likely to decompose to their elementary constituents. The chalcopyrite and the orthorhombic phases remained mechanically and dynamically stable at the selected pressure of our interest while the rhombohedral structure was only stable above the transition pressure of 1.78 Gpa. With the use of the MBJ functional, we were able to predict accurately the bandgap of the chalcopyrite and the orthorhombic structures. For the first time, the electronic properties of the rhombohedral structure were investigated and found that it has a bandgap of about 0.95 eV. From the GW calculations, the bandgaps of 1.24 eV and 1.40 eV for CH-AglnS<sub>2</sub> and OR-AglnS<sub>2</sub> respectively were not in agreement with 1.87 eV and 1.98 eV from the experimental available data. Similar discrepancy was found in other copper and indium based chacopyrite such as CulnS<sub>2</sub> and it was hypothesised that the orbitals of those atoms are not be well described within the GW method [202, 221]. Since, reliable bandgap and absorption could not be obtained from GW calculations, we then limited our efficiency of about 31.42%. CH-AglnS<sub>2</sub> and OR-AglnS<sub>2</sub> efficiencies were estimated at 21.10% and 21.10% respectively.

#### 10.2 What next?

- Most of these studies were done at zero temperature and pressure which are not the operating conditions of solar cells. Pressure phase transition were investigated in a few cases, but a complete study requires taking into account the effect of temperature. We intend to perform, in the future, a pressure and temperature phase transition study on these compounds. The quasiharmonical approximation could be used.
- Doping plays an important role on the electronics and optical properties of chalcopyrites. For example, defect levels could be created in the bandgap and offer a possibility of increasing the absorptivity. Such study may be performed in these materials.
- 3. It is predicted that a different starting point such as the hybrid functional or the COHSEX

method for the GW calculation could help to overcome the bandgap underestimation in  $AgInS_2$ . We shall explore this possibility since the it allows the used of the spectroscopy limited maximum efficiency (SLME) method for estimating solar cells performance.

4. There is need to investigate the possibility of using large bandgap materials such as  $AgAIS_2$ in intermediate band and tandem solar cells and also estimate the efficiency.

# Appendix A. Solving the KS equation

# A.1 Self-consistent procedure

If we look back at Equation 2.3.34 and examine the KS potential in more details, one can notice that the Hartree and the exchange-correlation contribution to the KS potential depend explicitly on the density itself. Thus, solving the Equation 2.3.23 become a cumbersome task since we have to construct the KS potential from the wave-function/density that is not known a priori. We can circumvent this kind of problem by using an iterative method also known as the Self-Consistent Field (SCF) procedure.



Figure A.1 Self-consistent iterative procedure for solving the KS equation

As we summarised in Figure A.1, the self consistent iterative procedure consists of constructing the KS potential from an initial guess of the density. Then solve KS Equation 2.3.23 to get the total energy  $E_i$ . If the SCF convergence criteria is satisfied, the energy  $E_i$  minimised the single particle energy. Otherwise, a new density has to be generated from the wave-function. This is then used as the new guess for the density and this iteration is repeated until the minimum energy is obtained. From the ground-state energy, other ground-state properties (forces, formation energy etc.) can be calculated.

#### A.2 Block's theorem

When solving the KS equation, one has to carefully choose the basis set for representing the KS orbitals. The choice is guided by the type of materials that one is interested in. For crystalline solids, the appropriate basis set are plane waves since one can simplify the problem using Bloch's Theorem. The collective behaviour of electrons in a single unit cell can be translated to the whole periodic system of an infinite number of electrons. According to Bloch's theorem, if the potential  $V(\mathbf{r})$  of the Hamiltonian H has a translational symmetry such that

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}) \tag{A.2.1}$$

with  $\mathbf{R}$  a lattice vector in the Bravais lattice The eigenstate of H can be written as

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k}.\mathbf{r}) \tag{A.2.2}$$

where  $u_{\mathbf{k}}(\mathbf{r})$  has the same periodicity as the potential V(**r**) and the wavevector **k** in the Brillouin Zone (BZ). As it is a periodic function,  $u_{\mathbf{k}}(\mathbf{r})$  can be expanded it in terms of a Fourier series

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} \exp\left(i\mathbf{G}\cdot\mathbf{r}\right)$$
(A.2.3)

where **G** represents the reciprocal lattice vectors defined such that  $\mathbf{G} \cdot \mathbf{R} = 2\pi n$  with n an integer number. By substituting (A.2.3) into (A.2.2), the electronic wave-function yields

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} \exp\left[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}\right]$$
(A.2.4)

