In this chapter we incorporate the ZORA equations (describing both scalar and spin-orbit relativistic effects) developed in chapter 4 in the formulation of the linear response of solids within TDCDFT. We obtain a spin-dependent version of the linear response formalism, which makes possible its further extension to the response to magnetic fields as well. As immediate application we can include the treatment of spin-orbit coupling in the optical property calculations. We test the method on metallic and nonmetallic systems. First we present the ZORA results for the dielectric functions of Au and W. With the treatment of the spin-orbit coupling new spectral features appear that are missing in the scalar ZORA spectra of these two metals, and that are in agreement with the experiment and with our speculations in chapters 5 and 6. Then we study the linear response of the zincblende semiconductors ZnTe, CdTe, and semimetal HgTe. We compare nonrelativistic, scalar ZORA, and ZORA relativistic results to show the impact of the scalar and spin-orbit effects on the spectra. Comparison of our ZORA results with experimental data shows an overall good agreement.

8.1 Introduction

In chapters 5, 6, and 7 we included the treatment of scalar relativistic effects in the linear response of heavy metals within the zeroth-order regular approximation [93,95,110]. Although the scalar relativistic effects induced major corrections in the
Chapter 8. Effect of the spin-orbit coupling on the linear response of solids

spectra [110, 146], some important features were still missing due to the neglect of spin-orbit coupling. For example, in the group VB and VIB bcc transition metals we have seen that the treatment of spin-orbit coupling is expected to yield an onset in the interband contribution to the absorption spectrum, while in the scalar relativistic calculations a constant absorption results at low frequency, even close to $\hbar \omega = 0$ [146]. In this chapter we will take into account also the effect of spin-orbit coupling in the linear response of extended systems, following our derivation given in chapter 4. Besides this immediate application, the inclusion of the spin in the formulation of the linear response of solids is a first step for the treatment of the magnetic response. Indeed, the spin-dependent Hamiltonian, which governs the linear perturbation of the Kohn-Sham ground state, contains the coupling between a spin-density operator and the magnetic field. At present we do not treat the response to magnetic fields. We give the ZORA equations, comprising both the dominant scalar relativistic effects and spin-orbit coupling, which we solve in the ground-state and in the linear response calculations. The response functions, which depend only on the ground-state orbitals and orbital energies, are to be changed in order to consider two-component spinors. To test our method we first calculate the ZORA dielectric functions of Au and W. As discussed in more detail in chapters 5 and 6, these two metals are expected to show visible changes in the spectra upon the inclusion of spin-orbit coupling in the ground-state and response calculations. Indeed the ZORA calculations show a smooth onset and a better visible second peak in the absorption of Au, and an onset with a sharp peak at about 0.46 eV in the absorption of W, in good agreement with the experimental data and with our predictions. We further apply the method to the most common II-VI semiconductors ZnTe and CdTe, and semimetal HgTe in the zincblende structure. These compounds have been extensively studied both experimentally and theoretically [147–157]. Their electronic structure is characterized by a moderately narrow ($\lesssim 1$ eV), fully occupied metal $d$ band-complex inside the valence bands around 7-11 eV below the Fermi level, which are visible in the photoemission spectra of all II-VI semiconductors [158–160]. The highest-lying $d$ bands play an important role in the electronic structure and optical properties of these materials. In particular they affect the fundamental band gap by mixing with the $p$-like states at the top of the valence band, resulting in wide and medium energy-gaps of 2.39 eV and 1.59 eV for ZnTe and CdTe, respectively [156]. Magnetoreflection data provide strong evidence that HgTe is a zero-gap semimetal with inverted band-structure at $\Gamma$ point, i.e., an inverted order of the bands at $\Gamma_6$ ($s$-like) and $\Gamma_8$ ($p$-like) with a resulting negative energy-gap of $-0.30$ eV [156], unlike ZnTe, CdTe, and most other zinc-blende compounds [147]. Spin-orbit coupling has a strong impact on the electronic structure, and thus on the optical spectra, of these compounds. Splittings appear at the top
valence bands and for the sp-like conduction bands at $\Gamma$, L, and X high-symmetry points. The experimental observation of such splittings, usually as double peaks in the optical spectra, has been very useful in the assignement of the optical spectra in terms of interband transitions [161]. We show the importance of scalar and spin-orbit relativistic effects on the ground-state band structures as well as on the optical properties of the three compounds. While the first two compounds are described as semiconductors both in nonrelativistic and relativistic calculations, HgTe appears as semiconductors in nonrelativistic calculations, but as semimetals in a relativistic description. The changes in the electronic structures due to the inclusion of relativity has a drastic effect on the dielectric constant and dielectric function of HgTe. In the frequency range 0-10 eV we find an overall good agreement between the ZORA results and experiments reported in literature. First we give the main ZORA equations discussed in chapter 4, which can be used to include relativistic effects in the linear response of solids within TDCDFT. Next we present our results for the dielectric functions of Au and W, and for the band structures, the dielectric constants, and the dielectric functions of ZnTe, CdTe, and HgTe, and compare these with available experimental data.

