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### Electronic and optical properties of crystalline and amorphous silica from first-principles

Dissertation présentée en vue de l'obtention du grade de Docteur en Sciences de l'Ingénieur par

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# Contents

	Tabl	le of Co	ontent	i
	List	of Figu	ures	v
	List	of Tabl	les	ix
1	Intr	oducti	ion	1
	1.1	Comp	utational studies of silica	3
	1.2	Scope	and outline	6
<b>2</b>	Met	thodol	ogy	9
	2.1	The q	uantum many-body problem	9
		2.1.1	Schrödinger equation	.0
		2.1.2	The Born-Oppenheimer approximation 1	1
	2.2	Classie	cal Molecular Dynamics	.3
		2.2.1	Basic theory 1	4
		2.2.2	Effective potentials	7
		2.2.3	Conclusion	20
	2.3	Densit	ty functional theory $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 2$	21
		2.3.1	Independent particles 2	21
		2.3.2	The Hartree and Hartree-Fock approximations 2	22
		2.3.3	Density Functional Theory 2	24
		2.3.4	DFT in practice 3	32
		2.3.5	Conclusion	86
	2.4	MBPT	$\Gamma$ and $GW$	36
		2.4.1	Response functions	37
		2.4.2	Green's functions and the quasiparticle concept 3	39
		2.4.3	Hedin's equations or how to get the self-energy 4	12

### Contents

		2.4.4	The $GW$ approximation $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	13
		2.4.5	Interpolation of $GW$ eigenvalues $\ldots \ldots \ldots \ldots \ldots$	16
		2.4.6	Conclusion	52
	2.5	Optica	l properties and the Bethe-Salpeter equation $5$	52
		2.5.1	The $2$ -particles propagator $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	53
		2.5.2	The Bethe-Salpeter equation	53
		2.5.3	Formulation as an eigenvalue problem 5	55
		2.5.4	Conclusion	58
3	Pur	e silica	5	59
	3.1	Genera	ation of amorphous silica models $\ldots \ldots \ldots \ldots $	60
	3.2	Structu	ural properties $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	62
		3.2.1	Radial distribution functions and bond lengths $\ . \ . \ \theta$	63
		3.2.2	Angular distribution functions and bond angles $\ensuremath{\mathfrak{G}}$	53
		3.2.3	Rings statistics	55
		3.2.4	Conclusion $\ldots \ldots \ldots$	66
	3.3	Electro	onic structure $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots $	67
		3.3.1	Valence density of states $\epsilon$	68
		3.3.2	Charge transfer $\ldots \ldots \ldots$	68
		3.3.3	Partial densities of states	70
		3.3.4	Band gap and excited states	71
	3.4	Optica	l properties	75
		3.4.1	Optical spectra of $\alpha$ -quartz $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$	78
		3.4.2	Optical spectra of amorphous silica 8	35
	3.5	Conclu	sion $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	88
4	Hyd	rogen-	containing silica 8	9
	4.1	Structu	ure of the different charged states $\ldots \ldots \ldots \ldots $	39
	4.2	Defect	energy levels	92
	4.3	Defect	formation energies	93
5	Size	effects	s in <i>GW</i> corrections 10	)1
	5.1	Oxyge	n vacancy in $\beta$ -cristobalite $\ldots \ldots \ldots$	)2
		5.1.1	Supercells	)4
		5.1.2	Computational details $\ldots \ldots \ldots$	)5

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	5.2	Size effects in the defect energy levels	. 105
	5.3	Conclusion	. 109
6	Δςς	essment of the plasmon-pole approximation	111
U	<b>6</b> .1	OP eigenvalues with and without plasmon-pole models .	. 111
	6.2	Analysis of the PPMs and dielectric function	. 114
	6.3	Conclusion	. 119
7	Ana	alysis of the TB09 XC potential	121
	7.1	Band gaps and widths	. 122
	7.2	Band structures	. 122
		7.2.1 Silicon and germanium	. 122
		7.2.2 Silicon dioxide	. 125
		7.2.3 Zinc oxide	. 130
		7.2.4 Tin oxides	. 130
		7.2.5 Calcium sulfide and calcium oxide	. 131
		7.2.6 Magnesium oxide	. 132
		7.2.7 Lithium fluoride	. 133
	7.3	Optical spectra of $\alpha$ -SiO <sub>2</sub>	. 133
	7.4	Effect of the $c$ parameter	. 135
	7.5	Conclusion	. 138
Co	onclu	sion and perspectives	141
A	ppen	ndices	147
$\mathbf{A}$	Bec	ke-Roussel potential	149
в	a-Si	$\mathbf{O}_2 \ \mathbf{models} : \mathbf{properties}$	151
$\mathbf{C}$	Con	nputational requirements in <i>GW</i>	155
	C.1	Memory	. 155
	C.2	Timings	. 156
D	Ban	nd structures with the TB09 functional	159
	D.1	Silicon and germanium	. 159

### Contents

	D.2	Silicon dioxide $\ . \ .$							•		•	•		•	•	•	•	•			160
	D.3	Zinc oxide			•				•	•				•	•						160
	D.4	Tin oxides						•	•			•		•	•	•	•				161
	D.5	Calcium sulfide						•	•			•		•	•	•	•				161
	D.6	Calcium oxide			•				•		•	•		•	•		•				164
	D.7	Magnesium oxide .					•	•	•		•	•		•	•	•	•	•			164
	D.8	Lithium fluoride .		•	•	•			•	•				•	•		•	•		•	165
$\mathbf{E}$	$\mathbf{List}$	of publications																			167
Bi	Bibliography 16						169														

iv

# List of Figures

1.1	Absorption bands in $SiO_2$	2
1.2	Experimental and theoretical band gaps of $SiO_2 \ldots \ldots$	5
2.1	Leap-frog algorithm	16
2.2	Effective potentials for silica.	19
2.3	Self-Consistent Field cycles	24
2.4	Jacob's ladder of density functional approximations	29
2.5	Pseudopotential approximation	35
2.6	Response of a material to a macroscopic external potential.	38
2.7	Spectral function of the one-particle Green's function. $\ .$ .	40
2.8	Schematic illustration of the quasiparticle concept	41
2.9	Hedin's equations and the $GW$ approximation	43
2.10	Frequency dependence of $\Sigma$	45
2.11	Polyfit interpolation of $GW$ eigenvalues	49
3.1	Tetrahedral structure of $a$ -SiO <sub>2</sub>	60
$3.1 \\ 3.2$	Tetrahedral structure of $a$ -SiO <sub>2</sub>	$\begin{array}{c} 60\\ 61 \end{array}$
3.1 3.2 3.3	Tetrahedral structure of $a$ -SiO <sub>2</sub>	60 61 62
3.1 3.2 3.3 3.4	Tetrahedral structure of $a$ -SiO <sub>2</sub>	60 61 62 64
<ol> <li>3.1</li> <li>3.2</li> <li>3.3</li> <li>3.4</li> <li>3.5</li> </ol>	Tetrahedral structure of $a$ -SiO <sub>2</sub>	60 61 62 64 65
<ol> <li>3.1</li> <li>3.2</li> <li>3.3</li> <li>3.4</li> <li>3.5</li> <li>3.6</li> </ol>	Tetrahedral structure of $a$ -SiO <sub>2</sub>	60 61 62 64 65 67
<ol> <li>3.1</li> <li>3.2</li> <li>3.3</li> <li>3.4</li> <li>3.5</li> <li>3.6</li> <li>3.7</li> </ol>	Tetrahedral structure of $a$ -SiO <sub>2</sub>	<ul> <li>60</li> <li>61</li> <li>62</li> <li>64</li> <li>65</li> <li>67</li> <li>69</li> </ul>
3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8	Tetrahedral structure of $a$ -SiO <sub>2</sub>	<ul> <li>60</li> <li>61</li> <li>62</li> <li>64</li> <li>65</li> <li>67</li> <li>69</li> <li>72</li> </ul>
3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9	Tetrahedral structure of $a$ -SiO <sub>2</sub>	60 61 62 64 65 67 69 72 74
3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 3.10	Tetrahedral structure of $a$ -SiO <sub>2</sub>	<ul> <li>60</li> <li>61</li> <li>62</li> <li>64</li> <li>65</li> <li>67</li> <li>69</li> <li>72</li> <li>74</li> <li>76</li> </ul>

3.12	Macroscopic dielectric function $\epsilon_2(\omega)$ in $\alpha$ -SiO <sub>2</sub> : rigid-
	shift and polyfit approximations
3.13	Macroscopic dielectric function $\epsilon_2(\omega)$ in $\alpha$ -SiO <sub>2</sub> : rigid-
	shift and polyfit approximations plus scissor 80
3.14	Macroscopic dielectric function $\epsilon_2(\omega)$ in $\alpha$ -SiO <sub>2</sub> using a
	model dielectric function
3.15	Convergence in $\mathbf{k}$ -points of the macroscopic dielectric func-
	tion $\epsilon_2(\omega)$ in $\alpha$ -SiO <sub>2</sub>
3.16	Macroscopic dielectric function in $a$ -SiO <sub>2</sub> for four differ-
	ent models
3.17	Macroscopic dielectric function in $a$ -SiO <sub>2</sub>
4.1	Structure of the positively charged hydrogen in $a$ -SiO <sub>2</sub> . 90
4.2	Structure of the negatively charged hydrogen in $a$ -SiO <sub>2</sub> . 91
4.3	Defect energy levels of hydrogen in $a$ -SiO <sub>2</sub> 92
4.4	Defect formation energies of hydrogen in $a$ -SiO <sub>2</sub> (DF <sup>*</sup> T). 95
4.5	GW formation energies
4.6	GW defect formation energies of hydrogen in $a$ -SiO <sub>2</sub> 97
5.1	Structure of ideal $\beta$ -cristobalite
5.2	Energy levels of oxygen vacancy in ideal $\beta$ -cristobalite 103
5.3	Convergence of the defect energy levels in DFT 106
5.4	Convergence of the defect energy levels in $GW$ 107
5.5	Convergence of the $GW$ corrections to the DFT defect
	energy levels
6.1	QP corrections obtained with and without plasmon-pole
-	models
6.2	Band structure of $\alpha$ -SiO <sub>2</sub> obtained in LDA and $G_0W_0$ 115
6.3	Real part of the RPA microscopic dielectric function along
0.0	the imaginary axis 116
6.4	BPA microscopic dielectric function along the real axis 117
6.5	Pole position and <i>f</i> -sum rule 118
0.0	
7.1	Theoretical and experimental band gaps
7.2	Band structure and DOS of silicon

vi

7.3	Band structure and DOS of germanium
7.4	Theoretical and experimental band widths
7.5	Band structure and DOS of silicon dioxide
7.6	Optical spectra of $\alpha$ -SiO <sub>2</sub> from the TB09 functional 134
7.7	Band width narrowing in DFT-TB09
7.8	Band gaps and widths as a function of the $c$ parameter
	in the TB09 functional
B.1	Structural properties of models 01 to 08
B.2	Structural properties of models 09 to 16
B.3	Structural properties of models 17 to 20
<b>D</b> 4	
D.1	Band structure and DOS of zinc oxide
D.2	Band structure and DOS of tin oxide
D.3	Band structure and DOS of tin dioxide
D.4	Band structure and DOS of calcium sulfide $\ldots \ldots \ldots \ldots 164$
D.5	Band structure and DOS of calcium oxide $\hdots$
D.6	Band structure and DOS of magnesium oxide $\ . \ . \ . \ . \ . \ . \ . \ . \ . \ $
D.7	Band structure and DOS of lithium oxide

# List of Tables

3.1	Bond lengths in $a$ -SiO <sub>2</sub>
3.2	Mean and standard deviation of bond angles in $a$ -SiO <sub>2</sub> 66
3.3	Bader and Hirshfeld charges
3.4	Band gaps in $SiO_2$
3.5	Peaks of $\epsilon_2(\omega)$ in $\alpha$ -SiO <sub>2</sub>
3.6	Macroscopic dielectric constant and birefringence in $\alpha$ -SiO <sub>2</sub> . 82
3.7	Peaks of $\epsilon_2(\omega)$ in <i>a</i> -SiO <sub>2</sub>
4.1	Hydrogen formation energies in DFT
4.2	Hydrogen formation energies in $GW. \ldots \ldots \ldots 96$
5.1	Supercells of cristobalite
5.2	Macroscopic dielectric constants in pure and defective sys-
	tems
6.1	Band gaps in $\alpha$ -SiO <sub>2</sub> with and without plasmon-pole model.113
7.1	Band gaps obtained in LDA, TB09, $G_0W_0$ @LDA and
	$G_0 W_0$ @TB09
7.2	Band widths obtained in LDA, TB09, $G_0W_0$ @LDA and
	$G_0 W_0$ @TB09
C.1	Memory requirements in $GW$ calculations for large systems. 156
C.2	Timings in $GW$ calculations for large systems 157

## Chapter 1

# Introduction

Silicon dioxide or silica (SiO<sub>2</sub>) is a material of particular technology interest for its exceptional combination of properties. Indeed, both its crystalline forms and amorphous phase are widely used in many electronic and optoelectronic technologies. Quartz clocks are regulated by the electronic oscillations of an  $\alpha$ -quartz ( $\alpha$ -SiO<sub>2</sub>) crystal. The frequency of these crystal oscillations are very precise and quartz clocks are amongst the most widely used time measurements standards. The amorphous form (a-SiO<sub>2</sub>), also known as *fused quartz*, *vitreous silica* or *silica glass*, is present in many electronic devices as a gate dielectric in metal-oxide-semiconductor (MOS) transistors [1]. Optical fibers are mostly made of amorphous silica as it shows a very good optical transmission over a large range of frequencies [2].

In the applications stated above, defects and impurities constitute an intrinsic part of the materials used. Indeed, atomic species are introduced in the material — either on purpose or accidentally — during the manufacturing process and are known to play a crucial role in the properties of the device. In optical fibers, these impurities can cause an attenuation of the optical signal and a decrease of the bandwidth. As shown in Fig. 1.1, several absorption bands can contribute to this attenuation [3]. Point defects in SiO<sub>2</sub> are also induced under particle irradiation. These radiation-induced defects can be at the origin of the degradation of its properties. The oxygen deficient center (ODC in Fig. 1.1) is one of the most harmful defects in silica as it gives rise



Figure 1.1: Absorption bands in  $SiO_2$ . NBOHC and ODC stand for non-bridging oxygen hole center and oxygen deficient center respectively. Adapted from Ref. [3].

to an absorption band at  $\sim 7.6$  eV and is the precursor of the E' center after irradiation [1]. The E' center has been known experimentally for a long time from absorption and electron spin resonance (ESR) experiments [4, 5], producing the corresponding absorption band at  $\sim 5.7$ eV, and has been studied extensively using first-principles computations [6, 7, 8]. Other fundamental defect centers related to the excess or deficiency of oxygen in silica are responsible for other absorption bands at a specific energy [1, 3]. These so-called color centers are strongly influenced by the presence of other impurities in the material, and in particular of hydrogen species. The latter can have both a positive and detrimental effect on the targeted properties [9, 10] of the sample.

An accurate understanding of the above-mentioned defects and processes thus appears to be essential in the development of quality glasses and in the improvement of their properties. In this line, first-principles calculations show up to be a very interesting tool to be combined with experimental studies. First, they can provide a strong support for the interpretation of experimental data in which some unexplained phenomena can then be understood on the basis of theoretical results. Second, first-principles computations can be used in the prediction of the properties of a particular combination of impurities and of unknown effects for which no experimental data is available yet. This in turn can lead to the discovery of new remedies against the radiation-induced degradation of the properties in silica.

In this introduction, an overview of the theoretical studies of the properties in  $SiO_2$  is sketched. The state of the art in the computation of the properties of the pure crystalline and amorphous phases with ab initio methods is surveyed. Defects in bulk systems and other properties obtained from first-principles is also reviewed, with a particular emphasis on those connected to this work. Finally, the outline of this thesis is presented.

### 1.1 Computational studies of silica

The first ab initio computation of  $SiO_2$  dates back to the late 1980's when the electronic structure of  $\alpha$ -quartz was obtained using density functional theory (DFT) [11] in the local density approximation (LDA) [12] by Chelikowsky and Schlüter [13] as well as by Calabrese and Fowler [14]. After these two precursory studies on  $\alpha$ -SiO<sub>2</sub>, other crystalline polymorphs were examined and compared using localized orbitals [15] and DFT. In particular, Allan and Teter [16] were able to determine the structural parameters of three polymorphs ( $\alpha$ -quartz,  $\alpha$ -cristobalite and stishovite) within less than 2% of the experimental values. The structural but also the elastic properties were then obtained for all known  $SiO_2$  polymorphs within LDA by Keskar and Chelikowsky [17] and then later compared to results with the generalized gradient approximation (GGA) [18] by Demuth et al. [19]. In this latter work, the GGA was found to predict an incorrect order of stability for the low-density phases at low pressures, with  $\alpha$ -quartz being energetically less favored than cristobalite or keatite for example. On the other hand, the high pressure phase transitions are not properly described by the LDA while the GGA corrects this wrong behavior as also observed by Hamann [20].

With the constant increase in computation power and with the development of elaborate methods and algorithms, other electronic and optical properties have started to be analyzed through first-principles calculations. Dielectric and vibrational properties of  $\alpha$ -quartz were obtained by Gonze *et al.* [21] using density functional perturbation theory (DFPT) [22, 23], with a rather good agreement with experimental results. For an accurate description of excited state and optical properties such as the band gap and absorption spectra, other theories are required in order to better reflect the electronic correlations than in the mean-field approach provided by DFT. Many-body perturbation theory (MBPT) [24, 25] brings up the framework for the description of such properties.

It is important to stress that the value of the band gap in SiO<sub>2</sub> is still a matter of debate, both theoretically and experimentally [26, 27]. Figure 1.2 illustrates published values for the band gap in  $\alpha$ -quartz (green) and amorphous silica (blue). The band gap and the optical absorption spectrum of  $\alpha$ -quartz were first computed by Chang *et al.* [28] using the *GW* approximation and the Bethe-Salpeter equation [29]. This study can be considered as one of the main findings in the field of crystalline silica as the excitonic character of the absorption spectrum was clearly proved, based on theoretical arguments. The excitonic properties and the self-trapping mechanism in  $\alpha$ -quartz were then further investigated by Ismail-Beigi and Louie [30].

Concerning the vitreous phase, the atomistic description of the amorphous structure itself is a subject on its own. Structural models can be obtained using a classical molecular dynamics approach in which the classical potentials are constructed on the basis of ab initio calculations as was done by van Beest *et al.* [31] and Carré *et al.* [32]. Many studies have concentrated on the description of the amorphous structure using periodic supercells of relatively small size [33, 34, 35, 36]. Ginhoven *et al.* [37] showed that the properties obtained from a sufficient number of small models with 72 atoms were equivalent to those obtained with larger supercells containing ~1500 atoms. We have thus chosen to work



Figure 1.2: Values published for the experimental (squares) and theoretical (triangles) band gaps of  $\alpha$ -quartz (green) and amorphous silica (blue).

with such small models in this thesis. Other cluster-based approaches have been used to model amorphous silica, in particular for the description of the defect centers [38]. In such techniques, the problem is solved in a basis made of localized functions (atomic orbitals, gaussians, ...). Apart from the fact that the computed properties are basis-dependent, the excited states are problematic due to their intrinsically high degree of non-locality [39].

The first ab initio (periodic) model of amorphous silica was produced by Sarnthein *et al.* [40, 41]. This model was successively used for the computation of several properties of amorphous silica. It was proven to reproduce the experimental neutron scattering properties by Pasquarello *et al.* [42] as well as the infrared absorption spectrum by Pasquarello and Car [43]. Further investigations on the vibrational properties showed that the presence of small rings in the sample was responsible for the appearance of specific lines in the Raman spectrum [44]. The same model was also used to obtain the dielectric properties and Raman spectrum by Umari *et al.* [45, 46]. The ultra-violet optical absorption was studied within DFT by Sadigh *et al.* [47] for varying temperatures and showed that the temperature dependence of the fundamental absorption edge in amorphous silica approximately follows the Urbach rule [48]. The band gap and the effect of small disorder in amorphous silica has also been extensively studied by Martin-Samos *et al.* [27, 49]. To the best of my knowledge, the optical properties of amorphous silica have not yet been studied within the Bethe-Salpeter formalism including the effects of excitons.

Turning to more realistic systems with the presence of defects and impurities, the computation of the resulting properties using periodic supercells is a delicate matter. Indeed, the defect itself can interact with its neighboring images and strongly affect the properties obtained if the supercell used is too small. Several correction schemes have been devised in order to account for the finite-size effects in DFT [50, 51, 52] and a good review for other methods beyond DFT can be found in Ref. [53].

Defects in amorphous silica have been studied using DFT and the GW method by several groups. In particular, the charged states of hydrogen were investigated by Godet and Pasquarello [54]. The neutral hydrogen species was found to be less stable than its positive and negative charged states. The mechanism of diffusion of the positive hydrogen has then been shown to be dominantly cross-ring [55]. Other hydrogen-related defects were also studied by Benoit *et al.* [56]. Oxygen-related defects have been described extensively in the literature using DFT [36, 57, 58, 59]. The oxygen self-interstitial has also been studied using MBPT by Martin-Samos *et al.* [60]. The diffusion mechanism of the O self-interstitial is a process for which the standard DFT approach fails badly. The agreement with experiment could be recovered by using a combined DFT/GW scheme [61].

### **1.2** Scope and outline

Although many of the electronic and optical properties of silica are known, a thorough description of the radiation-induced defects and their effects on the properties of the raw material are still not clearly established. This particularly ambitious objective lines up the motivations for this thesis. Indeed, the properties of pure and defective silica are investigated using different levels of theory and the results obtained in the following chapters are a step towards a better understanding of the physical processes occurring in devices containing silica. Emphasis is placed on the choice of the methods and approximations used as well as on their accuracy and reliability to predict the electronic and optical properties. Several techniques are indeed used, each of them having their advantages and limits. The results presented encompass a rather broad scope with possible applications in other fields and opens to perspectives of future work. The outline of this thesis is sketched in the following.

In **Chapter 2**, the methods used in this thesis are reviewed. Classical molecular dynamics is presented as an approximation to the full many-body problem. For systems in their ground-state, the Schrödinger equation is shown to be more easily solved using density functional theory (DFT) by reformulating the electronic problem in terms of the electronic density instead of the total wavefunction. As a ground-state theory, DFT is unable to predict excited states properties and MBPT is presented as a cure to accurately describe band gaps and optical properties.

The properties of pure silica are presented in **Chapter 3**. First, the amorphous silica models are presented and their structural properties are analyzed. The electronic properties in amorphous silica are then compared to those of the  $\alpha$ -quartz crystal. The value of the band gap in both the amorphous and crystalline forms is determined by combining Bethe-Salpeter computations and experimental optical spectra, suggesting. A publication is in preparation.

Hydrogen-containing silica is investigated in **Chapter 4**. The positive, neutral and negative charged states of hydrogen in silica are first introduced. The defect energy levels obtained from DFT and GW computations are then presented. Formation energies for the three charged states are calculated using the DFT formalism. Preliminary results are also obtained for GW-corrected formation energies, with some discrepancies which led to reexamine, in the following chapters, the approximations used until now.

In **Chapter 5**, the supercell-size dependence of the GW corrections of defect energy levels is investigated. The neutral oxygen vacancy in ideal  $\beta$ -cristobalite is used as a test case. The comparison of a simple quantity arising from the GW computations in the pure and defective samples is proposed as a minimal requirement for the supercell size convergence. A publication is in preparation.

The frequency dependence of the microscopic dielectric function is examined in **Chapter 6**. In particular, the plasmon-pole approximation of Godby and Needs is shown to be a very good estimate of the quasiparticle energies obtained with a full frequency treatment, for the states close to the Fermi level.

Finally, an alternative to the computationally demanding GW method is analyzed in **Chapter 7**. The Tran and Blaha (TB09) exchangecorrelation potential was recently proposed to overcome the well known "band gap problem" in DFT. It will be shown that indeed the band gaps are better reproduced with this functional but at the cost of a systematic degradation of the valence band structure. Further GW corrections starting from TB09 DFT electronic structure solve this problem and seem to be rather close to quasiparticle self-consistent GW schemes. Part of this work has been accepted for publication in Physical Review B as Ref. [62].

Final conclusions are addressed at the end of this manuscript.

## Chapter 2

# Methodology

### 2.1 The quantum many-body problem

In the early decades of the  $20^{\text{th}}$  century, an impressive amount of new progresses has been made in physics and chemistry, in particular in the knowledge of the composition of matter, molecules and atoms as well as the physical laws that determine their evolution. When the microand nano-worlds are considered, the laws of classical physics turn out to be insufficient because of the electronic nature of matter [63, 64, 65]. Indeed, for these length scales and their corresponding energies, the Planck's constant h cannot be neglected such that the atoms and electrons show both particle and wave characteristics. This is known as the theory of particle-wave duality, originally introduced by Louis de Broglie in 1924 in his doctoral thesis. As a consequence, the properties of the electrons cannot be described using classical mechanics. These findings have inspired the development of the quantum theory of manyparticle systems [66].

In this section, the important concepts of many-body quantum mechanics are sketched. First the Schrödinger equation [67] and its formidable difficulty are presented. The Born-Oppenheimer approximation [68] is then introduced as a simplification of the full quantum many-body problem. This important advance alleviates the complicated many-body problem and will actually be used in all this thesis.

#### 2.1.1 Schrödinger equation

In quantum mechanics, the state of a physical system is completely described by its many-body wavefunction  $\Psi_i^{\text{MB}}$ . For systems at equilibrium, this wavefunction and its associated eigenvalue can be obtained through the time-independent Schrödinger equation

$$\widehat{H}^{\mathrm{MB}}\Psi_i^{\mathrm{MB}} = E_i \Psi_i^{\mathrm{MB}} \tag{2.1}$$

where the many-body Hamiltonian  $\widehat{H}^{\rm MB}$  is the sum of the kinetic energy  $\widehat{T}$  and potential energy  $\widehat{V}$  :

$$\widehat{T} = -\sum_{i=1}^{N} \frac{\hbar}{2m_i} \nabla_{\mathbf{r}_i}^2$$
(2.2)

$$\widehat{V} = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(2.3)

where  $m_i$  and  $q_i$  are the mass and the charge of particle *i*.

The two terms of the Hamiltonian stated above are known exactly. The wavefunction  $\Psi_i^{\text{MB}}$  of the system can thus in principle be determined exactly but in practice, the solution is far from being computationally tractable except for trivial cases. Indeed, all the particle's motions are correlated through the potential energy operator such that the many-body wavefunction is a complicated mathematical representation of the system including the effects of this correlation. The aim of finding the wavefunction that satisfies Schrödinger's equation is thus almost impossible to achieve.

As a consequence, it is not quite surprising that a large part of this field of physics has been focused on trying to find approximations to the many-body Hamiltonian  $\hat{H}^{\text{MB}}$  and wavefunction  $\Psi_i^{\text{MB}}$  that can be managed in a reasonable human and/or computer time, while preserving the proper physics, or at least keeping the desired accuracy and physical understanding.

#### 2.1.2 The Born-Oppenheimer approximation

The complexity of the Schrödinger equation and its consequences led Born and Oppenheimer [68] (BO) to rationalize the full many-body problem. As the masses of the nuclei are at least 3 orders of magnitude larger than the electron mass, their dynamics are much slower than those of electrons. Born and Oppenheimer suggested that the motion of nuclei and electrons could be decoupled such that the full many-body wavefunction takes the following form :

$$\Psi^{\rm MB}(\{\mathbf{r}_i\}, \{\mathbf{R}_j\}) = \Psi^{\rm el}_{\{\mathbf{R}_j\}}(\{\mathbf{r}_i\})\Phi(\{\mathbf{R}_j\})$$
(2.4)

The full Hamiltonian can be separated as a sum of electronic  $\widehat{T}_{\rm el}$ and atomic  $\widehat{T}_{\rm nucl}$  contributions to the kinetic energy operator plus the electrostatic interactions between electrons  $\widehat{V}_{\rm el-el}$ , between nuclei and electrons  $\widehat{V}_{\rm nucl-el}$  and between nuclei  $\widehat{V}_{\rm nucl-nucl}$ 

$$\widehat{H}^{\rm MB} = \widehat{T}_{\rm el} + \widehat{T}_{\rm nucl} + \widehat{V}_{\rm el-el} + \widehat{V}_{\rm nucl-el} + \widehat{V}_{\rm nucl-nucl}$$
(2.5)

From now on and unless otherwise stated, atomic units will be assumed in the rest of this manuscript such that the electron mass  $m_e$ , the electron charge e, the reduced Planck constant  $\hbar$  and the Coulomb constant  $\frac{1}{4\pi\epsilon_0}$  are all set to one. All the components of the Hamiltonian in equation 2.5 are then defined as

$$\widehat{T}_{\rm el} = -\sum_{i=1}^{N_e} \frac{1}{2} \nabla_{\mathbf{r}_i}^2 \tag{2.6}$$

$$\widehat{T}_{\text{nucl}} = -\sum_{i=1}^{N_n} \frac{1}{2M_i} \nabla_{\mathbf{R}_i}^2$$
(2.7)

$$\widehat{V}_{\rm el-el} = \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(2.8)

$$\widehat{V}_{\text{nucl-el}} = -\sum_{i=1}^{N_e} \sum_{j=1}^{N_n} \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|}$$
(2.9)

$$\widehat{V}_{\text{nucl-nucl}} = \sum_{i=1}^{N_n} \sum_{j>i}^{N_n} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}$$
(2.10)

where  $N_e$  and  $N_n$  are the numbers of electrons and nuclei,  $\mathbf{r}_i$  is the position of electron i,  $\mathbf{R}_i$  is the position of nucleus i,  $M_i$  is the mass of atom i in atomic units and  $Z_i$  is the atomic number of nucleus i.

