Chapter 1

General Introduction

1.1 Introduction

All materials we are surrounded by are built from atoms. Atoms are enormously small particles, which themselves are built from a positively charged nucleus surrounded by negatively charged electrons. The electrons are attracted by the nucleus, and move with high speed in specific shells (also called orbitals) around the nucleus. This is understood by first looking at Coulomb's law,

$$\frac{q_1 q_2}{r_{12}^2} \propto F.$$  

(1.1)

It tells us that the force exerted on the electron by the nucleus is inversely proportional to the square of the distance between the electron and the nucleus. Electrons which are closer to the nucleus are, according to Coulomb's law, stronger bound, and thus have a lower potential energy. However the velocity of the electrons is much higher near the nucleus, and thus these electrons have a higher kinetic energy. That the electrons do not fall onto the nucleus comes from the fact that the potential energy loss and kinetic energy gain for the electron approaching the nucleus are balanced at a certain distance. In this way stable orbitals are formed. In general, the closer the electrons are to the nucleus, the lower the energy of the orbital in which the electrons are moving. It is a purely quantum mechanical effect that such orbitals can contain at maximum two electrons, with opposite spins according to the Pauli principle. The atoms can therefore be characterised by the energy levels of the orbitals in which the electrons are located. This is called the electronic structure of the atom.

In solids, the atoms are closely packed and arranged in an orderly way thereby forming a regular lattice. The atoms are so closely packed that the outer shells of neighbouring atoms start to overlap (See Fig. 1.1). The atomic picture of the electronic structure breaks down and a new picture emerges, in which the electrons are no longer attached to a single nucleus. In metals for instance, the electrons can 'jump' from one atom to another, and can more or less move freely through the solid. The electronic structure of a solid can, however, still be deduced from the constituent atoms. The energy levels of the atomic orbitals combine into so-called energy bands, as can be seen in Fig. 1.1 for a metal. The highest
energy level which is filled by electrons is called the Fermi level, which hence marks the separation between occupied and virtual states (See Fig. 1.1). Many properties of solids are determined by the behaviour of the electrons in the bands that have energies close to the Fermi level. Depending on the occupation of the energy bands a solid is called a metal, a semiconductor, or an insulator (See Fig. 1.2).

In metals the Fermi level is somewhere inside an energy band, which implies that it takes just a very small amount of energy to promote an electron to a higher energy level within
the same band. This characterises a metal and implies that the electrons can 'jump' freely from one atom to another, delocalising them over the complete metal. If the Fermi level is somewhere between a completely occupied (valence) band and an unoccupied (conduction) band, it takes a finite amount of energy to promote an electron from the valence band to the conduction band. One can show that in the latter case the electrons are more or less localised i.e., they can not easily 'jump' from one atom to the next. If the energy difference between the valence and the conduction band is big, the solid is called an insulator, and when it is small the solid is called a semiconductor.

As was already mentioned before, many properties of solids are determined by the dynamics of the electrons at the Fermi level. A prototypical example is the response of a solid to an electromagnetic field. Such an external field provides the solids with the energy needed to promote an electron to a higher energy level or band. The promoted electron leaves an empty level behind, which is often referred to as a 'hole'. Both the excited electron and the 'hole' are free to move. Therefore, the response of a solid to such an external field consists of the formation of electron-hole pairs, which respond to the electric field and cause electrical currents to flow in the solid. These induced currents give rise to an induced field, which tends to oppose, i.e., screen, the externally applied field. The perturbing field is effectively reduced inside the solid. In metals the electrons are able to flow over very large distances, as we already described before, they are able to completely screen the externally applied electric field to which the solid is exposed. However, at optical frequencies the screening can only be partial due to the inertia of the electrons. In insulators this screening is also restricted since in these materials the electronic charge can not flow over such large distances. The charge density then merely changes by, what is called polarization of the solid.

Many physical properties of many-particle systems have been under constant investigation during the past century. In general the description of the interacting many-particle systems is too complicated and approximations need to be made. By now several approximate methods are available to model the interacting many-particle systems. In the Born-Oppenheimer approximation the motion of the electrons is separated from the motion of the nuclei, which is much slower. This reduces the problem to the motion of the electrons only, with the nuclei at fixed positions. In principle, the motion of the electrons is described by the electronic wavefunction $\Psi_{el}(r_1, r_2, ..., r_n, t)$, which is the solution of the time-dependent Schrödinger equation

$$\hat{H}(t)\Psi_{el}(r_1, r_2, ..., r_n, t) = i\frac{\partial}{\partial t}\Psi_{el}(r_1, r_2, ..., r_n, t) ,$$

