Summary

Materials have been used throughout history for their structural properties, e.g. ductility, elasticity, hardness etc., and later also for their physical properties, i.e., for their characteristic response to external perturbances. These last properties have been investigated in this thesis by using quantum mechanics. The mutual interactions of the many-particles which constitute matter complicate its theoretical description enormously. Time-dependent density-functional theory provides a powerful tool to investigate these dynamic properties in atoms, molecules, and clusters. Indeed this theory maps the many-particle problem of interacting electrons in a time-dependent external field onto an auxiliary system of noninteracting particles in an effective field. The many-particle effects enter through so-called exchange-correlation contributions to the effective potentials describing this field. These effective potentials are uniquely determined by the time-dependent density for a given initial state. Essential in this formulation is that the time-dependent density is exactly the same in the real and auxiliary system. The time-dependent density can thus be obtained from the auxiliary system once we know the effective potentials, which in turn are functionals of the time-dependent density. This requires a self-consistent procedure in which one updates the approximate densities and potentials in an iterative way. In this thesis we have only considered systems, initially in the ground state, which are perturbed only weakly by an external electromagnetic field. In this so-called linear response regime the induced density is proportional to the applied field. The exchange-correlation potentials depend on the density in a nontrivial way: the potentials at time $t$ and position $\mathbf{r}$ depend in general on the density at all earlier times $t'$ and at all positions $\mathbf{r}'$. In the linear response regime this relation is expressed through a so-called exchange-correlation response kernel. The most common approximation for the exchange-correlation potentials is the adiabatic local density approximation (ALDA), in which these potentials
are instantaneous and local functionals of the density. The scenario becomes more complicated for solids, which can be treated as ‘open’ systems, i.e., systems without boundary. To fully describe these systems, the density is replaced by the current-density leading to time-dependent current-density-functional theory (TDCDFT). In this thesis we have formulated the linear response of metallic crystalline systems to an electric field within this theoretical framework. The method gives already reasonable results for the dielectric and electron energy-loss functions within the ALDA. Although this approximation describes well the interband region of the spectra, it is less satisfying in the intraband region, where relaxation processes, such as electron-electron and electron-phonon scattering, become more important. Indeed the ALDA fails to reproduce the Drude-like tail in the absorption spectra. Approximations to the exchange-correlation potentials which are local-functionals of the current-density and hence nonlocal-functionals of the density can be included in a natural way in our formulation. In these approximations the exchange-correlation kernels can have memory, and thus relaxation processes due to electron-electron scattering can be taken into account. Other types of deviations from experiments can be observed in systems containing heavy elements, if relativistic corrections are neglected. Our method can treat scalar relativistic effects and spin-orbit coupling both in the ground-state and response calculations by using the zeroth-order regular approximation (ZORA). The spin-dependent formulation of the method, which allows to treat spin-orbit coupling, represents a first step to describe the linear response to an external magnetic field.

In chapter 1 we have given a brief introduction to optical properties of solids, namely the dielectric function and the electron energy-loss function. These two quantities describe the response of the system to a macroscopic and to an external electric field, respectively. Although the experiments which measure these two quantities can appear so different, they actually contain the same information in the long-wavelength limit, i.e., for external fields characterized by wavelengths that are long if compared to the interatomic distance. In chapter 2 an overview of the theoretical framework used has been presented. Time-dependent current-density-functional theory is an extension of the earlier density functional theory. What makes a density functional approach so attractive for theoretical analysis is the use of the density as basic quantity. The density, rather than the many-particle wavefunction, is used to describe a quantummechanical system, since the ground-state properties of the system can be expressed as functional of this quantity. First we have discussed the fundamental theorems of Hohenberg and Kohn and the practical set of one-particle equations introduced later by Kohn and Sham. These equations describe an auxiliary system of noninteracting particles in an effective potential which reproduces the same density as in the real interacting system. We have then described the formulation of a density
Summary