8.2 Theory

We combine the ZORA formalism (comprising both scalar and spin-orbit relativistic effects) with the time-dependent current-density formulation of the linear response of solids to a macroscopic field. The first-order perturbation of the ground state of a Kohn-Sham system described by the ZORA equation

$$H^{ZORA}_\Psi(r) = \left[v_{\text{eff},0}(r) + \frac{c^2}{2c^2 - v_{\text{eff},0}(r)}\sigma \cdot p\right]\Psi(r),$$

is governed by the perturbation

$$\delta \hat{h}(r,t) = \int \left(\hat{\rho}(r')\delta v_{\text{eff}}(r',t) + \frac{1}{c}\hat{j}_p(r') \cdot \delta A_{\text{eff}}(r',t)ight) dr',$$

where,

$$\hat{\rho}(r') = \delta(r - r'),$$

$$\hat{j}_p(r') = -\frac{i}{2} \left[\hat{\rho}(r')K(r') - K(r')\hat{\rho}(r')\right],$$

$$\hat{s}(r') = \frac{1}{2}\hat{\rho}(r')\sigma.$$
Here $c$ is the velocity of light, $v_{\text{eff},0}(r)$ is the ground-state self-consistent effective potential, $\mathbf{\sigma}$ is the vector of Pauli matrices, and $K(r) = (1 - v_{\text{eff},0}(r)/2c^2)^{-1}$. One can then calculate the linear response of the system to this perturbation by solving self-consistently the sets of equations describing the induced density and induced current-density. These two quantities are expressed in terms of $q$-dependent Kohn-Sham response functions, which only depend on the ground-state orbitals, orbital energies, and occupations numbers,

$$\chi_{abq}(r, r', \omega) = \frac{1}{N_k} \sum_k \sum_{ia} \frac{(f_{ik} - f_{ak+q})}{1 + \delta_{i,a}} \times$$

$$\frac{\langle \Psi^*_i | \hat{a}_q(r) | \Psi_{ak+q} \rangle \langle \Psi^*_a | \hat{b}_q(r') | \Psi_i \rangle}{\epsilon_{ik} - \epsilon_{ak+q} + \omega + i\eta} + c.c. (-q, -\omega), \quad (8.6)$$

