## UNIVERSITY OF NOVA GORICA SCHOOL OF APPLIED SCIENCES

# THE PEROXY LINKAGE IN AMORPHOUS SILICA: ELECTRONIC AND OPTICAL PROPERTIES FROM AB-INITIO MODELING

MASTER THESIS

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Nova Gorica, 2014

## UNIVERZA V NOVI GORICI FAKULTETA ZA APLIKATIVNO NARAVOSLOVJE

# PEROKSIDNA VEZ V AMORFNEM SILICIJU: ELEKTRONSKE IN OPTIČNE LASTNOSTI IZ AB-INITIO MODELIRANJA

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Nova Gorica, 2014

# Acknowledgement

I would like to express my deepest gratitude to my mentor, doc. dr. Layla Martin-Samos for all the help provided in the making of the thesis. Many aspects of this work would not be possible without all the meaningful lectures, thorough guidance and your endless patience. Thank you!

This work was performed using the GENCI-CCRT High Performance Computing resources (DARI Grant number 2014096137).

I would also like to thank all of the staff from University of Nova Gorica for all the assistance throughout the study. Special mention to Ana for never giving up. Last but not least I would like to thank my family for their unconditional support, especially grandmother Helena.

#### Abstract

A major motivation to study point defects in silica is their role in the degradation of SiO<sub>2</sub>-based optoelectronic devices. One of the primary steps for understanding and controlling degradation processes is the one-to-one assignment between defect structure at the atomic scale and experimental signature (optical absorption bands, Electron Paramagnetic Resonance- EPR, Fermi contact/g-tensor, Photoluminescence bands, etc). Experimentally, bi-univocal assignments are not straightforward. Indeed, correlations have to be found between the results of different complementary spectroscopic techniques, such as Optical Absorption (OA), Photo-Luminescence spectra (PL) or(EPR combined with various treatments like irradiation, temperature, etc. Moreover, the sample itself contains always many different defects and impurities that make hard to detect and identify single signals against the background of other signals. In this context, ab-initio modelling plays a crucial role for calculating basic properties of defects.

Among other defects, the identification of the optical signature of Peroxy Linkage (POL) is still under debate. Experiments report values between 3.8 eV and 7 eV, while modelling, through mean-field theories, suggest absorption around 6.5 eV. In this work, electronic and optical properties have been modelled through what is nowadays considered the state-of-the-art approach, i.e. Density functional theory, GW approximation and solution of the Bethe-Salpeter equation. The DFT method provides good ground state configuration, GW approximation provides the quasi-particle band structure (N+1 and N-1 electronic excitations of the N electron gas), by properly including exchange and correlation effects. The Bethe-Salpeter Equation (BSE) takes into account electron-hole interactions through the diagonalization of an effective two-particle Hamiltonian (neutral excitations of the N electron gas) that contains parameter-free exchange and screening effects between holes and electrons. This study shows presence of three bands assigned to POL, however their very low oscillator strength indicates minimal possibility for their experimental detection reported in literature.

**Keywords:** *Ab-initio* modeling, Density functional theory (DFT), GW approximation, Bethe-Salpeter equation, silicon dioxide, point defects, peroxy linkage

## Povzetek

Študija točkastih deformacij silicija je zanimiva zaradi njihove vloge pri degradaciji optično-električnih naprav zgrajenih iz silicijevega dioksida - SiO<sub>2</sub>. Eden izmed prvih korakov pri razumevanju in nadzoru degradacije je povezovanje med defekti na atomski skali in eksperimentalnimi rezultati (optični absorpcijski pasovi, elektronska paramagnetna resonanca, fotolumiscenčni pasovi,... ), kar pa ni vedno enostavno razvidno. Posledično moramo poiskati korelacije med rezultati različnih komplementarnih spektroskopskih tehnik kot so: optična absorpcijska spektroskopija(OA), fotolumiscenčna spektroskopija (PL) ali elektronska paramagnetna resonanca (EPR) v kombinaciji z različnimi postopki npr. temperatura, obsevanje,... Poleg tega vzorec vedno vsebuje različne defekte in nečistoče zaradi katerih težko ločimo posamezne signale od ostalih signalov oz. ozadja. V tem kontekstu ima ab-initio modeliranje osrednjo vlogo pri izračunu osnovnih lastnosti defektov.

Med drugimi defekti je identifikacija optične sledi peroksidne vezi (PerOxyLinkage - POL) še vedno predmet študij. Eksperimentalna poročila opisujejo energijo absorpcije med 3.8eV in 7eV medtem ko rezultati modeliranja nakazujejo vrednost okrog 6.5 eV. V tem delu so predstavljene elektronske in optične lastnosti modelirane z najnaprednejšimi metodami: Gostotna funkcijska teorija ("Density Functional Theory- DFT), GW približkom in rešitvami Bethe-Salpeterjeve enačbe. DFT metoda služi izračunu osnovnega stanja, GW približek opisuje pasovno strukturo kvazi-delcev (N+1 in N-1 elektronskih vzbuditev N-elektronskega plina) z natančnim obravnavanjem izmenjevalnih ter korelacijskih efektov. Bethe-Salpeterjeva enačba (BSE) opisuje interakcijo elektron-vrzel z diagonalizacijo Hamiltonovega operatorja dveh delcev (nevtralno vzbujanje N-elektronskega plina) kateri vsebuje izmenjavo prek prostih parametrov in učinkov senčenja med vrzelmi in elektroni. Ta študija pokaže navzočnost treh absorpcijskih pasov izhajajočih iz peroksidnega defekta. Zelo nizke verjetnosti optičnega vzbujanja nakazujejo malo možnosti, da bi opisane prehode lahko zaznali z eksperimentalnimi metodami opisanimi v literaturi.

**Ključne besede:** *Ab-initio* modeliranje, gostotna funkcijska teorija (DFT), GW približek, Bethe-Salpeterjeva enačba, silicijev dioksid, točkaste deformacije, peroksidna vez

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## List of Acronyms

- a-SiO<sub>2</sub> Amorphous-SiO<sub>2</sub>
- BCB Bottom of conduction band
- BSE Bethe Salpeter equation
- CI Configuration interaction
- DFT Density functional theory
- EA Electron affinity
- EPR Electronic paramagnetic resonance
- HF Hartree Fock
- HOMO Highest occupied molecular orbital
- HPC High performance computing
- KS Kohn Sham
- LDA Local density approximation
- LUMO Lowest unoccupied molecular orbital
- MOSFET Metal oxide semiconductor field effect transistor
- OA Optical absorption
- PL Photo luminescence
- POL Peroxy linkage
- TDDFT Time dependant density functional theory
- TVB Top of valence band
- VIP Vertical ionization potential

## 1. Introduction

Amorphous Silicon dioxide (a- $SiO_2$ ), commonly referred as silica, is a high dielectric material widely used in many applications such as gate oxide in MOSFET, optical fibers and lithography. It can be easily manufactured at a relatively low cost. Its huge band gap (9.6 eV) and huge optical gap (9 eV) together with its dielectric properties and high thermal stability make silica a unique material, very difficult to replace. In all the modern applications, it is very important to control defects (and defect precursors) as they may create defect levels within the band-gap that could reduce the performance of silica-based devices (electronic losses and optical attenuations). For devices submitted to harsh environments, the knowledge and control of defects becomes even more crucial, as irradiation induces ionization of pre-existing defects and/or creation of new defects through knock-on processes, such modifying substantially (and most of the time irreversibly) the optoelectronic-properties. Is in particular for these kinds of environments, that the study of fundamental aspects of silica is getting an increased interest in the material science community. Indeed, in the field of nuclear technology, optical fibers based on silica are, at the moment, the sole candidates for communication and sensing.

Despite 50 years of intensive research and applications, a complete picture of silica and its defects is still missing. Experimentally a one-to-one assignment between defect signatures and guessed defect atomic structure needs the combination of many experimental techniques (among others, Electron Paramagnetic Resonance, various types of Luminescence, optical absorption) that comprise measurements at different conditions together with hypothesis on the atomic structure and how are defects created, how they recombine and how they are annihilated. In the case of silica, as it is an amorphous material, i.e. disordered, this assignment is even more difficult as defects may be "anything". Indeed, contrary to SiO<sub>2</sub> crystalline polymorphs, even the silica atomic structure, disregarding "defects", is unknown. The ideal a-SiO<sub>2</sub> is supposed to be a random network of SiO<sub>4</sub> tetrahedral, with an atomic density of 2.2 g/cm. The sole information about medium range arrangements comes from Raman experiments and modeling that have proven the presence of 3 and 4 tetrahedral rings [9]. In this context, it is clear that materials modeling may play a fundamental role.

In this thesis we will focus on optoelectronic properties of the PerOxy Linkage (POL). POL is an intrinsic defect arising from an excess of oxygen, from thermodynamic equilibrium with  $O_2$  gas or from the creation of an oxygen Frenkel pair. The atomic structure of the defect is  $a \equiv Si - O - O - Si \equiv$  bridge. It is of interest, because in most of the silica applications, silica-based devices are submitted to oxygen partial pressure.