The slow dynamics of nuclei as compared to the electron's lead to consider that the electrons evolve in a potential created by nuclei that are fixed. In that case, the nucleic kinetic energy term in Eq. 2.5 can be neglected as the nuclei do not move and the electrostatic interactions between nuclei is a constant. As a result, the electronic Hamiltonian  $\hat{H}^{\rm el}$  is expressed as

$$\widehat{H}_{\{\mathbf{R}_j\}}^{\mathrm{el}} = \widehat{T}_{\mathrm{el}} + \widehat{V}_{\mathrm{el-el}} + \widehat{V}_{\mathrm{nucl-el}}$$
(2.11)

The Schrödinger equation involving this electronic Hamiltonian then reads

$$\widehat{H}_{\{\mathbf{R}_{j}\}}^{\mathrm{el}}\Psi_{\{\mathbf{R}_{j}\}}^{\mathrm{el}}(\{\mathbf{r}_{i}\}) = E_{\{\mathbf{R}_{j}\}}^{\mathrm{el}}\Psi_{\{\mathbf{R}_{j}\}}^{\mathrm{el}}(\{\mathbf{r}_{i}\})$$
(2.12)

where  $E_{\{\mathbf{R}_j\}}^{\text{el}}$  is the electronic energy of the system with the fixed positions  $\{\mathbf{R}_j\}$  for the nuclei.

The total wavefunction of the system, including the nuclei, can in turn be obtained by reintroducing the atomic kinetic energy term :

#### 2.2. Classical Molecular Dynamics

$$\left[\widehat{T}^{\text{nucl}} + E^{\text{el}}_{\{\mathbf{R}_j\}}\right] \Phi_i(\{\mathbf{R}_j\}) = E^{\text{BO}}_i \Phi_i(\{\mathbf{R}_j\})$$
(2.13)

Though the BO approximation substantially simplifies the manybody problem by reducing the size of the problem, it is clear that solving Eq. 2.12 remains a burden as many electrons are involved in the electronic Hamiltonian. The individual motions of the electrons are indeed correlated through the electron-electron interaction  $\hat{V}_{\rm el-el}$ . In order to solve this problem, other approximations are needed. In the following sections, different methods for solving this problem will be presented. The different approaches are introduced in order of increasing complexity. The approach presented in Sect. 2.2 proposes to handle the complicated electronic interactions by simply including it in an effective potential that also comprises the nucleic interactions. The problem is thus reduced to a classical mechanical one. In Sect. 2.3, density functional theory deals with electronic interactions in an average way where the electronic density is used as the central variable for setting up the effective (electronic) potential. Finally, many-body perturbation theory in the GW approximation (Sect. 2.4) and Bethe-Salpeter approach (Sect. 2.5) uses perturbation expansion series of independent interactions to model the fully interacting electronic system, still within the realm of the BO approximation.

### 2.2 Classical Molecular Dynamics

Molecular Dynamics (MD) is the study of the evolution of the atomic configuration of a complex physical system by means of computer simulations. The movement of the atoms in the system is determined by numerically integrating Newton's equations of motion [69]. The BO approximation is used such that the electrons instantaneously adapt their dynamics to the atomic displacements. In its classical version, the hamiltonian is derived from an *effective potential* or *force field* which contains all the electronic, ionic and electron-ion interactions and depends only on the atomic positions. In this section, the basic theory of classical MD is reviewed. First, the relevant equations and algorithms used to simulate the motion of the system's atoms are introduced. Then the empirical potentials for silica used in this thesis are presented. Finally, the tools used to analyze the results and compare to available experimental data are described.

#### 2.2.1 Basic theory

#### Equations of motion and discretization

The trajectories of the N atoms are described by the laws of motion or equations of motion (EOM). Newton's second law is precisely the equation that describes the relationship between the force  $\mathbf{F}_i$  acting on an object with mass  $M_i$  (the atom) and its acceleration  $\mathbf{A}_i$ . The evolution of the N atoms in the system is thus described using a set of N equations :

$$\mathbf{F}_{i} = M_{i} \mathbf{A}_{i} = M_{i} \frac{\mathrm{d}^{2} \mathbf{R}_{i}}{\mathrm{d}t^{2}} \quad \text{with} \quad i = 1 \dots N$$
 (2.14)

The forces on the atoms are calculated from the derivative of a given effective potential (see Sec. 2.2.2)

$$\mathbf{F}_i = -\boldsymbol{\nabla}_{\mathbf{R}_i} V(\mathbf{R}_1, \dots, \mathbf{R}_N) \tag{2.15}$$

For the numerical study of the system, the N second-order differential equations 2.14 are rewritten as a set of 2N first-order equations involving the velocity  $\mathbf{V}_i$  of each atom :

$$\frac{\mathrm{d}\mathbf{R}_i}{\mathrm{d}t} = \mathbf{V}_i \tag{2.16}$$

$$\begin{cases}
M_i \frac{\mathrm{d}\mathbf{V}_i}{\mathrm{d}t} = \mathbf{F}_i$$
(2.17)

These two equations are then integrated by discretizing in time as  $t = t_0, t_1, \ldots$  using a constant time step  $\tau = t_{n+1} - t_n$ . Each time  $t_n$  is then obtained as  $t_0 + n\tau$ .

#### The MD algorithm

The basic MD algorithm follows a standard procedure :

- 0. The initial configuration of the system at t = t<sub>0</sub> is first set up
  : positions {R<sub>i</sub>}<sub>0</sub> and velocities {V<sub>i</sub>}<sub>0</sub> of all the particles in the system.
- 1. All the forces  $\mathbf{F}_i$  on each atom are then computed using Eq. 2.15 from which the new velocities can be derived using Eq. 2.17.
- 2. The configuration is then updated by integrating Eq. 2.16 with the new velocities.
- 3. Steps 1 and 2 are then iterated for the required number of steps or until some stationary state is achieved.

Several schemes exist for the integration of equations 2.16 and 2.17. The algorithm used here (the *leap-frog* algorithm) is described in the following.

**The** *leap-frog* **algorithm** In the leap-frog algorithm [70], which is represented schematically in Fig. 2.1, the positions and velocities of the particles are evaluated at time  $t_n$  and  $t_{n+\frac{1}{2}}$  respectively, where  $t_{n+\frac{1}{2}} = t_n + \frac{\tau}{2}$ :

$$\mathbf{R}(t_{n+1}) = \mathbf{R}(t_n) + \tau \mathbf{V}\left(t_{n+\frac{1}{2}}\right)$$
(2.18)

$$\mathbf{V}\left(t_{n+\frac{1}{2}}\right) = \mathbf{V}\left(t_{n-\frac{1}{2}}\right) + \frac{\tau}{m}\mathbf{F}(t_n)$$
(2.19)

This algorithm has the advantage that it is time-reversible. This guarantees the conservation of energy or any other conservable quantity and hence provides a robust algorithm to be used for NVT ensembles [71].

#### The NVT ensemble

The direct application of equations 2.15-2.17 produces quantities in the NVE or micro-canonical ensemble (constant number of particles, con-



Figure 2.1: Schematic view of the leap-frog algorithm. The configurations **R** of the particles are evaluated at each integer time step  $t_n$  using Eq. 2.18 using the velocities **V** evaluated at the preceding half-integer time step  $t_{n-\frac{1}{2}}$ .

stant volume and constant energy). However, the properties that are investigated are most often from the NVT or *canonical* ensemble where the number of atoms N, the volume V and the temperature T are fixed. For that purpose, the system is coupled to an external heat bath with the target temperature  $T^{\text{target}}$ .

In the Nosé-Hoover temperature coupling, which is the thermostat that has been used in this thesis, a friction term is added to equation 2.17:

$$M_i \frac{\mathrm{d}\mathbf{V}_i}{\mathrm{d}t} = \mathbf{F}_i - \frac{\xi}{M_i} \mathbf{V}_i \tag{2.20}$$

where the friction parameter  $\xi$  has its own equation of motion :

$$\frac{1}{2}Q\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{1}{2}\sum_{i=1}^{N}M_i\mathbf{V}_i^2 - \frac{1}{2}(N_f + 1)k_BT^{\mathrm{target}}$$
(2.21)

where  $N_f = 3(N-1)$  is the number of degrees of freedom of the system,  $k_B$  is the Boltzmann constant and the mass parameter Q of the heat bath determines the coupling strength of the thermostat.

When the kinetic energy of the system (first term in Eq. 2.21) is larger than the target kinetic energy of the system (second term in Eq. 2.21), the friction parameter  $\xi$  is increased such that more energy is extracted from the system in order to cool it down. On the opposite, when the system's temperature is lower than the target one,  $\xi$  is negative and the friction term causes the system to heat up. Actually, the coupling strength changes when the target temperature is varied. For that reason, the Q parameter is usually expressed in terms of the period  $\tau_{\rm NH}$  of the kinetic energy oscillations :

$$Q = \frac{\tau_{\rm NH}^2 T^{\rm target}}{4\pi^2} \tag{2.22}$$

Using  $\tau_{\rm NH}$  as the parameter for the thermostat is thus more justified, in particular when annealing, melting or quenching is simulated. In this thesis, a melt-and-quench procedure has been used to prepare amorphous silica models (see Sec. 3.1).

#### 2.2.2 Effective potentials

In a molecular dynamics simulation, one very important decision is the choice of the force field. Different types of force fields exist : bonded, non-bonded and electrostatic potentials. Usually for a given system, the total force field is a combination of bonded, non-bonded and electrostatic potentials.

Bonded interactions assume a predefined topology for the system which is then described using 2-, 3- and 4-body interactions. A given particle will usually have few bonded interactions mainly corresponding to its chemical bonds. These interactions are defined precisely from a fixed list of atoms. In contrast, non-bonded interactions are defined for all particles. These are typically the Lennard-Jones potential or other model pair-potentials. In principle, their range is infinite but in practice, the long-range part is usually small such that the interactions are computed only for the atoms within a certain radius. The Coulomb interaction is a particular case of non-bonded interactions as their range is much longer. For this reason, the are commonly dealt with using Ewald sums (see Sec. 2.2.2). Finally, specific constraints can also be defined with respect to the actual coordinate system.

#### Effective potentials for silica

Simple two-body unpaired potentials (CHIK) from Carré et al.[32] have been used in this thesis for the generation of the silica models. These potentials have the same form as the old van Beest, Kramer and van Santen (BKS) potentials [31] but have revealed to yield more accurate static and dynamical properties. In particular, the partial paircorrelation functions and angular distribution functions show results in closer agreement with experiment than the BKS potentials. The CHIK potentials are expressed as the sum of a Coulomb term and a short-range term in the Buckingham [72] form :

$$V_{\alpha\beta}(R) = \frac{q_{\alpha}q_{\beta}e^2}{R} + A_{\alpha\beta} \,\mathrm{e}^{-B_{\alpha\beta}R} - \frac{C_{\alpha\beta}}{R^6} \tag{2.23}$$

where  $R = |\mathbf{R}_i - \mathbf{R}_j|$  is the distance between particles *i* and *j* and the coefficients  $q_{\alpha}$ ,  $q_{\beta}$ ,  $A_{\alpha\beta}$ ,  $B_{\alpha\beta}$  and  $C_{\alpha\beta}$  depend on the types  $\alpha$  and  $\beta$ of species *i* and *j*.

As it can be seen in Fig. 2.2 (in which the inset shows the longitudinal force obtained by applying equation 2.15 to the potentials), the potentials thus defined (thin lines) have a nonphysical behavior at low separation such that if two particles appear to be too close to each other during the simulation, they might collapse due to the infinitely attractive potential. A strong repulsive part  $V_{\alpha\beta}^{\rm RP}(R)$  has thus been added to each of the potentials for distances under which the resulting force starts to decrease (branching point). This term has been chosen proportional to the inverse fourth power of the distance :

$$V_{\alpha\beta}^{\rm RP}(R) = v_{\alpha\beta}^0 + K_{\alpha\beta}(R - R_{\alpha\beta}^0)^{-4}$$
(2.24)

The strengths  $K_{\alpha\beta}$  of the hard repulsive parts were set to  $10^{22}$  erg/cm<sup>4</sup> (~ 33 eV/Bohr) while the parameters  $v^0_{\alpha\beta}$  and  $r^0_{\alpha\beta}$  were chosen in order to match the CHIK potentials and their first derivatives at the corresponding branching points.

#### Long-range electrostatic interactions and Ewald sums

Electrostatic interactions in a system correspond to the combination of all Coulomb repulsion or attraction of all pairs of particles with an (effective) charge. As already mentioned previously, this kind of interaction has long-range effects such that for periodic systems, the number of



Figure 2.2: Effective potentials used for the generation of the amorphous silica models (thin lines). For low separation of species, for which the resulting force starts to decrease (see inset), a repulsive part has been added (thick lines).

terms in the electrostatic potential acting on a given atom is very large. Indeed a given atom interacts with all the other atoms in the unit cell as well as with all the periodically replicated images of all atoms. Defining  $\mathbf{n} = (n_x, n_y, n_z)$  as the index of the cell, the total Coulomb energy reads

$$U^{\text{Coul}} = \frac{1}{2} \sum_{n_x} \sum_{n_y} \sum_{n_z} \sum_{i} \sum_{j'} \frac{q_i q_j}{R_{ij,\mathbf{n}}}$$
(2.25)

in which  $R_{ij,\mathbf{n}}$  is the distance between particle *i* in the origin cell  $\mathbf{n}_0 = \mathbf{0}$  and particle *j* in cell  $\mathbf{n} = (n_x, n_y, n_z)$  and the prime in the sum over *j* means that the i = j term has to be omitted when  $\mathbf{n} = \mathbf{n}_0$ .

Using the technique of Ewald summation [73, 74], this slowly converging sum is split into the sum of two rapidly converging ones and a constant term :

$$U^{\text{Coul}} = U^{\text{dir}} + U^{\text{rec}} + U^0 \tag{2.26}$$

$$U^{\rm dir} = \frac{1}{2} \sum_{n_x} \sum_{n_y} \sum_{n_z} \sum_{i} \sum_{j'} q_i q_j \frac{\operatorname{erfc}(\alpha R_{ij,\mathbf{n}})}{R_{ij,\mathbf{n}}}$$
(2.27)

$$U^{\rm rec} = \frac{1}{2\pi V_{cell}} \sum_{m_x} \sum_{m_y} \sum_{m_z} \sum_{i} \sum_{j'} q_i q_j \frac{e^{(-(\pi \mathbf{m}/\alpha)^2 + 2\pi i \mathbf{m} \cdot (\mathbf{R}_i - \mathbf{R}_j))}}{\mathbf{m}^2} \quad (2.28)$$

$$U^0 = -\frac{\alpha}{\sqrt{\pi}} \sum_{i}^{N} q_i^2 \tag{2.29}$$

The direct term  $U^{\text{dir}}$  is calculated in real space and is rapidly converging in  $R_{ij,\mathbf{n}}$  due to the complementary error function  $\operatorname{erfc}(\alpha R_{ij,\mathbf{n}})$  while the Fourier term  $U^{\text{rec}}$  is calculated in reciprocal space and converges rapidly due to the decreasing exponential  $e^{(-(\pi \mathbf{m}/\alpha)^2)}$  and the  $\frac{1}{\mathbf{m}^2}$  dependence.

#### 2.2.3 Conclusion

Classical molecular dynamics provides an efficient and fast way to describe molecular and solid state systems. As the electronic interactions are completely included in the effective classical potentials, it considerably reduces the complexity of the system. On the other hand, these effective potentials are empirical. Consequently, they have to be chosen carefully and vary from system to system. Another drawback of CMD lies in the underlying assumption of classical potentials. As quantum effects are not explicitly used in the theory, electronic properties cannot be obtained from CMD.

The CHIK potentials presented in Sect. 2.2.2 yield structural properties for amorphous silica in good agreement with experiment. Primary models can thus be generated using CMD and these CHIK potentials and used as starting point for further refinement. The next section presents density functional theory that allows for a more accurate and more suited description of a system composed of nuclei and electrons.

# 2.3 Mean field approaches and density functional theory

In this section, the basic ideas of mean field approaches, such as the Hartree-Fock method and density functional theory are sketched. First the concept of independent particles is introduced as well as the Hartree and Hartree-Fock approximations. The ground basis of density functional theory is then presented, namely the Hohenberg-Kohn theorems and the Kohn-Sham equations. The exchange-correlation approximations that were used throughout this thesis are then laid out. Finally, the notions of reciprocal space, basis sets and pseudopotentials are reviewed.

#### 2.3.1 Independent particles

Using Born-Oppenheimer approximation the atomic and electronic motions are separated, the electronic wavefunction of the system can be determined for a given arrangement of the atoms :

$$\widehat{H}^{\rm el}|\Psi_m\rangle = E_m^{\rm el}|\Psi_m\rangle \tag{2.30}$$

where  $\hat{H}^{\text{el}} = \hat{T}_{\text{e}} + \hat{V}_{\text{ee}} + \hat{V}_{\text{e}N\{\mathbf{r}\}}$  is the electronic Hamiltonian operator. In this operator,  $\hat{T}_{\text{e}}$ ,  $\hat{V}_{\text{ee}}$  and  $\hat{V}_{\text{e}N\{\mathbf{R}\}}$  correspond respectively to the electronic kinetic energy, the electron-electron interaction and the electron-nuclei interaction.

$$\begin{split} \widehat{T}_{\mathrm{e}} &= \sum_{i=1}^{N_{\mathrm{e}}} - \frac{\nabla_{\mathbf{r}_{i}}^{2}}{2} \\ \widehat{V}_{\mathrm{ee}} &= \sum_{\substack{(i,j)\\i < j}}^{N_{\mathrm{e}}} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} \\ \widehat{V}_{\mathrm{eN}} &= \sum_{i}^{N_{\mathrm{e}}} \sum_{j}^{N_{\mathrm{N}}} \frac{-Z_{j}}{|\mathbf{r}_{i} - \mathbf{R}_{j}|} = \sum_{i}^{N_{\mathrm{e}}} V_{\mathrm{ext}}(\mathbf{r}_{i}) \end{split}$$

If we consider the electrons as non-interacting, the  $\hat{V}_{ee}$  is neglected. The *N*-electrons problem can then be solved by using Slater determinants :

$$\Psi_{n}(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N}) = \frac{1}{\sqrt{N}} \begin{vmatrix} \psi_{1}(\mathbf{r}_{1}) & \psi_{2}(\mathbf{r}_{1}) & \dots & \psi_{N}(\mathbf{r}_{1}) \\ \psi_{1}(\mathbf{r}_{2}) & \psi_{2}(\mathbf{r}_{2}) & \dots & \psi_{N}(\mathbf{r}_{2}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{1}(\mathbf{r}_{N}) & \psi_{2}(\mathbf{r}_{N}) & \dots & \psi_{N}(\mathbf{r}_{N}) \end{vmatrix}$$
(2.31)

where the one-electron orbitals  $\psi_i(\mathbf{r})$  are eigenfunctions of the oneelectron Schrödinger equation :

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$
(2.32)

The total electronic energy is then obtained as the sum of the energies of each orbital. Similarly, the electronic density corresponds to the sum of the electronic density of each orbital.

#### 2.3.2 The Hartree and Hartree-Fock approximations

While verifying the Pauli exclusion principle, the solutions 2.31 completely neglect the electron-electron interaction. In the Hartree approximation, the many-body wavefunction is written as a product of the one-electron wavefunctions
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\dots\psi(\mathbf{r}_N)$$
(2.33)

and the electrons interact via the mean-field electrostatic potential arising from the other electrons. The effective potential  $V_{\text{eff}}$  is thus defined as the superposition of the *external* potential  $V_{\text{ext}}$  created by the ions and the Hartree potential  $V_H$ 

$$V_{\text{eff}}(\mathbf{r}) = V_H(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})$$
(2.34)

The Hartree potential is a functional of the electronic density :

$$V_{\rm H}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'$$
(2.35)

The electronic density is in turn obtained from the one-electron Schrödinger wavefunctions :

$$n(\mathbf{r}) = \sum_{j} \psi_{j}^{*}(\mathbf{r})\psi_{j}(\mathbf{r})$$
(2.36)

The wavefunctions are obtained from the solution of the one-electron Schrödinger equations 2.32 where  $V(\mathbf{r})$  is replaced by  $V_{\text{eff}}(\mathbf{r})$ :

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right)\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r})$$
(2.37)

In this way, a Self-Consistent Field (SCF) cycle is defined as illustrated in Fig. 2.3 (a). From a starting electronic density, the corresponding effective potential is calculated and used to obtain the wavefunctions. From these wavefunctions, a new electronic density can be calculated. This can be iterated until all the elements of the cycle reach a stationary solution.

In the Hartree approximation stated above, the Pauli exclusion principle is clearly not satisfied as the wavefunction should be antisymmetric upon interchange of two electrons :



Figure 2.3: Self-Consistent Field cycle (a) in the Hartree approximation and (b) within Density Functional Theory.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$$
(2.38)

In the Hartree-Fock method, the wavefunction is expressed as Slater determinants as in Eq. 2.31. The Pauli exclusion principle is then satisfied trivially by including an *exchange* term in the one-particle Hartree-Fock equations :

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right)\psi_j(\mathbf{r}) - \sum_k \int \frac{\psi_k^*(\mathbf{r}')\psi_j^*(\mathbf{r}')\psi_k(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}d\mathbf{r}' = \varepsilon_j\psi_j(\mathbf{r})$$
(2.39)

The Hartree-Fock equations do not contain any electronic correlation. Indeed, by assuming a single determinant for the electronic wavefunction, the dimensional space of possibilities for the total electronic wavefunction is reduced. This is indeed a strong hypothesis that can lead to poor electronic structures.

#### 2.3.3 Density Functional Theory

In the Hartree and Hartree-Fock methods, electronic correlation is neglected such that the computed properties can largely deviate from the real ones. One possibility relies in Density Functional Theory (DFT) in which the electronic exchange and correlation effects are taken into account by means of a model local potential. In this section, the underlying theorems of DFT will first be presented. The fundamental approximations used in DFT are then laid out. Finally, some important aspects of practical calculations are set down.

## Density as the fundamental variable : the Hohenberg-Kohn theorems

In 1964, Hohenberg and Kohn [11] (HK) published a paper on the inhomogeneous electron gas that would appear to be a very important step into the possibility to solve the Schrödinger equation for real systems. They proposed to address the complicated and fully interacting electronic problem by replacing it by a much more tractable one. The electronic density  $n(\mathbf{r})$  is considered as the fundamental variable of the problem and hence the space in which the problem is solved is reduced by a factor N. This section presents the two main theorems that come with this idea.

**Theorem 1.** The ground-state electronic density  $n(\mathbf{r})$  of a system of interacting electrons uniquely determines the external potential  $V_{\text{ext}}(\mathbf{r})$  in which the electrons evolve.

Conversely, the external potential  $V_{\text{ext}}(\mathbf{r})$  is a universal functional of the density within some additive constant. It follows that any property of the system is in fact a functional of the ground-state density  $n_0(\mathbf{r})$ . In particular, the total energy is obtained as

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$
(2.40)

where  $F[n(\mathbf{r})]$  is a universal (unknown) functional of the density.

**Theorem 2.** The universal functional for the energy  $E[n(\mathbf{r})]$  is defined in terms of the electronic density  $n(\mathbf{r})$ . The ground-state is obtained for the density  $n_0(\mathbf{r})$  that minimizes this functional. As a consequence, the ground-state of the system (and its total energy) can be obtained using conjugate gradient methods or other iterative minimization procedures [75].

#### The Kohn-Sham formulation

All the beauty of DFT resides in the existence of a universal functional  $F[n(\mathbf{r})]$  of the density defined in Eq. 2.40 and in the reduction of the complexity of the problem from a wavefunction in 3N dimensions to the density in 3 dimensions. However, the functional  $F[n(\mathbf{r})]$  is unknown. Kohn and Sham [12] split up this functional into three terms so that the energy functional  $E[n(\mathbf{r})]$  is rewritten as

$$E[n(\mathbf{r})] = \underbrace{T_{s}[n(\mathbf{r})] + E_{H}[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})]}_{F[n(\mathbf{r})]} + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \quad (2.41)$$

where

$$T_{\rm s}[n(\mathbf{r})] = -\frac{1}{2} \sum_{i=1}^{N} \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r}$$
(2.42)

$$E_{\rm H}[n(\mathbf{r})] = \frac{1}{2} \int n(\mathbf{r}) V_H(\mathbf{r}) d\mathbf{r} = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}$$
(2.43)

are the kinetic energy of the non-interacting electron gas with density  $n(\mathbf{r})$  and the Hartree energy of the same density. These two terms are known exactly while the last term  $E_{\rm XC}[n(\mathbf{r})]$ isthe exchange-correlation (XC) energy of the system and is formally defined by Eq. 2.41. This XC energy functional contains all the many-body effects of the interacting system and is in general not known. In fact, it has been calculated exactly only for simple model systems such as the homogeneous electron gas [76].

Using the second HK theorem (Theorem 2) with the additional constraint that the total number of electrons  $N_{\rm e}$  has to remain constant under any variation of the density, the ground-state density of the system is found by minimizing the energy :

#### 2.3. Density functional theory

$$\frac{\delta}{\delta n(\mathbf{r})} \left[ E[n(\mathbf{r})] - \lambda \left( \int n(\mathbf{r}) d\mathbf{r} - N_{\rm e} \right) \right] = 0 \tag{2.44}$$

$$\frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \lambda \qquad (2.45)$$

in which  $\lambda$  plays the role of a Lagrange multiplier for the constraint on the number of electrons. Equation 2.45 can then be rewritten as :

$$\frac{\delta T_{\rm s}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + V_{\rm KS}(\mathbf{r}) = \lambda \tag{2.46}$$

where the Kohn-Sham potential  $V_{\rm KS}({f r})$  is an effective potential expressed as

$$V_{\rm KS}(\mathbf{r}) = V_{\rm ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\rm XC}(\mathbf{r})$$
(2.47)

The two first terms in Eq. 2.47 have already been defined in Sect. 2.3.2. The exchange-correlation potential  $V_{\rm XC}(\mathbf{r})$  is derived from the exchangecorrelation energy  $E_{\rm XC}[n(\mathbf{r})]$ :

$$V_{\rm XC}(\mathbf{r}) = \frac{\delta E_{\rm XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$
(2.48)

With the equations and quantities stated above, the ground-state energy and density are obtained by solving equations 2.36 and 2.47 together with the following one-particle Schrödinger equations with the KS potential as the effective potential :

$$\left(-\frac{1}{2}\nabla^2 + V_{\rm KS}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$
(2.49)

This set of equations define a self-consistent cycle (SCF) as illustrated in Fig. 2.3 (b). This cycle has to be iterated until a stationary state is obtained for all the quantities involved. The Kohn-Sham equations thus give the theoretical basis for the description of a groundstate's system provided that the exchange-correlation energy  $E_{\rm XC}[n(\mathbf{r})]$ in Eq. 2.48 is known, which is usually not the case. Because of that, approximations for this functional have to be used in practice.

#### **Exchange-correlation functionals**

Many exchange-correlation functionals exist in the scientific community. In fact, plenty of them have been devised for many specific purposes. In an ideal world, the exchange-correlation functional should work for any system and for any property. In practice, this perfect exchangecorrelation does not exist and one then needs to choose one amongst all the possible approximations on the market. In this thesis, the *local density approximation*[77] (LDA) has been used for most of the results presented. Another functional proposed by Tran and Blaha [78] has also been tested in this work for the electronic properties.

**Local density approximation** In the local density approximation, the exchange-correlation energy is obtained by assuming that it depends locally on the exchange-correlation energy density  $\varepsilon_{\text{XC}}^{\text{HEG}}(n)$  of the homogeneous electron gas with the same density  $n = n(\mathbf{r})$ , which is known exactly from quantum Monte-Carlo simulations [76] and has been parametrized by Perdew and Wang [77] for any constant density n. The total exchange-correlation energy is then obtained by integrating the exchange-correlation energy density over the volume of the system :

$$E_{\rm XC}^{\rm LDA}[n(\mathbf{r})] = \int \varepsilon_{\rm XC}^{\rm HEG}(n(\mathbf{r})) \mathrm{d}\mathbf{r}$$
 (2.50)

Surprisingly and despite of its simplicity, LDA has been shown to give reasonable structral properties such as bond lengths, lattice parameters and atomic positions within 1 or 2 % over a large range of systems [79]. The computation of other energy-derived properties obtained from finite differences or from the more elegant density functional perturbation theory [22, 80, 81] within LDA can also be achieved with a relative accuracy of less than 5 % [82] for many systems.

Unfortunately, this approximation is not reliable for all the properties. Excited states and, in particular, the band gap energy are poorly described within LDA [83, 84]. In fact, except for the highest occupied and lowest unoccupied states, the eigenvalues obtained from the solution





Figure 2.4: Jacob's ladder of density functional approximations, from Perdew and Schmidt[85].

of the KS equations cannot in principle be interpreted as quasiparticle energies. They are indeed just Lagrange multipliers used to solve a minimization problem of a fictitious system of non-interacting particles that mimics the fully interacting one. This is not specific to LDA though and attempts are made to design new functionals capable of describing such properties.

Other functionals and Jacob's Ladder Many other approximations for the exchange-correlation functional exist in the literature besides the LDA. These range from local gradient expansion of the density [18] to more elaborate schemes involving semi-local or orbital-dependent terms [39]. Depending on the system and properties as well as on the desired accuracy one aims to look at, some type of functional might be preferred, keeping in mind that usually, a better accuracy implies a more complicated and more computationally demanding approximation.