where the summation is over the (partially) occupied bands $i$, with occupation number $f_{ik} = 1$, and the unoccupied bands $a$, with occupation number $f_{ak} = 0$. The operators $\hat{a}_q(r)$ and $\hat{b}_q(r)$ can be either $\hat{\rho}_q(r) = e^{-iqr} \rho(r)$ or $\hat{j}_q(r) = \hat{j}_p(r) + e^{-iqr} K(r) \nabla \times \hat{s}(r)$, with $\hat{j}_p(r) = -i (\hat{\rho}_q(r) K(r) \nabla - \nabla^\dagger K(r) \hat{\rho}_q(r))/2$. The Bloch orbitals $\Psi_{ik}(r)$ are now two-component spinors and are solutions of the ground-state ZORA equation (8.1). Note that for scalar relativistic calculations the ground-state Hamiltonian in Eq. (8.1) does not contain the Pauli vector $\mathbf{\sigma}$, and the perturbation (8.2) does not contain the last term on the right-hand side. Furthermore, in the response functions (8.6) the Bloch orbitals are scalar functions, and the occupation numbers are $f_{ik} = 2$ for occupied bands and $f_{ak} = 0$ for unoccupied bands.

From the macroscopic induced current one can calculate the macroscopic dielectric function, which (at a wavevector $q = 0$ and in the adiabatic local density approximation) can be defined as [84]

$$\epsilon(\omega) = (1 + 4\pi \chi^\text{inter}_e(\omega)) - \frac{4\pi i}{\omega} \sigma^\text{intra}_e(\omega). \quad (8.7)$$

Here the term in bracket on the right-hand side represents the interband contribution to the dielectric function, while the other term is the intraband contribution. The former is due to transitions between occupied and unoccupied bands, while the latter is due to transitions within the same partially occupied bands. Clearly, these last transitions are not possible in nonmetallic systems, which are characterized by bands that are either fully occupied or fully unoccupied.
8.3.1 Computational details

We performed ZORA calculations of the dielectric functions of Au and W in the spectral range 0-10 eV. We used the experimental lattice constants 4.08 Å for Au in a fcc lattice, and 3.16 Å for W in a bcc lattice. Furthermore, we calculated the ground-state band structures and the optical dielectric functions $\epsilon(\omega)$ in the spectral range 0-10 eV for the isotropic crystals of ZnTe, CdTe, and HgTe in a zincblende lattice. We used the experimental lattice constants 6.09 Å for ZnTe, 6.48 Å for CdTe, and 6.08 Å for HgTe. All calculations were performed using a modified version of the ADF-BAND program [29,30,61–63,84]. We checked that our results were converged with respect to the basis set size and the sampling density of the irreducible Brillouin zone. We made use of a hybrid valence basis set consisting of Slater-type orbitals (STOs) in combination with the numerical solutions of a free-atom Herman-Skillman program [64]. Cores were kept frozen up to 3$p$ for Zn, 4$p$ for Cd and Te, and 4$f$ for Hg, Au, and W. The spatial resolution of this basis is equivalent to a STO triple-zeta basis set augmented with two polarization functions. The Herman-Skillman program also provides us with the free-atom effective potential. The crystal potential was evaluated using an auxiliary basis set of STO functions to fit the deformation density in the ground-state calculation and the induced density in the response calculation. For the evaluation of the $k$-space integrals we used a quadratic (linear in the response calculations) numerical integration scheme, which was constructed by adopting a Lehmann-Taut tetrahedron method [59, 60]. We found converged results using 175 sample points in the irreducible wedge of the Brillouin zone for Au, W, ZnTe, and for CdTe and HgTe in the nonrelativistic calculations. Relativistic calculation results for W in the frequency range 0-3 eV converged using 1771 sample points, and for CdTe and HgTe using 1695 sample points. All the dielectric constants were obtained by using 1695 sample points. In all our ground-state calculations we used the Vosko-Wilk-Nusair parametrization [65] of the LDA exchange-correlation potential, which was also used to derive the ALDA exchange-correlation kernel for the response calculations.