Under the experimental point of view, optical absorption data on the POL are scarce and controversial. Imai et al. [17] have attributed a broad absorption bump in the region of 6.5-7.8 eV to POL, while Nishikava et al. [26] have assigned a weak band at 3.8 eV in the spectrum of a sample of synthetic silica. On the theoretical side, calculations are rare and performed with very drastic approximations. The first theoretical estimation gives a first optically active transition at 8.6 eV [15]. More sophisticated Quantum Chemistry calculations on very small SiO<sub>2</sub> clusters, have given a value of 6.5 eV for the lowest transition [13]. In this work, we will use state-of-the art first-principles approaches for modeling the optical signature of POL. Our approach allows for the parameter-free determination of the optical transitions and optical absorption spectra taking into account exchange and correlation effects, electron-hole interactions and the long-range dielectric behavior of the material under study.

In the first chapter of this thesis we will first present the theoretical framework and then discuss our results on the peroxy bridge.

# 2. Theoretical framework

#### 2.1 Introduction

Modeling optoelectronic properties needs the solution for the ground state of N interacting electrons through Coulomb potential plus the solution of charged and neutral excitations, see figures 2.1 and 2.2. Being a many body problem, only approximate solutions are accessible. In the field of quantum mechanical electronic modeling, two types are commonly used: first principle and semi-empirical methods. The latter utilize certain assumptions based on previous experimental data (empirical modeling, statistical input and fitting parameters) in order to simplify calculations and speed up the process. Reliance on empirical parameters can however greatly reduce accuracy of such approach. Methods based on first principle (often referred as *ab initio*) indisputably provide fundamental picture of the nature and its properties at the price of very demanding computational cost. [1]

Here we will concentrate on what is nowadays state-of-the-art approach for modeling opto-electronic properties from first principles, which is based on perturbative GW<sup>1</sup> on top of Density Functional Theory (DFT) calculations.

<sup>&</sup>lt;sup>1</sup>While symbols G and W represent certain quantities with physical/mathematical meaning, the method is never presented with their full name and simply referred as GW approximation



Figure 2.1: Left: Electrons in ground state, Middle: "Photo emission" - Electron is removed from crystal leaving a hole ie. N-1 particles in the system, Right: "Inverse photo emission" - Additional electron is introduced into system to fill an unoccupied state, producing N+1 particle system



Figure 2.2: Schematic view of a neutral excitation: formation of an interacting electron-hole pair

## 2.2 Basics of Density Functional Theory

Density functional theory (DFT) differs from other methods as it does not try to obtain approximate wave functions as diagrammatic expansions but it uses functionals of the electron density to describe interacting system of fermions. DFT only provides the ground state electronic density. It has been applied to a huge variety of systems giving very accurate results for ground-state properties. This theory was developed in 70's on the basis of Thomas-Fermi semi-classical method for many body electronic structure calculation and received multiple corrections especially in correlation parts constantly increasing accuracy and general scientific popularity [3].

DFT is based on the variational principle of Hohenberg and Kohn that allows the determination of the exact ground state density of a specified many-particle system. It is formulated for local, spin-independent external potentials leading to non-degenerate ground state.

The many fermion systems are characterized by a non-relativistic time independent Hamiltonian [3]

$$\hat{H} = \hat{T} + \hat{V} + \hat{W} \tag{2.1}$$

where T is kinetic energy, W coulomb energy and V energy produced by external field. Total energy functional for a set of doubly occupied electronic states  $\psi_i$  can be written as:

$$E[\{\psi_i\}] = 2\sum_i \int \psi_i \left[-\frac{\hbar^2}{2m}\right] \bigtriangledown^2 \psi_i d^3r + \int V_{ion}(r)n(r)d^3r + \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{XC}[n(r)] + E_{ion}(\{R_I\})$$
(2.2)

 $E_{ion}$  is the coulomb interaction between nuclei,  $V_{ion}$  static total electron-ion potential, n(r) electronic density  $(n(r) = 2\sum_{i} |\psi_i(r)|^2)$  and  $E_{XC}$  exchange-correlation functional. Only minimum value of this energy has physical value, so calculating total functional is redundant. By minimization of Kohn-Sham scheme self-consistent solutions can be obtained. These equations are generally written in the standard form as:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{\alpha} \int d^3 r \hat{\psi}^+_{\alpha}(\mathbf{r}) \bigtriangledown^2 \hat{\psi}_{\alpha}(\mathbf{r}) + \sum_{\alpha} \int d^3 r \hat{\psi}^+_{\alpha}(\mathbf{r}) v(\mathbf{r}) \hat{\psi}_{\alpha}(\mathbf{r}) + \frac{1}{2} \sum_{\alpha\beta} \int d^3 r \int d^3 r' \hat{\psi}^+_{\alpha}(\mathbf{r}) \hat{\psi}^+_{\beta}(\mathbf{r'}) w(\mathbf{r},\mathbf{r'}) \hat{\psi}_{\beta}(\mathbf{r'}) \hat{\psi}_{\alpha}(\mathbf{r})$$
(2.3)

We define a set  $\nu$  of local one-particle potentials with the property that the solution of each eigenvalue problem

$$H|\phi\rangle = (\hat{T} + \hat{V} + \hat{W})|\phi\rangle = E|\phi\rangle, \hat{V} \in \nu$$
(2.4)

leads to non-degenerate ground state for system of N fermions:

$$H\left|\phi\right\rangle = E_{gs}\left|\phi\right\rangle,\tag{2.5}$$

First Hohenbger-Kohn theorem states that ground state expectation of any observable  $\hat{O}$  is a unique functional of the exact ground state density (n)

$$\langle \Psi[n] | \hat{O} | \Psi[n] \rangle = O[n]$$
(2.6)

When ground state density is known it also determines the external potential of the system and if the kinetic and the inter-particle energy are specified, the entire Hamiltonian.

Second statement of Hohenberg-Kohn theorem defines variational character of the energy functional

$$E_{v_0}[n] := \langle \Psi[n] | \, \hat{T} + \hat{W} + \hat{V}_0 \, | \Psi[n] \rangle \tag{2.7}$$

where  $\hat{V}_0$  is the external potential of a specific system with ground state density  $n_0(r)$ and ground state energy  $E_0$ . The exact ground state density can be determined by minimization of:

$$E_0 = \min E_{v_0} [n]$$
 (2.8)

Kohn and Sham have established that is possible to map the many-body equation through N independent equations using N-particle orbitals. In the Kohn-Sham scheme the many-body ground state density is described in terms of lowest N-particle orbitals:

$$n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2$$
(2.9)

 $\phi_i(r)$  being lowest single particle orbital obtained from a Schrödinger like equation:

$$\left(-\frac{\hbar^2}{2m}\,\nabla^2 + v_s(r)\right)\phi_i(r) = \epsilon_i\phi_i(r), \epsilon_1 \le \epsilon_2\dots$$
(2.10)

Adding Hartree term into total energy functional followed by some calculations [3] yields final expression for external potential:

$$v_{s,0}(r) = v_0(r) + \int d^3 r' w(r, r') n_0(r') + v_{xc}\left([n_0]; r\right)$$
(2.11)

The theory is in principle exact but one has to know the exact universal exchange functional.

#### 2.3 Basics of GW

Most of quantum chemistry approaches use a diagrammatic expansion of the electronic interactions through the bare Coulomb potential, which makes the inclusion of electronic correlations extremely computationally demanding. The method described in this section was first presented by Lars Hedin in 1965 [7] and is often referred as the GW approximation. Conversely to quantum chemistry approaches [20] GW uses an expansion on the screened Coulomb potential where the screening is calculated through linear response.