This multitude of functionals can be classified into different groups by their level of simplicity or reversely by their level of accuracy. These groups can be represented in Fig. 2.4 in a so-called *Jacob's ladder* of density functional approximations after Perdew and Schmidt[85]. In this Jacob's ladder, the highest rung corresponds to the best accuracy that can be achieved from an exact treatment of exchange and partial correlation. This kind of technique is very demanding and cannot be applied to real large systems with the present status of computer and hardware. On the contrary, the lowest rung represents the LDA approximation, which is conceptually easy and computationally tractable for relatively large systems. The other rungs between these two are other levels in the theory, such as GGA functionals and other Meta- and Hyper-GGA's, with their own pros and cons.

Describing the bandgap with a semi-local functional : the Tran-Blaha exchange-correlation One of the main failure in DFT is the well known band gap problem and the correct description of excited states. Indeed, DFT is formally a ground-state theory and this issue has been known for years [83, 84]. In order to get reliable electronic structures, one needs to go to many-body perturbation theory (see Sect. 2.4) but with a considerable increase in computational time. For that reason, many attempts have been made to obtain better band gaps and to improve the quality of the excited states without using any computationally demanding many-body techniques. The  $\Delta$ SCF method [39] for atoms and molecules, further generalized to solids by Chan and Ceder as  $\Delta$ -sol, [86] leads to fundamental band gaps in closer agreement with experiment. However, the full band structure of the excited states remains quite approximate. Hybrid functionals [87, 88, 89] can have a positive effect on the accuracy of the bandgap and the position of higher excited states[90] but are more computationally demanding than standard XC functionals as they include some part of exact exchange.

In a recent letter by Tran and Blaha [78], a modified version of the Becke-Johnson exchange potential[91] combined with an LDA (Perdew-Wang [77]) correlation part was proposed to improve band gap predictions in DFT. This new XC functional (referred to as TB09) has already been applied to a large variety of systems[92, 93, 94, 95, 96, 97] and was able to predict bandgaps in close agreement with experiment.

#### 2.3. Density functional theory

The TB09 exchange-correlation potential is composed of a modified version of the Becke-Johnson[91] exchange potential and an LDA correlation part. The exchange part  $V_{\rm X}^{\rm TB09}(\mathbf{r})$  takes the following form :

$$V_{\rm X}^{\rm TB09}(\mathbf{r}) = c V_{\rm X}^{\rm BR}(\mathbf{r}) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_{\rm s}(\mathbf{r})}{n(\mathbf{r})}},\qquad(2.51)$$

where  $V_X^{BR}(\mathbf{r})$  is the Becke-Roussel potential [98] modeling the Coulomb potential created by the exchange hole (see Appendix A for the exact expression) and the parameter c results from the following equation :

$$c = \alpha + \beta \left( \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d\mathbf{r}' \frac{|\nabla n(\mathbf{r}')|}{n(\mathbf{r}')} \right)^{1/2}, \qquad (2.52)$$

where  $V_{\text{cell}}$  is the unit cell volume and where  $\alpha$  and  $\beta$  were fitted to experimental gaps in the original paper using a least-square procedure. The kinetic energy density  $t_s(\mathbf{r})$  reads

$$t_s(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{N} \nabla \psi_i^*(\mathbf{r}) \cdot \nabla \psi_i(\mathbf{r})$$
(2.53)

Limitations of this functional have been pointed out by some authors. First, there is no energy functional from which the potential is derived [99, 100], which prevents the description of any energy-related properties, such as defect formation energies or phase stability. Secondly, it is not intended to be used for systems without an electronic gap and indeed seems to be an issue for such systems[101]. Finally, effective masses are reported to be overestimated [97, 102], with an accompanying narrowing of the bands. There are other known drawbacks to the TB09 functional, namely the fact that it is not size consistent and that it is not gauge invariant.[103]. In this thesis, the band gaps and electronic structures of several compounds obtained with the TB09 functional will be compared to results obtained with LDA and the more accurate GW method.

#### 2.3.4 DFT in practice

All the theory presented here above is very general. The actual implementation of the Kohn-Sham equations and the way the different quantities are represented depend on the physical system under study. For atomic or molecular systems, one usually takes localized basis sets such as atom-centered gaussians or spherical harmonics. In this thesis, crystalline and amorphous solids are concerned. As it will be shown later on, amorphous structures can be described using a periodic supercell approach. The most appropriate type of basis set for periodic quantities is then made of plane waves. In this section, some important aspects for practical calculations in periodic systems such as the Bloch theorem and the use of pseudopotentials will be presented.

#### Periodicity and the Bloch theorem

In a solid, the electronic problem is a very complicated one as there is an infinitely large number of electrons. In practice, the solid is idealized as a perfect crystal where the atoms are periodically repeated in space. Because of this periodic arrangement of ions, the electrons evolve in an effective potential that has the same periodicity as the crystal. The physical system is completely characterized by the coordinates of the atoms in the primitive unit cell and the primitive translation vectors  $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$  that determine how the unit cell is replicated.

By definition of the periodic crystal, any real space property  $f(\mathbf{r})$  of the system such as its electronic density or the potential is invariant under any translation of the primitive translation vectors and integer combinations of them :

$$f(\mathbf{r} + \mathbf{R}) = f(\mathbf{r}) \tag{2.54}$$

with  $\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$  and  $n_1, n_2, n_3 \in \mathbb{Z}^3$ .

As a periodic quantity,  $f(\mathbf{r})$  can be expressed as a Fourier series

$$f(\mathbf{r}) = \sum_{\mathbf{G}} f_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$
(2.55)

in which  $\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$   $(m_1, m_2, m_3 \in \mathbb{Z})$  is a reciprocal space vector and  $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$  are the reciprocal space primitive vectors defined as

$$\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_{\text{cell}}}, \qquad \mathbf{b}_2 = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V_{\text{cell}}} \qquad \text{and} \qquad \mathbf{b}_3 = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V_{\text{cell}}} \qquad (2.56)$$

where  $V_{\text{cell}} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$  is the volume of the primitive unit cell.

The Fourier coefficients  $f_{\mathbf{G}}$  in Eq. 2.55 are obtained as

$$f_{\mathbf{G}} = \frac{1}{V_{\text{cell}}} \int_{V_{\text{cell}}} f(\mathbf{r}) \,\mathrm{e}^{-i\mathbf{G}\cdot\mathbf{r}} \,\mathrm{d}\mathbf{r}$$
(2.57)

The periodicity of the effective potential of the system implies that it must verify the condition of Eq. 2.54. A direct consequence of this lies in the Bloch theorem [104]:

**Theorem 3.** In a perfect crystal, one can choose the eigenfunctions of a Schrödinger equation in a periodic potential  $V(\mathbf{r})$  to be written as the product of a plane wave part  $e^{i\mathbf{k}\mathbf{r}}$  and a periodic function  $u_{n\mathbf{k}}(\mathbf{r})$  with the same periodicity as the potential :

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \tag{2.58}$$

where

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}) \tag{2.59}$$

and  $\mathbf{k}$  is a reciprocal space vector which can be seen as a quantum number arising from the translational symmetry of the potential.

In addition to the periodicity of the potential, the function  $u_{n\mathbf{k}}(\mathbf{r})$  is periodic in  $\mathbf{k}$  such that the electronic problem is entirely characterized if  $u_{n\mathbf{k}}(\mathbf{r})$  is known for all  $\mathbf{k}$  in the first Brillouin zone.

Using the Bloch theorem and a Fourier representation of the periodic function  $u_{n\mathbf{k}}(\mathbf{r})$  leads to rewrite the wavefunction of a system as :

$$\psi_{n\mathbf{k}} = \frac{1}{V_{\text{cell}}} \sum_{\mathbf{G}} c_{n\mathbf{k}+\mathbf{G}} \,\mathrm{e}^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} \tag{2.60}$$

In principle the sum in Eq. 2.60 is infinite but in practice, the basis set defined by the set of **G** vectors used is truncated and include plane waves up to a given kinetic energy cut-off  $E_{\text{cut}}$ :

$$\frac{|\mathbf{k} + \mathbf{G}|^2}{2} < E_{\text{cut}} \tag{2.61}$$

The truncation in the set of **G** vectors induces errors in the computed properties. In practice, this error can be reduced by increasing the kinetic energy cut-off defined in Eq. 2.61 until the desired accuracy is achieved. In particular, the total electronic energy of the system computed with a given  $E_{\rm cut}^1$  will always be smaller or equal to the total energy obtained with a smaller  $E_{\rm cut}^2 < E_{\rm cut}^1$ .

It is important to note that the all-electron wavefunction of a system has a very large oscillatory behavior close to the nuclei, implying a large kinetic energy cut-off and hence a large computational cost. Therefore, one usually makes another assumption about the separation of core and valence electrons leading to the pseudopotential approximation.

#### **Pseudopotentials**

In the frozen core approximation, we take advantage of the fact that the core electrons of the atoms are strongly localized and separated in space and energy from the other (valence) electrons. Indeed, as their binding energy is usually much lower, their properties are not much modified by the surrounding environment. On the contrary, the valence electrons are the ones participating in the bonding between atoms. Many properties of a given material thus depend mainly on the dynamical properties of these valence electrons.

The number of electrons explicitly included in the simulation is thus decreased. In addition to that, the pseudopotential are constructed in order to smooth the oscillatory behavior of the wavefunctions close to the nuclei, as illustrated in Fig. 2.5. This leads to a strong cut-down in the size of the basis sets needed. The actual procedure to generate a reliable pseudopotential is not trivial and will not be discussed further here.



Figure 2.5: Pseudopotential approximation. The all-electron and pseudo-wavefunctions for the silicon 3s-state are shown in the dashed blue and full green lines respectively. The corresponding pseudopotential for the *s*-angular momentum is shown as a full red line. The effective (with  $Z_{\rm ion} = 4$ ) Coulomb potential is also shown on the figure. For large radii, the pseudopotential is superimposed onto the effective Coulomb tail, meaning that far from the nucleus, the effective charge perceived by an electron is that of the ion with  $Z_{\rm ion} = Z_{\rm atom} - Z_{\rm core}$ .

#### 2.3.5 Conclusion

The physics of a many-electron system is often very complicated due to the correlated motion of the individual particles on all the other particles. These so-called exchange and correlation effects are present in all quantum systems and are almost impossible to account for exactly. Even though, for many cases, such as ground-state properties, a mean field approach such as density functional theory, where the exchange-correlation effects are approximated in an average way, is suitable. DFT is a reformulation of the full quantum many-body problem into a much more tractable one. Ground-state properties are usually obtained with a relatively good accuracy and hence, DFT is often used to compute equilibrium lattice parameters, total energy differences, phase diagrams, ... On the other hand, electronic properties are not well described, in particular the band gap. In order to get accurate electronic band structures, exchange-correlation effects should be included in a more appropriate way and this will be the subject of the next section.

### 2.4 Electronic structure within many-body perturbation theory and the GW approximation

The band gaps of semiconductors and insulators are often strongly underestimated within DFT and the standard exchange-correlation approximations. In order to get an accurate description of the electronic structure, one has to go beyond mean field theories and consider all the interactions between electrons. In the Many-Body Perturbation Theory (MBPT), the energies and wavefunctions of the system are obtained by solving the quasiparticle (QP) equation :

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_i^{\rm QP}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \omega = \varepsilon_i^{\rm QP})\psi_i^{\rm QP}(\mathbf{r}) = \varepsilon_i^{\rm QP}\psi_i^{\rm QP}(\mathbf{r}) \quad (2.62)$$

36

This equation is very similar to Eq. 2.49 where the self-energy  $\Sigma$ , a non-local, energy-dependent and non-hermitian operator, takes the role of the XC potential  $V_{xc}$ . The solution to the Many-Body problem is direct if the expression for the self-energy is known but for practical applications, the self-energy is always approximated as its complexity is of the same order as the many-electron wavefunction. The challenging part is to find such approximations that are accurate enough for the property we aim to look for. In particular, DFT assumes that  $\Sigma$  is energy-independent and depends only on the density of the system.

In this section, the main ingredients of Many-Body Perturbation Theory are presented. First, the fundamental response functions of a system to a given perturbation are defined. Next, the concept of Green's functions and quasiparticles are introduced. The general equations from Hedin needed to obtain the Green's functions and self-energy are then laid out. The GW approximation as well as the particular methods and technicalities used in this thesis to obtain accurate electronic structure are then described.

#### 2.4.1 Response functions

When a material is subject to an external potential  $V_{\text{ext}}$ , the groundstate density *n* is affected. This perturbation  $\delta n_{\text{ind}}$  of the density causes itself another *induced* potential  $V_{\text{ind}}$  as shown in Fig. 2.6. The total potential is then the sum of these two potentials  $V_{\text{tot}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{ind}}(\mathbf{r})$ .

Let  $\delta V_{\text{ext}}$  be a small change in the external potential, the change in the total potential is simply expressed as :

$$\delta V_{\rm tot} = \delta V_{\rm ext} + \delta V_{\rm ind} \tag{2.63}$$

where the induced potential is given by

$$\delta V_{\rm ind} = v \delta n_{\rm ind} \tag{2.64}$$

in which v is the Coulomb interaction.

The dielectric function and its inverse are then defined as



Figure 2.6: Response of a material to a macroscopic external potential. The total potential  $V_{\text{tot}}(\mathbf{r})$  at some position  $\mathbf{r}$  is the sum of the external potential  $V_{\text{ext}}(\mathbf{r})$  and the induced potential  $V_{\text{ind}}(\mathbf{r})$ .

$$\epsilon = \frac{\delta V_{\text{ext}}}{\delta V_{\text{tot}}} = 1 - v\tilde{P} \tag{2.65}$$

$$\epsilon^{-1} = \frac{\delta V_{\text{tot}}}{\delta V_{\text{ext}}} = 1 + vP \tag{2.66}$$

in which the *irreducible polarizability*  $\tilde{P} = \frac{\delta n_{\rm ind}}{\delta V_{\rm tot}}$  and the *reducible polarizability*  $P = \frac{\delta n_{\rm ind}}{\delta V_{\rm ext}}$  describe the linear response of the density with respect to a change in the total and external potential respectively. The same physics is contained in these two polarizabilities and the connection between them is easily obtained by combining Eqs. 2.65 and 2.66 :

$$P = \tilde{P} + \tilde{P}vP \tag{2.67}$$

From the dielectric function, one can define the screened Coulomb interaction W as

$$W = \epsilon^{-1} v \tag{2.68}$$

The response functions described in this section provide the theoretical basis for a perturbative expansion of the many-body problem. Before setting up the actual equations needed to solve this problem, one needs to define the central variable that is used in MBPT.

#### 2.4.2 Green's functions and the quasiparticle concept

In MBPT, the electronic problem is solved in terms of *Green's functions* or *propagators*. In the zero temperature limit, the one-particle Green's function G is defined in the Heisenberg representation as

$$G(\mathbf{x}_1, t_1, \mathbf{x}_2, t_2) = -i \langle \Psi_0 | \mathsf{T} \left[ \psi(\mathbf{x}_1, t_1) \psi^{\dagger}(\mathbf{x}_2, t_2) \right] | \Psi_0 \rangle$$
(2.69)

where  $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$  stands for space and spin coordinates,  $\Psi_0$  is the many-body ground-state wavefunction,  $\mathsf{T}$  is the time ordering operator<sup>1</sup> and  $\psi(\mathbf{x}_1, t_1)/\psi^{\dagger}(\mathbf{x}_2, t_2)$  are the annihilation/creation operators. The physical interpretation of the Green's function can be understood in terms of particle's propagation. For  $t_1 > t_2$ , the Green's function is the probability amplitude of finding an electron at point  $\mathbf{x}_1$  at time  $t_1$  which was added to the system at point  $\mathbf{x}_2$  and time  $t_2$ . For  $t_1 < t_2$  instead, the Green's function is the probability amplitude of the propagation of a hole from point  $\mathbf{x}_1$  at time  $t_1$  to point  $\mathbf{x}_2$  at time  $t_2$ .

The Green's function G is the fundamental variable in MBPT, in the same manner the electronic density is in DFT. All the properties of the interacting system can thus be extracted from G if it is known exactly. The electronic density itself is obtained as  $-iG(11^+)$ , where the *number* abbreviation for the space, spin and time coordinates is used, in which  $1 = (\mathbf{r}_1, \sigma_1, t_1), 1^+ = \lim_{\tau \to 0^+} (\mathbf{r}_1, \sigma_1, t_1 + \tau)$  and  $\tau$  is a positive infinitesimal, . When the Green's function is expressed in a spectral representation, the electron affinities and ionization potentials appear to be the poles of G:

$$G(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i} \frac{\Psi_{i}(\mathbf{r}, \omega) \Psi_{i}^{\dagger}(\mathbf{r}', \omega)}{\omega - E_{i}(\omega)}$$
(2.70)

The spectral function  $A(\omega)$  (schematically shown in Fig. 2.7), which is the quantity that is measured in photoemission experiments, is obtained from the one-particle Green's function as

 $<sup>\</sup>label{eq:tau} {}^1\mathsf{T}\left[\psi(\mathbf{x}_1,t_1)\psi^\dagger(\mathbf{x}_2,t_2)\right] = \theta(t_1-t_2)\psi(\mathbf{x}_1,t_1)\psi^\dagger(\mathbf{x}_2,t_2) - \theta(t_2-t_1)\psi^\dagger(\mathbf{x}_2,t_2)\psi(\mathbf{x}_1,t_1)$  in which  $\theta(t)$  is the step function.



Figure 2.7: Spectral function of the one-particle Green's function.

$$A(\omega) = \frac{1}{\pi} \operatorname{Im} G(\omega) \tag{2.71}$$

Figure 2.7 illustrates some features of the spectral function. The full red line is the spectral function of the fully interacting Green's function. The vertical thick blue line is the spectral function of an independent (KS) particle. What is usually called the *quasiparticle* energy corresponds to the main contribution in the spectral function. The width of this main peak in the spectral function is related to the inverse of the quasiparticle lifetime. It should be emphasized here that if the spectral function is not clearly peaked as in Fig. 2.7, then the quasiparticle concept might loose its physical meaning.

Another intuitive picture of the quasiparticle concept is illustrated in Fig. 2.8. The Coulomb potential  $v(\mathbf{r}, \mathbf{r}')$  at point  $\mathbf{r}'$  arising from a bare electron at position  $\mathbf{r}$  is shown in (a). In a real material, the electron gets surrounded by a positive charge cloud due to its negative charge as shown in Fig. 2.8 (b). More precisely, this cloud correspond to an induced charge  $n_{\text{ind}}(\mathbf{r}, \mathbf{r}'')$  at all points  $\mathbf{r}''$  due to the electron in  $\mathbf{r}$ . The screened Coulomb potential  $W(\mathbf{r}, \mathbf{r}')$  at point  $\mathbf{r}'$  arising from a quasi-electron at position  $\mathbf{r}$  is the sum of the bare Coulomb potential  $v(\mathbf{r}, \mathbf{r}')$  and all the small (opposite) contributions  $v(\mathbf{r}'', \mathbf{r}')$  due to the induced (positive) charge of the cloud.



Figure 2.8: Illustration of a the Coulomb interaction v for bare electrons and the screened Coulomb interaction W for quasielectrons.

This can also be inferred from the expression of the screened Coulomb interaction. Omitting the frequency dependence, the screened Coulomb interaction reads

$$W(\mathbf{r}, \mathbf{r}') = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}'') v(\mathbf{r}'', \mathbf{r}') d\mathbf{r}''$$
(2.72)

$$= v(\mathbf{r}, \mathbf{r}') + \int \underbrace{\left(\epsilon^{-1}(\mathbf{r}, \mathbf{r}'') - 1\right)}_{\int v(\mathbf{r}, \mathbf{r}'') P(\mathbf{r}''', \mathbf{r}'') d\mathbf{r}'''} v(\mathbf{r}'', \mathbf{r}') d\mathbf{r}''$$
(2.73)

where the underbraced term in Eq. 2.73 can be identified as an approximate mean induced charge. Moreover, by assuming that the values for  $\epsilon$ are on average larger than 1, so that the term  $(\epsilon^{-1} - 1)$  ranges between -1 and 0, the integral in Eq. 2.73 will be comprised between  $-v(\mathbf{r}, \mathbf{r}')$ and 0. The extreme case of an electron in vacuum, where  $\epsilon = 1$ , leads to  $(\epsilon^{-1} - 1) = 0$  such that the screened Coulomb interaction is exactly equal to the bare Coulomb interaction (no screening cloud as there is no available charge density).

The total energy of the system can also be extracted from the Green's function, by means of the Galitskii-Migdal formula [105] or the Luttinger-Ward formalism [106]. However, these approaches are extremely diffi-

cult to apply for real systems due to their large computational costs [105] and mean-field theories such as DFT usually lead to total energies and other ground-state properties in good agreement with experiment. The present theory will thus mainly be used for the electronic structure. In the following, the theory and methods used to solve the many-body problem are laid out.

#### 2.4.3 Hedin's equations or how to get the self-energy

In a completely general theory, the Green's function G and similarly the self-energy  $\Sigma$  are obtained by solving a set of five self-consistent integrodifferential equations which were originally introduced by Hedin [24] as illustrated schematically in Fig. 2.9 (a). Hedin's equations read

$$\Sigma(12) = i \int G(13)\Gamma(324)W(41)d34$$
 (2.74)

$$G(12) = G^{0}(12) + \int G^{0}(13)\Sigma(34)G(42)d34 \qquad (2.75)$$

$$\Gamma(123) = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d4567$$
(2.76)

$$\tilde{P}(12) = -i \int G(13)G(41)\Gamma(342)d34$$
(2.77)

$$W(12) = v(12) + \int v(13)\tilde{P}(34)W(42)d34 \qquad (2.78)$$

in which  $\Gamma(123)$  is the vertex function, W is the dynamical screened interaction and  $\tilde{P}$  is the irreducible polarizability.

In this way, the many-body problem is expressed in a form that casts up the essential physics. The polarizability  $\tilde{P}$ , which is the response of the system to the addition of an electron or hole, is set up from the creation at  $1 = (\mathbf{r}_1, t_1)$  of an electron and a hole (the two Green's function) that will propagate respectively to 3 and 4. The propagation depends on how the electron and the hole interact with each other, which is described by the vertex function  $\Gamma(342)$ .



Figure 2.9: (a) Schematic view of the set of integro-differential equations from Hedin. (b) The GW approximation to Hedin's equations neglecting vertex corrections.

#### 2.4.4 The GW approximation

Solving the full set of self-consistent Eqs 2.74-2.78 is practically impossible for real systems. For this reason, it is customary to neglect the vertex term, i.e.  $\Gamma(123) = \delta(12)\delta(13)$  in Eq. 2.76. Using this approximation, the Hedin's pentagon of Fig. 2.9 (a) reduces to the schematic view of Fig. 2.9 (b). In particular, the self-energy is written as the product of the Green's function G and the dynamical screened Coulomb potential W, leading to the so-called GW approximation

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega') e^{i\omega'\delta^+} d\omega'$$
(2.79)

Getting back to the physical interpretation of Hedin's equations, it is not quite surprising that the GW approximation has been successfully applied for charged electronic excitations. Indeed, experimental photoemission (PES) and inverse photoemission spectra (IPES) are rather well described within the GW method. For charged excitations, when a hole is created in the valence band while the electron is ejected from the system, the latter is completely out of the system such that its interaction with the hole (described by the vertex  $\Gamma$ ) can be neglected as a first approximation. Conversely, when an electron is added to the conduction band of a system, a hole is created in some other external system and the interaction between these two particles can also be considered as insignificant. It follows that the response of the system actually depends only on the propagation of the hole in the valence (for a  $N \rightarrow N-1$  electronic excitation) or of the electron in the conduction (for a  $N \rightarrow N+1$ electronic excitation).

#### Non self-consistent GW

Although the system of GW equations sketched in Fig. 2.9 (b) should in principle be solved self-consistently, most calculations hitherto have been carried out in a non self-consistent way leading to the so-called *oneshot* GW or  $G_0W_0$ . The idea of this one-shot approach is to stop after one cycle, provided that the starting point is close to the final result. In this thesis, the screened interaction  $W_0$  is calculated from a DFT-LDA bandstructure calculation, unless otherwise noted. This screened interaction  $W_0$  is in turn used to obtain the self-energy  $\Sigma_0 = iG_0W_0$ . It is important to stress here that while self-consistent GW is supposed to give the same results whatever the starting point is, the one-shot approach depends by essence on the initial Green's function  $G_0$ .

Assuming that  $\psi_i^{\text{QP}} \approx \psi_i^{\text{KS}}$ , the  $G_0 W_0$  method is usually applied within a perturbative approach. The first-order perturbation is obtained from the expectation value of the difference between the self-energy  $\Sigma$ and the XC potential  $V_{\text{xc}}$ :

$$\varepsilon_{i}^{\text{QP}} = \varepsilon_{i}^{\text{KS}} + \left\langle \psi_{i}^{\text{KS}} \right| \Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_{i}^{\text{QP}}) - V_{\text{xc}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \left| \psi_{i}^{\text{KS}} \right\rangle$$
(2.80)

In principle, Eq. 2.80 should be solved self-consistently as the selfenergy has to be evaluated at the corresponding QP energy  $\varepsilon_i^{\text{QP}}$ . Noting that the difference between QP and KS energies is relatively small, a first-order Taylor expansion of the self-energy around  $\varepsilon_i^{\text{KS}}$  is used to obtain its value at  $\varepsilon_i^{\text{QP}}$ :

$$\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_i^{\rm QP}) \approx \Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_i^{\rm KS}) + (\varepsilon_i^{\rm QP} - \varepsilon_i^{\rm KS}) \left. \frac{\partial \Sigma(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \right|_{\omega = \varepsilon_i^{\rm KS}}$$
(2.81)



Figure 2.10: Frequency dependence of  $\Sigma$ .

This leads to rewrite Eq. 2.80 as

$$\varepsilon_{i}^{\text{QP}} = \varepsilon_{i}^{\text{KS}} + Z_{i} \left\langle \psi_{i}^{\text{KS}} \right| \Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_{i}^{\text{KS}}) - V_{\text{xc}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \left| \psi_{i}^{\text{KS}} \right\rangle$$
(2.82)

with  $Z_i$  being the renormalization constant :

$$Z_{i} = \left[1 - \left\langle\psi_{i}^{\mathrm{KS}}\right| \left.\frac{\partial\Sigma(\mathbf{r},\mathbf{r}',\omega)}{\partial\omega}\right|_{\omega=\varepsilon_{i}^{\mathrm{KS}}}\left|\psi_{i}^{\mathrm{KS}}\right\rangle\right]^{-1}$$
(2.83)

This procedure is sketched in Fig. 2.10 and has been shown to yield very good results [107] for many applications.

#### **Plasmon-pole models**

The frequency dependence of the screened interaction W requires a large sampling of points on the frequency axis. When a plasmon-pole model (PPM) is used, all the spectral weight of the imaginary part of  $\epsilon_{\mathbf{GG}'}^{-1}(\mathbf{q}, \omega)$ is assumed to be concentrated at the plasmon frequency  $\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})$  with amplitude  $A_{\mathbf{GG}'}(\mathbf{q})$ :

$$\operatorname{Im} \epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q},\omega) = A_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) \times \left[\delta(\omega - \tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}))\right]$$
(2.84)

Using the Kramers-Kronig relations, the real part of the dielectric function is then obtained as

$$\operatorname{Re} \epsilon_{\mathbf{GG}'}^{-1}(\mathbf{q},\omega) = \delta_{\mathbf{GG}'} + \frac{\Omega_{\mathbf{GG}'}^{2}(\mathbf{q})}{\omega^{2} - \tilde{\omega}_{\mathbf{GG}'}^{2}(\mathbf{q})}$$
(2.85)

with  $\Omega^2_{\mathbf{GG}'} = -A_{\mathbf{GG}'}(\mathbf{q})\tilde{\omega}^2_{\mathbf{GG}'}(\mathbf{q}).$ 

This parametrized form for the dielectric function allows to reduce the computational cost for the calculation of the screened interaction. Indeed, the PPM parameters defined above are obtained from the dielectric function evaluated at one or two frequencies depending on the strategy used, while a full frequency treatment requires its computation for a large number of frequencies. The first approach, proposed in the famous GW implementation by Hybertsen and Louie [108], is to choose the PPM parameters in order to reproduce the static limit  $\epsilon_{\mathbf{GG'}}^{-1}(\mathbf{q}, \omega = 0)$  and to enforce Johnson's frequency sum (f-sum) rule

$$\int_{0}^{\infty} \omega \operatorname{Im} \epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q},\omega) d\omega = 2\pi^{2} \frac{(\mathbf{q}+\mathbf{G}) \cdot (\mathbf{q}+\mathbf{G}')}{|\mathbf{q}+\mathbf{G}|^{2}} n_{\mathbf{G}-\mathbf{G}'}$$
(2.86)

In the Godby and Needs [109] model, the parameters are fixed so that the static limit and another imaginary frequency  $i\omega_{\rm gn}$  (usually taken as the plasma frequency  $\omega_{\rm P} = \sqrt{4\pi n_0}$ ) are both reproduced. Even though both procedures are crude approximations, the latter has been proved to yield results in much better agreement with a full-frequency treatment for states close to the Fermi level [110, 111, 112].

#### 2.4.5 Interpolation of GW eigenvalues

The computation of an accurate density of states requires a dense sampling of k-points in the Brillouin zone. From a computational point of view, such large meshes are prohibitive when using the  $G_0W_0$  method. For optical properties, randomly shifted **k**-point meshes are usually preferred as the optical spectra converge more quickly but their computation in GW is not straightforward. Therefore it is preferable to avoid a full calculation by interpolating the GW eigenvalues on a very dense mesh from the results obtained on a coarser k-point grid.