8.3.2 Metals: spin-orbit effects

The electronic band structures and optical properties of Au and W have been analyzed in detail in chapters 5 and 6, respectively. In particular, in those chapters, we have discussed the effect of the scalar relativistic corrections in the linear response of the two metals. Some deviations from experiments have been attributed to the neglect of the spin-orbit coupling in the response calculations. Analysis of the band structure
Figure 8.1: Real (upper graph) and imaginary (lower graph) parts of the dielectric function of Au. The ZORA relativistic calculations (bold solid lines) are compared with experimental results (dotted-dashed lines) taken from Ref. [50].

Figure 8.2: Real (upper graph) and imaginary (lower graph) parts of the dielectric function of W. The ZORA relativistic calculations (bold solid lines) are compared with experimental results (dotted-dashed lines) taken from Ref. [106]. To show the peak at 0.42 eV in the experimental absorption we have reported only the interband contribution to the absorption, as extrapolated from experiments in Ref. [106].
calculated by including scalar and spin-orbit coupling effects, and assignment of the spectral features in terms of pairs of bands suggested an improvement in the low-frequency onset of the interband transitions and second main peak in the absorption of Au, and the appearance of a finite onset and a peak around 0.60 eV in W with the inclusion of the spin-orbit coupling in the response calculations. Here we present the results of the dielectric functions of Au and W calculated by including scalar and spin-orbit effects both in the ground-state and response calculations. Inspection of Figs 8.1 and 8.2 confirm our previous speculations, and show a good agreement with the experiments. Note that in Fig. 8.2 we report the experimental interband absorption of W, as extrapolated by Weaver et al. by their experiments [106], in order to show the onset and peak at 0.42 eV.

8.3.3 Nonmetals: band structures and dielectric functions

In Figs 8.3, 8.4, and 8.5 we report the ground-state band structures of ZnTe, CdTe, and HgTe, respectively. Each figure comprises results from nonrelativistic, scalar ZORA relativistic, and ZORA relativistic calculations. In order to facilitate the comparison among the three band structures, the energy levels are reported with respect
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Figure 8.4: Theoretical LDA ground-state band structures of CdTe. The thin dotted lines refer to nonrelativistic calculations, the dashed lines refer to scalar ZORA relativistic calculations, and the bold solid lines refer to ZORA relativistic calculations.

Figure 8.5: Theoretical LDA ground-state band structures of HgTe. The thin dotted lines refer to nonrelativistic calculations, the dashed lines refer to scalar ZORA relativistic calculations, and the bold solid lines refer to ZORA relativistic calculations.
to the respective Fermi levels. The valence and conduction bands are numbered at a given $k$ point starting from the lowest band. Some particular states at various high-symmetry points are labeled according to the respective double group representations. The $d$-band complexes, which for simplicity we have not reported in the figures, are located around 6-9 eV below the Fermi energy, and are almost dispersionless. As expected, scalar relativistic effects shift the band energies with respect to the non-relativistic results. In ZnTe and CdTe the dispersion of the valence and conduction bands is similar both in nonrelativistic and scalar relativistic band structures, thus nonrelativistic and scalar relativistic optical spectra can be expected to differ only in the energy position of the main spectral features. In HgTe relativistic effects induce drastic changes in the electronic structure and, thus, in the optical properties: already the inclusion of scalar relativistic effects changes the character of this compound from semiconductor, as appears to be in nonrelativistic calculations, to semimetal with an inverted band order. Indeed, the $s$-like $(6s \text{ Hg})$ states at $\Gamma_{1v}$ ($\Gamma_6$ in the double group representation) are stabilized more than the $p$-like $(5p \text{ Te})$ states at $\Gamma_{15v}$ ($\Gamma_8$ in the double group representation), resulting in a vanishing band gap and an inversion of the typical band order [162]. The inclusion of spin-orbit coupling leads in particular

Table 8.1: Calculated energy gaps (eV), centers of the $d$-band energies $\epsilon_d$ (eV), and spin-orbit splittings (eV) of valence bands at $\Gamma$ ($\Delta_0$) and $L$ ($\Delta_1$) for ZnTe, CdTe, and HgTe. The experiments are taken from Ref. [156].