To form a complete set for N-body system one would have to acquire all Slater determinant from single particle functions. Notation that specifies states by listing quantum labels  $k_1, k_2, \ldots, k_N$  is introduced:

$$(N)^{-1/2}det \{u_k(\mathbf{x}_l)\} \equiv |k, k_1, k_2, \dots, k_N\rangle$$
 (2.12)

"Creation/annihilation" operators  $a_k^+/a_k$  are defined as:

$$a_{k}^{+} |k_{1}, k_{2}, \dots, k_{N}\rangle = |k, k_{1}, k_{2}, \dots, k_{N}\rangle$$

$$a_{k} |k_{1}, k_{2}, \dots, k_{N}\rangle = |k, k_{1}, k_{2}, \dots, k_{N}\rangle$$
(2.13)

It is also important to mention that

$$a_k \left| k_1, k_2, \dots, k_N \right\rangle = 0 \tag{2.14}$$

For  $k \neq k_i$  for all *i*. From these definitions rest of commutation relations can be deduced:

$$\left[a_{k}, a_{k'}^{+}\right]_{+} = a_{k}a_{k'}^{+} + a_{k'}^{+}a_{k} = \delta_{kk'}, \quad \left[a_{k}, a_{k'}\right]_{+} = \left[a_{k}^{+}, a_{k'}^{+}\right]_{+} = 0$$
(2.15)

In purpose of shortening notation and not applying  $a_k^+/a_k$  to individual one-electron states wave field operators  $\psi(x)$  and  $\psi^+(x)$  are defined by:

$$\psi(\mathbf{x}) = \sum_{k} a_k u_k(\mathbf{x}) \tag{2.16}$$

Where **x** stands for space and spin degrees of freedom. For the interpretation of the many-body problem describing electrons interacting with each others we define a Hamiltonian H that contains two terms: The ground state  $H_0$  and a perturbing term  $H_1$ .  $\phi(\mathbf{x}, t)$  represents small external perturbing potential.

$$H = H_0 + H_1$$

$$H_0 = \int \Psi_+(\mathbf{x})h(\mathbf{x})\Psi(\mathbf{x})d\mathbf{x} + \frac{1}{2}\int \Psi_+(\mathbf{x})\Psi_+(\mathbf{x}')v(\mathbf{r},\mathbf{r}')\Psi(\mathbf{x}')\Psi(\mathbf{x})d\mathbf{x}d\mathbf{x}' \quad (2.17)$$

$$H_1 = \int \Psi_+(\mathbf{x})\Psi(\mathbf{x})\phi(\mathbf{x},t)d\mathbf{x}$$

The annihilation operator  $\Psi(\mathbf{x}, t)$  satisfies the equation of motion:

$$i\frac{\partial\Psi(\mathbf{x},t)}{\partial t} = [h(\mathbf{x}) + \phi(\mathbf{x},t)]\Psi(\mathbf{x},t) + \int v(\mathbf{r},\mathbf{r}')\Psi^{+}(\mathbf{x}',t)\Psi(\mathbf{x}',t)\Psi(\mathbf{x},t)d\mathbf{x}' \quad (2.18)$$

Using the relation  $d\Theta(t)/dt = \delta(t)$  and the commutation rules at equal times for  $\Psi(\mathbf{x}, t)$  and  $\Psi^+(\mathbf{x}, t)$  we obtain for the one electron Green function

$$[i(\partial/\partial t) - h(\mathbf{x}) - \phi(\mathbf{x}, t)] G(\mathbf{x}t, \mathbf{x}'t')$$
  
+ $i \int v(\mathbf{r}, \mathbf{r}'') d\mathbf{x}'' \langle N | T \{ \Psi^+(\mathbf{x}'', t) \Psi(\mathbf{x}'', t), \Psi(\mathbf{x}, t), \Psi^+(\mathbf{x}', t) \} | N \rangle$  (2.19)  
=  $\delta(\mathbf{x}, \mathbf{x}') \delta(t, t')$ 

This terms with four field operators contains two particle Green function and describes two-body correlations in the system. This equation can be used as basis for forming infinite chains for more complicated correlations.

To describe interaction of a particle with the rest of the system we generalize the notation with the introduction of a nonlocal time (or energy) dependent quantity called the self-energy operator  $\Sigma$  which is defined from equation 2.19 as:

$$[i(\partial/\partial t) - h(\mathbf{x}) - V(\mathbf{x}, t)] G(\mathbf{x}t, \mathbf{x}'t') - \int \Sigma(\mathbf{x}t, \mathbf{x}''t'') G(\mathbf{x}''t'', \mathbf{x}'t') d\mathbf{x}'' dt'' = \delta(\mathbf{x}, \mathbf{x}') \delta(t, t')$$
(2.20)

The quantity  $V(\mathbf{x}, t)$  is the total average potential in the system:

$$V(\mathbf{x},t) = \phi(\mathbf{x},t) + \int v(\mathbf{r},\mathbf{r}') \langle N | \Psi^+(\mathbf{x}'t)\Psi(\mathbf{x}',t) | N \rangle d\mathbf{x}'$$
(2.21)

It is more convenient to use frequency domain when dealing with energies hence the Fourier transform:

$$G(\mathbf{x}, \mathbf{x}'; \omega) = \int G(\mathbf{x}t, \mathbf{x}'t') exp\left[i\omega(t - t')\right] d(t - t')$$
(2.22)

This expression is not valid unless G depends only on time arguments, implying time independence (or zero value) of external potential  $\phi(\mathbf{x}, t)$ . Fourier transform of self energy operator 2.20 becomes

$$[\omega - h(\mathbf{x}) - V(\mathbf{x})] G(\mathbf{x}, \mathbf{x}'; \omega) - \int \Sigma(\mathbf{x}, \mathbf{x}''; \omega) G(\mathbf{x}'', \mathbf{x}'; \omega) = \delta(\mathbf{x}, \mathbf{x}')$$
(2.23)

which represents many-body character of G origins in energy dependence of the selfenergy  $\Sigma$ . If it did not depend on energy the set of equations could be solved for a set of eigenfunctions  $u_k$ . Since this in not the case one has to look for physically meaningful approximations. One of the most commonly used relatively simple estimations that makes  $\Sigma$  independent of energy applies Hartree and Hartree-Fock approximation to Green function theory:

$$\Sigma^{H} = 0; \quad \Sigma^{HF}(\mathbf{x}t, \mathbf{x}', t') = iv(\mathbf{x}, \mathbf{x}')G(\mathbf{x}t, \mathbf{x}'t')\delta(t - t' + \delta)$$
(2.24)

with fourier transform of  $\Sigma^{HF}(t-t^\prime)$  being

$$\Sigma^{HF}(\mathbf{x}, \mathbf{x}'; \omega) = -v(\mathbf{x}, \mathbf{x}') \langle N | \psi^+(\mathbf{x}' \psi(\mathbf{x}) | N \rangle = V_{ex}(\mathbf{x}, \mathbf{x}')$$
(2.25)

# Within the Hartree-Fock approximation electronic correlations are completely neglected.

When dynamical interactions are included the full Green function is needed, and the self energy has to be interpreted as a functional of G:  $\Sigma = \Sigma(G)$ . Formally it can be expressed from the dynamically screened function W:

$$W(12) = \int v(13)\epsilon^{-1}(32)d(3)$$
(2.26)

Using the following abbreviated notation:

(1) = 
$$(\mathbf{x}_1, t_1), \quad v(12) = v(\mathbf{r}_1, \mathbf{r}_2)\delta(t_1 - t_2)$$
 (2.27)

Inverse dielectric function  $\epsilon^{-1}$  obtained from classical theory measures screening of change  $\delta V$  due to small variation  $\delta \phi$  in the external potential.

$$\epsilon^{-1}(1,2) = \frac{\delta V(1)}{\delta \phi(2)} = \delta(12) + \int v(13) \frac{\delta \langle \rho(3) \rangle}{\delta \phi(2)} d(3)$$
(2.28)

The key quantity needed to be calculated is the irreducible polarizability P, as  $\epsilon$  relates to P as:

$$\epsilon(12) = \delta(12) - \int P(32)v(13)d(3). \tag{2.29}$$

As a function of P, W can be expressed as:

$$W(12) = v(12) + \int W(13)P(34)v(42)d(34)$$
(2.30)

The self energy  $\sigma$  and P can now be written as functional derivatives of G:

$$\Sigma(12) = -i \int v(1^+3)G(14\frac{\delta G^{-1}(42)}{\delta\phi(3)})d(34)$$
(2.31)

$$P(12) = i \int G(23)G(42) \frac{\delta G^{-1}(42)}{\delta V(1)} d(34)$$
(2.32)

Finally, the vertex  $\Gamma$  is defined as:

$$\Gamma(12;3) = -\frac{\delta G^{-1}(12)}{\delta V(3)} = \delta(12)\delta(13) + \frac{\delta \Sigma(12)}{\delta V(3)}.$$
(2.33)

Within the GW approximation the vertex is set to:

$$\Gamma(12;3) = \delta(12)\delta(13)$$
 (2.34)

This means that electron-hole interactions are not accounted for in the dielectric response function.

### 2.4 DFT in practice

The introduction of DFT has been briefly covered in section 2.2. The general idea of the approach is provided by the set of Kohn-Sham equations in 2.9, 2.10 and in 2.11. Looking at the equations it seems that the determination of the ground-state electronic density is an easy task. However, their practical implementation requires the use of some tricks and approximations [8].

#### 2.4.1 Approximation to exchange functional

The Kohn-Sham equations represent a mapping of the interacting many-electron onto a system of non-interacting electrons in the effective potential produced by all the other particles. Complete knowledge of universal exchange correlation energy functional would produce exact total density. However as the universal functional is unknown, approximations have to be used. The most common drawback of these approximate functionals is an over-counting of the electron-electron self-interaction in the Hartree term.

One of the first used approximations is Local Density Approximation (LDA), which states that exchange-correlation energy functional can be approximated by the one of the homogeneous electron gas:

$$\varepsilon_{XC}(\mathbf{r}) \approx \varepsilon_{XC}^{hom} [n(\mathbf{r})].$$
 (2.35)

Various methods exist for exchange-correlation energy calculation from homogeneous electron gas that give similar accuracy. They are all based on some parametrization and are formulated to compute global minimum of the system. **In all our calculations we have used Perdew-Zunger LDA functional** [25].