One possible technique is the Wannier interpolation [113, 114]. For valence states, this technique is reasonably easy to apply. Indeed, the valence wavefunctions are well localized and the generation of the Wannier functions is almost instantaneous. On the other hand, applying this procedure for the conduction states is not an easy task as these states are usually more delocalized. For this reason a different and much more straightforward procedure has been implemented here and used throughout this thesis.

#### The *polyfit* energy approximation

For simple materials such as  $SiO_2$ , the GW corrections are mainly a function of the energy. The fluctuations due to wave vector and state dependencies are present but can be neglected when the computation of band structures and densities of states are performed for plotting purposes. Moreover, it provides a more accurate interpolation than the *scissor* approximation (simple rigid shift of the conduction bands) that is usually assumed for *sp* semiconductors.

The QP corrections  $\Delta \varepsilon_i^{GW}$  to the Kohn-Sham eigenvalues  $\varepsilon_i^{\text{KS}}$  for state  $i = (n, \mathbf{k})$  obtained in the GW approach are obtained from Eq. 2.82 as

$$\Delta \varepsilon_i^{\rm GW} = \varepsilon_i^{\rm QP} - \varepsilon_i^{\rm KS} \tag{2.87}$$

In the *polyfit* energy approximation, the eigenvalues are interpolated using a least-squares polynomial fit by parts on the energies. In this way, the dependence of the GW correction  $\Delta \varepsilon_i^{GW}$  on the band index and k-point  $i = (n, \mathbf{k})$  is replaced by a function of the KS eigenvalues only :

$$\Delta \varepsilon_i^{GW} \longrightarrow \Delta^{GW}(\varepsilon_i^{\rm KS}) \tag{2.88}$$

First, the electronic bands are split into N separate groups depending on their energy range, using forbidden energy bands for the N-1 limits of the different intervals (so-called *energy pivots*) :

$$I_{1} = [-\infty, \xi_{1}]$$

$$\dots$$

$$I_{\alpha} = [\xi_{\alpha}, \xi_{\alpha+1}]$$

$$\dots$$

$$I_{N} = [\xi_{N-1}, \infty]$$
(2.89)

For each interval  $I_{\alpha}$ , a polynomial of order  $m_{\alpha}$  is employed as a fit for the *GW* corrections :

$$\Delta^{GW}(\varepsilon_i^{\text{KS}}) = p_\alpha^{m_\alpha}(\varepsilon_i^{KS}) \quad \text{for} \quad \varepsilon_i^{KS} \in I_\alpha$$
 (2.90)

The polynomial can be constrained to go through the endpoints of each group of bands in order to preserve the bandwidths. An example of this fitting procedure is given in Fig. 2.11 for the case of  $\alpha$ -SiO<sub>2</sub> with third-order polynomials. The upper panel shows the polynomial fits obtained for the *GW* corrections.

This interpolation scheme is obviously not perfect. The error  $\theta_i$  made for each state *i* gives an estimate of the overall error of the fit. For each explicitly calculated state, it is evaluated as the difference between the polyfit and the real correction  $\Delta \varepsilon_i^{GW}$  from Eq. 2.87 :

$$\theta_i = \Delta^{GW}(\varepsilon_i^{\rm KS}) - \Delta \varepsilon_i^{GW} \tag{2.91}$$

The errors for  $\alpha$ -SiO<sub>2</sub> are given in the lower panel of Fig. 2.11. For the valence states, this error is always smaller than 0.1 eV whereas for the highest excited states displayed in the figure, the error goes up to 0.25 eV. As previously stated, this procedure is expected to give this kind of errors for *sp* semiconductors. For other compounds where strong hybridization occurs, such as in transition metal oxides or other complex



Figure 2.11: Interpolation of GW corrections to the KS eigenvalues with the *polyfit* energy approximation. Example for  $\alpha$ -SiO<sub>2</sub> in LDA. Upper panel :  $G_0W_0$  corrections for the valence (blue crosses) and conduction (red circles) states with respect to DFT eigenvalues. The vertical dashed green lines corresponds to the *energy pivots* chosen to separate the different groups of bands. The black lines are the polynomial fits obtained for each group of band. Lower panel : Error made by the *polyfit* approximation used in the upper panel.

systems, the error can be much larger as the GW corrections are usually different depending on the character of the state considered.

GW band structures The polyfit approximation provides a very fast method to obtain GW band structures without the need of constructing localized Wannier functions or using other human-demanding method. The band structures are easily obtained by application of the energy interpolation defined in Eq. 2.90. The exact same process is applied in order to get GW-corrected randomly shifted **k**-point grids used in the computation of optical properties.

GW density of states The use of the polyfit approximation is also very convenient for a direct calculation of the GW density of states from the DFT density of states. The density of states g(E) is defined as

$$g(E) = \frac{\mathrm{d}N_{<}(E)}{\mathrm{d}E} \tag{2.92}$$

where  $N_{\leq}(E)$  is the number of states in the system whose energy is lower than E. Let  $N_{\leq}^{\text{DFT}}(E)$  be the number of states lower than energy E in DFT. Provided that the GW corrections expressed by a polyfit approximation  $\Delta^{GW}(E)$  do not give rise to any permutation, i.e.  $\frac{d\Delta^{GW}(E)}{dE} > -1$ , it is clear that

$$N_{<}^{\rm DFT}(E) = N_{<}^{GW}(E + \Delta^{GW}(E))$$
 (2.93)

By taking the derivative of Eq. 2.93 with respect to E and rearranging the terms, the GW density of states  $g^{GW}(E')$  at the energy  $E' = E + \Delta^{GW}(E)$  is obtained straightforwardly as a function of the DFT density of states  $q^{\text{DFT}}(E)$ :

$$g^{GW}(E') = \frac{g^{\text{DFT}}(E)}{1 + \frac{d\Delta^{GW}(E)}{dE}}$$
(2.94)

The same technique can be used to obtain GW partial (angular and atom projected) densities of states. This procedure is of course assuming that the ratio's of state characters are unchanged by the GW corrections. GW effective masses If the effective mass  $m_{\rm KS}^*$  from a Kohn-Sham calculation is known, the computation of the GW effective masses with the polyfit is also straightforward. The effective mass of a hole (electron) whose energy is close to a maximum (minimum) of the valence (conduction) band is obtained as :

$$m_{\rm KS}^* = \left[\frac{{\rm d}^2 \varepsilon^{\rm KS}}{{\rm d}k^2}\right]^{-1} \tag{2.95}$$

The effective mass using QP energies  $\varepsilon^{\text{QP}} = \varepsilon^{\text{KS}} + \Delta^{GW}(\varepsilon^{\text{KS}})$  from a GW polyfit interpolation can be thus derived as

$$m_{GW}^{*} = \left[\frac{\mathrm{d}^{2}\varepsilon^{\mathrm{QP}}}{\mathrm{d}k^{2}}\right]^{-1}$$
(2.96)
$$= \left[\frac{\mathrm{d}^{2}\varepsilon^{\mathrm{KS}}}{\mathrm{d}k^{2}} + \underbrace{\frac{\mathrm{d}^{2}\Delta^{GW}(\varepsilon^{\mathrm{KS}})}{\mathrm{d}k^{2}}}_{\mathrm{correction \ term}}\right]^{-1}$$
(2.97)

Using Faà di Bruno's formula [115] for the second derivative of a composite function, the correction term in Eq. 2.97 is obtained as :

$$\frac{\mathrm{d}^2 \Delta^{GW}(\varepsilon^{\mathrm{KS}})}{\mathrm{d}k^2} = \left. \frac{\mathrm{d}\Delta^{GW}}{\mathrm{d}\varepsilon} \right|_{\varepsilon^{\mathrm{KS}}} \frac{\mathrm{d}^2 \varepsilon^{\mathrm{KS}}}{\mathrm{d}k^2} + \left. \frac{\mathrm{d}^2 \Delta^{GW}}{\mathrm{d}\varepsilon^2} \right|_{\varepsilon^{\mathrm{KS}}} \left( \frac{\mathrm{d}\varepsilon^{\mathrm{KS}}}{\mathrm{d}k} \right)^2 \quad (2.98)$$

where the second term vanishes from the fact that we are close to a minimum or maximum. Finally, the GW effective mass is obtained as :

$$m_{GW}^* = \left[ \frac{\mathrm{d}^2 \varepsilon^{\mathrm{KS}}}{\mathrm{d}k^2} + \left. \frac{\mathrm{d}\Delta^{GW}}{\mathrm{d}\varepsilon} \right|_{\varepsilon^{\mathrm{KS}}} \frac{\mathrm{d}^2 \varepsilon^{\mathrm{KS}}}{\mathrm{d}k^2} \right]^{-1}$$
(2.99)

$$= \left[ \frac{\mathrm{d}^2 \varepsilon^{\mathrm{KS}}}{\mathrm{d}k^2} \left( 1 + \frac{\mathrm{d}\Delta^{GW}}{\mathrm{d}\varepsilon} \Big|_{\varepsilon^{\mathrm{KS}}} \right) \right]^{-1}$$
(2.100)

$$= \frac{m_{\rm KS}}{1 + \frac{{\rm d}\Delta^{GW}}{{\rm d}\varepsilon}\Big|_{\varepsilon^{\rm KS}}}$$
(2.101)

#### 2.4.6 Conclusion

The GW method described in this section provides an accurate method to compute reliable quasiparticle electronic structure of materials. In particular, the band gap, which is well underestimated within DFT, is corrected by the GW technique, leading to values in much closer agreement with experiment. The main advantage of the method is that the quasiparticle eigenvalues are obtained as a first-order perturbation of a previous Kohn-Sham set of eigenvalues. The polyfit approximation, a very efficient and straightforward procedure to interpolate GW eigenvalues and densities of states, was developed and used in many parts of this thesis.

In spite of the considerable improvement in the computation of the band gap, the GW method is unsuitable for excitations involving two particles such as optical absorption. Indeed, it does not include any two-particle interaction term in its derivation. Electron-hole or *excitonic* interactions are thus neglected and optical spectra are not well reproduced for materials in which these are important, such as SiO<sub>2</sub>. The following section describes the theory needed in order to correctly include excitonic effects.

# 2.5 Optical properties and the Bethe-Salpeter equation

In an absorption process, an electron is promoted to a conduction band, leaving a hole in the valence band and creating an interacting electronhole pair. The one-particle Green's functions used are not sufficient to describe the evolution of the coupled electron-hole pair as their motions are correlated. In the Bethe-Salpeter (BS) formalism, the response of the system is described in terms of two-particles propagators involving fourpoint quantities. In this section, the main ingredients needed to obtain accurate optical spectra by means of the BS equation are presented.

#### 2.5.1 The 2-particles propagator

Whereas the one-particle Green's function defined in Eq. 2.69 describes the propagation of one particle (electron or hole), the 2-particles Green's function G(1'2'12) is the mathematical object describing the probability amplitude for two particles to go from one starting configuration to another :

 $\overbrace{(1,2)}^{\text{initial configuration}} \xrightarrow{final configuration} \overbrace{(1',2')}^{final configuration}$ 

where the time coordinate of (1', 2') and (1, 2) are t' and t respectively<sup>2</sup>. Formally, it is defined as

$$G(1'2'12) = (-i)^2 \langle \Psi_0 | \mathsf{T} \left[ \psi(1')\psi(1)\psi^{\dagger}(2)\psi^{\dagger}(2') \right] |\Psi_0\rangle$$
 (2.102)

The two-particle excitations (coupled electron-hole pair) can be obtained from the poles of the two-particle Green's function. Now that the mathematical object containing all the physical information useful for two-particles excitations is defined, all what is left is to find the equation that describes the concurrent motion of the electron and hole.

#### 2.5.2 The Bethe-Salpeter equation

The key quantity for this purpose is the four-point or electron-hole polarizability polarizability L

$$L(1234) = L^{0}(1234) - G(1234)$$
(2.103)

$$L^{0}(1234) = iG(13)G(42) \tag{2.104}$$

The independent electron-hole polarizability  $L^0$  in Eq. 2.103 namely describes the evolution of an electron and a hole separately. The 4-point

<sup>&</sup>lt;sup>2</sup>This way of specifying the time coordinates implies that the Green's function is in fact the particle-hole Green's function, as needed for the computation of optical absorption. Other time orderings can exist, defining particle-particle Green's functions used for example in the description of Auger processes.

polarizability comes from the solution of the so-called Bethe-Salpeter equation (BSE) :

$$L(1234) = L^{0}(1234) + \int L^{0}(1256)K(5678)L(7834)d5678 \qquad (2.105)$$

with the BS kernel K being defined as

$$K(1234) = \delta(12)\delta(34)\overline{v}(13) + i\frac{d\Sigma(13)}{dG(24)}$$
(2.106)

The modified Coulomb interaction  $\overline{v}$  is equal to :

$$\overline{v}(\mathbf{q}) = \begin{cases} 0 & \text{for} & \mathbf{G} = \mathbf{0} \\ v(\mathbf{q}) & \text{for} & \mathbf{G} \neq \mathbf{0} \end{cases}$$
(2.107)  
(2.108)

The BS kernel in Eq. 2.106 is made up of two terms. The first one corresponds to the Coulomb interaction between the electron and the hole. The second represent the change in the self-energy with respect to a change of the Green's function. As the self-energy is usually unknown, some approximation has to be used for this last term. Using the GW approximation for which the self-energy is expressed as  $\Sigma = iGW$ , the second term of Eq. 2.106 becomes

$$i\frac{\mathrm{d}\Sigma}{\mathrm{d}G} = -\frac{\mathrm{d}GW}{\mathrm{d}G} \tag{2.109}$$

$$= -W + G\frac{\mathrm{d}W}{\mathrm{d}G} \tag{2.110}$$

$$\approx -W$$
 (2.111)

Going from Eq. 2.110 to Eq. 2.111 follows from the fact that the term  $G\frac{\mathrm{d}W}{\mathrm{d}G}$ , which can be seen as the excitation self-screening (the change in the screening due to the excitation itself), is expected to be small [116]. Finally the BS equation reduces to

$$L(1234) = L^{0}(1234) + \int L^{0}(1256)(\delta(56)\delta(78)v(57) - \delta(57)\delta(68)W(56))L(7834)d5678$$
(2.112)

#### 2.5.3 Formulation as an eigenvalue problem

In order to solve the BS equation 2.112, it is easier to reformulate the problem as an effective eigenvalue problem. As the purpose of the problem is the description of electron-hole pairs, a clever idea is to use a basis made of the wavefunctions obtained from the solution of a one-particle Hamiltonian. The elements in the basis of this *transition space* are then built from the product of two single-particle wavefunctions  $\psi_i \psi_j$  such as, for example, products of KS  $\psi_i^{\text{KS}}$  or QP  $\psi_i^{\text{QP}}$  wavefunctions obtained from a prior DFT or *GW* calculation. It is expected that a relatively small number of wavefunctions will be sufficient to form a complete set for the range of solutions that are looked for. Any four-point function F(1234) is then expanded in this basis as :

$$F(1234) = \sum_{(n_1n_2)(n_3n_4)} \psi_{n_1}^*(1)\psi_{n_2}(2)F_{(n_1n_2)(n_3n_4)}\psi_{n_3}(3)\psi_{n_4}^*(4) \quad (2.113)$$

where the  $n_i$ 's stand for spin, **k**-point and band index and  $F_{(n_1n_2)(n_3n_4)}$ is given by

$$F_{(n_1n_2)(n_3n_4)} = \int F(1234)\psi_{n_1}(1)\psi_{n_2}^*(2)\psi_{n_3}^*(3)\psi_{n_4}(4)d1234 \quad (2.114)$$

The independent electron-hole polarizability in Eq. 2.104 can then be expressed in transition space as

$$L^{0}_{(n_{1}n_{2})(n_{3}n_{4})}(\omega) = \frac{f_{n_{2}} - f_{n_{1}}}{(\varepsilon_{n_{2}} - \varepsilon_{n_{1}} - \omega)} \delta_{n_{1}n_{3}} \delta_{n_{2}n_{4}}$$
(2.115)

and is diagonal in this representation.

By defining an effective or excitonic two-particle hamiltonian  $H^{\rm exc}$  :

$$H_{(n_1n_2)(n_3n_4)}^{\text{exc}} = (\varepsilon_{n_2} - \varepsilon_{n_1})\delta_{n_1n_3}\delta_{n_2n_4} + (f_{n_1} - f_{n_2})K_{(n_1n_2)(n_3n_4)}$$
(2.116)

the BS equation 2.105 can be rewritten in this transition space as

$$L_{(n_1n_2)(n_3n_4)} = \left[ H_{(n_1n_2)(n_3n_4)}^{\text{exc}} - I\omega \right]^{-1} F$$
 (2.117)

where I is the identity matrix and F is given by

$$F = \begin{array}{c} (n_1 n_2) \downarrow | \xrightarrow{(n_3 n_4)} (v'c'\mathbf{k}') & (c'v'\mathbf{k}') \\ F = \begin{array}{c} (vc\mathbf{k}) & \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{array}$$
(2.118)

Supposing that the material under study is a spin-unpolarized semiconductor and considering we are only interested in the long wavelength  $(\mathbf{q} \to \infty)$ , the excitonic hamiltonian has the following block structure :

$$H^{\text{exc}} = \begin{array}{c} (n_1 n_2) \downarrow | \xrightarrow{(n_3 n_4)} & (v'c'\mathbf{k}') & (c'v'\mathbf{k}') \\ (vc\mathbf{k}) & \begin{pmatrix} H^{\text{res}} & H^{\text{coupl}} \\ -H^{\text{coupl}*} & -H^{\text{res}*} \end{pmatrix}$$
(2.119)

The matrix elements of the resonant part are obtained as

$$H_{(vc\mathbf{k})(v'c'\mathbf{k}')}^{\text{res}} = (\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}})\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'} + 2\overline{v}_{(vc\mathbf{k})(v'c'\mathbf{k}')} - W_{(vc\mathbf{k})(v'c'\mathbf{k}')} \quad (2.120)$$

where the elements of  $\overline{v}$  and W are defined as

2.5. Optical properties and the Bethe-Salpeter equation

$$\overline{v}_{(vc\mathbf{k})(v'c'\mathbf{k}')} = \iint \psi_{v}(\mathbf{r})\psi_{c}^{*}(\mathbf{r})\overline{v}(\mathbf{r},\mathbf{r}')\psi_{v'}^{*}(\mathbf{r}')\psi_{c'}(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \qquad (2.121)$$
$$W_{(vc\mathbf{k})(v'c'\mathbf{k}')} = \iint \psi_{v}(\mathbf{r})\psi_{v'}^{*}(\mathbf{r})W(\mathbf{r},\mathbf{r}',\omega=0)\psi_{c}^{*}(\mathbf{r}')\psi_{c'}(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \qquad (2.122)$$

in which the static approximation ( $\omega = 0$ ) to the screened Coulomb interaction is used.

For bulk systems, the coupling terms are usually neglected, leading to the so-called Tamm-Dancoff approximation [117]. This approximation to the BS kernel is known to accurately describe optical absorption in solids while largely reducing the computational cost [118].

Once the solution of Eq. 2.117 is obtained, the macroscopic dielectric function can be computed from the two-point contraction  $\hat{\chi}(12) = L(1122)$  of the resulting 4-point polarizability :

$$\varepsilon_M(\omega) = 1 - \lim_{\mathbf{q} \to 0} v(\mathbf{q}) \hat{\chi}_{00}(\mathbf{q}, \omega)$$
(2.123)

whose imaginary part is the absorption spectrum.

The solution of Eq. 2.117 requires a diagonalization of a very large matrix in order to get the excitonic eigenvalues and wavefunctions. As our concern is to get optical spectra, an iterative method based on the Haydock algorithm [118, 119] is used instead. This technique provides a much faster way to compute the optical spectra but does not explicitly solve Eq. 2.117 such that the excitonic wavefunctions are not obtained.

The convergence of the BS technique with respect to the **k**-point grid is crucial. In fact, accurate optical spectra require a large sampling. This in turn implies that the screened Coulomb interaction should be calculated with this dense mesh. This is very computationally demanding and can be avoided by using a model dielectric function [120, 121] in which the static dielectric constant is used as a parameter.

#### 2.5.4 Conclusion

In the Bethe-Salpeter formalism, accurate optical properties can be achieved from first-principles calculations. The problem is solved in a so-called transition space made of products of wavefunctions. This allows to rewrite the BS equation as an eigenvalue problem. The optical spectra are then obtained from a solution of this eigenvalue problem either from a full diagonalization or from an iterative algorithm (the Haydock technique).
### Chapter 3

## Pure silica

Since the publication of the random network theory of glass structure by Zachariasen [122] and the early X-ray studies of Warren and coworkers[123, 124] in the 1930s, the structure of amorphous silicon dioxide  $(a-\text{SiO}_2)$  is known to form a network of randomly interconnected tetrahedra. These tetrahedra are composed of one silicon atom at the center and four oxygen atoms at the corners where each oxygen atom is shared by two tetrahedral units such that the total number of O atoms is twice that of the number of Si atoms. This short-range (SR) arrangement is illustrated for two corner-sharing tetrahedra in Fig. 3.1 in which the main SR structural properties such as bond lengths and angles can be identified.

Before studying the electronic and optical properties, an essential preliminary step is to generate a-SiO<sub>2</sub> models that are representative of a real vitreous structure. It has been shown that a sufficiently large set of small models is able to reproduce the structural features of experimental glass samples [37]. This chapter presents the results gathered from several a-SiO<sub>2</sub> models. First, the procedure used to generate the models combining classical MD (CMD) and ab initio refinement within DFT is presented. An extensive analysis of the structural properties is then performed in order to assess the quality of the models. The models are then used for electronic structure analysis in DFT and GW. Finally, the optical properties are presented.



Figure 3.1: Tetrahedral structure of a-SiO<sub>2</sub>.

#### 3.1 Generation of amorphous silica models

The amorphous silica models used in this thesis were prepared in two steps [35]. In the first step, an amorphous system is obtained within classical molecular dynamics using a melt-and-quench procedure. The resulting structure is then relaxed using DFT. The models thus obtained will be shown to describe the overall structural properties with a good accuracy.

The initial configurations for each model needed at the beginning of the MD simulations are set up by arranging randomly the atoms in a box whose volume is fixed to reproduce the experimental density  $\rho = 2.2 \text{g/cm}^3$ . Twenty different models each containing 72 atoms have been prepared using CMD and then further relaxed within DFT. Ten additional models with 648 atoms have also been produced with CMD in order to compare their structural properties to the smaller models. The CHIK potentials and the additional repulsive part for small radii presented in sect. 2.2.2 were used for the MD simulations. The integration of the EOMs is done using the leap-frog algorithm and a time step  $\tau = 1$  fs. For the temperature coupling, the Nosé-Hoover thermostat has been used with a time constant  $\tau_{\rm NH} = 0.02$  ps for the coupling strength. The melting and quenching is performed using the following temperature profile as illustrated by the solid red line in Fig. 3.2



Figure 3.2: Melting and quenching of a-SiO<sub>2</sub>. Temperature profile.

- The samples are melted at high temperature (5000 K) for 100 ps (I in Fig. 3.2).
- The system is then quenched down to 300 K at a cooling rate  $\gamma_1=10$  K/ps from 5000 K to 1000 K and  $\gamma_2=5$  K/ps from 1000 K to 300 K (II and III in Fig. 3.2).
- The system is then annealed at 300 K during 160 ps (IV in Fig. 3.2).

Figure 3.2 also shows the real temperature of the system as obtained in Eq. 2.21. The inset of the figure shows the evolution of the total energy of the system. At the end of the simulation, the configuration is taken as an input for further ab initio refinement of the structure.

The internal coordinates of the atoms have been relaxed in DFT using the Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm until the forces on all the atoms were less than  $1.10^{-5}$  Ha/Bohr. Other computational and technical details concerning the parameters for the DFT calculations are described in the next section. This first-principles relax-



Figure 3.3: Supercell of a-SiO<sub>2</sub>. The silicon and oxygen atoms are shown in green and red respectively. The purple and light blue highlighted atoms spot the presence of small rings of size n = 3-4.

ation resulted in slight changes in the structure, the overall connectivity of the network being unchanged. One of these models is illustrated in Fig. 3.3.

From the twenty models generated, 5 have been rejected because of a wrong coordination of some silicon and/or oxygen atoms or because of the presence of two edge-sharing tetrahedra. In the following sections, statistics are collected on the 15 remaining models. Appendix B gathers the properties of all the models generated in this work.

#### **3.2** Structural properties

Before going further in the analysis of the electronic and optical properties of pure a-SiO<sub>2</sub>, it is necessary to validate the models obtained from the combined CMD+DFT approach. For that purpose, the properties of the samples are compared to available experimental data. Basically, the structural properties in amorphous solids can be separated in four ranges : I. the structural unit (tetrahedron), II. the connection between these units (bond angles, ...), III. the overall network connectivity and IV. the long range density fluctuations. In this section, the two first ranges will be analyzed through the radial distribution functions, the bond lengths, the angular distribution functions and the bond angles whereas the rings statistics will be used to characterize the network connectivity. The last range will not be discussed in this thesis as it involves inhomogeneities that are on a more macroscopic scale.

# 3.2.1 Radial distribution functions and bond lengths

The total g(r) and partial radial distribution functions (RDF)  $g_{\text{Si}-\text{O}}(r)$ ,  $g_{\text{Si}-\text{Si}}(r)$  and  $g_{\text{Si}-\text{O}}(r)$  of pure *a*-SiO<sub>2</sub> are shown in Fig. 3.4. The CMD RDF is given by the dashed orange line while the ab initio relaxed one is the full black line. Obviously, the CMD already yields a very good initial configuration for the models and DFT does not bring any major change in the RDF's.

Bond lengths can be extracted from Fig. 3.4 and can be compared to experimental values [125]. For each pair Si-O, Si-Si and O-O, the two first peaks are clearly identified and are attributed to first and second neighbors. The results for both the CMD and ab initio relaxed (LDA) values are reported in Table 3.1.

The distances obtained are within 1-2% of the experimental values and in good agreement with previously reported theoretical values [33, 35, 36, 40]. This is already a first validation of the models generated. The first neighbor distances mainly characterize the short-range order while second neighbors give some information about the connectivity between the tetrahedral units.

#### 3.2.2 Angular distribution functions and bond angles

Another important aspect in the structure of an amorphous model consists in the bond angles. In a binary compound such as  $SiO_2$ , six different types of bond angles can be identified and the corresponding angle distribution functions are represented in Fig. 3.5. For the O-Si-O (inside the



Figure 3.4: Total and partial radial distribution functions in a-SiO<sub>2</sub>.

Table 3.1: Bond lengths in a-SiO<sub>2</sub> (in Å). The average  $\overline{r}$  Si-O, Si-Si and O-O distances for the first and second neighbors are given for the CMD simulations as well as for the ab initio relaxed models. The standard deviation  $\sigma$  is also reported.

		MD		LDA		Expt. [125]
		$\overline{r}$	$\sigma$	$\overline{r}$	$\sigma$	
Si-O	$1^{\mathrm{st}}$	1.63	0.04	1.61	0.02	1.62
	$2^{\mathrm{nd}}$	4.09	0.47	4.05	0.45	4.15
Si-Si	$1^{\mathrm{st}}$	3.12	0.11	3.16	0.12	3.12
	$2^{\mathrm{nd}}$	5.20	0.53	5.15	0.53	5.18
0-0	$1^{\mathrm{st}}$	2.65	0.10	2.60	0.09	2.65
	$2^{\mathrm{nd}}$	5.07	0.35	4.98	0.34	4.95



Figure 3.5: Angle distribution functions in a-SiO<sub>2</sub>.

tetrahedral unit) and Si-O-Si (between two tetrahedra) distributions, there is only one main peak in the distribution. The other bond angles clearly have two peaks in their distributions. Each peak can be identified to a particular angle in Fig. 3.1. For example, the first (blue) O-O-O peak corresponds to angles with the three atoms belonging to the same tetrahedron (O<sub>1</sub>-O<sub>2</sub>-O<sub>3</sub>) whereas the second one (green) appears to be connected to angles with the oxygen atoms in two adjacent tetrahedra (O<sub>1</sub>-O<sub>2</sub>-O<sub>5</sub>).

Table 3.2 reports the mean and standard deviation of the different bond angles illustrated in Fig. 3.5. For the Si-Si-Si, the small peak at about 60° is attributed to models where small rings (n = 3 - 4) as already noted in [126]. The agreement is good with the experimental values and other CMD/DFT values.

#### 3.2.3 Rings statistics

The medium-range structure (network connectivity) can be characterized by analyzing the rings in the amorphous structure. Many different types of rings can be defined. The type of rings analyzed here follows the shortest path criterion [128] : a ring is the shortest path between two of the nearest neighbors of a given atom. This definition differs slightly from the King's criterion [129] in which a ring is the shortest path that

	peak	MD		LDA		Expt./Theor.
		$\overline{ heta}$	$\sigma$	$\overline{ heta}$	$\sigma$	
O-Si-O	$\operatorname{main}$	109.4	6.4	109.4	5.5	$109.5 \ [125]$
Si-O-Si	$\operatorname{main}$	148.8	13.7	149.3	14.3	$147.9-151 \ [125, \ 127]$
Si-Si-Si	$\operatorname{main}$	108.1	19.9	108.5	19.3	107.7 [36]
0-0-0	a	59.0	5.4	59.0	5.1	$60 \ [126]$
	b	120.3	25.4	121.3	25.4	
O-O-Si	с	35.3	3.3	35.2	2.8	35 [126]
	d	124.7	26.8	126.1	26.5	
O-Si-Si	е	15.5	7.0	15.3	7.2	
	f	108.8	15.0	109.0	14.2	

Table 3.2: Mean and standard deviation of bond angles in a-SiO<sub>2</sub> (in °).

comes back to a given atom starting from one of its neighbors. In that case, some rings in the network might not be taken into account (see [128] for a detailed discussion).