In reciprocal space, each electron occupies a single state defined by the  $\mathbf{k}$  vector. An advantage of using the Bloch's theorem is that the problem of finding the infinite number of electronic state is simplified. This is done by finding a finite number of electronic states in the unit cell with an infinite number of  $\mathbf{k}$ -points within the BZ. The new problem can be tackled easily. Here, the wave-functions representing sufficiently close  $\mathbf{k}$ -points are very similar and thus, they can be

represented by a single wave-function. Hence, the integral over the BZ can be replaced by a discrete sum over a grid of  $\mathbf{k}$  points [222]:

$$\frac{\Omega}{(2\pi)^3} \int_{BZ} \dots \Theta(E_F - E_{\mathbf{k}}) d\mathbf{k} \to \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} f_{\mathbf{k}} \dots$$
(A.2.5)

where  $\Theta$  is a *Heaviside step function* and  $f_{\mathbf{k}}$  represents the occupation number which is equal to 1 for an occupied state and 0 otherwise. There are many ways of sampling the BZ and the most common one is the uniform sampling method proposed by Monkhorst and Pack [135]. The number of **k**-points sufficient for sampling the BZ is obtained through a series of convergence tests where the total energy of different **k**-point grids are compared. Convergence is reached when the energy remains almost constant for different sets of **k**-point grids. An example is shown in Figure A.2a below.



**Figure A.2** Illustration of the **k**-points and cutoff energy convergence tests for the case study of AgAIS<sub>2</sub>. Convergence was reach when energy difference between two scf step was last then 2 meV.  $K_i$  is the value of the **k**-point along *i* direction (i = x, y, z). It can be seen that from  $K_z$ =5, there is not a significant change in energy. Hence, 5 can be taking as the converge value of  $K_z$ . Simillar tests should be performed along  $K_x$  and  $K_y$  directions. For the cut off energy, it starts converging from  $E_{cut} \simeq 310$  eV.

#### A.3 KS equation in reciprocal space

For a periodic system, the electronic wave-functions can be written as a Bloch wave function (Equation A.2.4). If we consider that all the potentials contributing to the KS potential are periodic, they can also be written as

$$V(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{V}(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r}), \qquad (A.3.1)$$

Substituting Equation A.2.4 into the KS Equation ?? and multiplying both sides of the latter by  $\exp(i(\mathbf{k} + \mathbf{G}').\mathbf{r})$  leads the KS equation in the reciprocal space

$$\sum_{\mathbf{G}'} \left[ \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_{KS} (\mathbf{G} - \mathbf{G}') \right] c_{\mathbf{k},\mathbf{G}'} = E_{\mathbf{k}} c_{\mathbf{k},\mathbf{G}'}$$
(A.3.2)

where  $V_{KS}(\mathbf{G} - \mathbf{G}')$  is the Fourier transform of the KS potential. In practice, Equation A.3.2 is solved by diagonalisation. The size of the matrix depends on the number of plane waves included in the calculation. Because of the infinite number of plane waves, one has to determine how many of them are sufficient for getting accurate eigenvalues for Equation A.3.2. This number is defined by the kinetic energy cutoff  $E_{cut}$  defined in such a way that

$$\frac{1}{2}|\mathbf{k}+\mathbf{G}|^2 \le \mathsf{E}_{cut}.\tag{A.3.3}$$

As in the case of the BZ sampling, a convergence test of  $E_{cut}$  versus total energy has to be performed in order to get an accurate  $E_{cut}$ . An example of such a test is given in Figure A.2b.

## A.4 Pseudopotential and Projector Augmented Waves (PAW)

The potential in the region around the core of an atom is very deep and leads to a rapid oscillation of the wave-function compared to the valence region where it is fairly smooth. As a result of this

oscillation, core and the valence states can hardly be described by the same wave-function accurately. However, it is known that the core electrons are more localised than the valence electrons and do not contribute that much to the chemical properties of solids and molecules [223]. Hence, the strong potential around the core can be replaced by a much weaker *pseudopotential* and the wave-function by a much smoother *pseudo wave-function*. The reason being that it requires a small number of Fourier coefficients if it is to be represented by a plane wave basis set. There are two different approaches for defining the pseudopotentials. Namely, the empirical method where the parameters are fitted to the data from atomic or solid state databases, and the ab initio potential constructed to fit the valence properties calculated for the atoms.