#### 2.4.2 Plane wave expansion and Bloch theorem

Problem of dealing with multiple non-interacting electrons moving in static background potential is covered by Bloch theorem, which states that in a periodic lattice, wave function can be written as a periodic part and a wavelike part [6]:

$$\psi_i(r) = \exp\{i\mathbf{k}r\}f_i(r). \tag{2.36}$$

The cell-periodic part becomes:

$$f_i(r) = \sum_G c_{i,G} exp\{iGr\},$$
(2.37)

where G are reciprocal lattice vectors defined as  $\mathbf{G} \cdot \mathbf{l} = 2\pi m$ . I are lattice vectors and m integers. In full form electronic wave functions are expressed as:

$$\psi_i(\mathbf{r}) = \sum_G c_{i,\mathbf{k}+\mathbf{G}} \exp\left[i(\mathbf{k}+\mathbf{G}\cdot\mathbf{r})\right]$$
(2.38)

In principle an infinite set of plane vectors is needed. However coefficients  $c_{i,\mathbf{k}+\mathbf{G}}$  for plane waves with smaller kinetic energy  $(\hbar^2/2m)|\mathbf{k}+\mathbf{G}|^2$  are usually more important. A cut off value can be used to truncate the basis set. This approximation allows a description of wave functions with a discrete set of plane waves, i.e. with a finite basis set. Convergence has to be checked with respect to this cut-off. A correction factor can be calculated [11] for estimating the difference between theoretical infinite number and practical finite basis sets.

Inserting plane wave function 2.38 into Kohn-Sham equation 2.10 followed by integration over  $\mathbf{r}$  greatly simplifies expression:

$$\sum_{G'} \left[ \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_{ion}(\mathbf{G} - \mathbf{G}') + V_H(\mathbf{G} - \mathbf{G}') + V_{xc}(\mathbf{G} - \mathbf{G}') \right] c_{i,\mathbf{k}+\mathbf{G}'} = \epsilon_i c_{i,\mathbf{k}+\mathbf{G}}$$
(2.39)

In this form kinetic energy term is diagonal and potential are described in terms of their Fourier transforms. Size of the matrix depends on the cutoff energy  $(\hbar^2/2m)|k+G_c|^2$ .

One of the Bloch theorem limitations is its description of defects or effects in direction perpendicular to the lattice. In case of defects one must assume super-cell containing defects and not every single defect in lattice. It is essential to include a bulk large enough so the defects do not interact with each other.

#### 2.4.3 The pseudo potential approximation

In practice plane-wave basis set provides very limiting platform for computation of all-electron structure in real crystal as this would require extremely large cut-off for describing the strongly oscillating electronic wave functions in the core region. The pseudo potential approximation allows the electronic wave functions to be build from much smaller basis set. The basis for this approximation comes from the fact that most of the physical and chemical properties of materials depends on the valence electrons. Thus effect of core levels are replaced by weaker pseudo potentials that act on set of pseudo wave functions rather than the true valence wave functions. Pseudo potential is build in such a way that scattering properties or phase shifts for pseudo functions are identical to core level electrons and ion interaction, but with no remaining radial nodes in the core region. The most general form of pseudo potential is:

$$V_{NL} = \sum_{lm} |lm\rangle V_l \langle lm|$$
(2.40)

where  $|lm\rangle$  are the spherical harmonics and  $V_l$  is the pseudo potential for angular momentum l. This operator decomposes the wave function into spherical harmonics, each one is then multiplied with the relevant pseudo potential  $V_l$ . Local pseudo potential means that same angular momentum components are used in a system. It is possible to produce predetermined phase shifts for each state but limitations arises with the number of those shifts maintaining sufficient smoothness. Without a smooth and weak pseudo potential, it becomes difficult to expand the wave functions using reasonable number of plane-wave basis states. It is important that not only spatial dependences of real and pseudo functions are the same but also absolute magnitudes in order to produce same charge densities.

Total ionic potential of the solid is obtained by placing a pseudo potential at the position of each ion. Information about positions can be expressed in the terms of the structure factor for each wave vector  $\mathbf{G}$  at atomic position  $R_I$ :

$$S_{\alpha}(\mathbf{G}) = \sum_{I} exp \left[ i\mathbf{G} \cdot \mathbf{R}_{I} \right]$$
(2.41)

where the sum runs over all positions of defined specie  $\alpha$  in single unit cell. Periodicity of the system restricts nonzero components to reciprocal lattice vectors.

Total ionic potential  $V_{ion}$  is formulated as a product of the structure factor and pseudo potential over all the atomic species:

$$V_{ion}(\mathbf{G}) = \sum_{\alpha} S_{\alpha}(\mathbf{G}v_{\alpha(\mathbf{G})})$$
(2.42)

At large distances pseudo potential is reduced to bare Coulomb potential (Z/r) where Z is the valence of the atom). More interesting is the behavior for small wave vectors as it follows from Fourier transform that pseudo potential diverges as  $Z/G^2$ . But since it does not behave as pure Coulomb potential for small values it can be treated as difference between the two. For a certain atomic specie ionic potential becomes:

$$v_{\alpha,core} = \int \left[ Z/r - v_{\alpha}^{0}(r) \right] 4\pi r^{2} dr \qquad (2.43)$$

with  $v_{\alpha}^{0}$  is pseudo potential for l = 0 angular momentum. This integral is nonzero only within core region because the potentials are identical outside. There is no contribution to total energy from  $Z/G^{2}$  component at **G**=0 due to cancellation of divergence but the non-Coulomb part contributes with:

$$N_{el}\Omega^{-1}\sum_{\alpha}N_{\alpha}v_{\alpha,core} \tag{2.44}$$

where  $N_{el}$  is the number of electrons in the system,  $N_{\alpha}$  is total number of particular specie's atoms and  $\Omega$  volume of the unit cell.

#### 2.4.4 Ewald summation

The Coulomb energy is difficult to calculate using either real or reciprocal space as the interaction is always long range. Ewald developed a rapidly convergent method for Coulomb summation over a periodic lattice:

$$\sum_{l} \frac{1}{|\mathbf{R}_{l} + l - \mathbf{R}_{2}|} = \frac{2}{\sqrt{\pi}} \sum_{l} \int_{\eta}^{\infty} exp \left[ -|\mathbf{R}_{1} + \mathbf{l} - \mathbf{R}_{2}| 2\rho^{2} \right] d\rho + \frac{2\pi}{\Omega} \sum_{G} \int_{0}^{\eta} exp \left[ -\frac{|\mathbf{G}|^{2}}{4\rho^{2}} \right] exp \left[ i(\mathbf{R}_{1} - \mathbf{R}_{2}) \cdot \mathbf{G} \right] \frac{1}{\rho^{3}} d\rho$$
(2.45)

where l are the lattice vectors, **G** reciprocal-lattice vectors and  $\Omega$  volume of the unit cell. This identity rewrites the lattice summation for the Coulomb energy between ion position on  $\mathbf{R}_2$  and an array of atoms placed at the points  $\mathbf{R}_1 + l$ . It holds for all the positive  $\eta$ . At first sight the infinite summation has been replaced by two sums, one over real and other for reciprocal space. However it has property of much faster convergence in personal space when applied with correct  $\eta$ . Yet there is a problem, as the separation of sum into two spaces does not give the exact value of final total energy. So additional terms need to be included into equation 2.45.

$$E_{ion} = \frac{1}{2} \sum_{I,J} Z_I Z_J e^2 \left[ \sum_l \frac{erfc(\eta | \mathbf{R}_1 + \mathbf{l} - \mathbf{R}_2 |)}{|\mathbf{R}_1 + \mathbf{l} - \mathbf{R}_2|} - \frac{2\eta}{\sqrt{\rho}} \delta_{IJ} + \frac{4\pi}{\Omega} \sum_{G \neq =0} \frac{1}{|\mathbf{G}^2|} exp \left\{ -\frac{|\mathbf{G}|^2}{4\eta^2} \right\} cos \left[ (\mathbf{R}_1 - \mathbf{R}_2) \cdot \mathbf{G} \right] - \frac{\pi}{\eta^2 \Omega} \right]$$
(2.46)

where  $Z_I$  and  $Z_J$  are the valences of the ions I and J. Erfc is complementary error function. As ions do not interact with their own Coulomb charge, l = 0 term must be omitted from the real space when I=J.