in which $\hat{H}$ is the many-particle Hamiltonian. Many approaches in quantum chemistry try to find this very complicated electronic wavefunction $\Psi_{el}(r_1, r_2, ..., r_n, t)$. As a first approximation one could model the Hamiltonian in Eq. 1.2, by replacing all the interactions between the particles by some effective mean field. Still the computational effort for evaluating the electronic wavefunction in several of such approximations is very high. However, there exist a set of theorems (the Hohenberg-Kohn theorems), which state that such an approach can actually be exact, at least for the stationary state of the system,
and, as turned out, much lower computational costs. The strong and attractive point of these theorems, called density functional theory (DFT), comes from the fact that it is not necessary to calculate the electronic wavefunction $\Psi_{el}(r_1, r_2, ..., r_n, t)$ for a full description of the system, but it is sufficient to look at the electron density $\rho(r)$. In the Kohn-Sham approach to DFT, one models the interacting many-particle system in terms of an effective non-interacting particle system (also called Kohn-Sham system). The external field is hereby replaced by an effective external field, which incorporates the interparticle interactions in an average way. The effective potential has to be modelled in such a way that the density of the Kohn-Sham system $\rho_{ks}(r)$ reproduces exactly the density of the real interacting many-particle system $\rho_{\text{real}}(r)$. Further, for the effective potential in such a Kohn-Sham system, it can be shown that it is completely determined by the electron density of the true interacting many-particle system.

Figure 1.3: Theoretical versus experimental dielectric constant for various elementary and binary crystals. The sodium chloride crystals (◦) of the I-VI type MX (M=Li, Na, K, Rb, Cs; X=F, Cl, Br, I) and (+) of the II-VI type NY (N=Mg, Ca, Sr, Ba; Y=O, S, Se, Te). The crystals in the diamond structure (×) (C, Si, Ge) and in the zincblende structure (○) for the III-V type LZ (L=Al, Ga, In; Z=P, As, Sb) and (●) for the II-VI type NY (N=Zn, Cd; Y=S, Se, Te).

In the time-dependent version of DFT, one not only needs to consider the effective scalar potential, but also the effective vector potential of the non-interacting many-particle system. Both these potentials have to be modelled in such a way that the density and current density of the Kohn-Sham system, $\delta \rho_{\text{ks}}(r, t)$ and $\delta j_{\text{ks}}(r, t)$, reproduce the exact density and current density of the real interacting many-particle system, $\delta \rho_{\text{real}}(r, t)$ and $\delta j_{\text{real}}(r, t)$.

In this thesis we describe the macroscopic optical properties of solids, by looking at the dynamics of the moving electrons as a response to an externally applied perturbing field. We have successfully applied time-dependent density functional theory to calculate such properties, as can be seen in Fig. 1.3. In Fig. 1.3 we compiled the theoretical (TDDFT)
versus experimental results for the dielectric constant $\epsilon_\infty$ for various elementary and binary crystals.

1.2 Outline of this thesis

In this thesis we describe \textit{time-dependent density functional theory for periodic systems}. We hereby aim to describe if, and in which way, the theoretical concepts of time-dependent density functional theory (TDDFT) can be applied to systems with periodicity in multiple dimensions (polymers, surfaces and solids). Throughout the thesis we give the development of a computer implementation to test these theoretical ideas and concepts.

In the \textbf{chapter 2}, a brief summary of the theoretical concepts of time-dependent density functional theory is given. We describe density functional theory (DFT), which was first introduced in 1965 by Hohenberg and Kohn [2] (section 2.1 and 2.2). The practical implementation of DFT was given one year later by Kohn and Sham [3], and resulted into a self-consistent scheme (section 2.3). The time-dependent version of DFT, was not given before the 1980s by Runge and Gross [4] (section 2.4).

In \textbf{chapter 3}, we address the problem of what is exactly the definition of polarization in a dielectric medium. Together with the question of how to define properly and uniquely polarization in such dielectric media. Therefore, in this chapter, polarization in a dielectricum is introduced as the dynamic response of the system to an externally applied electric field. (section 3.1). The dynamic response of the system consists of electric currents flowing through the system. Thereby an electromagnetic field is generated, which tends to oppose this external field and effectively reduces the perturbing field inside the dielectricum. In section 3.2 we show that if the system can be decomposed into an assembly of localised elements which are all charge neutral and independently polarizable, the macroscopic polarization can be considered in a simple discrete dipole model. For such a discrete dipole model the Clausius-Mossotti relation is valid. In section 3.3 the proper definition for polarization in an extended system is considered. The polarization as it was used in a discrete dipole model is, in general, ill-defined because it depends on the particular choice of partitioning the system into the separate elements. There is no unique way to do this partitioning. The definition for polarization in terms of the induced current provides a simple way to avoid this problem. Therefore, it provides a unique definition for polarization in extended systems. The induced current which flows through the interior of the system is also directly related to the intrinsic charge that piles up at the surface of the system. Thus it is not necessary to consider the surface of the system explicitly, and, in addition to the above, this makes the definition for the polarization in terms of the induced current more attractive.