Nowadays, the latter method is the most common used in DFT codes. Several techniques for generating the pseudopopentials have been developed ranging from the norm-conserving to the ultrasoft pseudopotentials. Details about these pseudopentials can be found in many seminal DFT books including that of Richard Martin [51]. However, we will elaborate on a more convenient method to treat the potential known as the Projector Augmented Wave (PAW) method [224]. The aim of the PAW method is to develop a more accurate method for describing both core and valence states at a reasonable computational cost, for all the atoms in the periodic table. Within the PAW method, the valence states are represented by a smooth wave-function in terms of plane waves. To define a full wave-function, we look for a linear transformation operator  $\mathcal{T}$  that links the smooth pseudo (PS) wave-function  $|\tilde{\psi}_n\rangle$  of the valence region to the all electron (AE) wave-function  $|\psi_n\rangle$ :

$$|\psi_n\rangle = \mathcal{T}|\tilde{\psi}_n\rangle$$
 (A.4.1)

A suitable transformation operator should be defined such a way that  $|\psi_n\rangle$  only differs from  $|\tilde{\psi}_n\rangle$ in the region around the core. Hence, Blöchl [224] defined  $\mathcal{T}$  as

$$\mathcal{T} = 1 + \sum_{a} \mathcal{T}^{a} \tag{A.4.2}$$

$$\mathcal{T}^{a} = \sum_{i} \left( |\phi_{i}^{a}\rangle - |\tilde{\phi}_{i}^{a}\rangle \right) \langle \tilde{p}_{i}^{a}|$$
(A.4.3)

where i is an index for angular momentum and magnetic quantum number. Since  $\mathcal{T}^a$  is a local operator, the PS partial smooth wave-function, the AE partial wave-function and the projector must be chosen such that:

- \*  $\phi_i^a(\mathbf{r}) = \tilde{\phi}_i^a(\mathbf{r})$  for  $\mathbf{r} \ge \mathbf{r}_c^a$ ,
- \*  $|\tilde{p}_i^a\rangle$  is localised inside the augmentation sphere and orthogonal to the PS partial smooth wave-function i.e.  $\langle \tilde{p}_i^a | \tilde{\phi}_j^a = \delta_i \delta_j$ ,
- \* adjacent augmentation spheres must not overlapped.

Inserting the transformation operator (A.4.3) to Equation A.4.1, the AE KS wave-function yields

$$\psi_n(\mathbf{r}) = \tilde{\psi}_n(\mathbf{r}) + \sum_a \sum_i \left( \phi_i^a(\mathbf{r}) - \tilde{\phi}_i^a(\mathbf{r}) \right) \tilde{p}_i^a | \tilde{\psi}_n \rangle \tag{A.4.4}$$

In the PAW method, it is assumed that the core states of an isolated atom are not modified during the formation of molecules. This is known as the *frozen core approximation* [225]. An advantage of this approximation is that the smooth PS wave-function  $\tilde{\psi}_n(\mathbf{r})$  can be used in lieu of the AE wave-function  $\psi_n(\mathbf{r})$  as variational parameter during the calculations. Moreover, it enables one to obtain the observable quantities as expectation of values  $\tilde{\psi}_n(\mathbf{r})$ . The expectation value of some operator A is given by [88, 224]

$$\langle A \rangle = \sum_{n} f_n \langle \tilde{\psi}_n | \tilde{A} | \tilde{\psi}_n \rangle$$
 (A.4.5)

where n is the band index and  $f_n$  the occupation number of the state and the PS operator  $\tilde{A}$  has the form where n is the band index;  $f_n$  is the occupation number of the state and the PS operator  $\tilde{A}$  has the form,

$$\tilde{A} = \mathcal{T}^{\dagger} A \mathcal{T}$$
  
=  $A + \sum_{i,j} |\tilde{p}_i\rangle \Big( \langle \phi_i | A | \phi_j \rangle - \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle \Big) \langle \tilde{p}_j |.$  (A.4.6)

Following the above description, the charge density and the total energy, respectively, are given by

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^{1}(\mathbf{r}) - \tilde{n}^{1}(\mathbf{r})$$
 (A.4.7)

and

$$E) = \tilde{E} + E^{1} - \tilde{E}^{1}$$
 (A.4.8)

with  $n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r})$  and  $E^1 - \tilde{E}^1$  vanishing outside the augmentation spheres. Under the constraints given above, there is a freedom to choose  $|\phi_i^a\rangle$ ,  $|\tilde{\phi}_i^a\rangle$  and  $|\tilde{p}_i^a\rangle$ . In our calculations, we adopted the Kresse and Joubert [133] derivation as implemented in the Vienna Ab initio Package (VASP) [134]. Here the PS partial wave-function  $|\tilde{\phi}_i^a\rangle$  is expanded in terms of a linear combination of Bessel's functions and the projector is obtained using the Vanderbilt ultrasoft pseudopotential scheme [226].
## Appendix B. Geometric optimisation: the equation of state

Geometry optimisation involves searching for the most convenient atomic configuration for a given structure. The structural quantities to be considered include the atomic position, the shape of the unit cell and its volume. In order to reach the global energy minimum, the optimisation is done in two steps: Firstly, a full relaxation calculation where the stated parameters are allowed to change is carried out until the minimum energy is reached following the conjugate gradient algorithm. A threshold value of the Hellmann-Feyman force on each ion should also be considered. The Hamiltonian is then diagonalised using an appropriate diagonalisation method such as the Block Davidson Algorithm [227]. Thereafter, ionic relaxations at different volumes are performed and fitted to a third order Birch-Murnaghan equation of state (EOS) [146].