#### 2.4.5 Born-Oppenheimer approximation

Since now, we have only presented the approximations that are used for the electronic degree of freedom, assuming that the ions are frozen at a given position. When modeling material properties, however, one needs to take into account also atomic relaxations. The knowledge of the ground-state of a system implies the finding of the global minimum of the system, including both electrons and ions. In principle, this search needs the solution of a quantum equation where the electronic and ionic degrees of freedom are entangled. However, as the mass of electrons is insignificant compared to ionic masses it can be assumed that electrons will instantly respond to any atomic movement. This assumption is called the Born-Oppenheimer approximation and allows for the separation of electronic and nuclear wave functions:

$$\Psi_{total} = \Psi_{electronic} \Psi_{nuclear} \tag{2.47}$$

Moreover, as most of the atomic elements have a De Broglie wave-length very small, the atomic degrees of freedom are always treated classically. The finding of the ground state then is implemented with two loops: the internal one, search for the electronic ground-state at fixed ionic positions, the external one, solve classical Newton equations for the ions. These were some of the fundamental approaches and approximation used for total energy calculation of solid states. Standard procedure is shown in figure 2.3. It requires initial guess (or very simplified self consistent calculation) for electronic charge density from which Hartree potential and exchange correlation can be calculated. Hamiltonian matrices are then constructed for each k-points from equation 2.39.



Figure 2.3: Procedure for calculation of total energy using conventional matrix diagonalization

Kohn-Sham eigenvalues are calculated from diagonalization of this matrix. This procedure is used until convergence is achieved. Total energy usually depends more on the ionic potential than configuration potential so calculations are performed using an energy cutoff and number of  $\mathbf{k}$  points at which energy differences have converged rather than absolute energy convergence.

#### 2.5 GW in practice

Foundations of GW approximation [2] [7] have been described in the section 2.3. GW approach can be seen as generalized Hartree-Fock where correlations are taken into account through linear response. Basic equations are too difficult (or time consuming) for practical use in their original form, so again some tricks and approximations are used.

We begin with the assumption of a periodic system with unit cell of volume  $\Omega$ , set up by N number of cells, such as limit goes to  $N \to \infty$ . Every function is represented as sum of normalized plane waves and depends on spatial coordinates.

$$\Psi_{nk}(x) = \frac{1}{\sqrt{N\Omega}} \sum_{G} \psi_{nk}(G) e^{i(k+G)\mathbf{x}}$$
(2.48)

Where G runs over reciprocal lattice. Products of the two Kohn-Sham states in real space is:

$$M_{nk,n',k'}(x) = \sqrt{N\Omega}\psi_{nk}^{*}(x)\psi_{n',k'}(x)$$
(2.49)

Preferably functions are expressed in phase space and require Fourier transformation. For example polarizabiliy becomes:

$$P(xx';\omega) = \frac{1}{N\Omega} \sum_{kGG'} e^{i(k+G)\mathbf{x}} P_k(G,G';\omega) e^{-i(k+G')\mathbf{x'}}$$
(2.50)

Sum over k vectors runs through a set of uniformly spaced points in first Brillouin zone. Same convention is used for bare Coulomb potential  $v^c$  resulting in reciprocal spaced diagonal matrix:

$$v^{c}(x,x') = \frac{2}{|x-x'|}$$
(2.51)

$$v_k^c(G,G') = \frac{8\pi}{(G+q)^2} \delta_{GG'}$$
(2.52)

The first step for GW calculation is evaluation of polarizability  $P_0$ . Only the imaginary value of frequency is included:  $\omega = is$ . The expression in reciprocal space is:

$$P_q(GG'; is) = -\frac{4}{N\Omega} \sum_{cvqk} \theta(\epsilon_{ck} - \mu) \theta(\mu - \epsilon_{vk+q}) M^*_{ck,vk+q}(G')$$

$$\frac{2(\epsilon_{ck} - \epsilon_{vk+q})}{(\epsilon_{ck} - \epsilon_{vk+q})^2 + s^2}$$
(2.53)

 $\mu$  in the Fermi energy, so the  $\theta$  function selects a band index v, which belongs to occupied bands (valence) and bands c representing unoccupied states (conduction). Ideally sums over k and q should be performed over infinitely dense mesh in first Brillouin zone. In practice special points technique is used: Fourier quadrature of the integrand. It is also useful to consider analytical behavior of P when  $q \rightarrow 0$  as:

$$P_q(G=0,G'=0;\omega) \sum_{\alpha\alpha'} q_\alpha S^{\alpha\alpha'}(\omega) q_{\alpha'}$$
(2.54)

$$P_q(G, G'=0; \omega) \sum_{\alpha} L^{\alpha}(G; \omega) q_{\alpha}$$
(2.55)

$$P_q(G=0,G';\omega) \sum_{\alpha} q_{\alpha}(R^{\alpha}(G';\omega)) *$$
(2.56)

where  $\alpha$  and  $\alpha'$  run over three spatial coordinates. For imaginary frequencies P is Hermitian.

Second step is to compute screened Coulomb potential, obtained as:

$$W(is) = [1 - \nu^c P(is)]^{-1} \nu^c$$
(2.57)

For imaginary frequencies W is Hermitian as well. We split the screened Coulomb potential into pure exchange and pure correlation by subtracting  $v^c$ . This way the exchange self-energy is given by:

$$\langle nk | \Sigma_x | n'k \rangle = -\frac{1}{N\Omega} \sum_{vq} \sum_G \theta(\mu - \epsilon_{vk-q}) M^*_{vk-q,nk}(G) v^c_q(G) M_{vk-q,n'k}(G)$$
(2.58)

and correlation by:

$$\langle nk | \Sigma_{c}(\omega) | n'k \rangle = -\frac{1}{N\Omega} \sum_{n"q} \sum_{GG'} M_{n"k-q,nk}^{*}(G) M_{n"k-q,n'k}(G')$$

$$\frac{-1}{2\pi i} \int d\omega' \frac{W_{GG'(q;\omega')}^{P} e^{-i\delta\omega'}}{\omega + \omega' - \epsilon_{n"k-q} - i\eta sign(\mu - \epsilon_{n"k-q})}$$
(2.59)

Setting  $\sigma_c$  to zero will give Hartree-Fock approximation. This integral is problematic to solve and computationally demanding for systems with more than a few electrons. Usually plasmon-pole models are used for the screening. In our calculations we have used the Godby-Needs [24] plasmon-pole that allows for an analytical solution of the energy integral.

#### 2.5.1 The plasmon-pole model

The dynamical behavior of the dielectric matrix is given by a parametrized model of the dielectric function in reciprocal space:

$$\varepsilon_{GG'}^{-1}(q;\omega) = \delta_{GG'} + \frac{\Omega_{GG'}^2(q)}{\omega^2 - \omega_{GG'}(q)^2}$$
(2.60)

~ 0

where  $\Omega_{GG'}$  (effective bare plasma frequency) and  $\omega_{GG'}$  are the two parameters of the model. These frequencies are chosen, when  $\epsilon^{-1}$  is actually computed, as:  $\omega = 0$  and  $\omega = i\omega_p$  ( $\omega_p$  is an estimate for plasmon frequency). This should only work, in principle, for systems where plasmons are well defined. However, it has been also applied to molecules and has given very accurate results. Once the screening is known, the correlation part of self energy from equation 2.59 can be evaluated analytically by choosing an integration part with an arc in the lower half plane ( $e^{-i\delta\omega'}$ ). We obtain:

$$\frac{-1}{2\pi i} \int d\omega' \frac{W_{GG'}^P(q;\omega')e^{-i\delta\omega'}}{\omega + \omega' - \epsilon_{n^*k-q} - i\eta sign(\mu - \epsilon_{n^*k-q})} = \frac{-1}{2\pi i} \int d\omega' \frac{(\epsilon_{GG'}^{-1}(q;\omega') - \delta_{GG'})v_C(G'+q)e^{-i\delta\omega'}}{\omega + \omega' - \epsilon_{n^*k-q} - i\eta sign(\mu - \epsilon_{n^*k-q})} = (2.61)$$

$$\frac{-\Delta_{GG'}^2 v_C(G'+q)}{2\delta_{GG'}(q)} \left[ \frac{\theta(\mu - \epsilon_{nk})}{\omega + \tilde{\omega}_{GG'}(q) - \epsilon_{nk} - i\eta} + \frac{\theta(\epsilon_{nk} - \mu)}{\omega + \tilde{\omega}_{GG'}(q) - \epsilon_{nk} + i\eta} \right]$$

#### 2.5.2 Perturbative GW, GW@DFT

The most important computational approximation is that, even if in principle GW equations form a set of complete equations that should be solved self-consistently, this is almost never achieved. Indeed in the majority of the cases, it is sufficiently accurate (and computationally affordable) to perform a one-shot GW on top of some reasonable DFT initial guess. In other words, the DFT initial wave functions are assumed to be very close to the "real" quasi-particle wave functions and are not re-calculated, while DFT Kohn-Sham energies are corrected with a diagonal GW self-energy. In the literature this approximation is often referred as GW@DFT or  $G_0W_0$ . As the GW correction does not come from a diagonalization, and DFT exchange-correlation potentials fail in describing energy differences between electronic states of different nature (delocalized-localized, occupied un-occupied) some times a change in the energy ordering of the states may appear between DFT and GW@DFT. In all our calculations we have performed  $G_0W_0$  on top of DFT-LDA.