The number of rings of each size is shown in Fig. 3.6. The number of rings has been normalized to one tetrahedron. The five small panels correspond to five different models that were generated and the main panel is the average ring size distribution of the fifteen 72-atom models generated and the average ring size distribution of ten 648-atom models. It is clear that separately, the small models do not reproduce the ring size distribution of the larger models but averaging over the fifteen small models leads to satisfactory agreement and reproduces previously published results [128].

#### 3.2.4 Conclusion

Fifteen models have been prepared and validated in this section. These models will be used in the following sections to investigate the electronic and optical properties of amorphous silica.



Figure 3.6: Rings statistics in a-SiO<sub>2</sub>. Each of the small figures correspond to a particular 72-atom model while the larger is the average distribution of the fifteen 72-atom models generated (in blue) and of ten 648-atom models generated (in orange).

#### **3.3** Electronic structure

Electronic structure calculations have been performed on the relaxed models presented in the previous sections. The ground-state densities have been computed using DFT. Using Bader analysis, the charge transfer from silicon to oxygen has been obtained and the Bader charges were used to compute atom and angular momentum projected densities of states. The band gap and the excited states have been computed using the GW approximation. Comparisons with crystalline SiO<sub>2</sub> in the  $\alpha$ -quartz structure ( $\alpha$ -SiO<sub>2</sub>) have also been performed for some of the above-mentioned properties.

In all the calculations of this chapter, norm-conserving pseudopotentials (see Sect. 2.3.4) have been employed and the LDA has been used as the exchange-correlation functional in DFT. The wavefunctions were expanded using plane waves up to 40 Ha energy cut-off. The relaxations in the previous section were done with the  $\Gamma$ -point only. The *GW* calculations have been performed using the Godby and Needs (GN) plasmon-pole model (see Chapter 6 for a detailed analysis of the model in the case of  $\alpha$ -SiO<sub>2</sub>) for the frequency dependence of the dielectric function. This dielectric matrix was expanded using plane waves with a maximum energy cut-off of 6 Ha. The *extrapolar method* [130, 131] has been used with a compensation energy of 2 Ha in order to reduce the number of empty states included in the computation of the polarizability and the self-energy.

#### 3.3.1 Valence density of states

The valence density of states (DOS) has been obtained for the 15 models selected previously and compared to X-ray photoemission spectra [132]. Two different methods were used and are illustrated in Fig. 3.7. The DOS obtained with the tetrahedron method [133] on a  $2 \times 2 \times 2$  **k**-point mesh followed by a gaussian smearing is given by the filled blue curve for DFT and by the filled orange curve for GW (obtained using Eq. 2.94) while a simple gaussian smearing on a  $\Gamma$ -point only computation is represented by the full blue line (DFT only). A good agreement between the two DFT DOS is achieved, which corroborates the sufficient convergence on the number of **k**-points. Both the DFT and GW DOS agree reasonably well with experimental curves in black and red (enlarged for the higher valence states) though GW tends to broaden the DOS and push the states further from the Fermi level.

Except for a much more peaked structure, the DOS of  $\alpha$ -SiO<sub>2</sub> is essentially similar to the *a*-SiO<sub>2</sub> one. One can identify mainly three groups of electronic states : the first group ranges from -20 eV to -16 eV and totalizes 4 electrons, the second, from -5 eV to -10 eV, with 4 electrons also, and the upper valence group, from the Fermi level to -5 eV, summing up the last 8 electrons. These groups will be analyzed in more detail from the projected DOS.

#### 3.3.2 Charge transfer

The valence electronic charges have been reported in Table 3.3. The Hirshfeld [135] and Bader [136] analysis have both been computed from the ground-state densities. As expected from the electronegativities of



Figure 3.7: Valence density of states (DOS) and integrated density of states (IDOS) of a-SiO<sub>2</sub> and  $\alpha$ -SiO<sub>2</sub> in DFT (filled blue curve) and GW (filled orange curve). The DOS are normalized to one SiO<sub>2</sub> unit. The DOS have been obtained with the tetrahedron method (2×2×2 **k**-point mesh for a-SiO<sub>2</sub> and 4×4×4 **k**-point mesh for  $\alpha$ -SiO<sub>2</sub>,) smeared with a gaussian whose FWHM=0.4 eV. For a-SiO<sub>2</sub>, the green line is the DFT DOS obtained with a simple gaussian smearing (same FWHM) on a  $\Gamma$ -point computation. The integrated DFT DOS is given by the dashed blue line. The X-ray photoemission spectra [132, 134] are illustrated by the black and red lines.

	Ba	der	Hirshfeld		
	a-SiO <sub>2</sub>	$\alpha$ -SiO <sub>2</sub>	a-SiO <sub>2</sub>	$\alpha$ -SiO <sub>2</sub>	
Silicon	0.89	0.91	3.56	3.58	
Oxygen	7.55	7.55	6.22	6.21	

Table 3.3: Valence Bader and Hirshfeld electronic charges in a-SiO<sub>2</sub> and  $\alpha$ -SiO<sub>2</sub> (in electrons).

the oxygen and silicon atoms, there is a transfer of electrons from the silicon atoms to the oxygen atoms. The Bader charges lead to a much larger transfer than the ones obtained with the Hirshfeld method. This large quantitative difference is a known effect of the two analysis.

The atomic charges for a-SiO<sub>2</sub> and  $\alpha$ -SiO<sub>2</sub> differ by a very small amount (on the order of the errors of the methods). Indeed, the local environments of the atoms in both solids are very similar : both share the same tetrahedral unit and the Si-O bond length (1.61 Å) in  $\alpha$ -SiO<sub>2</sub> is almost equal to the average value in a-SiO<sub>2</sub>. One can note that the Bader electronic charges are close to the usual assumption of the Si<sup>4+</sup> and O<sup>2-</sup> configurations in SiO<sub>2</sub> (Si<sup> $\sim$ 3.2+</sup> and O<sup> $\sim$ 1.55-</sup> from Bader). These Bader charges have thus been used to define an *equivalent Bader radius* for each atom for which the integrated charge inside the corresponding sphere is equal to the Bader charge. For the silicon atom, this radius is  $\sim$  1.56 Bohr in both  $\alpha$ -SiO<sub>2</sub> and a-SiO<sub>2</sub>. For the oxygen atom, the equivalent Bader radius is  $\sim$  2.53 Bohr and  $\sim$  2.57 Bohr in  $\alpha$ -SiO<sub>2</sub> and a-SiO<sub>2</sub> respectively. The angular projected DOS have been computed inside the spheres defined by these equivalent Bader radii.

#### 3.3.3 Partial densities of states

The partial densities of states (pDOS) are shown in Fig. 3.8. They have been normalized to each atom's Bader volume in which the projections were performed. In this case, the pDOS are then given per unit of volume and can be superimposed with the DOS per volume, for a better comparison. On the other hand, this normalization increases the scale for the silicon by a factor  $\sim 9$  and cuts out some information about the real proportion of silicon/oxygen states.

The projected densities of states allows to better identify the three groups in the valence. The lowest lying group has a strong oxygen *s*-character and a very small amount of silicon *s*- and *p*-states and is clearly identified as the oxygen 2*s*. The states between -5 eV and -10 eV are mainly composed of oxygen *p*- and some silicon *s*- and *p*-orbitals  $(sp^3 \text{ hybrid states})$  and correspond to bonding  $O_{2p}$ -Si<sub>sp3</sub> states. The remaining group between -5 eV and the Fermi level is almost entirely made of oxygen *p*-states and is attributed to  $O_{2p}$  non-bonding orbitals.

#### 3.3.4 Band gap and excited states

The experimental band gap in a-SiO<sub>2</sub> and  $\alpha$ -SiO<sub>2</sub> is still a matter of debate [26, 137] with values ranging from 7.5 to 11.5 eV [138, 139, 140, 141] (see Table 3.4). While it is generally accepted that the optical absorption in a-SiO<sub>2</sub> is slightly red-shifted (0.1-0.5 eV) with respect to  $\alpha$ -SiO<sub>2</sub> [137, 142], no strong evidence has been put forward about the difference between their respective band gaps [27, 49].

The theoretical band gaps obtained within DFT and the GW approximation are reported in Table 3.4. As expected, DFT strongly underestimates the band gaps of both materials. The GW corrections open the gap to values closer to the experimental ones. In both cases, the GW correction amounts to approximately 3.2 eV. This is not in agreement with what is shown in [49], where the GW correction for amorphous structures is larger than for  $\alpha$ -quartz. They explain this difference from the presence of small rings (3- and 4-membered) in a-SiO<sub>2</sub>, which are not found in  $\alpha$ -SiO<sub>2</sub> (which only contains 6- and 8-membered rings). This straight conclusion is surprising and indeed, the large diversity of ring sizes and the presence of small rings (see the highlighted atoms in Fig. 3.3) in the amorphous models presented here do not lead to significant differences in the GW corrections. The discrepancy between the values obtained and the experimental values is rather to be found in one of the approximation used, namely the use of a one-shot GW instead of



Figure 3.8: Partial densities of states in a-SiO<sub>2</sub>. The thick blue, blue green and red lines correspond to the GW s-, p- and d-projected DOS for silicon in three upper panels and for oxygen in the three lower panels. The thin black lines correspond to the DFT pDOS in each panel. The total DFT and GW DOS are given as the filled blue and orange curves. All the DOS have been normalized to the volume onto which they were computed.

	LDA	$G_0W_0$	Theor.	Expt.
a SiO-	. 5 2		$5.6^{\rm a},  5.36^{\rm b}, 9.3^{\rm c}$	$9.3^{\rm d},11^{\rm e},1111.5^{\rm f}$
$a-51O_2$	$\sim 0.5$	$\sim 0.0$	$9.4-9.6^{\rm g},10.1^{\rm h}$	$8.8\text{-}8.9^{\rm i}, 7.64\text{-}9.56^{\rm j}$
$\alpha$ -SiO <sub>2</sub>	6.06	9.27	$5.8^{\rm k},  5.9^{\rm l},  9.4^{\rm m}, 10.1^{\rm n}$	$8.29-9.55^{\circ}, 8.9^{p}$
<sup>a</sup> DFT-L	DA [40] a	nd [27] <sup>b</sup>	DFT-LDA [60] $^{\circ}G_0W_0@I$	LDA [60] <sup>d</sup> [139] <sup>e</sup> [26]

Table 3.4: Theoretical and experimental (direct) band gaps in a-SiO<sub>2</sub> and  $\alpha$ -SiO<sub>2</sub> (in eV).

<sup>a</sup> DFT-LDA [40] and [27] <sup>b</sup> DFT-LDA [60] <sup>c</sup>  $G_0 W_0$ @LDA [60] <sup>d</sup> [139] <sup>e</sup> [26] <sup>f</sup> [138] <sup>g</sup>  $G_0 W_0$ @LDA [49] <sup>h</sup> COHSEX [27] <sup>i</sup> [140] <sup>j</sup> [141] <sup>k</sup> DFT-LDA [60] <sup>l</sup> DFT-LDA [27] <sup>m</sup>  $G_0 W_0$ @LDA [60] <sup>n</sup>  $G_0 W_0$ @LDA [28], COHSEX [27] and QPscGW [97] <sup>o</sup> [141] <sup>p</sup> [140]

a fully or partially self-consistent scheme. This is unfortunately out of reach for large systems with the present computational resources.

As shown in Table 3.4 and from the above discussion, the value of the quasiparticle band gap of a-SiO<sub>2</sub> is not yet clearly determined. This issue will be put forward again when discussing the optical properties in the next section. As a matter of fact, a good description of the excited states, and in particular of the band gap, is a prerequisite for optical calculation.

The electronic structure for the excited states is also obtained within the GW method. The GW density of states has already been presented in Fig. 3.7 and 3.8. The overall energy dependence of the GW corrections obtained using the polyfit energy approximation is shown in Fig. 3.9 for one model with two different sets of **k**-points : (a) the  $\Gamma$ -point (referred to as Pfit<sub> $\Gamma$ </sub>) and (b) a 2×2×2 mesh (referred to as Pfit<sub>222</sub>). The rigidshift approximations Sciss<sub> $\Gamma$ </sub> and Sciss<sub>222</sub> from the two **k**-point sets are also shown in the figure as the dashed lines in (a) and (b). The error arising from using the polyfit on these two **k**-point sets is shown in (c) and the corresponding GW DOS aligned to the Fermi level are plotted in (d). The inset in (d) is an enlarged view of the conduction DOS. As shown in (c), the error amounts to maximum 0.1 eV for valence states



Figure 3.9: GW corrections in a-SiO<sub>2</sub>.

and 0.2 eV for conduction states and the use of the  $Pfit_{\Gamma}$  as compared to the  $Pfit_{222}$  leads to a red shift of the conduction DOS by ~0.1 eV.

From the GW DOS obtained from the previous polyfits, one can calculate a joint density of states  $J(\omega)$  (JDOS) as :

$$J(\omega) = \int N_{\rm v}(E) N_{\rm c}(E+\omega) \mathrm{d}E \qquad (3.1)$$

where  $N_{\rm v}(E)$  and  $N_{\rm c}(E)$  are the valence and conduction DOS respectively. As a very rough approximation, the optical absorption spectrum can be considered proportional to this JDOS (neglecting oscillator matrix elements and excitonic effects). It corresponds to the density of possible independent transitions of a given energy and is illustrated in Fig. 3.10 (a).

The inset in Fig. 3.10 (a) shows that the JDOS obtained from  $\text{Pfit}_{\Gamma}$  is red-shifted by ~0.1 eV, as expected from the conduction shift mentioned previously. The lower panel (b) illustrates the minimum, maximum and mean errors in the transition energies obtained from the two polyfits where the mean error for each polyfit is roughly constant. This justifies the use of the polyfit interpolation of the quasiparticle energies used in the electron-hole basis sets for the computation of optical properties. Additionally, the use of a polyfit obtained from a *GW* calculation at the  $\Gamma$ -point gives rise to a small and constant lowering of the transition energies and can thus be corrected for *a posteriori*.

#### **3.4** Optical properties

The joint density of states presented in the previous section provides an approximation for the imaginary part of the dielectric constant, neglecting excitonic effects and transition probabilities (also called optical matrix elements). Instead, by using the JDOS weighted by these optical matrix elements, one can define the non-interacting or *random-phase* approximation (RPA) of the dielectric function. As clearly illustrated in Fig. 3.11 (b) for  $\alpha$ -SiO<sub>2</sub>, the RPA macroscopic dielectric function do not reproduce the experimental spectra (black line) when using the DFT eigenvalues (full red line). Adding the *GW* corrections using a



Figure 3.10: (a) Joint density of states using the polyfit approximations  $\operatorname{Pfit}_{\Gamma}$  (thin blue line) and  $\operatorname{Pfit}_{222}$  (thin orange line) as compared to the exact one (thick black line) and to the rigid-shift approximations  $\operatorname{Sciss}_{\Gamma}$  (green line) and  $\operatorname{Sciss}_{222}$  (red line) taken respectively on the  $\Gamma$ and  $2 \times 2 \times 2$  **k**-point grids *GW* calculations. The red ruler in the inset shows the error from  $\operatorname{Pfit}_{\Gamma}$ . (b) Maximum, minimum (upper and lower thin lines) and mean (thick line) errors in the transition energies using  $\operatorname{Pfit}_{\Gamma}$  (blue) and  $\operatorname{Pfit}_{222}$  (orange). The mean errors using the rigid-shift approximations  $\operatorname{Sciss}_{\Gamma}$  and  $\operatorname{Sciss}_{222}$  are given as the green and red lines respectively.



Figure 3.11: (a) Schematic illustration of the rigid-shift and polyfit approximations (b) Independent-particle approximation of  $\epsilon_2(\omega)$  in  $\alpha$ quartz. The full red line corresponds to the RPA approximation using the Kohn-Sham (LDA) levels while the dashed green and full blue curve corresponds to the RPA approximation using the *GW*-corrected levels obtained respectively from a rigid shift of the KS conduction states and from a polyfit interpolation. The experimental spectrum is shown in black.

rigid-shift (dashed green line) or a polyfit approximation (full blue line) does not improve the agreement with the experiments. As mentioned in Sect. 2.5, this discrepancy is due to the lack of electron-hole interaction in the computation of the dielectric function.

In this section, the optical properties are obtained from the solution of the Bethe-Salpeter equation. The optical spectra of crystalline and amorphous silica will be presented. Emphasis will be put on the different levels of approximations that can be used. Results obtained with a rigid shift of the unoccupied states are compared to those obtained with the polyfit interpolation. Additionally, the use of a model dielectric function [120, 121] for the static screening matrix in the BS kernel is found to yield very satisfactory results as compared to a computation performed with the exact dielectric function. Finally, it is shown that the actual quasiparticle band gaps of a-SiO<sub>2</sub> and  $\alpha$ -SiO<sub>2</sub> can be deduced through reverse engineering by comparing the theoretical and experimental spectra.

#### **3.4.1** Optical spectra of $\alpha$ -quartz

Using the formalism introduced in Sect. 2.5, the absorption spectra of  $\alpha$ -SiO<sub>2</sub> are in a much better agreement with the experimental ones. This has already been shown for the crystalline form in previous studies [28, 30, 97]. First, these results for  $\alpha$ -SiO<sub>2</sub> are reproduced analyzed in details. In particular, the rigid-shift approximation is found to be insufficient and a more decent approximation for the electron-hole basis set as given by the polyfit interpolated values leads to a much better agreement with experiment. The procedure is used to obtain optical spectra for the amorphous phase, which has not yet been done to our knowledge.

The imaginary part of the macroscopic dielectric function of  $\alpha$ -SiO<sub>2</sub> computed with the quasiparticle eigenstates from a rigid shift (in red) and from a polyfit interpolation is illustrated in Fig. 3.12 where the experimental spectrum [143] is given as the thick black line. In the same figure, the corresponding RPA dielectric function obtained using the same QP eigenstates is given by the dot-dashed lines. The results were obtained with a  $4 \times 4 \times 4$  randomly shifted **k**-point grid including 18 occupied and 24 unoccupied states in the electron-hole basis set. The BS kernel has been constructed using the DFT-RPA screened Coulomb interaction.

First of all, the inclusion of excitonic effects by using the BS equation clearly improves upon RPA but the overall structure appears to be slightly too low in energy. This is most probably due to the QP gap which is underestimated with respect to its (not so well known) experimental value. Indeed, Kresse *et al.* [97] obtained a value of 10.1 eV for the direct gap at  $\Gamma$  by using quasiparticle self-consistent *GW* [144] (sc-QP*GW*). On the other hand, Chang *et al.* came up with the same value for the gap from a one-shot *GW* but using a plasmon-pole that artificially increases the band gaps [111, 112] (see also Chapter 6). Using



Figure 3.12: Macroscopic dielectric function  $\epsilon_2(\omega)$  in  $\alpha$ -SiO<sub>2</sub> : rigidshift (in red) and polyfit (in green) approximations (BS spectra : full lines. RPA spectra : dot-dashed lines). The black line corresponds to the experimental spectrum [143].

an additional scissor for both the rigid-shift and polyfit approximations in order to get this same value for the direct gap (results referred to as Sciss<sup>+</sup> and Pfit<sup>sciss</sup>) lead to the optical spectra in Fig. 3.13.

When this additional correction for the QP gap is used, the agreement with experiments in much better for Pfit<sup>sciss</sup>. In particular, the position of the peaks are much closer to the experimental ones and to other reported theoretical results as shown in Table 3.5. For the Sciss<sup>+</sup> results, the agreement is as good for the first peak but worsens for the other peaks. This follows from the fact that the energy dependence of the *GW* particle corrections is not taken into account. This results in a red-shift of the transition energies as previously shown in the joint density of states for a-SiO<sub>2</sub> in Fig. 3.10 which in turn leads to the squeezing observed in the dielectric spectrum.

The comparison of the dielectric function obtained with the Pfit<sup>sciss</sup> approximation with and without excitonic effects reveals that the two first peaks are clearly excitonic, as already mentioned by Chang *et al.* [28]. However, they also described the third and fourth peaks as



Figure 3.13: Macroscopic dielectric function  $\epsilon_2(\omega)$  in  $\alpha$ -SiO<sub>2</sub> : rigidshift (Sciss<sup>+</sup>, in red) and polyfit (Pfit<sup>sciss</sup>, in green) approximations plus scissor (BS spectra : full lines. RPA spectra : dot-dashed lines). The black line corresponds to the experimental spectrum.

Table 3.5: Position of the peaks of  $\epsilon_2(\omega)$  in  $\alpha$ -SiO<sub>2</sub> (in eV). The relative positions of the 2<sup>nd</sup>, 3<sup>d</sup> and 4<sup>th</sup> peaks with respect to the first one is given between parenthesis. Theoretical results obtained by Chang *et al.* [28] and Kresse *et al.* [97] are also reported.

$n^{\rm th}$ peak	$1^{\mathrm{st}}$	$2^{\mathrm{nd}}$	$3^{d}$	$4^{\mathrm{th}}$
$\mathrm{Pfit}^{\mathrm{sciss}}$	10.55	$11.5 \ (0.95)$	14.15(3.6)	16.8(6.25)
$\mathrm{Sciss}^+$	10.3	$11.2 \ (0.9)$	$13.65\ (3.35)$	16(5.7)
Chang <i>et al.</i>	10.1	11.3(1.2)	13.5(3.4)	17.5(7.4)
Kresse <i>et al.</i>	10.3	11.45(1.15)	14.0(3.7)	17 (6.7)
Expt. [142, 145]	10.45	11.55(1.1)	14.2(3.75)	$16.7 \ (6.25)$

being largely excitonic while this is not so clear in Fig. 3.13. Indeed, in the range from 13 to 18 eV, the GW-RPA spectrum show features that are very similar to the BS spectrum. An analysis of the excitonic wavefunctions would certainly help the interpretation but goes beyond the scope of this thesis.

In the work by Chang *et al.*, the set of QP eigenvalues used to construct the electron-hole basis set has been obtained from a one-shot GWcalculation starting from a DFT-LDA calculation, as in this work. On the contrary, they used the Hybertsen and Louie (HL) plasmon-pole model [108] and included some kind of self-consistency in the BS computation while the Godby and Needs model [109] has been used here. The former has been shown to artificially increase the band gap with respect to a full-frequency GW computation [110, 111, 112] (see also Chapter 6). As a matter of fact, the one-shot GW is unable to determine the correct QP gap of  $\alpha$ -SiO<sub>2</sub> while self-consistent GW with vertex corrections seems to remedy this problem as shown by Kresse et al. [97]. The HL model also leads to an overestimation of the dispersion of the quasiparticle eigenvalues, which could explain the necessity to include self-consistency in their BS approach. Here, though the GW gap itself is underestimated, the relative position of the peaks is well described. This indicates that the dispersion is fairly well represented, without any self-consistency in the BS computation, similar to what was done in Kresse et al. [97].

Table 3.6 reports the values of the macroscopic dielectric constants and the birefringence value  $\Delta n = n_e - n_o \simeq \sqrt{\epsilon_e} - \sqrt{\epsilon_o}$  (e and o stands for the extraordinary and ordinary rays, along and perpendicular to the trigonal axis respectively) obtained with the different approximations. The KS-RPA values are surprisingly close to the experimental values. On the contrary, the GW-RPA (whatever the scheme used for the interpolation of the QP eigenvalues) leads to a large underestimation while the BSE recovers a good agreement, the best interpolation scheme being the Pfit<sup>sciss</sup>.

As already mentioned previously, the RPA screened Coulomb interaction W from the Kohn-Sham DFT eigenvalues has been used in

Table 3.6: Electronic contribution to the macroscopic dielectric constants and birefringence  $\Delta n$  in  $\alpha$ -SiO<sub>2</sub> using the different approximations mentioned in the text, as compared to experiment [146] and to results obtained using density functional perturbation theory with (DFPT<sup>sciss</sup>) and without (DFPT) a scissor correction of 1.8 eV [21]. The two components  $\epsilon_{\infty}^{xx} = \epsilon_{\infty}^{yy}$  and  $\epsilon_{\infty}^{zz}$  correspond to the dielectric constant in the hexagonal plane and in the z direction (along the trigonal axis) respectively.

		$\epsilon_{\infty}^{xx}{=}\epsilon_{\infty}^{yy}$	$\epsilon_{\infty}^{zz}$	$\Delta n$
KS-RPA		2.377	2.403	0.0084
$GW ext{-}RPA$	$\operatorname{Pfit}^{\operatorname{sciss}}$	2.052	2.067	0.0052
	$\mathrm{Sciss}^+$	2.079	2.095	0.0055
	Pfit	2.097	2.113	0.0055
BSE	$\operatorname{Pfit}^{\operatorname{sciss}}$	2.335	2.365	0.0098
	$\mathrm{Sciss}^+$	2.387	2.417	0.0097
	Pfit	2.419	2.451	0.0103
Expt		2.356	2.383	$\sim 0.009$
DFPT		2.527	2.566	0.0122
$\mathrm{DFPT}^{\mathrm{sciss}}$		2.353	2.385	0.0104



Figure 3.14: Macroscopic dielectric function  $\epsilon_2(\omega)$  in  $\alpha$ -SiO<sub>2</sub> with (in green) and without (in blue) using a model dielectric function. The experimental spectrum is shown in black.

the construction of the excitonic hamiltonian (see Eq. 2.120). This is a customary procedure whose justification lies in the fair agreement with experiment of the KS-RPA value of the static (electronic) dielectric constant  $\epsilon_{\infty} = \epsilon_1(\omega = 0)$ . Another commonly used approximation for the screened Coulomb interaction used in the BS equation is to derive it from a model dielectric function [120, 121] (MDF). The only (external) parameter for the MDF is precisely the value of the static dielectric constant  $\epsilon_{\infty} = \sim 2.39$  (chosen here as the average of the two components in Table 3.6). One then avoids the computation of the full RPA dielectric function for each **q**-point and reduces drastically the computational time. The results with a MDF-derived (blue line) and with the full KS-RPA (green line) screened Coulomb interaction are compared in Fig. 3.14. The agreement is very good, in particular for the position of the peaks which are almost unaffected.

Using a MDF, the convergence with respect to the number of **k**points is much easier. Up to here, all the spectra presented were obtained using a randomly shifted  $4 \times 4 \times 4$  **k**-point grid. As shown in Fig. 3.15, the macroscopic dielectric function is not completely converged with this



Figure 3.15: Convergence in **k**-points of the macroscopic dielectric function  $\epsilon_2(\omega)$  in  $\alpha$ -SiO<sub>2</sub>. The red, green and blue curves correspond respectively to a 2×2×2, a 4×4×4 and a 6×6×6 **k**-point grid.

grid but the position of the peaks is only slightly affected, even for the smaller **k**-point grid. The first peak is pretty much the same with the two larger grids while the lowest one leads to a cutting-down in amplitude. On the other hand, the second peak shows some structured variation at  $\sim 13.2$  eV in the  $4 \times 4 \times 4$  grid that are not present in the experimental spectrum while the third and fourth peaks are pretty much converged. These observations will serve as a basis for the amorphous models as these imply a much larger cost in computational time and memory and for which BS calculations are performed with only one **k**-point.

The results obtained in this section shed some light on the actual value of the direct gap in  $\alpha$ -SiO<sub>2</sub>. It is based on the comparison of the experimental spectrum of  $\epsilon_2(\omega)$  with the theoretical one, solution of the BS equation. The relative peak positions are fairly well reproduced as observed in Table 3.5 and this constitutes some indirect evidence of the reliability of the overall energy dispersion of the  $G_0W_0$  eigenvalues of both the valence and conduction states though the value of the band gap is clearly underestimated. The band gap can thus in turn be obtained by shifting the spectrum in order to reflect the absolute peak positions. Its actual value appears to be approximately equal to the sc-QPGW value of 10.1 eV. Of course, in the process discussed above, several approximations are used, but based on the errors in the relative positions of the peaks, one can reasonably estimate the error on the band gap inferred here to be about 0.2 eV. This is consistent with recent experimental results in a-SiO<sub>2</sub> and  $\alpha$ -SiO<sub>2</sub> [26] and thus partially solves the problem of the band gap in quartz. A full analysis of the excitonic wavefunctions should indeed be performed in order to confirm these findings and is thus a possible route for future work.

#### 3.4.2 Optical spectra of amorphous silica

For a-SiO<sub>2</sub>, a similar procedure involving the polyfit interpolation of the  $G_0W_0$  eigenvalues followed by an additional rigid shift has been used. The results presented here are performed with a model dielectric function. As for  $\alpha$ -SiO<sub>2</sub>, the RPA-KS static dielectric constant  $\epsilon_{\infty}$  is rather well described with a mean value of 2.14 to be compared with the experimental value ranging from 2.11 to 2.18 [147, 148] and with the theoretical value of 2.14 from Ref. [46]. This value has been used as the parameter for the MDF.

The macroscopic dielectric function has been obtained for four different models. The computations were carried out separately on four different **k**-points. Three different directions of the **q** vector of light were obtained and averaged for each model and **k**-point. The resulting macroscopic dielectric function is given in Fig. 3.16 (a) to (d) for each model (in blue). A common additional rigid shift of 1.27 eV had to be chosen in order to align the first peak with the experimental spectra [142]. The *GW*-RPA dielectric function is given by the dot-dashed green line. Another possibility is to align each model separately, in which case the shifts needed to align the first peak are respectively 1.38, 1.42, 1.17 and 1.1 eV for the models in (a)-(d). These two alternatives have been used for the averaging procedure.