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left( \left[ \left(\frac{V_0}{V}\right)^{2/3} - 1 \right]^3 B'_0 + \left[ \left(\frac{V_0}{V}\right)^{2/3} - 1 \right]^2 \left[ 6 - 4 \left(\frac{V_0}{V}\right)^{2/3} \right] \right)$$
(B.0.1)

where  $E_0$ ,  $V_0$ ,  $B_0$  and  $B'_0$  are the equilibrium cohesive energy, volume, bulk modulus and its derivatives respectively. The cohesive energy defines the energy required to separate atoms infinitely far apart from a solid by breaking the atomic bonds [1] and the bulk modulus is the the resistance of a material subject to a uniform compression.

## Appendix C. Stability

To be used for technology applications, the material has to go through a series of tests in order to make sure it can resist different kinds of deformations when it is subjected to stress. Theoretically, the parameters to be checked included but are not limited to the bulk modulus, the cohesive and formation energy, and, the elastic constants. Lattices dynamics shall also be investigated.

#### C.1 The formation and the cohesive energy

For the case of chalcopyrites structure with general formula ABC<sub>2</sub>, the cohesive energy  $(E_{coh})$  is given by

$$E_{coh} = \frac{E_{sol} - N\left(E_{atom}^A + E_{atom}^B + 2E_{atom}^C\right)}{4N}$$
(C.1.1)

where N is the number of ABC<sub>2</sub> units per unit cell and  $E_{sol}$  the total energy of the bulk ABC<sub>2</sub> system.  $E_{atom}^{i}$  is the atomic energy of the atom i (i=A, B, C). It corresponds to the total energy of an isolated i atom and should not be confused with the total energy of the bulk system of i atoms. In practice, it is approximated as the total energy of a system made of a large unit cell containing one atom at its center. The large unit cell is adopted in order to avoid interaction with adjacent cells related to the use of the periodic boundary condition. At the ground-state (Temperature = 0K, Pressure = 0GPa), it can be used to select the most stable structure of a material if it exists with different phases. We will come back to it in subsection (C.2). The formation energy helps to predict the possibility of the formation of a material relative to its constituents. It is defined as the the energy difference between cohesive energy of a compound and those of constituents from which it is obtained:

$$E_f = E_{coh}(products) - E_{coh}(reactants)$$
(C.1.2)

In the case of ternary compounds, if the compound, say  $ABC_2$ , is obtained from its elementary constituents, the formation energy is given by

$$E_f(\mathsf{ABC}_2^{sol})) = E_{coh}(\mathsf{ABC}_2^{sol}) - \frac{\left[E_{coh}(\mathsf{A}^{sol}) + E_{coh}(\mathsf{B}^{sol}) + 2E_{coh}(\mathsf{C}^{sol})\right]}{4}$$
(C.1.3)

However, the chemical precursors used in the synthesis of a ternary compound can also be binary compounds. For instance,  $AgInS_2$  can be formed from  $Ag_2S$  and  $In_2S_3$  following the chemical process

$$\mathsf{AgInS}_2 \rightleftharpoons \frac{1}{2}\mathsf{Ag}_2\mathsf{S} + \frac{1}{2}\mathsf{In}_2\mathsf{S}_3. \tag{C.1.4}$$

In this case,  $E_f$  is calculated as

$$E_f(\ln AgS_2^{sol})) = E_{coh}(AgInS_2^{sol}) - \frac{\left[\frac{1}{2}E_{coh}(Ag_2S^{sol}) + \frac{1}{2}E_{coh}(In_2S_3^{sol})\right]}{4}$$
(C.1.5)

Positive formation energy is an indication that a material is likely to be transformed to its constituents under the given conditions.

#### C.2 Phase stability

Under specific conditions, a compound may undergo a pressure or temperature phase transition from one phase to another. For instance, most of the chalcopyrite materials convert to an orthorhombic phase at high temperature. The transition is analysed using the Gibbs free energy

$$G = E_{coh} + PV - TS \tag{C.2.1}$$

where T and P are the independent variables. As we pointed out in the previous subsection, it can be seen that at the ground-state, the Gibbs free energy turns into the cohesive energy. At T = 0 K and P  $\neq$  0 GPa, Equation C.2.1 turns into the enthalpy

$$H = E_{coh} + PV. \tag{C.2.2}$$

At a constant pressure P, the more stable structure is that with the smaller enthalpy. The transition pressure P<sub>t</sub> between two phases can be determined in two different ways. The first method involves constructing the common tangent on the energy-volume equation of state curves of the two phases. P<sub>t</sub> is then taking as the slope ( $P_t = -dE/dV$ ) of the common tangent. The second method entails plotting the enthalpy versus pressure curve for the two phases and taking P<sub>t</sub> as the crossing point where the two phases have the same enthalpy. After the transition, the favourable phase is that with the lowest enthalpy from P<sub>t</sub> upwards.