#### 2.6 Bethe-Salpeter equation

Eigenstate  $|E\rangle$  and energy  $\Omega$  of "unknown" excitonic state can be calculated from [12]:

$$\bar{H} \left| E \right\rangle = \Omega \left| E \right\rangle \tag{2.62}$$

 $|E\rangle$  can be written in the basis of single-particle orbitals as:

$$\Psi(xx') = \sum_{nn'k} \psi_{nk}^{qp}(x)\psi_{n'k}^{qp*}(x')$$
(2.63)

Excitation energies are solution of an eigenvalue problem and it is necessary to find a form of effective two-particle Hamiltonian of eq. 2.62. In the context of neutral excitations, this effective two-particle Hamiltonian is called the Bethe-Salpeter equation, describing electron-hole pairs.

The information about this excitation is given as two-particle Green-Function:

$$G_2(x_1t_1, x_2t_2, x_3t_3, x_4t_4) = (-i)^2 \langle N | T\{\Psi(x_1t_1)\Psi(x_2t_2)\Psi^{\dagger}(x_3t_3)\psi^{\dagger}(x_4t_4)\} | N \rangle$$
(2.64)

 $G_2$  describes the propagation of created electron-hole pair and  $|N\rangle$  is the ground state of N particle system.

Four point independent particle polarizability from equation 2.32 is:

$$P^{0}(1,1';2,2') = -iG(1',2')G(2,1)$$
(2.65)

Generalized form for response function is then:

$$\chi(1, 1', 2, 2') = P_0(1, 1', 2, 2') + \int P_0(1, 1', 3, 3')[v(3, 3', 4, 4') - W(3, 3', 4, 4')]\bar{P}(4, 4', 2, 2')d3d3'd4d4'$$
(2.66)

Expression for polarizability differs only in term of long range Coulomb potential  $(v \rightarrow \bar{v})$ .

In practice all of the quantities are calculated in frequency domain thus requiring Fourier transform:

$$\chi(1, 1', 2, 2') = \chi(x_1 t_1, x_1' t_1^{\dagger}, x_2 t_2, x_2' t_2^{\dagger}) \to \chi(x_1, x_1', x_2, x_2', \omega) \delta(x_1 - x_1') \delta(x_2 - x_2')$$
(2.67)

Another important assumption implemented is energy dependence of the screen potential which is neglected assuming  $W(\omega) = W(\omega = 0)$ . In theory this could be solved with inverting the matrix for each possible frequency  $\omega$ . However there exists more practical way, reformulating the problem into effective eigenvalue problem. First step consists of changing the basis set, consisting of single particle eigenfunctions  $\psi_n(x)$ (the subindex n has to be read as n = (n, k), it now contains the information of the band and k point). In this basis four point quantities become:

$$S(x_1, x_{1'}, x_2, x_{2'}) = \sum_{(n_1, n_{1'})(n^*, n_{2'})} \psi^*_{n_1}(x_1) \psi_{n_1'}(x_1') \psi_{n_2}(x_2) \phi^*_{n_2}(x_{2'}) S_{(n_1, n_{1'})(n_2, n_{2'})}$$
(2.68)

Active eigenvalue problem now becomes:

$$\sum_{(n_1,n_{1'})(n_2,n_{2'})} H_{(n_1,n_{1'})(n_2,n_{2'})^{2p}} A^{\mu}_{(n_2,n_{2'})} = E^{\mu} A^{\mu}_{(n_2,n_{2'})}$$
(2.69)

where two-particle Hamiltonian is:

$$H_{(n_1,n_{1'})(n_2,n_{2'})^{2p}} = (\epsilon_{n_{1'}} - \epsilon_{n_1})\delta_{(n_1,n_2)(n_{1'},n_{2'})} + (f_{n_1} - f_{n_{1'}})\Xi_{(n_1,n_{1'})(n_2,n_{2'})}$$
(2.70)

with  $\epsilon_{n_{1'}}$  and  $\epsilon_{n_1}$  being quasi particle energy eigenvalues and  $\Xi_{(n_1,n_{1'})(n_2,n_{2'})}$  presenting the interaction kernel, defined as:

$$\Xi_{(n_1,n_{2'})(n_2,n_{2'})} = -\int dx_1 dx_{1'} \psi_{n_1} \psi^*_{n_{1'}}(x_{1'}) W(x_1,x_{1'}) \psi^*_{n_2}(x_1) \psi_{n_{2'}}(x_1) + \int dx_1 dx_{1'} \psi_{n_1}(x_1) \psi^*_{n_{1'}}(x_1) v(x_1,x_{1'}) \psi^*_{n_2}(x_{1'}) \psi_{n_{2'}}(x_{1'})$$
(2.71)

In general  $A^{\mu}$  are not orthogonal. In the case of semiconductors this expression can be simplified:  $(f_{n_1} - f_{n_{1'}})$  is different from zero only for transitions for which  $(n_1, n_{1'})$ = (occupied, unoccupied) or vice versa.

The matrix representation of the two body Hamiltonian for a semiconductor-insulator is:

$$\begin{pmatrix} & v_c, c_2 & c_2, v_2 & v_2, v_{2'} & c_2, c_{2'} \\ \hline v_1, c_1 & H_{(v_1c_1)(v_2c_2)}^{2p} & \Xi_{(v_1c_1)(c_2v_{2'})} & \Xi_{(v_1c_1)(v_2v_{2'})} & \Xi_{(v_1,c_1)(c_2c_{2'})} \\ c_1, v_1 & -\Xi_{(c_1,v_1)(v_2c_2)} & -H_{(c_1v_1)(c_2v_2)}^{2p} & -\Xi_{(c_1v_1)(v_2v_{2'})} & -\Xi_{(c_1v_1)(c_2c_{2'})} \\ v_1, v_{1'} & 0 & 0 & e_v \delta_{(v_1,v_2)(v_{1'},v_{2'})} & 0 \\ c_1, c_{1'} & 0 & 0 & 0 & e_c \delta_{(c_1,c_2)(c_{1'},c_{2'})} \end{pmatrix}$$
(2.72)

where  $e_v = (E_{v_{1'}} - E_{v_1})$  and  $e_c = (E_{c_{1'}} - E_{c_1})$ .  $v_i$  and  $c_i$  stand for valence and conduction states, respectively.

In "block" representation matrix for  $H^{2p}$  is:

$$\begin{pmatrix} H_{(v_1c_1)(v_2c_2)}^{2p-resonant} & \Xi_{(v_1c_1)(c_2v_2)}^{coupling} \\ -\left[\Xi_{(v_1c_1)(c_2v_2)}^{coupling}\right]^* & -\left[H_{(v_1c_1)(v_2c_2)}^{2p-resonant}\right]^* \end{pmatrix}$$
(2.73)

 $H^{2p-resonant}$  is Hermitian and corresponds to positive absorption energy while  $-[H^{2p-resonant}]$  gives de-excitation energies. Ignoring the coupling part of the matrix eigenvalue problem is reduced to:

$$\sum_{(v_2,c_2)} H^{exc,2p\ resonant}_{(v_1,c_1)(v_2,c_2)} A^{\mu}_{(v_2,c_2)} = E^{exc}_{\mu} A^{\mu}_{(v_1,c_1)}$$
(2.74)

This resonant part is the one that is diagonalized in all our calculations.

## 3. Peroxy linkage defect in silica

It has been briefly commented in the introduction that previous works on the optical properties of POL are scarce and the results quite controversial [13].

Experimentally only very few results report peroxy bridge measurements. In one case it has been assigned to a very broad peak in the 6.5-7.8 eV region [17], while ref. [26] reports a band at 3.8 eV with a very low intensity. Ref. [26] and [17] justify the presence of POL with absence of any EPR signals because POL defect is indeed a paramagnetic defect. Their second argument is the decrease of the observed optical absorption peak after hydrogen treatment, possibly due to following reaction:

$$\equiv Si - O - O - Si \equiv +H_2 \rightarrow \equiv Si - O - H + H - O - Si \equiv (3.1)$$

First theoretical estimation was proposed by O'Reilly and Robertson [15]. They used a tight-binding Hamiltonian model on a 243 atoms  $\alpha$ -quartz cell. Peroxy bridge configuration was considered to be the same as in the  $H_2O_2$  molecule: 1.49 Å distance between O atoms and dihedral angle between O-O-H of approximately 100°. This first attempt is, of course, very rough as it is well known that tight-binding like methods completely miss the description of solid-state effects, which are crucial in bulk materials. The simple use of the crystalline polymorph quartz may not be too bad, as the local structure of quartz and a-SiO<sub>2</sub> is very similar. Indeed, quartz and silica are based on a network of SiO<sub>4</sub> tetrahedral. In ref. [15], it is shown that POL induces two states: a  $p\sigma$  resonance at -4.4 eV and an empty  $p\sigma*$  state at 4.2 eV, which produce optically active transition at 8.6 eV. From the numbers, it is clear that electron-hole interaction has completely been neglected. We expect that this electron-hole interaction would be very important in silica, leading to strongly bounded excitons, as silica has a very low dielectric constant.