The theoretical spectra obtained are not in a so good agreement with the experiments as for the  $\alpha$ -SiO<sub>2</sub> case. The first peak is rather well described in amplitude while its position is fixed by construction. On



Figure 3.16: Macroscopic dielectric function in a-SiO<sub>2</sub>. Four different models (in blue) are shown in panels (a) to (d). The BS and GW-RPA spectra are given by the full blue and dot-dashed green lines respectively. The experimental spectrum [142] is given by the black line.

the other hand, the second peak is clearly underestimated and its maximum value does not correspond with the experimental position of the peak. As discussed in the previous section for  $\alpha$ -SiO<sub>2</sub>, the second peak is quite affected by **k**-point convergence. This discrepancy is thus likely to be attributed to the underconverged **k**-point grid (only one **k**-point in each computation). The missing spectral weight is expected be recovered by including more than one  $\mathbf{k}$ -point in the electron-hole basis set which in turn could reconcile the theoretical position of the peak with the experimental one. Concerning the other two peaks, their respective position is relatively well reproduced in each model. In the crystalline case, these peaks were not as influenced by **k**-point convergence as the second one, which tends to justify the validity of these peaks. The averaged spectra for the four models is given in Fig. 3.17 and the positions of the peaks are reported in Table 3.7. Except for the first peak which is slightly broadened when using a common shift, the resulting spectra are not much changed when using a common shift or separate shifts



Figure 3.17: Macroscopic dielectric function in a-SiO<sub>2</sub> averaged over four models. The BS and *GW*-RPA spectra are given by the full and dot-dashed lines respectively. The blue and green colors correspond to the spectra obtained with a common additional shift for the models and a separate shift for each model respectively. The experimental spectrum [142] is given by the black line.

for each model. In particular, the positions of the peaks remain almost unaffected.

In view of the above discussions, the value of the QP band gap in amorphous silica can also be inferred from the value of the additional rigid shifts needed to align the theoretical spectra with the experimental one. The direct QP band gaps obtained for the four models presented are respectively 9.85, 9.73, 9.73 and 9.68 eV, with a mean value of 9.75 eV. This latter value is slightly smaller than the QP gap in  $\alpha$ -quartz and is consistent with the known trend of small disorder implying a small closure of the gap. Similarly to what was found in the work by Martin-Samos *et al.* [49], the quasiparticle corrections to the LDA gap (including the additional shifts) are slightly larger for the amorphous phase than for  $\alpha$ -quartz. On the contrary, the actual values obtained in Ref. [49] are smaller than those obtained here. The reliability of the QP gaps determined in this work is supported by the optical absorption

Table 3.7: Position of the peaks of  $\epsilon_2(\omega)$  in *a*-SiO<sub>2</sub> (in eV). The relative positions of the 2<sup>nd</sup>, 3<sup>d</sup> and 4<sup>th</sup> peaks with respect to the first one are given between parenthesis. Experimental results [142, 145] are also reported.

$n^{\rm th}$ peak	$1^{\mathrm{st}}$	$2^{nd}$	$3^{d}$	$4^{\mathrm{th}}$
$\mathrm{Pfit}^{\mathrm{sciss}}$	10.5	$11.45\ (0.95)$	14.1 (3.6)	16.6(6.1)
Expt. $[142, 145]$	10.5	11.85(1.35)	13.9(3.4)	16.6(6.1)

results, which were not investigated in Ref. [49]. The results obtained for a-SiO<sub>2</sub> are of course more questionable than those of  $\alpha$ -SiO<sub>2</sub> due to **k**-point convergence and further computations with larger **k**-point grids should be performed in order to reproduce the experimental spectrum more accurately and verify the correctness of the gap inferred.

#### 3.5 Conclusion

Models of amorphous silica containing 72 atoms have been prepared using classical molecular dynamics and ab initio relaxation. The resulting structures have been analyzed in detail. Their structural properties (bond lengths, bond angles, rings statistics) are in good agreement with experimental data and with previously published results. Using DFT and the *GW* approximation, the electronic structure of *a*-SiO<sub>2</sub> has been compared to the most commonly found crystalline polymorph :  $\alpha$ -quartz. The optical properties have then been investigated by solving the Bethe-Salpeter equation. The one-shot *GW* technique has been found to be insufficient to reproduce the QP gap in SiO<sub>2</sub>. It has been shown that the direct QP gap can be obtained from a reverse-engineering procedure instead. The present results indicate that the direct QP gap in *a*-SiO<sub>2</sub> (9.75 eV) is slightly smaller than the direct QP gap in  $\alpha$ -SiO<sub>2</sub> (10.1 eV). The models generated here will be used in the next chapter for the analysis of charged states of hydrogen in amorphous silica.

### Chapter 4

# Hydrogen-containing silica

Defects are inevitably present in the materials due to their fabrication process. In the manufacturing of optical fibers, MOS transistors and other devices using SiO<sub>2</sub>, hydrogen atoms can be trapped in the bulk material in several forms : molecular H<sub>2</sub>, neutral H<sup>0</sup>, O-H<sup>+</sup>, Si-H<sup>-</sup>, .... Their presence can affect the electronic and optical properties. Moreover, when the device is used in a given environment, with high temperature, potential irradiation and other possibly harmful conditions, these sites can be excited, resulting in other defect centers and a degradation of the properties [1, 149]. In this chapter, the neutral and charged states of hydrogen are investigated by means of DFT and *GW* electronic structure calculations. The structure of these defects is first presented. The corresponding energy levels are computed from *GW* computations. Defect formation energies obtained from DFT are then presented. Finally, some *GW*-corrected formation energies are put up in a perspective of future work.

#### 4.1 Structure of the different charged states

The hydrogen atom has been investigated in the neutral, positive and negative charge states. In each case, a variety of minimum 15 different initial configurations in 5 different models of amorphous silica have been gathered. For both the positive and negative charged states, at least 9 of the closest atoms were relaxed in order to reach a total energy



Figure 4.1: (a) Structure of the positively charged hydrogen in a-SiO<sub>2</sub>. (b) Density profile in a plane along the O-H bond. The high density regions are shown in red while the low density regions appear in blue.

convergence of less than 0.05 eV. For the neutral state, only the hydrogen atom was relaxed in order to get the same convergence criterion. The resulting structures are fundamentally different from each other.

In the neutral state, the hydrogen atom  $H^0$  is localized in the larger voids of the system. The silica network is not distorted at all from the inclusion of this neutral hydrogen. Using a Bader charge analysis, its electronic charge is almost equal to one, showing that charge density corresponding to the electron provided by the H atom remains close to the proton. The state is clearly of *s*-character from a partial density of states analysis.

The positively charged hydrogen gets bonded to an oxygen atom as shown in Fig. 4.1 (a). The O-H bond length is about 1 Å while the bonds between the O atom and its first neighboring Si atoms increase to ~ 1.75Å as compared to the mean Si-O distance in pure *a*-SiO<sub>2</sub>, resulting in slightly distorted tetrahedrons. The charge density along the O-H bond is illustrated in Fig. 4.1 (b), in which a charge transfer from the O atom to the H atom is clearly seen. From a Bader analysis, the O atom, whose electronic charge without the H atom is ~ 7.55, looses ~ 0.5 electrons in favor of the H atom whose Bader electronic charge is ~ 0.75. The remaining charge comes from the other atoms of the unit cell.

In the negative charged state, the H atom forms a Si-H bond instead with a quite large deformation of the tetrahedron to which the Si atom



Figure 4.2: (a) Structure of the negatively charged hydrogen in *a*-SiO<sub>2</sub>. (b) Density profile in a plane along the Si-H bond. The high density regions are shown in red while the low density regions appear in blue.

belongs to (see Fig. 4.2 (a)). The Si-H bond length is about 1.5 Å and the Si-O bonds are largely affected. The bond between the Si atom and the H-opposed O atom (O<sub>1</sub>) amounts to ~1.8 Å while the three other Si-O bond lengths are increased to ~1.7 Å, resulting in a larger tetrahedron. In Fig. 4.2 (b), the charge density along the Si-H bond shows a larger extent of the charge around the H atom than in the positive charge case. Indeed, the Bader electronic charge of the H atom is ~ 1.6 electrons, and a small part (0.1 electron) of the remaining charge goes to the Si atom.

The structural properties found in this work are in fair agreement with other ab initio investigations of hydrogen in crystalline [150] and amorphous silica [54]. In the latter work, another kind of defect structure was found for the negative charged state in addition to the one observed here. This could be due either to the initial configurations used for finding the most stable configurations or to the fact that these structures are less favored energetically or to the different exchangecorrelation used in this work. Indeed, the LDA has been chosen in this work as it correctly predicts the order of stability of the low-density SiO<sub>2</sub> polymorphs whereas the GGA leads to unrealistic phase transitions with cristobalite being more stable than quartz [19]. Nevertheless, the electronic structure and formation energies will be analyzed in the following sections for the different structures obtained here.



Figure 4.3: Schematic illustration of the defect energy levels of hydrogen in a-SiO<sub>2</sub> in (a) positive charge state H<sup>+</sup>, (b) neutral charge state H<sup>0</sup> and (c) negative charge state H<sup>-</sup>. For each charge state, the DFT (left) and GW (right) energy levels are shown.

#### 4.2 Defect energy levels

As most point defects or impurities do, hydrogen introduces energy levels in the electronic structure of a-SiO<sub>2</sub>. These defect states can be evaluated from standard DFT calculations or from GW computations. Fig. 4.3 shows schematically the energy levels introduced by the hydrogen in a-SiO<sub>2</sub>.

In the positive charge state, a level is lowered in the  $O_{2s}$  region at  $\sim -21$  eV due to the bond formed between the H atom and an O atom. There is no occupied state in the gap but an unoccupied level appears close to the conduction band minimum. This absence of occupied defect state in the gap will lead to take this positive charge state as a reference for the calculation of the GW formation energies in the next section.

In the neutral charge state, the hydrogen introduces one occupied level with spin up and one unoccupied level with spin down in the gap. These two levels correspond to the 1s H orbital. In GW, the occupied H<sub>1s</sub> level is merged or almost merged with the valence band. The position of the unoccupied level with respect to the conduction band minimum is almost unaffected by the GW corrections. In the negative charge state, one doubly occupied state is introduced around 2.5 eV above the valence band maximum. Two other gap states close to each other are also introduced around 0.7 eV and correspond to the non-bonding  $O_{2p}$  from the oxygen opposed to the Si-H bond ( $O_1$  in Fig. 4.2 (a)). *GW* corrections do not change significantly the position of all these states with respect to the valence band maximum.

#### 4.3 Defect formation energies

The defect formation energies (DFE) of the hydrogen atoms have been calculated in DFT using the following equation

$$E_{\rm f}(D^q) = E_{\rm tot}(D^q) + E^{\rm corr}(q) - E^{\rm ref}_{\rm tot} - \sum_i n_i \mu_i + q(\epsilon_{\rm F} + \epsilon_{\rm v} + \Delta V) \quad (4.1)$$

in which  $D^q$  is a defect D in charge state q  $(H^+, H^0 \text{ or } H^-)$ ,  $E_{\text{tot}}(D^q)$ is the total energy of the system containing the defect.  $E^{\text{corr}}(q)$  is the electrostatic correction term for  $q \neq 0$  [151]. This term, which amounts to 0.92 eV, has been obtained from the computation of the electrostatic energy of a periodic array of a point charge in a neutralizing background of the opposite charge, divided by the dielectric constant.  $E_{\text{tot}}^{\text{ref}}$  is the total energy of the reference system (pure amorphous silica).  $n_i$  is the number of atoms of type i that have been added to  $(n_i > 0)$  or removed from  $(n_i < 0)$  the system to form the defect with  $\mu_i$  being their corresponding chemical potentials.  $\epsilon_{\text{F}}$  is the Fermi level referenced to the maximum of the valence band,  $\epsilon_{\text{v}}$  is the energy of the valence band maximum in the reference system and  $\Delta V$  is an alignment potential that accounts for the difference in the mean KS potential between the defective and reference systems [52].

The formation energies of the positively charged, neutral and negatively charged hydrogen atoms are represented in Fig. 4.4 and reported in Table 4.1 together with the results obtained by Godet and Pasquarello [54]. The formation energies are slightly different but as already menTable 4.1: Average hydrogen formation energies in DFT for a Fermi energy at the valence band maximum and charge transition level  $\epsilon(+/-)$  between the positive and negative charge states of hydrogen. The standard deviation of the formation energies obtained in the different configurations and models is given between parenthesis. All values are in eV.

	$E_{\rm f}^{H^+}(\epsilon_{\rm F}=0)$	$E_{\rm f}^{H^0}(\epsilon_{\rm F}=0)$	$E_{\rm f}^{H^-}(\epsilon_{\rm F}=0)$	$\epsilon(+/-)$
This work	-1.41 (0.18)	$2.31 \ (0.05)$	5.84(0.31)	3.62(0.18)
Ref. [54]	-1.28(0.20)	2.24(0.04)	5.22(0.44)	3.25(0.24)

tioned, the exchange-correlation used is not the same and could explain the different results observed here.

A common criticism about DFE computed using DFT relies in the presence of defect states in the gap. Because of the well known band gap underestimation, these gap states are likely to be misplaced. This in turn has effects in the formation energy. In the following, a combined DFT+GW scheme recently proposed by Rinke and coworkers [61, 152] is tested in order to compute GW-corrected defect formation energies.

The method is depicted schematically in Fig. 4.5. For the positively charged hydrogen, because there is no occupied state within the gap, the formation energy is computed within DFT (point 1). In order to get the formation energy of the neutral state (point 2), the change in energy from the positive to the neutral charge state is split in two parts : the "relaxation" energy  $\Delta E^{\text{rel}}(q_i, \mathbf{R}_1 \to \mathbf{R}_2)$  at fixed charge  $q_i$  (horizontal transitions :  $\mathbf{1} \to b$  or  $a \to \mathbf{2}$ ) and the energy to add one electron or electron affinity  $A(q_1, \mathbf{R}_i)$  for a given configuration  $\mathbf{R}_i$  (vertical transitions :  $b \to \mathbf{2}$  or  $\mathbf{1} \to a$ ). As the initial and final states are equal, the two paths should give the same formation energies.

The relaxation energy is calculated within DFT while the electron affinities are computed with the GW method. In a sense, one takes the best of both worlds : energy differences between different configurations without change in the particle number are supposed to be well described in DFT while GW is expected to give reliable electron addition and removal energies for a given configuration. For the energy to


Figure 4.4: Defect formation energies of hydrogen in a-SiO<sub>2</sub> (DFT). The shaded areas indicate the standard deviation of the values.

add one electron, these can be obtained either from the electron affinity of the system with N electrons or as the ionization energy of the system with N + 1 electrons. In principle, these are equivalent but in practice, the approximations used (one-shot GW, plasmon-pole model, ...) introduce differences between them and it has been shown that it is preferable to take the average of the two in order to get reliable electron addition energies [153].

A similar procedure is applied for the formation energy of the negative hydrogen, starting from the formation energy of the neutral hydrogen.

The results for one particular case are given in Table 4.2 and illustrated in Fig. 4.6. The energy to add one electron is clearly different whether it is computed from the affinity A(q) of with the ionization energy I(q-1) of the system with the additional electron. In particular, for the negative charge state, the difference between the two goes up to 2.3 eV in the case of the  $\mathbf{2} \to c \to \mathbf{3}$  path. The different ranges of formation energies thus obtained are shown by the colored areas in Fig. 4.6. Using the mean value of A(q) and I(q-1) leads to values in good agreement for the two different paths [153].



Figure 4.5: GW formation energies.

Table 4.2: Hydrogen formation energies in GW for a Fermi energy at the valence band maximum. The paths indicated in the table reference to the points in Fig. 4.5. All values are in eV.

	Path	A(q)	I(q-1)	(A+I)/2	DFT
$E_{\rm f}^{H^+}(\epsilon_{\rm F}=0)$					-1.36
$E_{\rm f}^{H^0}(\epsilon_{\rm F}=0)$	$1 \rightarrow a \rightarrow 2$	2.84	3.69	3.27	9 37
	$1 \rightarrow b \rightarrow 2$	2.81	3.59	3.20	2.01
$E_{\rm f}^{H^-}(\epsilon_{\rm F}=0)$	<b>2</b> ightarrow c  ightarrow <b>3</b>	4.92	7.24	6.08	6.04
	<b>2</b> ightarrow d  ightarrow <b>3</b>	5.80	6.30	6.00	0.04



Figure 4.6: GW-corrected defect formation energies of hydrogen in a-SiO<sub>2</sub>. The shaded areas indicate to the range of values obtained depending on the path used and on the computation of the electron addition energies.

For the neutral charge state, this procedure leads to an increase of the formation energy and the neutral hydrogen is even less favored. For the negative hydrogen, the formation energy obtained from this scheme is almost identical to the DFT formation energy. The position of the charge transition level  $\epsilon(+/-)$  is thus almost unaffected by this correction scheme for this particular case.

Unfortunately, no other conclusive results could be obtained for other cases. Specifically, the agreement between the two different paths was not recovered by using the mean value of A(N) and I(N + 1), with deviations as large as 1 eV. The reasons for these discrepancies are not yet fully understood. One possible perspective would be to examine the defect formation energies of hydrogen in the  $\alpha$ -quartz system by means of this DFT+GW scheme. Indeed, the amorphous character complicates the identification of the possible origins of the problems encountered here. This thus opens perspectives of future work as it will certainly help understand these problems by using a simpler system.

The applicability of this DFT+GW scheme for the charged states of hydrogen in a-SiO<sub>2</sub> is thus questionable. In fact, the method was initially applied in Ref. [61] to the silicon self-interstitial for which the structural changes from one charged state to another are quite small. This is very different here where the stable configurations for each charged state are very different from one another and could explain the problems encountered here. This complicates the search of the minimum steady-state in DFT for points **a**, **b**, **c** and **d** in Fig. 4.5. If the system gets stuck in some metastable state, which does not correspond to the global ground-state minimum, the method used here can lead to wrong results such as those obtained for the other cases tested while the results obtained in Table 4.2 were surprisingly consistent. Therefore, more technical aspects of the computations performed until now will be reexamined in the following chapters in order to better understand the discrepancies encountered here.

On the technical aspects, one possible source of error might be found in the actual GW corrections. In fact, it is customary to neglect finitesize effects in the GW corrections obtained in a relatively small supercell and use them as is to adjust the DFT energy levels of larger supercells. This leads to the next chapter for the analysis of the size effects in GW corrections.

# Chapter 5

# Size effects in *GW* corrections

In the previous chapter, the hydrogen energy levels in a-SiO<sub>2</sub> have been obtained in DFT and further adjusted within the GW approximation. In this latter correction process, supercell size effects are assumed to be negligible. The GW defect energy levels  $\varepsilon_{def}^{GW}$  are then usually obtained from supercell size corrected DFT levels  $\varepsilon_{def}^{DFT}(L \to \infty)$  to which GWcorrections without any correction for size effects are added :

$$\varepsilon_{\rm def}^{GW} = \varepsilon_{\rm def}^{\rm DFT}(L \to \infty) + \Delta_{\rm def}^{GW}(L_{\rm small})$$
(5.1)

This size-independency of the GW corrections is a customary assumption that has been used in other studies [154, 155, 156]. It is based on the fact that the screening effects are rather localized but to my knowledge, it has never been formally checked so far. In order to do that, one should test these size effects for a large range of defects in different systems with different charged states. This chapter is a step in this direction as it starts with the analysis of the size effects in the GWdefect energy level of one defect in its neutral state.

The tests have been performed for an oxygen vacancy in the idealized form of SiO<sub>2</sub> known as  $\beta$ -cristobalite or *high* cristobalite. The structure of cristobalite and the oxygen vacancy are first presented. The supercells used in the study of the size effects are then described. The defect energy



Figure 5.1: Structure of ideal  $\beta$ -cristobalite and oxygen vacancy. (a) Conventional (cubic) cell of ideal  $\beta$ -cristobalite and (b) Oxygen vacancy in the conventional cell. The silicon atoms that were initially bonded to the missing oxygen atom get closer to each other and form a bond (in blue).

levels obtained in DFT and GW are then given and final conclusions on this topic are drawn.

# 5.1 Oxygen vacancy in $\beta$ -cristobalite

Ideal  $\beta$ -cristobalite is a SiO<sub>2</sub> polymorph usually found at high temperatures (in volcanic rocks for example). In this form, the SiO<sub>4</sub> tetrahedrons are arranged in a very ordered way as shown in Fig. 5.1 (a). The structure is in fact a face-centered cubic system where the silicon atoms are positioned as in the diamond structure and the oxygen atoms are inserted in the middle of the Si-Si bonds. The (pure) primitive unit cell has been relaxed in DFT-LDA and the obtained lattice parameter (a=13.83 Bohr) has been used for the construction of the defective supercells. The great advantage is that the study of finite-size effects with this structure is easier as one can use supercells as multiples of the primitive (6 atoms) or conventional (24 atoms) unit cell.



Figure 5.2: Energy levels of oxygen vacancy in ideal  $\beta$ -cristobalite. The band structure is given along the M- $\Gamma$ -R-X- $\Gamma$ -M path in the conventional cell. The black and grey lines correspond to valence and conduction states respectively. The blue and red line are the two gap states introduced by the oxygen vacancy, the lowest one (def1) being occupied with 2 electrons while the highest one (def2) remains unoccupied in the neutral charge state.

In Fig. 5.1 (b), the structure of the oxygen vacancy  $V_O^0$  in its neutral charge state that is studied in this chapter is shown. The two silicon atoms to which the missing oxygen was bonded have been relaxed in the conventional unit cell. These two atoms gets closer to each other (2.93 Å, to be compared with the standard Si-Si distance of 3.17 Å), making a new Si<sub>sp3</sub>-Si<sub>sp3</sub> bond, as shown from a partial density of states analysis.

The presence of the oxygen vacancy introduces two defect energy levels in the band gap as shown in Fig. 5.2 (DFT band structure along the M- $\Gamma$ -R-X- $\Gamma$ -M path in the conventional cell). The lowest energy level (blue line, referred to as "def1") is occupied with two electrons and correspond to the bonding  $sp^3$  hybridized states forming the Si-Si bond mentioned above. The highest energy one (red line, referred to as "def2") is unoccupied and is attributed to antibonding  $sp^3$  states.

In the following sections, the convergence of the position of these defects with respect to the size of supercell used will be analyzed in

Name	$n \times n \times n$	Cell	$N_{\rm at}$	$V_{\rm SC}~({\rm Bohr}^3)$	$d_{\min}^{\text{def}}$ (Bohr)	$N_{\rm d}$
$C_{111}$	$1 \times 1 \times 1$	С	23	2643.9	13.83	6
$P_{222}$	$2 \times 2 \times 2$	Р	47	5287.9	19.56	12
$P_{333}$	3  imes 3  imes 3	Р	161	17846.5	29.33	12
$C_{222}$	$2 \times 2 \times 2$	С	191	21151.4	27.66	6
$P_{444}$	$4 \times 4 \times 4$	Р	383	42302.9	39.11	12
$C_{333}$	$3 \times 3 \times 3$	Р	647	71385.3	41.48	6
:	:	:	:	:	:	

Table 5.1: Supercells of cristobalite.

details. In particular, the GW corrections to the DFT energy levels will be obtained for four different supercells.

#### 5.1.1 Supercells

The different supercells that have been used corresponds to multiples of the unit cell (containing 6 atoms) and the primitive cubic cell (containing 24 atoms). One can then successively build supercells of increasing size as given in Table 5.1 where the multiplying factor n, the initial cell type (primitive P or conventional C) that is multiplied, the number of atoms in the supercell  $N_{\rm at}$  and the volume  $V_{\rm SC}$  of the supercell. The minimum distance between defects in neighboring images  $d_{\rm min}^{\rm def}$  and the defect coordination number  $N_{\rm d}$  (the number of defect images at a distance  $d_{\rm min}^{\rm def}$  of the defect in the origin cell) are the main parameters that controls the convergence of the defect energy levels with respect to the supercell size and are also given in the table.

Each of the supercells defined in Table 5.1 have been used to obtain the defect energy levels within DFT. The GW corrections were calculated for the first four of them. Indeed, the computational time and memory requirements become rapidly very high as shown in the following.

#### 5.1.2 Computational details

The parameters used for the simulations were carefully chosen as small as possible in order to reduce the computational needs to their minimum for an acceptable convergence criterion of 0.05 eV. For the ground-state calculations, an energy cut-off of 30 Ha has been used for the plane wave basis set. For the  $C_{111}$  and  $P_{222}$  supercells, a non-shifted  $2 \times 2 \times 2$ **k**-point grid has been used whereas only the  $\Gamma$ -point was needed for the larger supercells. The calculation of the dielectric matrix was expanded using an energy cut-off of 6 Ha for the plane waves. In order to get an accuracy of 0.05 eV on the defect energy positions, the number of unoccupied states included amounts to 18-20 times the number of occupied ones. For both the dielectric matrix and the self-energy corrections, the extrapolar method [130] with a compensation energy of 2 Ha has been used so that the number of unoccupied states required for the desired accuracy could be decreased to only 5 times the number of occupied states in all the supercells. An estimate of the computational requirements is given in Appendix C for the five first supercells.

# 5.2 Size effects in the defect energy levels

In DFT, the finite-size effects on the defect energy levels have been extensively studied for many systems [50, 51, 157, 158, 159, 160]. The convergence for the two defect levels in DFT is shown in Fig. 5.3 with respect to the inverse of the volume (left) and with respect to the inverse of the minimum distance between defects. The energy levels are referenced to the valence band maximum. It is interesting to note that the energy levels obtained from  $C_{nnn}$ -type supercells (multiples of the conventional cell, blue squares) seem to converge faster than those from  $P_{nnn}$ -type supercells (multiples of the primitive cell, green triangles) even when the minimum distance between defects is larger. This can be understood in terms of the defect coordination number  $N_d$  of  $P_{nnn}$ -type supercells which is twice that of  $C_{nnn}$ -type supercells.

The infinite size energy levels can be obtained by extrapolation using for example  $\varepsilon_{\text{def}}(L) = \varepsilon_{\text{def}}(L \to \infty) + \alpha L^{-1}$  with cells C<sub>222</sub> and C<sub>333</sub>.



Figure 5.3: Convergence of the defect energy levels in DFT.

The corresponding values for def1 and def2 are 0.74 eV and 5.23 eV and are shown in Fig. 5.3 by the dot-dashed line.

Turning to the GW computations, the GW energy levels and GW corrections are given in Figs 5.4 and 5.5. While the difference between the GW energy levels in the two larger supercells is less than 0.05 eV, the ones obtained in the 23- and 47 atom supercells differ by up to 0.3 eV. This observation is also present in the GW corrections with differences of ~ 0.2 eV between the two smallest and the two larger supercells. As the system studied here is neutral, for which supercell size effects are usually small, the convergence with respect to the supercell size could be important not only at the DFT level but also at the GW level. This indeed questions the reliability of GW defect energy levels calculated with small supercells, such as, for example, in Refs. [154, 155].

In the calculation of the GW corrections, the first step involves the computation of the dielectric function  $\epsilon_{\mathbf{GG}'}(\mathbf{q})$ . This dielectric function is then used to build the screened Coulomb interaction that enters Eq. 2.79 for the evaluation of the self-energy corrections.



Figure 5.4: Convergence of the defect energy levels in GW.



Figure 5.5: Convergence of the GW corrections to the DFT defect energy levels.

Table 5.2: Macroscopic dielectric constants in pure cristobalite and in defective supercells.

C <sub>111</sub>	$\mathbf{P}_{222}$	$P_{333}$	$C_{222}$	Pure
2.17	2.10	2.03	2.02	2.00

As the self-energy corrections depend on the screened Coulomb interaction, it is worth examining the latter in more in details. It is derived from the microscopic dielectric function of the defective system as

$$W(\mathbf{r}, \mathbf{r}') = \int \frac{1}{|\mathbf{r}'' - \mathbf{r}'|} \epsilon^{-1}(\mathbf{r}, \mathbf{r}'') \mathrm{d}\mathbf{r}''$$
(5.2)

In the above integral, the inverse dielectric function  $\epsilon^{-1}(\mathbf{r}, \mathbf{r}'')$  for large distances  $\mathbf{r} - \mathbf{r}''$  should be close (equal for an isolated defect in an infinite medium) to the macroscopic dielectric constant  $\epsilon_{\infty} = 1/\epsilon_{\mathbf{G}=\mathbf{G}'=0,\mathbf{q}=0}^{-1}$  of the pure compound. If the value of  $\epsilon_{\infty}$  obtained from a finite supercell computation differs too much from its value in the pure system, it will invariably induce deviations in the self-energy. The comparison of this quantity in the defective and pure system is thus expected to provide an indication of convergence of the *GW* corrections with respect to the size of the supercell. As shown in Table 5.2, the value of  $\epsilon_{\infty}$  in the two smaller supercells does not reproduce the pure bulk value, while this is the case for the two larger supercells.

The dielectric constant in the two larger supercells is converged within 1.5% of the pure bulk one and the GW defect energy levels are equal to each other within the 0.05 eV convergence criterion. This confirms that the comparison of the static dielectric constant in the pure bulk and in the defective supercell is an important parameter to be considered. This analysis could be done in other compounds and with other point defects in different charged states in order to validate the proposition and suggest an actual convergence criterion on the dielectric constant.