#### C.3 Lattice dynamics and thermal properties

Phonons can be defined as collective excitation associated with the lattice vibration of a crystal (periodic system). We will first give a brief summary of the lattice vibration, we adopt the description and the notation of Ref. [143]. At the ground-state, atoms in a crystalline structure occupy their equilibrium position  $\mathbf{r}(lk)$  where l and k denote the unit cells and the atom in each unit cell. During the vibration, the atoms move from the equilibrium to a new position  $\mathbf{R}(lk) = \mathbf{r}(lk) + \mathbf{u}(lk)$  where  $\mathbf{u}(lk)$  is the displacement.  $\mathbf{u}(lk)$  is assumed to be very small compared to the interatomic distance in order to remain within the harmonic approximation. The atomic configuration is governed by a crystal potential  $\Phi$  which can be expanded in Taylor series around the equilibrium position as

$$\Phi = \Phi_0 + \sum_{lk} \Phi_\alpha(lk) u_\alpha(lk) + \frac{1}{2} \sum_{ll'kk'} \Phi_{\alpha\beta}(lk, l'k') u_\alpha(lk) u_\beta(l'k') + \dots$$
(C.3.1)

where  $\alpha, \beta$  denote the Cartesian coordinates. The first term of the expansion is constant and referred to as the equilibrium configuration where atoms are at  $\mathbf{r}(lk)$  and can be fixed at zero. The coefficients  $\Phi_{\alpha}(lk)$  and  $\Phi_{\alpha\beta}(lk, l'k')$  are respectively the first and the second order force constants. Force constants are equivalent to the spring constant in one-dimensional system. The first order term  $\Phi_{\alpha}(lk)$  is equivalent to the force acting on an atom

$$F_{\alpha}(lk) = -\frac{\partial \Phi}{\partial u_{\alpha}(lk)}$$
(C.3.2)

and it goes to zero at the equilibrium. The second order force constant is given by

$$\Phi_{\alpha\beta}(lk,l'k') = -\frac{\partial F_{\beta}(l'k')}{\partial u_{\alpha}(lk)} = \frac{\partial^2 \Phi}{\partial u_{\alpha}(lk)\partial u_{\beta}(l'k')}.$$
(C.3.3)

Within the harmonic approximation, the higher terms of Equation C.3.1 are negligible. The dynamical matrix is the Fourier transform of the force constant matrix

$$D_{\alpha\beta}^{kk'}(\mathbf{q}) = \frac{1}{\sqrt{M_k M_{k'}}} \sum_{l'} \Phi_{\alpha\beta}(0k, l'k') e^{i\mathbf{q}[\mathbf{r}(l'k') - \mathbf{r}(0k)]}$$
(C.3.4)

where  $M_k$  are the atomic masses. The normal phonon modes are obtained from the dynamical matrix by solving the eigenvalues problem [141, 143]

$$\sum_{\beta k'} D_{\alpha\beta}^{kk'}(\mathbf{q}) e_{\mathbf{q}j}^{\beta k'} = \omega_{\mathbf{q}j}^2 e_{\mathbf{q}j}^{\alpha k}$$
(C.3.5)

where **q** and j are the wavevector and the band index respectively. There are two main methods for the phonon calculations: the direct method also known as supercell approach [228] and the linear response method sometimes labelled as the Density Functional Perturbation Theory (DFPT) [141, 142]. The main difference between the two approaches being the way the force constant is calculated.

The direct method is based on the fact that within the harmonic approximation, for any displacement  $u_{\alpha}(lk)$ , the force felt by the atom at l'k' is given by

$$F_{\beta}(l'k') = \sum_{lk} \Phi_{\alpha\beta}(lk, l'k') u_{\alpha}(lk).$$
(C.3.6)

Hence, knowing the displacement and the Hellmann-Feynman (HF) forces on all other atoms, the force constant is obtained as the coefficient of the linear relation above. Using the direct method, caution should be taken when choosing the size of the unit cell. The method relies on

short-ranged nature of force constant matrix by supposing that the forces vanish at long range. The assumption is that the small displacements only affected the atoms within the unit cell. But, because of the periodic arrangement of the cells, the forces acting on the atoms from the same cell are possibly influenced by atoms from the other cells. Hence, the unit cell (here the supercell) should be made as large as possible such that the element of the force constants matrix are negligible at the boundary of the supercell.