In \textbf{chapter 4} we show how time-dependent density functional theory becomes feasible in a real-space description for the calculation of the static and frequency-dependent dielectric function $\epsilon(\omega)$ of nonmetallic crystals. A combination of a lattice-periodic \textit{microscopic} scalar potential with a uniform \textit{macroscopic} electric field as perturbation in a periodic structure calculation is used (section 4.3). The induced density and microscopic potential
can be obtained self-consistently for fixed macroscopic field by using linear response theory in which Coulomb interactions and exchange-correlation effects are included. An iterative scheme, in which the density and the potential are updated in every cycle, is used (section 4.4). The explicit evaluation of Kohn-Sham response kernels is avoided and their singular behavior as function of the frequency is treated analytically (section 4.8). Coulomb integrals are evaluated efficiently using auxiliary fitfunctions (section 4.9) and a screening technique is applied for the lattice sums (section 4.7). The dielectric functions $\epsilon(\omega)$ for diamond, silicon, and gallium arsenide, within the adiabatic local density approximation, are obtained from the induced current (section 4.5). In particular in the low-frequency range no adjustment of the local density approximation band gap seems to be necessary to get good agreement for the static dielectric function $\epsilon_\infty$ with experiment.

In chapter 5 the results, of the TDDFT method as introduced in chapter 4, for a wide range of nonmetallic crystals are given for the dielectric constant $\epsilon_\infty$ (at optical frequencies). The crystals have the sodium chloride, the fluoride, the wurtzite, the diamond, and the zinc-blende lattice structure (section 5.4). The frequency-dependent dielectric function $\epsilon(\omega)$ for the crystals in the diamond and zincblende lattice structure are also presented (sections 5.5). The calculated results are compared with experimental data and other theoretical investigations. For the dielectric constants $\epsilon_\infty$ and the dielectric functions $\epsilon(\omega)$ the results are in good agreement with the experimental values. The average deviation is 4-5% from experiment for the group IV and III-V compounds in the wurtzite, zincblende and diamond lattice structure, 8-9% for the II-VI and I-VII compounds in the zinc-blende and sodium chloride lattice structure, and up to 14% deviation for the fluoride lattice structure. The spectral features of the dielectric functions $\epsilon(\omega)$ appear in the calculations at somewhat too low energies compared to experiment.

In chapter 6 the effects of including relativistic effects in time-dependent density functional theory for the optical response properties of nonmetallic crystals are investigated. The dominant scalar relativistic effects have been included using the zeroth-order regular approximation (ZORA) in the ground-state DFT calculations, as well as in the time-dependent response calculations (section 6.3). It is derived that this theory can also be applied to indium antimonide (InSb) and mercury selenide (HgSe) in the zinc-blende structure, notwithstanding the fact that they turn into semimetals when scalar relativistic effects are included (section 6.8). Results are given for the band structure, the static dielectric constant $\epsilon_\infty$ and the dielectric function $\epsilon(\omega)$ of InSb (section 6.5) and HgSe (section 6.6), for the various levels on which relativity can be included, i.e., nonrelativistic, only in the ground-state, or also in the response calculation. With the inclusion of scalar relativistic effects, the band structure of InSb and HgSe become semimetallic within the local density approximation and we find a deviation of 5% from experiment for the static dielectric constant of InSb. Also the dielectric functions are improved and the spectra are now in good agreement with experiment.

In chapter 7 a new approach is proposed to calculate optical spectra, which for the first time uses a polarization dependent functional within current density functional theory, as proposed by Vignale and Kohn [108] (section 7.3). This polarization dependent functional includes exchange-correlation contributions in the effective macroscopic electric
field. The functional is tested and used to calculate the optical absorption spectrum of the semiconductors: silicon, diamond, gallium phosphide, gallium arsenide and zinc sulfide (section 7.5). In all cases a better agreement with experiment is obtained than before.

In chapter 8 we demonstrate that time-dependent density-functional theory, within the adiabatic local density approximation, describes the excitonic effects for the insulators CaF$_2$, SiO$_2$, and GaN correctly. Results for the electronic band structure, the density of states and the optical spectra ($\epsilon_2$) are reported for these wide band gap insulators (section 8.4). The optical spectra calculated by TDDFT are compared directly with experimental measurements, and with the $\epsilon_2$’s as calculated by a Green’s function approach (DFT/GW/BSE). In DFT/GW/BSE, these excitons are explicitly taken into account by evaluating the two-body Green’s function $G_2$. The features in the optical absorption spectra, that are attributed to excitonic effects according to the DFT/GW/BSE results, are also found in the TDDFT calculations. This contradicts the common assumption that TDDFT is not able to describe these excitonic effects properly.

In chapter 9 the linear optical polarizability of several infinite conjugated polymers is examined within the time-dependent density functional theory approach, by making use of the periodicity in these systems. The polymeric chains examined were the model system polyhydrogen (H), polyacetylene (PA), polydiacetylene (PDA), polybutatriene (PBT), polythiophene (PT), polysilane (PSi) and polymethineimine (PMI). The results for the longitudinal polarizability, i.e., along the polymeric backbone $\alpha_{zz}$, were highly overestimated by TDDFT in comparison with the more traditional calculation methods (like e.g., Hartree-Fock and coupled cluster) for all the considered polymeric chains. The overestimation is most likely due to the incorrect description of the macroscopic exchange-correlation (xc) electric field contribution by the LDA and GGA approximation for the xc-functional. An estimate for this macroscopic exchange-correlation contribution $E_{xc,mac}$, is given for the polymeric chains considered.