179

functional approach for systems subjected to time-dependent external longitudinal fields, by giving the statement and the proof of the Runge-Gross theorem. Finally we have introduced time-dependent current-density-functional theory, that allows to treat also transverse fields and to treat the linear response in extended systems. The theory was first formulated by Ghosh and Dhara, but we have reported the main steps of a more recent demonstration given by Vignale. The current-density is the basic variable and uniquely determines the scalar and vector potentials which act on the system. This approach has been used by Kootstra et al. to formulate in an elegant way the linear response of nonmetallic systems to a macroscopic electric field. The dynamical response of the system is described by solving the time-dependent one-electron Kohn-Sham equations for the auxiliary noninteracting system in effective induced scalar and vector potentials which give the same density and current-density of the real system. One can express the density and the current-density induced by the perturbing potentials in terms of Kohn-Sham response functions, which only depend on the ground-state orbitals and orbital energies. Upon solving self-consistently the set of equations that describe the induced density and current-density, the dielectric function can be calculated from the macroscopic current. We have extended this formulation in order to treat the linear response of metallic crystalline systems as well. The derivation of the method is given in chapter 4. In treating the response of a metal to an external perturbation the Kohn-Sham response functions have to include both interband and intraband transitions with accurate treatment of the Fermi surface in the Brillouin-zone integrations. The intraband contributions, in particular, have to be evaluated using a wavevector-dependent description. To achieve this we have considered a general perturbation with wavevector $q$ and frequency $\omega$, and we have derived the linear response of the system for vanishing $q$, but finite $\omega$. This is the regime describing optical properties. We have found that within the ALDA and in the optical limit $q \to 0$ we can solve separately the self-consistent-field equations which describe the inter- and intraband contributions to the response. Upon solving these equations, one can calculate the dielectric function $\epsilon(\omega) = [1 + 4\pi\chi_{\text{inter}}(\omega)] - 4\pi i/\omega \sigma^{\text{intra}}(\omega)$, with $\chi_{\text{inter}}(\omega)$ the interband contribution to the electric susceptibility, and $\sigma^{\text{intra}}(\omega)$ the intraband contribution to the macroscopic conductivity tensor. We have also shown that we retrieve in our approach the well-known relation between the electron energy-loss function and the dielectric function, i.e., $2\pi/(q^2 V) S(q, \omega) = 3\{-1/\epsilon_L(q, \omega)\}$, with $S(q, \omega)$ the dynamical structure factor, and $\epsilon_L(q, \omega)$ the longitudinal dielectric function. We have applied the method to calculate the dielectric and electron energy-loss functions of copper and silver and the agreement with the experiments is very good. However, strong deviations from the experimental spectra can be expected for heavy metals. Here relativistic effects
play an important role. In chapter 3 we have given an introduction to a relativistic formulation of density functional theory, which is based on quantum electrodynamics. Analogously to the nonrelativistic stationary case, one can prove a one-to-one mapping between the external four-component potential and the four-component current of the system. We have described how to arrive at the Dirac-Kohn-Sham equations and how to reduce the four-component Hamiltonian to a two-component pseudorelativistic one by using the zeroth-order regular approximation. The ZORA Hamiltonian contains, already at zeroth order, the dominant relativistic effects. In chapter 5 we have combined this approach with our formulation of linear response and we have calculated the dielectric function of gold. We have shown that in a nonrelativistic calculation gold has the onset of interband absorption at about 3.5 eV, while the treatment of scalar relativistic effects red-shifts the onset at \( \sim 1.9 \) eV, very close to the experiments, thus explaining the yellow color of gold. In chapter 6 we have analyzed in detail the band structures, the Fermi cross-sections, and the optical properties of the group VB and VIB bcc transition metals V, Nb, Ta, and (paramagnetic) Cr, Mo, and W, respectively. Here it becomes clear how accurate and versatile our method is. Some deviations from experiments can be due to the neglect of spin-orbit coupling. In the chapter 8 we have presented a preliminary spin-dependent formulation of the method, which has the aim to treat the linear response to magnetic fields as well. As immediate application we have included the spin-orbit coupling both in the ground-state and response calculations. We have shown the main changes that need to be done in the response functions in order to be expressed in terms of two-component spinors. We have tested the method on metallic and nonmetallic systems. The ZORA calculations of the dielectric functions of Au and W show some spectral features which were missing in the scalar ZORA spectra, and are in agreement with our predictions (chapters 5 and 6) and with the experiments. We have analyzed the impact of the relativity on the ground state and optical properties of ZnTe, CdTe, and HgTe. Whereas the first two of the series are semiconductors both in nonrelativistic and relativistic calculations, HgTe becomes a semimetal when relativity is considered. The inclusion of spin-orbit coupling is immediately visible in the spectra, since a splitting of the low-frequency peak appears, which reproduces very well the experiments, although the spectra are red-shifted by \( \sim 1 \) eV with respect to the experiments.

Although the calculated spectra are in overall good agreement with experiments, the low-frequency Drude like absorption is missing in our calculations. This absorption is due to relaxation processes, and thus cannot be described within the adiabatic local density approximation where the response kernel is instantaneous. In chapter 7 we have used a functional which goes beyond the ALDA: the exchange-correlation vector potential is approximated as a local functional of the current-density using the
expression derived by Vignale and Kohn. The self-consistent-field equations describing the inter- and intraband contributions to the response become coupled. Within this approximation the response kernel has memory, hence it can take into account relaxation processes due to electron-electron scattering. We have calculated the dielectric and electron energy-loss functions of the noble metals Cu, Ag, and Au and our results reproduce reasonably well the experiments.