Chapter 1

Introduction

The development of new materials and the understanding of their physical properties is at the heart of technological as well as scientific progress. The study of semiconductors opens new possibilities for applications which make it interesting from a purely scientific point of view. The range of applications covers infrared detectors, in light emitting devices, as infrared lasers in fibre optics (Agarwal et al., 1993), as thermoelectric materials, in solar energy panels, and in window coatings and in quantum dots as monolayer (Justo et al., 2010; Hicks et al., 1996; Chatterjee et al., 1993; Nair et al., 1990; Bozin et al., 2010). Ferroelectric substance has wide applications in non-linear optics, ceramics, micro wave and sensor industries (Tagantsev et al., 2003; Kell, 1963) as well as in microelectronics.

Applied scientific research depends on the existence of accurate theoretical models. In particular, highly reliable *ab-initio* methods are in-dispensable for designing novel materials as well as for a detailed understanding of their properties. The development of such theories describing the electronic structure of atoms, molecules, and solids has been one of the success stories of physics in the 20\textsuperscript{th} century. Among these, density functional theory (DFT) of Hohenberg and Kohn (1964), Kohn et al., (1965) and others (Jones et al., 1989; Kohn, 1999) have proven to yield ground state properties for a vast number of systems in a very precise manner. DFT forms the basis of all electronic ground state calculations carried out in the present work.

In this work, we are mainly interested in optical properties, thus we are concerned with the interaction of external electro-magnetic waves with electron-hole excitations in
the system. We will limit our calculations to weak external perturbations which can be treated within the linear response regime. This can be treated rigorously within many-body perturbation theory, expressed in terms of the equation of motion for the electron-hole two-particle Green's function, the so-called Bethe-Salpeter equation (BSE) (Sham et al., 1966; Hanke et al., 1975, 1979, 1980; Hanke, 1975; Strinati, 1982,1984). To zeroth order, the electron and the hole can be treated as independent particles, which results in the random phase approximation (RPA) for the optical properties. However, solutions of the BSE in an *ab-initio* framework, appearing in the literature in the past few years, have shown that electron-hole interactions are indeed important in order to correctly describe quantitative (oscillator strengths) as well as qualitative (bound excitons) features of optical spectra of semi-conductors and insulators (Albrecht et al., 1997,1998; Benedict et al.,(1998), Rohlfing et al.,1998,1999; Van der Horst et al.,1999; Arnaud et al., 2001).

In the present work, we choose full potential linearized augmented plane waves (FP-LAPW) method (Hashemifar et al., 2005; Hedin et al., 1971), which is one of the most accurate and successful band structure methods available. We will apply this method to semiconductors and ferroelectric materials. All wave-functions entering the calculations are commonly expressed in terms of given basis functions. We have used a computer program WIEN2k code of Blaha et al., (2008) which is an implementation of the full-potential LAPW method, for all computations presented in this thesis. The calculations focus mainly on the influence of inter-molecular interactions on the electronic and optical properties of semiconductors.

This work is organized as follows. In Chapter 2 we give a short description of density functional theory (DFT) which provides the framework for treating ground state
properties of systems of interacting electrons. We will discuss the basic theorems and equations that form the foundations of DFT (Hohenberg et al., 1964; Kohn et al., 1965), and the relevant approximations entering the theory. In chapter 3 we will give a detailed method for the full potential linearized augmented plane waves (FP-LAPW) method. In chapter 4, we will discuss a methodology for optical study starting from Maxwell's equations in the presence of matter and we will derive the macroscopic dielectric function (DF) in the random phase approximation by using the self-consistent field method following the presentation of Adler (1962) and Wiser (1963). Chapter 4 contains the main outcome of the theoretical developments attained within this work.

In Chapter 5, the density of states, electronic band structures and optical properties for systems like BeX, PbX, ZnX, (where X= S, Se, Te) and ferroelectric material SbTaO₄ will be presented. In chapter 6, we will present the conclusion of the thesis, which will be followed by references and appendices.