In contrast the to the direct method, the force constant within the linear respond method is obtained as second derivative of the total energy. The ionic contribution to the total energy can be easily obtained, however, the electronic contribution requires the sophisticated DFT treatment of the electronic system. According to the HF theorem [229, 230], when the system is perturbed by a small displacement  $u_{\alpha}$ , the first derivative of the energy is given by

$$\frac{\partial E}{\partial u_{\alpha}} = \int n_{\mathbf{u}}(\mathbf{r}) \frac{\partial V_{\mathbf{u}}(\mathbf{r})}{\partial u_{\alpha}} d\mathbf{r}$$
(C.3.7)

and the second derivative as

$$\frac{\partial^2 E}{\partial u_{\alpha} \partial u_{\beta}} = \int \frac{\partial V_{\mathbf{u}}(\mathbf{r})}{\partial u_{\alpha}} \frac{\partial n_{\mathbf{u}}(\mathbf{r})}{\partial u_{\beta}} d\mathbf{r} + \int n_{\mathbf{u}}(\mathbf{r}) \frac{\partial^2 V_{\mathbf{u}}(\mathbf{r})}{\partial u_{\alpha} \partial u_{\beta}} d\mathbf{r}.$$
 (C.3.8)

The electronic density derivative  $\frac{\partial n_{\mathbf{u}}(\mathbf{r})}{\partial u_{\beta}}$  can be obtained from the DFT KS scheme. For a perturbation  $\delta V_{KS}$  of the KS potential, the variation of the density is given by [142]

$$\delta n(\mathbf{r}) = 4\Re e \sum_{v} \psi_{v}^{*}(\mathbf{r}) \Delta \psi_{v}(\mathbf{r}), \qquad (C.3.9)$$

where

$$\Delta \psi_v(\mathbf{r}) = P_c \frac{1}{\epsilon_v - H_{KS}} P_c \delta V_{KS} \psi$$
(C.3.10)

with c and v are the conduction and valence states respectively and  $P_c$  the projector over conduction states. Practically,  $\Delta \psi_v(\mathbf{r})$  can be obtained from the self-consistent solution of the Stenrheimer-like [142] equation

$$(\epsilon_v - H_{KS}) P_c \Delta \psi_v(\mathbf{r}) = P_c \delta V_{KS} \psi_v.$$
(C.3.11)

A detailed discussion of the DFPT can be found from the review articles of Baroni et *al.* [142] and Gonze [231]. The DFPT is not as computationally straightforward as the direct method, but it does not require the use of a supercell for the calculation of the dynamical matrix. The calculations are directly performed in the reciprocal space. Moreover, the so called longitudinal optical-transverse optical (LO-TO) splitting [150] is not taken into account in the direct method. LO-TO splitting comes from a dynamical matrix which includes the Born effective charge tensors and the high frequency static dielectric tensor [231]. The DFPT method is used for our phonon calculations. Initially, force constants are calculated using the VASP code. Thereafter, by means of the PHONOPY code [143] the elements of the dynamical matrix are computed from the force constant matrix and used as input for the secular Equation C.3.5. Knowing the phonon frequencies, the phonon contributions to the thermal properties at constant volume of the system such as the Helmholtz free energy F, the entropy S and the heat capacity  $C_v$  can be computed as functions of temperature [143, 150]:

$$F = \frac{1}{2} \sum_{\mathbf{q}_j} \hbar \omega_{\mathbf{q}_j} + k_B T \sum_{\mathbf{q}_j} ln \left[ 1 - \exp\left(\frac{-\hbar \omega_{\mathbf{q}_j}}{k_B T}\right) \right], \qquad (C.3.12)$$

$$S = -k_b \sum_{\mathbf{q}_j} ln \left[ 1 - \exp\left(\frac{-\hbar\omega_{\mathbf{q}_j}}{k_B T}\right) \right] - \frac{1}{T} \sum_{\mathbf{q}_j} \left[ \frac{\hbar\omega_{\mathbf{q}_j}}{\exp\left(\frac{-\hbar\omega_{\mathbf{q}_j}}{k_B T}\right) - 1} \right]$$
(C.3.13)

and

$$C_{v} = k_{b} \sum_{\mathbf{q}_{j}} \left(\frac{\hbar\omega_{\mathbf{q}_{j}}}{k_{B}T}\right)^{2} \frac{\exp\left(\frac{\hbar\omega_{\mathbf{q}_{j}}}{k_{B}T}\right)}{\left[\exp\left(\frac{\hbar\omega_{\mathbf{q}_{j}}}{k_{B}T}\right) - 1\right]^{2}},$$
(C.3.14)

where  $\omega_{\mathbf{q}_j}$  is the phonon frequency at the wavevector  $\mathbf{q}$  and band index j.  $k_B$ ,  $\hbar$  and T are respectively the Boltzmann constant, the Planck's constant and the temperature. It worth pointing out that the thermal properties can also be calculated at constant pressure within the quasi-harmonic approximation (QHA) [232]. However that aspect is not investigated in our work.