G. Pacchioni and G. Ierano studied peroxy bridge defect in silica using the Hartree-Fock (HF) approximation followed by various configuration interaction (CI) corrections [13]. Calculations were performed on small cluster models passivated with H (the biggest cluster was  $Si_2O_8H_6$ ). The use of cluster models precludes a correct treatment of the long-range dielectric behavior of the system under study. Another limitation lies in the use of localized basis sets for which the completeness of the basis can not be stated a-priori, and consequently the results may strongly depend on the basis choice. The relaxed distance between O-O atoms is 1.43 Å. The results show that the lowest transition occur at  $6.5 \pm 0.3$  eV with a very low intensity approximately  $10^{-4}$ . It is supposed to occur from doubly occupied  $\pi$ \* orbital from just above oxygen 2p band localized on O-O to the conduction band. This study does not show presence of an empty  $\sigma$ \* defect state, contrary to the model proposed by Robertson [15].

In ref. [13] there are also presented some calculations on the hydrogen peroxide molecule that is used as a very simplify model for POL. Various configuration interaction treatments show that the lowest transition occurs at  $(6.2\pm0.2)$  eV. As there are no experimentally detected absorption bands below 6.7 eV, the only option is to compare this result with other theoretical reports. In ref. [16] a similar transition energy (6.24 eV) has been calculated. In the case of molecules, we expect that the use of localized basis may not give an accurate description of the optical transitions in H<sub>2</sub>O<sub>2</sub>, as such basis completely fails in modeling scattering states. Scattering states may be crucial when dealing with H<sub>2</sub>O<sub>2</sub>, as its electron affinity (EA) is negative. A negative EA always induces the presence of scattering states between the vacuum level and the lowest unoccupied molecular orbit (LUMO).

In the last referred study [18], Time Dependent Density Functional Theory was used with standard exchange-correlation functionals and with 20% fraction of Fock potential. It is well known that the accuracy of TDDFT can not be assessed a-priori, indeed citing the authors of [18]: "the absolute value are likely to be underestimated ... we focus only on comparing the transition energies for the various sites ...".

## $3.1 \quad H_2O_2$

Similarly to previous studies we consider  $H_2O_2$  molecule as the "toy model" of POL. In the first step we relaxed the molecule with minimization of total energy using DFT-



Figure 3.1: Left - Unrelaxed  $H_2O_2$  structure, Right - Relaxed  $H_2O_2$  structure [19]

LDA with the Quantum ESPRESSO package [22].  $H_2O_2$  was considered to be totally isolated, with a cell parameter of 30 Å and Martyna-Tuckerman correction. Martyna-Tuckerman approach simply cuts off any long distance Coulomb interactions, isolating molecules from their periodic replicas. The convergence with respect to the plane-wave basis set has been achieved with 80 Ry cutoff for a total energy difference of 0.0001 eV. Pseudo-potentials were obtained from quantum-espresso database [23].

During the atomic relaxation, while the inter atomic distance changed from 1.48 Å to 1.4785 Å, which is negligible, the dihedral angle changes significantly from  $109.47^{\circ}$  to  $98.12^{\circ}$ , see figure 3.1.

With the relaxed atomic configuration we computed the Kohn-Sham states and their eigenvalues. 12 Kohn-Sham states are shown in table 3.1. Highest occupied molecular orbital (HOMO) is, as expected, localized on the 2 p non-bonding O orbitals, while LUMO appears to be a  $\sigma^*$  orbital (H<sub>2</sub>O<sub>2</sub> has 14 valence electrons).

Knowing the DFT electronic structure we proceed to calculate GW corrections. We reached a convergence of less than 0.1 eV for energy differences by considering 160 empty states. In table 3.2 GW corrections to KS states are shown. It is clear from last column of table 3.2, the GW correction does not appear as simple scissor shift. This is indeed the signature of the usual "fail" of DFT due to the approximate nature of known exchange-correlation functionals. This "fail" is always more evident for empty states,

Band	EigenValue	Plot	Band	Eigen Value	Plot
1	-27.79 eV		2	-22.34 eV	
3	-13.01 eV		4	-12.57 eV	
5	-9.60 eV		6	-9.034 eV	<b>Y</b>
7-НОМО	-5.90 eV		8-LUMO	-1.87 eV	
9	-0.80 eV		10	0.110 eV	
11	0.111 eV		12	0.47 eV	

Table 3.1: Kohn-Sham eigenvalues and square modulus of the corresponding wavefunction. O atoms are in red and H atoms in blue

of course, as DFT deals with electronic density and hence with "occupied states".

Experimentally no data exists for the Electron Affinity (EA) of hydrogen peroxide, as it has a negative electron-affinity. Quantum Chemistry theoretical calculations place the EA at -2.5 eV [28]. Many scattering states will be present between LUMO and vacuum level such enabling more complex electronic transitions. Experimental measurements of vertical ionization potential (VIP) placed it around 11.6 eV [30] [31]. Theoretical calculations have shown that the VIP value strongly depends on the dihedral angle [27]. With these two values for IP and EA we can estimate the HOMO-LUMO gap for  $H_2O_2$  to be around 14 eV. Within GW we obtained a HOMO-LUMO gap of 13.3 eV, which is in very good agreement with the few results available in the literature.

GW has provided with the N-1 and N+1 electronic excitations. We proceeded with the solution of Bethe-Salpeter equation. The imaginary part of the macroscopic dielectric tensor, molar absorptivity (related to the absorption spectra), is calculated from excitonic oscillator strength (probability of coupling with light), see figure 3.2. Results containing first four transitions are shown in Table 3.3. The lowest excitonic transition

Ν	KS energy (eV)	$\Delta$ GW (eV)
1	-27.79	-4.22
2	-22.34	-7.72
3	-13.01	-3.51
4	-12.57	-4.62
5	-9.60	-4.22
6	-9.03	-4.19
7	-5.90	-4.19
8	-1.87	5.13
9	-0.80	2.31
10	0.11	1.69
11	0.11	0.30
12	0.47	0.28

Table 3.2: GW corrections for  $H_2O_2$  molecule

occurs at 2.34 eV. Its oscillator strength is very low. The most relevant exciton, in terms of oscillator strength, has a transition energy of 6.79 eV. All of the excitations arise from non-trivial transitions from HOMO and different empty states. Many of those empty states are scattering states located between the vacuum level and LUMO. Weight describes probability of individual transition within particular exciton and sum of all weights is always 1. Even if our 6.79 eV excitation energy agrees well with ref. [13], these numbers are not comparable at all, as in ref. [13] scattering states were not taken into account. Similarity of results origins from the fact that some correlation effects are included in CI calculations.

Table 3.3: List of the first four electron-hole excitations with their respective oscillator strength

Exciton	V	C	Weight	Max. Osc. Strength	Transition energy	
1	7	8	0.584	0.0013	2.24  eV	
1	7	10	0.130		2.34 6 V	
2	7	9	0.513	0.0005	4.40 eV	
	7	10	0.295	0.003	03 5.56 eV	
3	7	16	0.128			
	7	16	0.128			
	7	12	0.293	0.019	0.019 6.79 eV	
4	7	18	0.218			6.79 eV
	6	8	0.177			



Figure 3.2: Plot of the absorption spectrum with respect to the photon energy. An artificial broadening of 0.001 eV has been used.

## 3.2 Silica

To model the POL defect in silica, we have used a 108-atoms non-defective model in which we have added an O atom. The silica model has been obtained through quenching from a melt, see [29]. As the system is disordered with 72 oxygen sites, there are 72 possible different configurations for inserting the additional O atom, see figure 3.3.



Figure 3.3: Silica model with lowest formation energy. Silicon atoms are represented in blue and oxygen atoms in red. Peroxy bridge defect is highlighted

The GW-BSE calculations are "very expensive": In order to have some statistic, but saving computer time, we have only considered five different configurations containing  $\equiv$  Si - O - O - Si  $\equiv$  bridge defect. The total number of valence electrons is 582 (291 occupied states). The non-defective 108 atoms silica model is used as reference. All the structures were fully relaxed with DFT-LDA [22]. After the atomic relaxation, the average distance for -O-O- bond is 1.4994 Å and for  $\equiv$  Si-O- bond 1.6707 Å.

The POL DFT electronic structure is schematically represented in figure 3.4. POL induces the creation of two strongly localized defect states in band gap. State 291 is similar to the H<sub>2</sub>O<sub>2</sub> HOMO, while 292 is similar to the LUMO (see table 3.1). The two states are the defect -O-O- 2p and =O-O-  $\sigma^*$  states, respectively. The energy difference between this two states is 4.3 eV, very close to the DFT HOMO-LUMO gap of 4 eV for H<sub>2</sub>O<sub>2</sub>. The 291 state is at 0.47 eV from the top of valence band (TVB), while 292 is at 4.77 eV. The DFT band gap is 5.49 eV (DFT always underestimates energy differences between occupied and unoccupied states).