# 5.3 Conclusion

The defect energy levels induced by an oxygen vacancy in the neutral charge state have been obtained using the DFT and GW methods for several sizes of supercells in the ideal  $\beta$ -cristobalite. The GW corrections are shown to depend on the supercell size, in particular for small cells. Results with larger cells (383 atoms, 647 atoms, ...) would most likely show that the GW corrections are reasonably converged for the larger cells used here. Due to computational resources, the GW corrections could not be performed for those cells. Regarding the macroscopic dielectric constant, it is very close to the one of the pure system for the 161- and 191-atom cells while the relative difference for the 23- and 47-atom cells amounts to  $\sim 9\%$  and  $\sim 5\%$  respectively. The macroscopic dielectric constant can thus be suggested as a convergence criterion for the GW corrections. In fact, the long range part of the microscopic dielectric function (i.e. the  $\mathbf{G} = \mathbf{G}' = 0$  term) could be fixed to its value in the pure bulk system. In that case, we would expect the GW corrections to be converge more rapidly with the supercell size. Another possible test would be to add a Coulomb cut-off for the long-range interactions. This has been shown to improve the convergence of the GW corrections with respect to the supercell size [161].

Further investigations should of course be performed for larger cells and in the case of charged states. Finally, this same procedure could be applied to other compounds in order to draw some rule of thumb depending on the macroscopic dielectric function of the pure system.

# Chapter 6

# Assessment of the plasmon-pole approximation

In the previous chapters, the Godby and Needs (GN) plasmon-pole model (PPM) has been used for the GW calculations. In a plasmon-pole approximation, the frequency dependence of the inverse dielectric matrix  $\epsilon^{-1}$  is assumed to have a particular form given by Eqs 2.84 and 2.85 where all the spectral weight of the imaginary part is reduced to a single delta peak. This particular assumption for the frequency dependence can have a strong effect on the computed QP eigenvalues. In this chapter, the QP electronic structure and the RPA dielectric function of  $\alpha$ -SiO<sub>2</sub> are obtained using two different PPMs and compared to results without any PPM approximation by performing a full-frequency computation.

# 6.1 QP eigenvalues with and without plasmonpole models

In order to obtain the full-frequency results, the contour deformation technique (CD) has been employed. It is of course much more computationally demanding but leads to a more accurate evaluation of the correlation term of the self-energy. For a detailed discussion of the technique, the reader is referred to Ref. [162]. The GN PPM and the Hybertsen and Louie (HL) PPM (see Sect. 2.4.4) have been studied here. The wavefunctions were expanded in a plane-wave basis set with an energy cut-off of 40 Ha. A non-shifted  $2 \times 2 \times 2$  **k**-point grid has been used for the computation of the self-energy terms while the same grid was shifted by  $(0, 0, \frac{1}{2})$  for the evaluation of the screened Coulomb interaction W. This smaller grid (with respect to the one used in Chapter 3) was used in order to facilitate the full-frequency treatment. It leads to a roughly systematic underestimation of the gap by ~0.1 eV with respect to a fully converged **k**-point grid. The energy cut-off for the this screening matrix was set to 6 Ha. The QP energies have been converged within 0.05 eV for the chosen **k**-point grid.

In Fig. 6.1 (a), the effects of using a PPM approximation are probed by looking at  $G_0W_0$  corrections  $\Delta^{G_0W_0}$  to the KS-LDA eigenvalues  $\varepsilon_{\text{LDA}}$ . The results computed with the GN and HL PPMs are compared to those calculated without resorting to any approximation on the frequencydependence of the dielectric matrix (i.e. using the CD technique). In the range of energies close to the Fermi level, the results obtained with the GN PPM are in excellent agreement with the CD results, not only for the band gap but also for the absolute values of the  $G_0W_0$  shifts. The latter are critical for band offsets studies [110, 163]. For the lowest energies (O<sub>2s</sub>-like states, between -20 and -15 eV), the reliability of the GN PPM is not as good. On the other hand, these states are very low in energy and are often not taken into account for the computation of other properties such as optical properties (see Sect. 3.4).

When using the HL PPM, the QP eigenvalues differ largely from the CD results for the whole range of energies. In particular, the band gap is overestimated with respect to its full-frequency value. The fundamental and direct band gaps obtained with the CD technique and with the two PPMs are gathered in Table 6.1 together with the LDA gap and the real QP gap as inferred in Sect. 3.4.

The LDA and  $G_0W_0$  band structures and density of states (DOS) are plotted in Fig. 6.2. The  $G_0W_0$  results are obtained using the polyfit



Figure 6.1: (a) Quasiparticle corrections obtained with and without plasmon-pole models (b) Error of each PPM investigated in this study with respect to full-frequency results (CD). The CD results are shown by the blue circles while the GN and HL PPMs correspond to the green crosses and red pluses respectively. The shaded areas correspond to the valence states.

Table 6.1: Fundamental  $E_{\rm g}$  and direct  $E_{\rm g,d}$  band gaps in  $\alpha$ -SiO<sub>2</sub> computed within LDA and  $G^0W^0$  using the CD technique, the GN and the HL PPMs. The real QP gap reported here corresponds to the value of the gap obtained in this work in Sect. 3.4.

	LDA	CD	GN PPM	HL PPM	Real QP gap
$E_{\rm g}$	5.77	8.89	8.88	9.36	$\sim 9.8$
$E_{\rm g,d}$	6.06	9.16	9.16	9.65	$\sim 10.1$

interpolation presented in Sect. 2.4.5. Only the upper valence bands corresponding to the bonding  $Si_{3s,3p}-O_{2p}$  and antibonding  $O_{2p}$  orbitals are shown in the figure.

It is proven here that the GN PPM is quite accurate approximation as compared to full-frequency results in a large of frequencies around the gap. As already demonstrated in Sect. 3.4, the one-shot GW is not sufficient to correctly predict the QP gap in  $\alpha$ -SiO<sub>2</sub>. Quasiparticle self-consistent GW with vertex corrections [144] has been shown [97] to yield a better agreement for the QP gap.

# 6.2 Analysis of the plasmon-pole models and dielectric function

The properties of the dielectric matrices obtained with the CD technique and with the PPMs are analyzed in order to further investigate the reasons leading to the discrepancies in the QP eigenvalues. In Fig. 6.3, the real part of the dielectric matrix  $\mathcal{R}\epsilon^{-1}(i\omega)$  along the imaginary frequency axis for  $\mathbf{q} = 0$  at  $\mathbf{G} = \mathbf{G}' = 0$  computed with the PPMs is compared to the more accurate values obtained with the CD technique. It is clear that the GN PPM is much closer to the CD result. Indeed, the GN PPM parameters are determined from the value of  $\epsilon^{-1}$  for the static limit ( $\omega = 0^+$ ) and for another frequency  $i\omega_p$  along the imaginary axis, the value of which corresponds to the intersection of the CD and GN curves in Fig. 6.3. It is thus not surprising that the GN PPM reproduces the behavior of the dielectric matrix along the imaginary axis fairly well. In contrast, the HL PPM strongly underestimates the behavior of the CD results over the whole frequency range.

The real part of  $\epsilon^{-1}(\omega)$  along the real frequency axis is shown in the upper panel of Fig. 6.4 for  $\mathbf{q} = 0$  at  $\mathbf{G} = \mathbf{G}' = 0$ . Both PPMs reproduce the static limit  $\omega = 0^+$  by construction. Even though the two PPMs are both crude approximations, the GN PPM is closer to the exact behavior of  $\mathcal{R}\epsilon^{-1}(\omega)$ , in particular for frequencies larger than the position of the main pole. The GN PPM is also a better approximation for frequencies smaller than 10 eV (see inset). These small frequencies correspond to



the full blue lines, green circles and dashed red lines correspond to the CD, the GN-PPM and the HL-PPM results Figure 6.2: Band structure of  $\alpha$ -SiO<sub>2</sub> obtained in LDA (left panel) and  $G_0W_0$  (middle panel). In the middle panel, respectively. The corresponding densities of states are given in the right panel. All the energies are referenced to the top of the valence band.



Figure 6.3: Real component of the RPA microscopic dielectric function  $\epsilon^{-1}$  at  $\mathbf{G} = \mathbf{G}' = 0$  and  $\mathbf{q} = 0$  plotted along the imaginary axis. The contour deformation technique, the Godby-Needs PPM and the Hybertsen-Louie PPM are given by the solid blue, the dot-dashed green and the dotted red lines.

the range needed for the evaluation of the QP corrections to the states close to the band gap.

The imaginary part of  $\epsilon^{-1}$  is shown in the middle panel of Fig. 6.4. The arrows indicate the position of the Dirac delta peaks for the PPMs where all the spectral weight of  $\mathcal{I}\epsilon^{-1}(\omega)$  is concentrated. The GN pole peak seems to better account for the overall peak structure of  $\mathcal{I}\epsilon^{-1}(\omega)$ . In the lower panel of Fig. 6.4, the integrand of the *f*-sum rule (Eq. 2.86) is shown. The blue shaded area is the integral corresponding to the CD results while the green and blue rectangles corresponds to the GN and HL PPMs. For higher **G**, **G'** vectors, the position of the peaks for the GN and HL PPMs is affected differently. The sum rule imposed by the HL model pushes the delta peak ever further on the real axis as can be seen in the upper panel of Fig. 6.5. This seems to result in an overestimation of the pole contribution along the imaginary axis, in particular for the low frequency region.

Turning to the analysis of the f-sum rule, it is trivially fulfilled by the HL PPM by construction, while in the GN PPM, the parameters fix the integral of the imaginary part of the inverse dielectric function. When



Figure 6.4: Real (upper panel) and imaginary (middle panel) components [at  $\mathbf{G} = \mathbf{G}' = 0$  and  $\mathbf{q} = 0$ ] of the RPA microscopic dielectric function  $\epsilon^{-1}$  as computed with the contour deformation technique (full blue line), the Godby-Needs PPM (dot-dashed green line), and the Hybertsen-Louie PPM (dotted red line) plotted along the real axis. The inset in the upper panel is a zoom of the real component for frequencies between 0 and 16 eV. The lowest panel shows the imaginary part multiplied by the frequency, as an illustration of the *f*-sum rule.



Figure 6.5: Position of pole (upper panel) and fulfillment of the *f*-sum rule (lower panel) for the diagonal elements ( $\mathbf{G} = \mathbf{G}'$ ) of  $\epsilon^{-1}$  within the GN (dot-dashed green) and HHL (dotted red) PPMs as a function of the corresponding kinetic energy  $(\frac{1}{2} |\mathbf{G}|^2)$ . The blue curves corresponds to the results obtained with CD technique for different number of unoccupied bands  $N_{\rm b}$  included in the calculation of  $\epsilon^{-1}$ . The CD band gap is converged with ~400 unoccupied states.

 $\mathcal{I}\epsilon^{-1}(\omega)$  is calculated explicitly, the integral depends on the number of empty states included in the sum. In the lower panel of Fig. 6.5, the fulfillment of the sum rule is shown as a function of the kinetic energy  $\frac{1}{2} |\mathbf{G}|^2$  of the diagonal matrix elements of  $\mathcal{I}\epsilon^{-1}(\omega)$ . The compliance with the sum rule is slowly achieved by the CD technique. On the other hand, the band gap and the QP eigenvalues in the range of energies between -10 eV and 15 eV are converged with only 400 bands, for which the sum rule is obviously not fulfilled for most diagonal matrix elements. For the GN PPM, the fulfillment is rather poor.

From the discussion stated above, the fulfillment of the f-sum rule is neither a minimum nor a sufficient condition to ensure reliable QP energies.

# 6.3 Conclusion

The reliability of the GN and HL PPMs has been studied by comparing them to results obtained with a full-frequency treatment using the CD technique. These results show that the GN PPM is able to reproduce the QP eigenvalues obtained from the CD method with good accuracy for a large range of energies around the Fermi level. The analysis of the PPMs also shows that the fulfillment of the f-sum rule is not an essential requirement for getting accurate results.

As a consequence, it is clear that the band gap obtained in Sect. 3.3.4 is underestimated by the one-shot GW method starting from an LDA electronic band structure. The HL PPM seems to give a better estimate of the QP gap but for the wrong reasons. In order to improve the prediction of the QP gap, it is thus necessary to go beyond the one-shot approach. The self-consistent GW schemes being very computationally demanding, it is advised to use a better starting point than LDA. The next chapter analyzes the TB09 exchange-correlation potential which has been claimed to give much more accurate band gaps while remaining in a KS-like formulation.

# Chapter 7

# Analysis of the TB09 exchange-correlation potential

In the previous chapters, it was shown that DFT with the LDA as the exchange-correlation functional was unable to predict correctly the band gaps and defect energy levels in SiO<sub>2</sub>. The application of a one-shot GW using the DFT-LDA electronic structure as a starting point also revealed the limits of the method. One would then need to use more sophisticated approaches involving some kind self-consistent solution of Hedin's equations such as QPscGW [144, 164] or self-consistent COHSEX+ $G_0W_0$  [165].

Alternatively, Tran and Blaha [78] recently proposed a modified version of the Becke-Johnson potential [91] leading to an improved description of the band gaps in semiconductors and insulators. This new XC functional (referred to as TB09) has already been applied to a large variety of systems [92, 93, 94, 95, 96, 97, 166] and was able to predict band gaps in close agreement with experiment. In this chapter, the TB09 functional is analyzed in details for a series of ten semiconductors and oxides (see also Ref. [62]).

# 7.1 Band gaps and widths

In the following, a systematic comparison of electronic band structures obtained from the LDA and TB09 functionals is performed. These are compared with the more accurate band structures obtained through oneshot GW calculations, and available experimental data. Several oxides and other technologically or theoretically interesting materials are investigated : silicon, germanium, silicon dioxide, tin monoxide and dioxide, zinc oxide, calcium sulfide, calcium oxide, magnesium oxide and lithium fluoride. As shown in Table 7.1 and Fig. 7.1, the TB09 delivers band gaps in much better agreement with experiment than the simple LDA. The  $G_0 W_0$  calculations are performed starting from LDA eigenvalues and wavefunctions (referred to as  $G_0W_0$ @LDA), but also from TB09 eigenvalues and wavefunctions (referred to as  $G_0W_0$ @TB09). The difference is non-negligible. In fact, the one-shot GW band gaps obtained starting from TB09 are close to those from quasiparticle self-consistent GW calculations, at a much reduced cost. For the specific case of  $\alpha$ - $SiO_2$ , the  $G_0W_0$ @TB09 band gap is much closer to the value inferred in Sect. 3.4.

# 7.2 Band structures

The experimental lattice parameters have been used for all the compounds studied. The GW eigenvalues and densities of states have been interpolated using the polyfit approximation developed in Sect. 2.4.5. The discussion presented in this section is based on the band structures and densities of states presented in Appendix D (except for Si, Ge and  $\alpha$ -SiO<sub>2</sub>) in which the computational details used for the calculations are also reported.

#### 7.2.1 Silicon and germanium

The silicon and germanium band structures and densities of states (DOS) are presented in Figs. 7.2 and 7.3 respectively. The DOS are compared to experimental X-ray photoemission spectra [177, 178] (XPS). It is clear

Table 7.1: Fundamental ( $E_g$ ) and direct ( $E_{g,d}$ ) band gaps of all the materials in this study in the LDA, TB09,  $G_0W_0$ @LDA and  $G_0W_0$ @TB09 approximations. Experimental and QPscGW values are also reported [28, 97, 144, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176].

		DFT		$G_0$	$W_0$		
		LDA	TB09	@LDA	@TB09	$\mathrm{QPsc}GW$	Expt.
Si	Eg	0.51	0.98	1.21	1.38	1.24	1.12
	$E_{g,d}$	2.56	3.04	3.25	3.44	3.30	3.20
Ge	$E_{g}$	0.20	0.71	0.70	0.93	0.95	0.66
	$E_{g,d}$	0.23	0.89	0.73	1.12		0.80
$\mathrm{SiO}_2$	$E_{g}$	5.77	9.82	8.96	10.09	9.7	$\sim 9$
	$E_{g,d}$	6.06	10.01	9.27	10.36	10.1	$\sim 9$
ZnO	$E_g$	0.67	3.44	2.32	3.73	3.8	3.6
$\operatorname{SnO}$	$E_{g}$	0.27	0.48	0.74	0.78	1.38	0.7
	$E_{g,d}$	2.17	3.17	2.92	3.82	3.88	2.77
$\mathrm{SnO}_2$	$E_{g}$	0.89	4.35	2.72	4.17	4.28	3.6
CaS	$E_{g}$	2.15	3.31	4.28	4.89		4.43
	$\mathrm{E}_{g,d,\Gamma}$	3.89	4.76	5.57	7.06		5.80
	$\mathbf{E}_{\mathbf{g},\mathbf{d},X}$	2.97	4.01	5.13	5.77		5.34
CaO	$E_{g}$	3.49	5.30	6.02	7.39	7.57	7.0
	$E_{g,d,\Gamma}$	4.55	7.04	6.49	10.36		7.0
	$\mathbf{E}_{\mathbf{g},\mathbf{d},X}$	3.87	5.62	6.46	7.85		7.3
MgO	$E_g$	4.73	8.32	7.48	8.97	9.16	7.83
LiF	$E_g$	8.82	14.31	13.45	15.09	15.9	14.2



Figure 7.1: Comparison of the theoretical and experimental band gaps (in eV) for all the different materials considered in this study. The different XC approximations for both DFT and GW calculations are given as black dots (DFT-LDA), red squares (DFT-TB09), green diamonds ( $G_0W_0$ @LDA), blue triangles ( $G_0W_0$ @TB09), and yellow dots (QPscGW). Corresponding band gap values are also reported in Table 7.1. Inset: Table of the mean error (ME), the mean absolute error (MAE), the mean relative error (MRE, in %), and the mean absolute relative error (MARE, in %) for the various XC functionals.

from the figures that both LDA and TB09 provide a rather fair description of the valence DOS. The main features of the band structure are indeed correctly reproduced by both XC approximations. The more elaborate  $G_0W_0$ -corrected DOS does not give rise to any major change in the valence electronic structure. The direct and indirect band gaps have already been presented in Table 7.1 while the valence band widths as well as first conduction band widths are given in Table 7.2. The valence band widths computed with the different approximations are reported in Fig. 7.4, together with those of the other compounds studied in this chapter. As expected, the band gaps obtained with TB09 are fundamentally improved over LDA.  $G_0W_0$ @TB09 opens the gap further, overshooting the experimental values. When compared to XPS results, our DFT results show that both XC functionals yield too small band widths. Further  $G_0 W_0$  correction even worsens this narrowing although the relative error with respect to experiment is reasonable in all four cases.

#### 7.2.2 Silicon dioxide

Silicon dioxide has already been presented extensively in Chapter 3. Its QP gap has been shown to be underestimated by  $\sim 4 \text{ eV}$  within DFT-LDA. It is thus a more challenging case than Si and Ge, to test the accuracy of the electronic structure obtained with the TB09 functional.

Figure 7.5 shows the band structures and DOS obtained with LDA, TB09,  $G_0W_0$ @LDA and  $G_0W_0$ @TB09. The fundamental gap is indirect, from K to  $\Gamma$ . The band gaps and different band widths of  $\alpha$ -quartz obtained with the different XC approximations, in DFT and  $G_0W_0$  are reported in Table 7.1 and Table 7.2.

As expected, the TB09 fundamental and direct gaps are closer to the reported experimental values (see Table 3.4 in Chapter 3) than the LDA ones and to the gaps obtained in Sect. 3.4. Comparing the DOS with recent XPS experiment [134], it is clear that the TB09 drastically underestimates the valence band widths. Applying  $G_0W_0$  corrections rectifies this error, leading to a  $G_0W_0$ @TB09 valence band structure



Figure 7.2: Band structure and DOS of bulk silicon in the diamond structure computed in DFT with (a) the LDA XC, (b) the TB09 XC and in one-shot GW using (c) DFT-LDA and (d) DFT-TB09 as a starting point. In the left panel, the dashed (black) lines correspond to the DFT-LDA band structure and the full (red) lines represent the DFT-TB09 band structure. In the middle panel, the dashed (green) lines correspond to the  $G_0W_0$ @LDA band structure and the full (blue) lines represent the  $G_0W_0$ @TB09 band structure. In the right panel, the valence DOS is compared to XPS spectrum [177] (black line).



Figure 7.3: Band structure and DOS of bulk germanium in the diamond structure computed in DFT with (a) the LDA XC, (b) the TB09 XC and in one-shot GW using (c) DFT-LDA and (d) DFT-TB09 as a starting point. The XPS spectrum is from Ref. [178]. The color scheme is the same as in Fig. 7.2.

Table 7.2: Valence band widths (VBW) and first conduction band widths (1CBW) of all the materials in this study. Experimental values [164, 170, 179, 180, 181, 182, 183, 184, 185, 186] are also reported when available.

		$\mathrm{DFT}$		$G_0 W_0$		
		LDA	TB09	@LDA	@TB09	Expt.
Si	VBW	11.96	11.72	11.19	11.43	12.50
	1CBW	3.71	3.51	3.69	3.54	
Ge	VBW	12.50	12.26	11.86	11.92	12.60
	1CBW	4.16	4.06	4.14	4.16	
$\mathrm{SiO}_2$	$VBW_{O_{2p}}$	3.27	2.65	3.66	3.70	4.0
	$\operatorname{VBW}_{\operatorname{O}_{2p}\operatorname{Si}_{3s,3p}}$	4.81	3.98	5.09	5.15	5.0
	$VBW_{O_{2s}}$	2.38	1.99	2.17	2.19	2.5
	1CBW	2.92	2.72	3.20	3.51	
ZnO	VBW	6.19	5.41	6.43	6.49	9.0
	1CBW	7.11	6.55	7.53	7.25	
$\operatorname{SnO}$	VBW	9.11	9.12	9.67	10.00	12.0
	1CBW	2.98	3.22	3.35	3.60	
$\mathrm{SnO}_2$	VBW	8.38	6.78	8.29	8.32	10.4
	1CBW	5.08	4.13	5.48	4.97	
CaS	VBW	3.18	2.59	3.13	3.18	3.9
	1CBW	3.09	3.07	3.43	4.28	
CaO	$VBW_{O_{2p}}$	2.68	1.92	2.82	2.72	
	$VBW_{O_{2s}}$	1.22	0.86	0.88	1.42	
	$VBW_{O_{2p}}\Gamma$ -X	1.76	1.36	1.89	1.85	1.2
	$VBW_{O_{2s}}\Gamma$ -X	0.55	0.37	0.40	0.76	0.6
	1CBW	3.47	2.55	3.72	4.36	
MgO	VBW	4.71	3.71	5.05	5.01	4.8
	1CBW	6.79	6.10	7.28	6.68	
LiF	VBW	3.12	2.00	3.39	3.21	3.5
	1CBW	5.84	5.64	6.24	6.21	



Figure 7.4: Comparison of the theoretical and experimental band widths (in eV) for all the different materials considered in this study. The different XC approximations for both DFT and GW calculations are given as black dots (DFT-LDA), red squares (DFT-TB09), green diamonds ( $G_0W_0$ @LDA), and blue triangles ( $G_0W_0$ @TB09). Corresponding band width values are also reported in Table 7.1. Inset: Table of the mean error (ME), the mean absolute error (MAE), the mean relative error (MRE, in %), and the mean absolute relative error (MARE, in %) for the various XC functionals.



Figure 7.5: Band structure and density of states of  $\alpha$ -quartz computed in DFT with (a) the LDA XC, (b) the TB09 XC and in one-shot GWusing (c) DFT-LDA and (d) DFT-TB09 as a starting point. The XPS spectrum is from Ref. [134]. The color scheme is the same as in Fig. 7.2.

very close to the  $G_0W_0$ @LDA one. The band gaps obtained with the  $G_0W_0$ @TB09 approach are also even closer to the QPscGW ones [97].

#### 7.2.3 Zinc oxide

The band structures and DOS are given in Fig. D.1. As already shown in other previous studies, [187, 188, 189, 190] LDA fails to provide a correct description of the Zn 3d levels and gives rise to a strong hybridization of these levels with the O and Zn *p*-states. The same authors suggest to add a Hubbard U term in order to lower the position of the Zn 3d-states and actually decouple them from the *p*-states. This results at the same time in an increased band gap closer to measurements. In any case, the same hybridization problem is observed when using the TB09 even if a tiny internal band gap around -4 eV is obtained. Nevertheless, considering all these states as a single group, the valence band width is once more clearly narrowed with the TB09 (5.41 eV) compared to LDA (6.19 eV). The  $G_0W_0$  corrected band structures are much closer to each other, at least for the highest p states (from -4 eV to the Fermi level). In Table 7.2, the present theoretical results are compared to the experimental band width (9 eV) [181, 191] corresponding to the sum of p states (5.3 eV), d states (2.5 eV) and the separating internal band gap (1.2 eV). This experimental band width is also in rather good agreement with the XPS spectrum reported in Fig. D.1.

The TB09 yields a band gap value of 3.44 eV which is again in much better agreement with experimental one (3.6 eV [169]) than the LDA (0.67 eV). The  $G_0W_0$  correction to LDA leads to a larger band gap (2.34 eV), still too low with respect to the experimental value while starting from the TB09 electronic structure leads to a  $G_0W_0$  gap of 3.73 eV, close to the QPscGW value.

### 7.2.4 Tin oxides

The band structures and DOS are given in Figs. D.2 and D.3. The highest group of valence bands of both oxides is rather well described even if some discrepancies appear between LDA and TB09, especially for the band width in the case of  $SnO_2$ . For SnO, it is clear that the
highly localized d states (lying at ~23-24 eV below the Fermi level) are better described with the TB09 as they are pushed down in energy, closer to the  $G_0W_0$  corrected ones. The O *s*-states (around ~18-20 eV below the Fermi level) are better positioned with TB09 than with LDA as confirmed by the  $G_0W_0$  results. In contrast with SiO<sub>2</sub> and ZnO, but similarly to Si and Ge, the valence band widths in SnO are not narrowed with the TB09 leading to a surprisingly good description of the valence states for this particular case.

The fundamental band gap of SnO is indirect from  $\Gamma$  to M. TB09 leads to larger fundamental and direct band gaps than LDA but both DFT fundamental band gaps are still lower than the measured values. The addition of a  $G_0W_0$  leads to indirect band gaps in very close agreement with the experiment whereas the direct experimental gap at  $\Gamma$  is overestimated by  $G_0W_0$ @TB09 but is closer to the QPscGW result.

For tin dioxide, the flat bands corresponding to d states (around -22 eV to -20 eV) are also somewhat better positioned in energy with the TB09 than within LDA but are slightly narrowed. The group of bands around -16 eV to -18 eV which is composed of O s states and some Sn s and p states is clearly shrunk with the TB09 compared to the LDA and  $G_0W_0$  structures. The highest valence bands are also strongly contracted with TB09.

Concerning the band gap, it is clearly underestimated within DFT-LDA while the TB09 leads to a value larger than the experimental one [171], very close to the QPscGW one. The  $G_0W_0$ @LDA band gap is still lower than in experiments while the  $G_0W_0$ @TB09 theoretical gap is closer to the measured value.

#### 7.2.5 Calcium sulfide and calcium oxide

The band structures and DOS of CaS are given in Fig. D.4. The fundamental band gap is indirect from  $\Gamma$  to X. The TB09 leads to increased values of the band gaps as shown in Table 7.1 while the LDA underestimates the experiments. The  $G_0W_0$ @LDA band gaps are closer to experiment.  $G_0W_0$ @TB09 strongly overestimates the direct band gap at  $\Gamma$  while the direct band gap at X and the indirect band gap are within 5% of the experimental values. Unfortunately, no QPscGW results were available in literature for this large band gap semiconductor.

The upper valence band composed of sulfur *p*-states is again clearly narrowed by TB09. In contrast, LDA is in much better agreement with the  $G_0W_0$  values. The band widths obtained with  $G_0W_0$ @LDA and  $G_0W_0$ @TB09 are in close agreement with each other.

The band structures and DOS of CaO are shown in Fig. D.5. The conduction band structure is somewhat different with the LDA and the TB09. In LDA, there is a local minimum in the conduction band at  $\Gamma$  while this band is pushed upwards with the TB09. In both cases, the gap is indirect from  $\Gamma$  to X. The band gaps obtained are gathered in Table 7.1. There is some controversy on the exact value and on the indirect character of the fundamental gap such that no reliable experimental value could be compared with our results.

Concerning the valence electronic structure, the upper valence bands are once more narrowed by TB09 when compared to LDA or  $G_0W_0$ corrected band structures.

#### 7.2.6 Magnesium oxide

The band structures and DOS of MgO are shown in Fig. D.6. The band gap is underestimated within DFT-LDA while the TB09 leads to a value larger than the experimental value. The  $G_0W_0$ @LDA band gap is closer to experiments while  $G_0W_0$ @TB09 pushes the gap even further away from the measured value. In fact, the  $G_0W_0$ @TB09 gap is very close to the reported QPscGW result.

The valence bands are clearly shrunk when using the TB09. Comparing the DOS with XPS experiments [192] shows evidently that the distance between the two peaks in the DOS of the upper valence band is much smaller than the experimental value when using the TB09 while the LDA and the  $G_0W_0$ -corrected band structures are in much better agreement. The valence band widths and band gap values obtained with the different methods are collected in Table 7.1 and Table 7.2.

### 7.2.7 Lithium fluoride

The band structures and DOS are shown in Fig. D.7. There is a strong narrowing of the valence band when using the TB09. Comparing the DOS with XPS experiments [186] shows obviously that the valence band is much smaller than the experimental value when using the TB09 while the LDA and the  $G_0W_0$ -corrected band structures are in better agreement. The two-peak structure in the XPS spectrum is also much better rendered with the LDA DOS whereas the TB09 is far from the experiment. Both  $G_0W_0$ -DOS fairly reproduce this peak structure.