#### C.4 Mechanical stability: Elastic constant

Elastic constants are of great experimental interest. It can provide useful information about the structural stability of a material. Elastic constants describe the response of a system when it is subjected to a strain. Once they are known, some relevant mechanical parameters such as Young's modulus, the Poisson ratio, and the bulk modulus can also be determined. Experimentally, they are calculated from Brillouin scattering or inelastic neutron scattering using the phonon or sound wave velocity ( $v = C_{ij}/\rho$ )<sup>1/2</sup> with  $\rho$  the density of the material). Within the limits of Hooke's Law (small strains), they relate the stresses  $\varepsilon$  to the strains  $\sigma$  in a linear form

$$\sigma = C_{ij}\varepsilon_j.\tag{C.4.1}$$

Theoretically, they correspond to the second derivative of the total energy of a solid under an infinitesimal strain:

$$E(\varepsilon) = E(V_0, \varepsilon = 0) + \frac{1}{2}V_0 \sum_{i,j} C_{ij}\varepsilon_i\varepsilon_j + O(\varepsilon^3)$$
(C.4.2)

with

$$C_{ij} = \frac{1}{V_0} \left( \frac{\partial^2 E(\varepsilon)}{\partial \varepsilon_i \partial \varepsilon_j} \right)$$
(C.4.3)

and  $V_0$  is the ground-state equilibrium volume. With addition of hydrostatic pressure, the volume of the system changes and the total energy is given by [191]:

$$E(\varepsilon) = E(V^*, \varepsilon = 0) + V^* \sum_i \sigma_i \varepsilon_i + \frac{1}{2} V^* \sum_{i,j} C_{ij} \varepsilon_i \varepsilon_j + O(\varepsilon^3)$$
(C.4.4)

where  $V^*$  is the volume of the system at a given pressure. A structure is stable with respect to the elastic constants when it obeys a certain general condition known as the Born stability criteria [193,194]. These conditions as well as the number of independent elastic constants depend on the symmetry of the system under investigation. Each specific condition will be stated when necessary in the next chapters.

# Appendix D. Frequency dependant dielectric response functions

The complex dielectric function  $\varepsilon(\omega)$  is the fundamental quantity used to determine optical properties of a material. It describes the response of the material to electromagnetic radiation. The imaginary part  $\varepsilon_2(\omega)$  is computed by summation over all pairs of occupied and virtual states [233]:

$$\varepsilon_{\alpha\beta}^{im}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{v,c,\mathbf{k}} 2w_{\mathbf{k}} \delta\left(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega\right) \langle u_{c\mathbf{k}+e_{\alpha}q} | u_{v\mathbf{k}} \rangle \langle u_{v\mathbf{k}} | u_{c\mathbf{k}+e_{\beta}q} \rangle, \tag{D.0.1}$$

where the indices c and v are restricted to the conduction and the valence band states respectively and  $\Omega$  denotes the unit cell volume. The vectors  $e_{\alpha}$  are unit vectors for the three Cartesian directions. The real part is obtained from the imaginary part using the Kramers-Kronig relation [234]

$$dfghj$$
 (D.0.2)

Other frequency dependant dielectric response functions such as the absorption coefficient  $\alpha(\omega)$ , the refractive index  $n(\omega)$ , the reflectivity  $R(\omega)$  can be derived from  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  [235] as:

$$\alpha(\omega) = \sqrt{2}\omega \left[ \left( \varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) \right)^{\frac{1}{2}} - \varepsilon_1(\omega) \right]^{\frac{1}{2}}, \qquad (D.0.3)$$

$$n(\omega) = \frac{1}{\sqrt{2}} \left[ \left( \varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) \right)^{\frac{1}{2}} + \varepsilon_1(\omega) \right]^{\frac{1}{2}}$$
(D.0.4)

and

$$R(\omega) = \left| \frac{\left[\varepsilon_1(\omega) + i\varepsilon_2(\omega)\right]^{\frac{1}{2}} - 1}{\left[\varepsilon_1(\omega) + i\varepsilon_2(\omega)\right]^{\frac{1}{2}} - 1} \right|^2$$
(D.0.5)