Figure 3.4: Schematic presentation of electronic structure in POL defect induced silica

One-shot GW calculation has been done on top of the previous DFT-LDA results. Table 3.4 displays the difference of the two methods and results are schematically shown in figure 3.5. We can quickly observe that the energies of states 292 and 293 have shifted and LUMO now appears in the conduction band. First defect state (291) in positioned at 0.44 eV from the TVB. This value is very close to the 0.47 eV given

by DFT. GW method places energy difference between two defect states at 9.5 eV. The calculated silica band gap is 9.16 eV. Similar to hydrogen peroxide GW correction does not appear as simple scissor shift.

N	KS energy (eV)	GW energy (eV)	
290	0.684	-1.289	
291 - Defect	1.155	-0.839	
292 - Defect	5.461	8.661	
293	6.170	7.867	
294	7.595	9.615	

Table 3.4: Comparison of calculated KS and GW energies



Figure 3.5: Schematic presentation of electronic structure in POL defect induced silica

Comparison of the two approaches shows that they both predict similar energy difference between valence and first defect state (0.44 eV and 0.47 eV) but differ strongly with occupied-unoccupied energy differences (i.e. 5.49 eV DFT and 9.16 eV GW for the band gap). As described in theoretical part of this work (section 2.4), DFT within the Kohn-Sham scheme provides the ground-state electronic density. Simplified one could say it is basically an "occupied state" theory, and occupied KS states are usually a good approximation for N-1 quasi-particle states. However, the situation is quite different for empty states. The most important error arises from known exchangecorrelation potentials, that do not cancel properly the Hartree self-interaction term. We proceed with the solution of BSE for obtaining the excitonic structure, including electron-hole interactions. First excitation is at 3.95 eV, and, as expected, arises from a quasi pure transition between the two strongly localized defect states (291 and 291). Second excitation occurs between the TVB and the unoccupied defect level (292) and has an excitation energy of 4.65 eV. Third transition of 7.0 eV is between the occupied defect state (291) and bottom of conduction band (BCB) 7.00 eV. Important observation is the very low oscillator strength which makes all the excitations quasi optically dark. This is the reason why the experimental results were controversial. The POL signature is almost invisible and in experimental measurement would probably be hidden by the signals of more optically active defects. The transition between the TVB and the unoccupied defect level has the highest oscillator strength around  $5 \cdot 10^{-4}$ . Comparison with  $H_2O_2$  (see table 3.3) shows that the single-particle transitions are the origin of the POL excitonic states in silica, contrary to the  $H_2O_2$  example where transitions are mostly combined. This is a direct consequence of the bulk nature of silica. Indeed, scattering states do not exist in "infinite" bulk systems. Comparison between the schematic representation of electronic structure calculated with the GW approach (figure 3.5) and transition energies from BSE (table3.5) displays the magnitude of the electron-hole interaction. The first excitation from table shows that the BSE gives transition energy of 3.95 eV while the difference between states 291 and 292 from GW calculation is 9.5 eV. The binding energy is as high as 5.5 eV. This shows importance of electron-hole interaction when states are heavily localized. When the states are less bonded difference is naturally smaller: GW predicts valence-conduction band gap of 9.16 eV while BSE place it at 7.45 eV. Binding energy is 1.71 eV.

Exciton	V	C	Weight	Max. Osc. Strength	Transition energy
1	291	292	0.935	0.0009	3.95 eV
2	290	292	0.845	0.005	4.65 eV
3	291	293	0.922	0.0009	7.00 eV
4	290	293	0.918	0.0007	7.45 eV

Table 3.5: List of first four excitons for the POL in silica model with lowest formation energy

Figure 3.6 shows the theoretical absorption spectra of pure silica with respect to all calculated configurations. The plots are sorted by formation energy from lower (bottom) to highest (top). Despite different excitonic energies the origin of the excitations is very similar for all the POL configurations: the first exciton arises from a transition between the two defect states, the second arises from a transition between TVB and the unoccupied defect level etc. Black arrows are used to indicate positions of peaks

as some are indeed so small that sometimes they cannot be even seen. Qualitatively excitation 2 from table 3.5 appears to be the most probable POL induced transition from all configurations. Some differences in transition energies are visible among different graphs. Qualitatively they can be estimated to shift transitions up to 1 eV. Their origin is probably slight difference in POL defect geometry between different configurations. Further research is needed to fully understand significance of defect geometry to optical properties.



Figure 3.6: Absorption spectra of "pure" silica and defect induced models. Black arrows are used to indicate POL induced excitons that have very small oscillator strengths.

## 4. Conclusion

In this work, we have studied from first-principles the opto-electronic properties of the peroxy bridge defect in pure silica. We have used state-of-the art Density Functional Theory with local density approximation, followed by GW@DFT and the solution of the BSE. Through this combination of approaches we can model parameter-free N-1 and N+1 electronic and neutral excitations including polarization, solid state effects and electron-hole interactions.

We have found that, there are three quasi-dark excitations at 3.95 eV, 4.65 eV and 7.00 eV and that can be bi-unequivocally associated to the POL. However as they are quasi-dark, it is very difficult (almost impossible) to experimentally distinguish the POL excitations from the background generated by other optically active defects. This is the reason why previous experimental results were controversial. Previous theoretical works on the topic were giving misleading results due to the intrinsic limitations of the methods that were used. Of course, at that time, those approaches were the only possibility, as the needed computational resources for addressing the issue of optical excitations in silica through GW and BSE are enormous. Only recently such kind of calculations became possible on High Performance Computing Facilities.

## **Bibliography**

- A. Kordon, Aplying computational intelligence: How to create value, Springer Science & Business Media, New York (2009)
- [2] L. Hedin and S. Lundqvist, Solid state physics, Volume 23, Academic Press, New York, London (1969)
- [3] R. M. Dreizler, E. K. U. Gross, Density functional theory: An approach to the quantum many-body problem, Springer-Verlag, Berlin (1990)
- [4] D. Griffiths, Introduction to Quantum mechanics, Prentice Hall Inc., New Jersey (1995)
- [5] G. Baiagaluppi, A. Valentini, Quantum theory at the crossroads, Cambridge university press (2009)
- [6] N. W Ashcroft, N. D. Merminn, Solid state physics, Harcourt Inc. (1976)
- [7] L. Hedin, Phys. Rev. 139 a796 (1965)
- [8] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, J. D. Joannopoulos, Reviews of modern physics 64, 1045 (1992)
- [9] A. Pasquarello and Roberto Car, Phys. Rev. Lett. 80, 5145 (1998)
- [10] J. F. Janak, Phys. Rev. B. 18, 7165 (1978)
- [11] G. P. Francis, M. C. Payne, J. Phys: Condens. matter 17, 1643 (1990)
- [12] L. M. Samos, G. Bussi, SaX: An open source package for electronic-structure and optical properties calculations in the GW approximation, Computer physics communications 180, 1416 (2009)
- [13] G. Pacchioni, G Ieranom Phys. Rev. B 57, 818 (1998)

- [14] C. Kittel, Introduction to Solid State Physics 8th ed. Wiley, 2005
- [15] E. O'Reilly and J. Robertson, Phys. Rev. B 27, 3780 (1983)
- [16] A. Rauk, M. Barrel, Chem Phys. 25, 409 (1977)
- [17] H. Imai, K. Arai, H. Hosono, Y. Abe, T. Arai and H. Imagawa, Phys. Rev. B 44, 1812 (1991)
- [18] D. Ricci, G. Pacchioni, M. A. Szymanski, A. L. Shluger, A Marshall Stoneham. Phy. Rev. B 65, 224104 (2001)
- [19] A. Kokalj, Comp. Mater. Sci., 2003, Vol. 28, p. 155
- [20] T. Helgaker, P. Jorgensen, J. Olsen, Molecular electronic structure, Wiley, 2000
- [21] L. M. Samos, G. Bussi, et al, http://www.sax-project.com
- [22] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, J. Phys. Condens. Matter 21, 395502 (2009).
- [23] Quantum ESPRESSO pseudopotential data base: http://www.quantumespresso.org/pseudopotentials
- [24] R. W. Godby, R. J. Needs, Phys. Rev. Lett. 62 (1989) 1169
- [25] J. P. Perdew, A. Zunger, Phys. Rev. B 23, 5048 (1981)
- [26] H. Nishikawa, R. Tahmon, Y. Ohki, K. Nagasawa, Q. Hama, J. Appl. Phys. 65, 4672 (1989)
- [27] T. Minato, D. P. Chong, Can. J. Chem., 61, 550 (1983)
- [28] J. Hrusak, H. Friedrichs, H. Schwarz, H. Razafinjanahary, H. Chermete, J. Phys. Chem. 100 (1996), 100
- [29] L. Martin-Samos, Y. Limoge, J.-P. Crocombette, G. Roma, N. Richard, E. Anglada, E. Artacho, Phys. Rev. B 71, 014116 (2005)

- [30] K. Osafune, K. Kimura, Chem. Phys. Lett. 25, 47 (1974)
- [31] R. S. Brown, Can. J. Chem. 53, 3439 (1975)