The valence band width and band gap values obtained with the different methods are gathered in Table 7.1 and Table 7.2. As for the other materials, the band gap is underestimated within DFT-LDA while the TB09 corrects this, yielding a value of 14.31 eV in much closer agreement with the experimental value [176] of 14.2 eV. The  $G_0W_0$  correction opens the LDA band gap closer to experiment while  $G_0W_0$ @TB09 opens the gap even further, overshooting the experimental value by almost 1eV. It is again very close to the QPscGW band gap.

### 7.3 Optical spectra of $\alpha$ -SiO<sub>2</sub>

From the overall accurate prediction of the experimental band gaps, the TB09 or the  $G_0W_0$ @TB09 would be expected to be a good candidate to build the electron-hole basis set needed in a BS calculation. This has been tested for the case of  $\alpha$ -SiO<sub>2</sub> and the resulting optical spectra is shown in Fig. 7.6 (a) and (b) for TB09 and  $G_0W_0$ @TB09 respectively.

Using the DFT-TB09 for the electron-hole basis set leads to an optical spectra that is red-shifted by about 1.5 eV as shown in (a) while the  $G_0W_0$ @TB09 in (b) yields a reasonable agreement of the position of the peaks of  $\epsilon_2(\omega)$ . On the other hand, in both cases, the amplitude of the peaks and the overall weight of the spectrum is strongly underestimated. As shown from the corresponding RPA spectra, this is not due to the excitonic effects but rather comes from the optical matrix elements. These are computed from the TB09 wavefunctions and are not comparable to those obtained from the LDA computations. This



Figure 7.6: Optical spectra of  $\alpha$ -SiO<sub>2</sub> from the TB09 functional. For TB09,  $G_0W_0$ @LDA and  $G_0W_0$ @TB09, the electron-hole basis sets in the BS or RPA computation are built from the TB09 eigenvalues and wavefunctions, from the  $G_0W_0$ @LDA eigenvalues and LDA wavefunctions and from the  $G_0W_0$ @TB09 eigenvalues and TB09 wavefunctions respectively.

discrepancy can most likely be traced back to the fact that it is not, strictly speaking, a Kohn-Sham system, as there is no energy functional from which the TB09 potential derives [99, 100]. As a consequence, the f-sum rule is not guaranteed to be fulfilled by the RPA-TB09 dielectric function, while this is the case for LDA [193].

### 7.4 Effect of the *c* parameter

As shown in the previous section, the TB09 functional allows to determine the band gaps of materials without any large additional computational cost and with a relatively good agreement with experiment. The exchange potential of the TB09 functional takes the form

$$V_{\rm X}^{\rm TB09}(\mathbf{r}) = c V_{\rm X}^{\rm BR}(\mathbf{r}) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_{\rm s}(\mathbf{r})}{n(\mathbf{r})}},\tag{7.1}$$

All the terms in Eq. 7.1 have been defined in Sect. 2.3.3. We focus here on the c parameter which is usually obtained following the standard self-consistent procedure (Eq. 2.52) proposed by Tran and Blaha. This parameter will also be varied manually in order to better identify its effects on the band gap and on the electronic structure.

Defining the narrowing factor as the ratio of the upper valence band width in LDA to the upper valence band width in TB09, the experimental fundamental gap of the materials shows an overall linear correlation to the narrowing factor as shown in Fig. 7.7. It is indeed clear that the narrowing of the bands is more pronounced for materials with wider band gaps. This gives some hint on how the TB09 leads to larger gaps. Indeed, exact exchange methods such as Hartree-Fock lead to an overestimation of the band gaps. Similarly, the TB09 opens the gaps by mixing in more local exchange in the system thanks to the adjustment of the c parameter. As a consequence of a more attractive exchange potential, the electrons are more localized and their electronic bands are narrowed.

Following this discussion, the effect of the c parameter on the computed band width is shown in Fig. 7.8 for  $\alpha$ -SiO<sub>2</sub>, ZnO, SnO<sub>2</sub> and MgO.



Figure 7.7: Graph of the *narrowing factor* (VBW<sub>LDA</sub>/VBW<sub>TB09</sub>) of the upper valence band as a function of the fundamental band gap  $E_g$  of the materials considered in the present study. Materials with larger band gaps exhibit a stronger narrowing of the valence bands.

The modification of the upper valence band width and the conduction band is shown for various values of the c parameter ranging from 1.0 to 1.7. As already mentioned in Ref. [78], the band gap is increases as a function of the c parameter. On the other hand, it is clear from the figure that the band widths are decreased when the c parameter is increased. This is also observed in the other compounds investigated and confirms the conjecture that the TB09 leads to band gaps larger than LDA by introducing a larger contribution of local exchange which at the same time contracts the electronic bands. Unfortunately, any attempt to obtain a better estimation of this c parameter would never correct the TB09's failure to describe the ground state correctly. The band widths obtained with LDA (black horizontal dashed lines) are always closer to the more reliable  $G_0W_0$  results (green horizontal continuous lines) than those obtained with the TB09.

Recently the authors of the TB09 proposed an improvement [194] of the original XC by redefining the parameters  $\alpha$  and  $\beta$  entering in the evaluation of the *c* parameter of the functional using a larger set



obtained by fixing the value of the c parameter in Eq. (2.51) for  $\alpha$ -SiO<sub>2</sub>, ZnO, SnO<sub>2</sub> and MgO. The red crosses indicate Figure 7.8: Fundamental band gaps  $E_g$ , upper valence band widths VBW and first conduction band widths 1CBW the c parameter that will reproduce the experimental band gap. The solid green horizontal lines in the VBW and 1CBW correspond to the  $G_0W_0$  result. The black dashed horizontal lines correspond to the LDA value obtained in the present study. The black triangles are the actual results obtained with the TB09. It is clear that the best c value for the band gap will always narrow the band widths.

of materials. They claimed that the TB09 and its revised version yield very accurate electronic band structures and gaps. According to the present study, the ground state valence band structures obtained with the TB09 is not guaranteed to reproduce the  $G_0W_0$  band structures nor the experiment. In particular, for large band gap materials, the valence band widths are strongly contracted.

### 7.5 Conclusion

A systematic investigation of the electronic structure obtained either from the LDA or TB09 XC functionals has been performed for ten semiconductors and oxides. The results show that although very appealing for its efficiency and simplicity and for its performance in reproducing experimental band gaps of pure bulk materials, the TB09 must be used with great caution if any other property than the band gap itself is under investigation. In particular, optical properties for  $\alpha$ -SiO<sub>2</sub> reveal a severe deficiency of the TB09 functional in the fact that the RPA dielectric function do not fulfill the *f*-sum rule. The perspectives of this kind of approaches are yet promising and there are possible avenues for the design of better XC functionals. Their forms should be given for the XC energy so that they correspond to real Kohn-Sham system where the exchange-correlation potential is derived from the XC energy functional. In order to better reflect the actual many-body effects, a local XC functional should take into account some part of semi-locality such as what is done with the TB09 functional.

Comparisons with  $G_0W_0$  results using both the DFT-LDA and the DFT-TB09 as starting points have been carried out for all the materials revealing that the TB09 can strongly underestimate the band widths. This contraction of the bands is found to be more pronounced for materials with a larger band gap. This follows from the fact that the TB09 opens the gaps by virtually adding a larger part of local exchange to the system through the adjustment of the *c* parameter. This stronger exchange part results in a stronger localization of electron hence narrowing the band widths.

#### 7.5. Conclusion

As a consequence, the ground-state electronic band structure is not well described for medium to large band gap materials. This is expected to be detrimental for any further investigations such as defect studies, analysis of surfaces or interfaces, etc. It is shown that any modification of the c parameter aiming to reproduce exactly the experimental band gap would not lead to any improvement. Indeed, the band widths of the materials are roughly proportional to the inverse of this parameter and will invariably be compressed.

Finally, the TB09 could be tested as a starting point for QPscGW computations in the perspective of reducing the number of self-consistent iterations needed to converge the QP wavefunctions and energies. Indeed, for the case of  $\alpha$ -SiO<sub>2</sub>, the  $G_0W_0$ @TB09 eigenvalues seem to be already rather close to the real QP ones as shown from the inspection of the BS spectrum obtained using these for the electron-hole basis set. The TB09 thus opens the perspectives of a better description of excited states in SiO<sub>2</sub>.

This study has been accepted for publication in Phys. Rev. B as Ref. [62].

# Conclusion and perspectives

This PhD project started four years ago, with the ambitious objective of describing the electronic and optical properties of amorphous silica containing various radiation-induced defects. Above all, this implies a very strong understanding of the properties in the pure, nondefective, bulk material. Clearly, modeling the amorphous state is not trivial and particular care has to be taken for the generation of such models. A large part of the work performed during this thesis concerned this aspect as well as the analysis and determination of the properties of the pure phase in order to assess the reliability of the models. From there onwards, impurities and defects can be introduced in the samples in order to investigate their effects on the properties of the perfect bulk system. This also appeared to be intricate and problematic in some cases. As a consequence, this thesis covers a mix of both technical and more physically oriented topics and results. The main outcomes are summarized in the following lines.

From a methodological point of view, the *polyfit interpolation* scheme has been developed in order to facilitate the interpolation of the quasiparticle energies obtained from GW computations. Indeed, these cannot be obtained easily for large **k**-point meshes as needed for BSE computations or for a given **k**-point path for the visualization of the band structure along specific symmetry lines. The polyfit interpolation is easier to apply than other techniques such as the Wannier interpolation. Besides, it is almost completely automatic and does not require any human time for the generation of the quasiparticle band structure. Densities of states, random **k**-point meshes and effective masses are also obtained straightforwardly. This approach is of course not perfect as it neglects the dependence of the GW corrections on the character of the state considered but it appeared to be very satisfactory in the case of SiO<sub>2</sub> and for most compounds presented in Chapter 7. Moreover, the polyfit has been proven to be efficient in many of the topics presented in this work and has already been used for publications.

On the scientific part, twenty models of amorphous silica were generated and analyzed in detail. In particular, their structural properties have been proven to be well described. Their electronic structure has been successfully obtained within DFT and perturbative GW and compared to XPS experiments. The different models were also characterized using atomic charge analysis and projected densities of states. We have shown that those pure silica models were in good agreement with experiments and previous theoretical studies. As already mentioned, this preliminary step was essential in order to assess the quality of the models.

One important scientific outcome of this thesis lies in the determination of the actual quasiparticle gap in amorphous silica (9.75 eV) and  $\alpha$ -quartz (10.1 eV). This longstanding problem, for which experimental studies have often been contradictory, has been solved by means of a reverse-engineering procedure. The correct gap was found by a matching procedure in which the positions of the peaks in the absorption spectrum obtained from the solution of the Bethe-Salpeter equation were aligned to those of experiments. The resulting optical spectrum of a-SiO<sub>2</sub> obtained in this thesis is also a significant achievement though its accuracy should be improved by further computations using more refined grids. It is interesting to note that the band gaps of both the crystalline and the amorphous form obtained using the above-mentioned procedure are larger than those obtained from a perturbative GW. This pushed the need to validate the main approximation of the latter method, namely the use of a plasmon-pole model. Concerning the defects, the positively charged, neutral and negatively charged states of hydrogen have been investigated. Their structure and formation energies have been obtained using DFT and shown to reproduce previous studies. The induced gap states have been successfully determined within GW. Preliminary results for GW-corrected formation energies have been discussed and led to consider a reexamination of the technical details and approximations used in this correction procedure.

The first technical issue discussed in this thesis is the supercell size convergence of the GW corrections. This important point has often been neglected while no formal study had ever been performed to address this problem. It has been shown for a defect model, the neutral oxygen vacancy in cristobalite, that supercells with 24 or 48 atoms are not large enough to converge the quasiparticle corrections, while such small cells have been used in the past to compute defect energy levels within GW. The macroscopic dielectric constant was found to be a relevant parameter for testing the convergence of the quasiparticle corrections with respect to the supercell size. This is still work in progress though and other cases should be tested, such as other charged states.

Two plasmon-pole models have been thoroughly tested and compared to full-frequency results. The Hybertsen and Louie PPM showed large deviations with respect to the latter results. On the contrary, the Godby and Needs PPM that was used in this work has been proven to be a very good estimate of the full-frequency results. Another important outcome from this detailed analysis concerns f-sum rule. Indeed, its fulfillment does not seem to be a necessary condition to ensure reliable results as it is clearly not satisfied with the GN PPM despite its good accuracy. This thus validated the previous GW results from that point of view. As a side effect, the one-shot GW with LDA as a starting point is thus unable to predict the band gap in SiO<sub>2</sub> (as inferred previously) and more involved theories such as quasiparticle self-consistent GW should be used to solve this issue.

From a computational point of view, even a partial self-consistency in the GW method is very demanding. For that reason, a *better starting*  point than LDA is strongly advised. The Tran and Blaha exchange potential, as claimed by their authors, was shown to yield much better band gaps than LDA, coming up as an interesting candidate as a starting point for self-consistent GW. On the other hand, the valence band widths were found to be strongly contracted, in particular for large band gap materials such as SiO<sub>2</sub>. Another issue concerns the optical matrix elements that seem to be largely underestimated, as observed in the optical spectrum. This thus questions the reliability of this already widely used functional.

Following the previous lines, many technical issues have been clarified, which opens perspectives for future work. In particular, the description of defects is far from being a closed subject. The electron addition and removal energies in defective systems are still a subject of debate and the present study brings up possible solutions. Indeed, these computed electron affinities may vary depending on the charge state in which they are computed. The GW defect formation energies of hydrogen in SiO<sub>2</sub>, which is still an open issue, could be reexamined in view of the analysis performed for the finite-size effects.

Another somewhat related point concerns the determination of the universal method needed to compute accurate band gaps. The reverseengineering procedure applied for  $SiO_2$  can indeed be generalized and used for other compounds but is not completely ab initio as it involves comparison with some experimental data. It can nevertheless be used to confirm and support results obtained with other methods such as the quasiparticle self-consistent scheme with vertex corrections. This latter approach seems to be universal but is at present out of reach for large systems such as the ones involved here.

Concerning the methods, there are many possible improvements to the polyfit interpolation developed in this work. In particular, the state and character dependence can be accounted for by using an approach based on the overlaps of the wavefunctions. Instead of interpolating the GW corrections using a simple energy dependence, the interpolated values would be obtained from an overlap-weighted average of the GW corrections of other states. This procedure is in fact already in progress and will very likely be continued soon.

On a broader view, the different topics addressed in this thesis form a sound basis for other studies. As stated in the introduction, an accurate knowledge of the defects at the nanoscale and of their effects on the properties is essential in order to develop new materials and improve existing ones. Ab initio computations can now be used to predict the properties of a particular compound and/or combination of defects and impurities before actually synthesizing it. In this context, first-principles approaches are becoming a standard for the discovery of new and highquality materials.

## Appendices

## Appendix A

## Expression of the Becke-Roussel potential

The expression of the Becke-Roussel potential reads

$$V_{\rm X}^{\rm BR}(\mathbf{r}) = -\frac{1}{b(\mathbf{r})} \left( 1 - e^{-x(\mathbf{r})} - \frac{1}{2}x(\mathbf{r}) e^{-x(\mathbf{r})} \right)$$
(A.1)

where  $b(\mathbf{r})$  is computed as

$$b(\mathbf{r}) = \left(\frac{x^3(\mathbf{r}) e^{-x(\mathbf{r})}}{8\pi n(\mathbf{r})}\right)^{1/3}$$
(A.2)

and  $x(\mathbf{r})$  is obtained from the solution of a non-linear equation involving the density  $n(\mathbf{r})$ , the gradient  $\nabla n(\mathbf{r})$  of the density, the laplacian  $\nabla^2 n(\mathbf{r})$ of the density and the kinetic energy density  $t_s(\mathbf{r})$  as defined in Eq. 2.53:

$$\frac{x(\mathbf{r}) e^{-2x(\mathbf{r})/3}}{x(\mathbf{r}) - 2} = \frac{2}{3} \pi^{2/3} \frac{n(\mathbf{r})^{5/3}}{Q(\mathbf{r})}$$
(A.3)

with

$$Q(\mathbf{r}) = \frac{1}{6} \left( \nabla^2 n(\mathbf{r}) - 2\gamma D(\mathbf{r}) \right)$$
(A.4)

$$D(\mathbf{r}) = 2t_s(\mathbf{r}) - \frac{1}{4} \frac{(\nabla n(\mathbf{r}))^2}{n(\mathbf{r})}$$
(A.5)

.

and  $\gamma=0.8$  is a fixed parameter.

### Appendix B

# Structural properties of the amorphous silica models

Some of the relevant structural properties of each model generated in this thesis are reported in this appendix. The radial distribution functions for the Si-O and O-O bonds are shown in the first columns of Figs. B.1 to B.3. The Si-Si-Si bond angle distribution is illustrated in the second columns while the rings statistics for each model are represented in the last columns. The figures also report the total energy  $\Delta E_{tot}$  of each model with respect to the one with the minimum total energy (model 05). Models with a wrong coordination (02, 07, 10 and 17) or with edge-sharing tetrahedra (15) have been rejected. This kind of defects is indeed present in a real SiO<sub>2</sub> glass but in a much smaller proportion than that of the models. These models are thus not expected to be representative of the real material.



Figure B.1: Structural properties of models 01 to 08.



Figure B.2: Structural properties of models 09 to 16.



Figure B.3: Structural properties of models 17 to 20.

### Appendix C

# Size effects in *GW* corrections : computational requirements

### C.1 Memory

The computational requirements for GW computations in large supercells are extremely large. Indeed, for the wavefunctions, many unoccupied states need to be stored in memory in addition to the valence states. The number of states included and the number of plane waves  $N_{\rm PW}^{\rm WF}$  needed are roughly proportional to the volume of the cell so that the size of the wavefunctions is roughly proportional to the volume squared. For the dielectric and screening functions, the size of the matrices ( $N_{\rm PW}^{\epsilon} \times N_{\rm PW}^{\epsilon}$ ) involved are also proportional to the volume squared. The memory requirements are gathered in Table C.1 for the five first supercells (as defined in Table 5.1).

As shown in this table, the memory needed grows fast. Hence, this project has been done on the large Curie cluster (see for example http://www-hpc.cea.fr/en/complexe/tgcc-curie.htm) within a PRACE preparatory access. The computations were performed in conjugation with algorithmic and optimization developments. These include developments towards an hybrid programming model consisting in a mix of

Table C.1: Memory requirements in GW calculations for large systems.  $N_{\rm PW}^{\rm WF}$  is the number of plane waves used to represent the wavefunctions (WF) and  $N_{\rm PW}^{\epsilon}$  is the number of plane waves used in the dielectric matrix. The names of the supercells correspond to those defined in Table 5.1.

Name	$N_{\rm at}$	$N_{ m PW}^{ m WF}$	WF size (GB)	$N_{\rm PW}^\epsilon$	$\epsilon$ size (GB)
$C_{111}$	23	$\sim 20750$	$\sim 0.1$	$\sim \! 1850$	$\sim 0.1$
$P_{222}$	47	$\sim \! 41500$	$\sim 0.4$	$\sim \! 3700$	$\sim 0.4$
$P_{333}$	161	$\sim \! 140000$	$\sim 4.9$	$\sim \! 12550$	$\sim 4.7$
$C_{222}$	191	$\sim \! 166000$	$\sim 6.9$	$\sim \! 14850$	$\sim 6.6$
P <sub>444</sub>	383	$\sim \! 332000$	$\sim 28.3$	$\sim 29700$	$\sim 26.3$

shared memory (OpenMP) and message passing interface (MPI) standards. Indeed, this kind of computations for these large systems would not have been possible without such developments as the maximum available memory for each MPI process is limited. On the cluster used, the largest nodes consist of 32 processors which share 128 GB of memory.

### C.2 Timings

The most computationally demanding part when the self-energy corrections are needed for a few states only, as it is the case when gap states are involved, is the computation of the dielectric function. Table C.2 reports the timings for the computation of the dielectric function in the different supercells.

This study is still work in progress and other developments have been performed that would allow the computation of the dielectric function for larger systems, such as the 383-atom supercell.

Table C.2: Timings in GW calculations for large systems.  $N_{\rm MPI}$  is the number of MPI processes while  $N_{\rm threads}$  is the number of threads for each MPI process, the total number of cores used being the product  $N_{\rm MPI} \times N_{\rm threads}$ . The names of the supercells correspond to those defined in Table 5.1.

Name	$N_{\rm at}$	$N_{\rm MPI}$	$N_{\rm threads}$	Time (hours)	Total time (hours)
C <sub>111</sub>	23	23	1	$\sim 0.5$	$\sim 12$
$P_{222}$	47	65	1	$\sim \! 13$	$\sim\!865$
$P_{333}$	161	116	4	$\sim 11$	$\sim 5200$
$C_{222}$	191	140	8	$\sim \!\! 17$	$\sim \! 18700$

158

### Appendix D

# Band structures with the TB09 functional

The computational details for all the compounds studied in Chapter 7 and the band structures of ZnO, SnO, SnO<sub>2</sub>, CaS, CaO, MgO and LiF are given in this appendix. In all the figures D.1 to D.7, the band structures and densities of states (DOS) are shown as obtained from DFT with (a) the LDA XC, (b) the TB09 XC and from one-shot GW using (c) DFT-LDA and (d) DFT-TB09 as a starting point. In the left panels, the dashed (black) lines correspond to the DFT-LDA band structure and the full (red) lines represent the DFT-TB09 band structure. In the middle panels, the dashed (green) lines correspond to the  $G_0W_0$ @LDA band structure and the full (blue) lines represent the  $G_0W_0$ @TB09 band structure. The corresponding DOS are shown in the right panels. When available, the experimental XPS spectrum is shown by the black line in the right panels.

### D.1 Silicon and germanium

Silicon in the diamond structure has been studied with the experimental lattice parameter [195] a=5.43 Å. Silicon has an indirect band gap from  $\Gamma$  to a point located about 80% of the way along the path  $\Gamma$ -X. Germanium possesses the same zinc-blende crystalline structure  $(Fd\overline{3}m)$  with an

experimental lattice parameter [195] a=5.66 Å and has an indirect band gap from  $\Gamma$  to L.

The wavefunctions have been expanded in a plane wave basis set with a kinetic energy cutoff of 20 Ha. The **k**-point grids used were  $6 \times 6 \times 6$ unshifted and  $8 \times 8 \times 8$  unshifted meshes for silicon (Si) and germanium (Ge) respectively. For the *GW* calculations, the size of the dielectric matrix used was determined by a kinetic energy cutoff of 10 Ha for Si and 20 Ha for Ge. The band structures and DOS are presented in Chapter 7 (Figs 7.2 and 7.3).

### D.2 Silicon dioxide

The  $\alpha$ -quartz polymorph (P3<sub>2</sub>21) has been considered with the experimental lattice parameters and internal coordinates from Wyckoff [195] (a=4.91 Å, c=5.40 Å, u<sub>Si</sub>=0.465, x<sub>O</sub>=0.415, y<sub>O</sub>=0.272, z<sub>O</sub>=0.12). An energy cut-off of 40 Ha for plane waves and a 4×4×4 k-point mesh have been used. Finally, the dielectric matrix was expanded with an energy cutoff of 8 Ha. The band structures and DOS are shown in Chapter 7 (Fig. 7.5).

### D.3 Zinc oxide

Zinc oxide (ZnO) is a widely studied material due to its application as a transparent conducting oxide. The wurtzite structure ( $P6_3mc - B4$ ) of ZnO has been considered here with the experimental lattice parameters from Kihara and Donnay. [196] It is also a benchmark case for band gap predictions as there is no consensus on the theoretical gap obtained from DFT or *GW* methods, with reported *GW* values ranging from 2.1 eV to 4.2 eV (see Ref. [111] and references therein).

The pseudopotential for the zinc atom includes the whole n=3 shell in the valence configuration. A  $\Gamma$ -centered  $8 \times 8 \times 5$  k-point mesh has been used and the plane-wave energy cut-off used for the wavefunctions and dielectric matrix are 150 Ha and 20 Ha respectively. The band structures and densities of states are shown in Fig. D.1.



Figure D.1: Band structure and density of states of ZnO. The XPS spectrum is from Ref. [197]. The range of energies from -6 eV to the Fermi level has been magnified with respect to the rest of the XPS spectrum.

### D.4 Tin oxides

Two forms of tin oxides have been considered : stannous SnO and stannic  $SnO_2$  oxide. Stannous oxide crystallizes in the P4/nmm (B10) structure while stannic oxide adopts the rutile form  $(P4_2/mnm)$ . Their experimental lattice parameters and internal coordinates are taken from Refs. [198] and [199] respectively. For both systems, an energy cutoff of 100 Ha was used for the wavefunctions. The k-point meshes used were  $4 \times 4 \times 3$  and  $4 \times 4 \times 6$  for SnO and SnO<sub>2</sub> respectively. The dielectric matrix was expanded using a cutoff energy of 10 Ha. The band structures and densities of states are shown in Figs. D.2 and D.3.

### D.5 Calcium sulfide

Calcium sulfide (CaS) has been studied in the rock salt structure  $(Fm\overline{3}m - B1)$  using the experimental lattice parameters. [195] The energy cut-



Figure D.2: Band structure and density of states of SnO. The XPS spectrum is from Ref. [182].



Figure D.3: Band structure and density of states of  $SnO_2$ . The XPS spectrum is from Ref. [182].



Figure D.4: Band structure and density of states of CaS.

off used for the wavefunctions was 45 Ha and the reciprocal space was discretized using 29  $\mathbf{k}$ -points in the irreducible Brillouin zone. The dielectric matrix was expanded using an energy cut-off of 10 Ha. The band structures and densities of states are shown in Fig. D.4.

### D.6 Calcium oxide

Calcium oxide (CaO) has been investigated in the rock salt structure  $(Fm\overline{3}m - B1)$ . The experimental lattice parameters [200] have been used. An energy cut-off of 38 Ha and 29 **k**-points in the irreducible Brillouin zone have been used for the wavefunctions. The dielectric matrix was expanded using an energy cut-off of 10 Ha. The band structures and densities of states are shown in Fig. D.5.

### D.7 Magnesium oxide

The most stable phase of magnesium oxide (MgO) is in the rock-salt structure  $(Fm\overline{3}m)$ . The experimental lattice parameter a=4.203 Å has been used [201]. The fundamental gap, which is direct at  $\Gamma$ , amounts to 7.83 eV. [175] The wavefunctions were expanded using 80 Ha as the



Figure D.5: Band structure and density of states of CaO.

energy cutoff for the plane waves and 44  $\mathbf{k}$ -points in the irreducible Brillouin zone. An energy cut-off of 16 Ha has been used for the plane wave representation of the dielectric matrix. The band structures and densities of states are shown in Fig. D.6.

### D.8 Lithium fluoride

The rock-salt structure  $(Fm\bar{3}m)$  of lithium fluoride (LiF) has been studied using the experimental lattice parameter [202] a=4.028 Å. The wavefunctions were expanded using 40 Ha as the energy cutoff for the plane waves and 29 **k**-points in the irreducible Brillouin zone. A kinetic energy cut-off of 16 Ha has been used for the plane wave representation of the dielectric matrix. The band structures and densities of states are shown in Fig. D.7.



Figure D.6: Band structure and density of states of MgO. The XPS spectrum is from Ref. [192].



Figure D.7: Band structure and density of states of LiF. The XPS spectrum is from Ref. [186].
## Appendix E

## List of publications

- M. Stankovski, G. Antonius, D. Waroquiers, A. Miglio, H. Dixit, K. Sankaran, M. Giantomassi, X. Gonze, M. and Côté and G.-M. Rignanese, G<sup>0</sup>W<sup>0</sup> band gap of ZnO: Effects of plasmon-pole models, Phys. Rev. B 84, 241201 (2011).
- A. Miglio, D. Waroquiers, G. Antonius, M. Giantomassi, M. Stankovski, M. Côté, X. Gonze and G.-M. Rignanese, *Effects of plas*mon pole models on the G<sup>0</sup>W<sup>0</sup> electronic structure of various oxides, Eur. Phys. J. B 85, 322 (2012).
- D. Waroquiers, A. Lherbier, A. Miglio, M. Stankovski, S. Poncé, M. J. T. Oliveira, M. Giantomassi, G.-M. Rignanese, and X. Gonze, Band widths and gaps from the Tran-Blaha functional : Comparison with many-body perturbation theory, accepted in Phys. Rev. B.
- D. Waroquiers, M. Giantomassi, M. Stankovski, G.-M. Rignanese and X. Gonze, *Quasiparticle gap and optical spectra in amorphous silica with excitonic effects*, in preparation.
- D. Waroquiers, M. Giantomassi, G.-M. Rignanese and X. Gonze, *Finite size effects in defect energy levels from a GW approach*, in preparation.

- F. Da Pieve, D. Waroquiers, M. Stankovski, T. Rangel, M. Giantomassi, G.-M. Rignanese, J. Paul, D. Lamoen and X. Gonze, *Electronic properties of pure and Al-doped TiO2 for pigment applications: Blue shift of the band gap and polaronic states*, submitted to Phys. Rev. B.
- F. Da Pieve, D. Waroquiers, M. Stankovski, M. Verstraete, M. Giantomassi, G.-M. Rignanese, J.Paul and X. Gonze, *Electronic properties of native defects in TiO*<sub>2</sub> by many body perturbation theory, to be submitted to Phys. Rev. B.
- B. Bertrand, S. Poncé, D. Waroquiers, M. Stankovski, M. Giantomassi, M. Mikami and X. Gonze, *Accurate electronic structure* of oxynitride green phosphors for white-LED, in preparation.

168

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