## Appendix E. Si efficiency code

The code is written in Python. The bandgap of silicon is 1.12 eV. The same procedure can be followed for the efficiency calculation at any bandgap.

```
,, ,, ,,
 necessary modules
,, ,, ,,
from __future__ import division
from scipy import integrate as itg
from scipy import interpolate as interp
import numpy as np
import matplotlib.pyplot as pylab
""" global variables
,, ,, ,,
eV = q = 1.60217662e - 19
Kb = 1.38064852e - 23
hplanck=6.62607004e-34
c = 3.e8
Tcell = 300.
Tsun = 6000.
""" Planck equation for the solar radiation"""
def Nc(Xg):
        Kst1 = 2.*((Kb*Tcell)**3)/((hplanck**3)*(c**2))
```

```
F = \text{lambda } x: (x**2)/(np.exp(x))
```

```
MaxXg = (4.43107249758 * eV) / (Kb * Tcell)
        valF = (itg.quad(F,Xg,np.inf)[0]) * Kst1
        return valF
def Diode(v):
        """ radiative and non radiative recombination of electons,
        think about an ideal diode"""
        cst=q/(Kb*Tcell)
        return q*np.pi*(np.exp(cst*v))
if __name__ == "__main__":
        ,, ,, ,,
            Ultimate efficieny assuming that each absorbed photon
        will produce an electron-hole pair.
        The sun here is assuming to be a blackbody at 6000K.
        More details can be found here
        http://cdn.intechopen.com/pdfs-wm/47490.pdf
        or http://dx.doi.org/10.5772/5891. Here, experimental data
        of the solar spectrum are considered insted of the black
        body assumption. The standard AM1.5G data are used. It can
        download for from http://rredc.nrel.gov/solar/spectra/am1.5/
        Details about the convertion from wave lenght to energy can
        be found in 30Nov.py"""
        AM15data=np.loadt×t("Dat.dat")
        am15=AM15data [:, 2]; Lambda=AM15data [:, 0]; dLambda=0.5
        M⊨len (am15)
        """ convert the wavelenght in energy (eV) and the am15 in
        energy unit too."""
        Energy = ((hplanck * c)/1e - 9)/Lambda;
```

```
AM15=((am15*(Lambda**(2)))/(hplanck*c))
Pin=-itg.simps(AM15,Energy*1e-9);
print "The Sun power is" ,Pin, "W/m2"," "
""" should multiply by 1e-9 because the AM1.5[:,2} are per
namometer. Remember to do the same during the integration
S(E)dE"""
```

eg=1.12\*eV; Index = np.where(Energy>=eg)[0][-1]

""" np.where(condition) return the position of all the element which satisfy the CONDITION. Here the condition is the position of all the energy greater than the gap. Since the array Energy is sort from max to min, [-1] will pick last eenergy grather than gap and we integrate AM15 from that element. More details abt np.where please google!!!! np.where(x>=1)[0][-1] return the index of last elemnt x greater than 1 and x[np.where(x>=1)[0][-1]] returns its value """

N = (AM15/Energy)/1.12

jsc112=Energy[Index]\*(-itg.simps(N[:Index],Energy[:Index]\*1e-9)) """ Ns here is the photon flux calcuting from by integrating the AM1.5 spectral photon distribustion. The later is deducded from the the spectral power AM1.5. N= np.array([AM15[k]/Energy[k] for k in range(M)]) """

N = np.array([AM15[k]/Energy[k] for k in range(M)]) """

""" this plot is the photon flux from the sun at the earth's surface vs energy (bandgap) using AM1.5G data""" fig=pylab.figure() ax = fig.add\_subplot(111)

```
BE112=Nc((1.12*eV)/(Kb*Tcell))
Volt=np.linspace(0,1.,M)
diode=Diode(Volt)
J=jsc112-diode*BE112;
lns1=ax.plot(Volt, J, label='current', color='red');
ax.set_ylabel("Current (A.\$m^{-2}\$)", fontsize=15)
ax.set_xlabel("Voltage (V)", fontsize=15)
ax.set_ylim (0,500); ax.set_xlim (0,1)
P=Volt*J
Pmax= max(Volt*J); print Pmax;
position=np.array(P).argmax()
print Volt[position]; print J[position]
eff=100*Pmax/Pin; print eff
jp=J[position]
ax.axhline(jp,linewidth=1,color = 'k',linestyle = '--')
ax2=ax.twinx()
lns2=ax.plot(Volt, P, label='power', color='green')
a \times 2.set_y lim(0,500)
lns=lns1+lns2;labs=[l.get_label() for l in lns]
ax.legend(lns,labs,loc='best')
vp=Volt[position]
a \times 2. a \times v \text{line}(vp, \text{linewidth} = 1, \text{color} = 'k', \text{linestyle} = '--')
ax2.plot(vp,Pmax, color='red', marker='d',markersize=7)
pylab.show()
```

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