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Gamma_8 - \Gamma_6$</th>
<th>$\epsilon_d$</th>
<th>$\Delta_0$</th>
<th>$\Delta_1$</th>
<th>$\Delta_0$</th>
<th>$\Delta_1$</th>
<th>Exp$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTe</td>
<td>2.03</td>
<td>-7.21</td>
<td>0.93</td>
<td>0.54</td>
<td>2.39</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.99</td>
<td>-6.97</td>
<td>0.91</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdTe</td>
<td>1.62</td>
<td>-8.45</td>
<td>0.89</td>
<td>0.54</td>
<td>1.59</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>-8.06</td>
<td>0.90</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgTe</td>
<td>1.52</td>
<td>-8.15</td>
<td>1.12</td>
<td>0.57</td>
<td>0.30</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.88</td>
<td>-6.84</td>
<td>0.81</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$data taken from Ref. [156].
to a splitting of the states at $L_{3v}$ point (in the single group representation), as well as along the line $\Gamma_{15v}-L_{3v}$, in $L_6$ and $L_{4.5}$ (in the double group representations), at $\Gamma_{15v}$ point in $\Gamma_7$ and $\Gamma_8$, and at $X_{5v}$ point in $X_6$ and $X_7$. Some of these splittings are well visible in the optical spectra as we will shortly show. In table 8.1 we compare nonrelativistic, scalar ZORA, and ZORA band gaps, centers of the $d$-band energies $\epsilon_d$, and spin-orbit splittings at $\Gamma_{15v}$ and $L_{3v}$ with the observed values collected in Ref. [156] for ZnTe, CdTe, and HgTe. Inspection of this table reveals the well-known underestimation of the band gap in semiconductors by using the local density approximation. The inclusion of relativity decreases even more the band gap. In HgTe

![Figure 8.6: Real (upper graph) and imaginary (lower graph) parts of the dielectric function of ZnTe. In the left panel we compare nonrelativistic calculations (thin lines), scalar ZORA relativistic calculations (dashed lines), and ZORA relativistic calculations (bold lines). To facilitate the comparison we have rigidly shifted upwards nonrelativistic ($\epsilon(\omega) + 10$) and scalar relativistic ($\epsilon(\omega) + 5$) curves. In the right panel we compare the ZORA relativistic calculations with the experiments (dotted-dashed lines) from Ref. [163].](image-url)
relativity is essential to describe the negative band gap, which is, however, overestimated in the calculations with respect to the observed value. The energies of the $d$-band complexes improve with the inclusion of scalar and spin-orbit relativistic effects in ZnTe and CdTe, whereas in HgTe the nonrelativistic results are the closest to the experiments. However, in the calculations the $d$-band complexes are less bound than the observed ones. This has already been observed in previous calculations on gold and bcc metals from the groups VB and VIB \cite{110,146}, and it is a failure of the local density approximation. The main important splittings are well reproduced in our calculations. In Figs 8.6-8.8 we report the calculated and measured \cite{149,163} real

![Diagram](image_url)

Figure 8.7: Real (upper graph) and imaginary (lower graph) parts of the dielectric function of CdTe. In the left panel we compare nonrelativistic calculations (thin lines), scalar ZORA relativistic calculations (dashed lines), and ZORA relativistic calculations (bold lines). To facilitate the comparison we have rigidly shifted upwards nonrelativistic ($\epsilon(\omega) + 10$) and scalar relativistic ($\epsilon(\omega) + 5$) curves. In the right panel we compare the ZORA relativistic calculations with the experiments (dotted-dashed lines) from Ref. [163].
and imaginary parts of the dielectric function for the three compounds. In order to facilitate the comparison with the experiments we used the scissors operator to shift the calculated optical spectra of ZnTe and CdTe to higher energies such that the zero crossings of the real parts of the calculated dielectric functions coincide with the experiments. The shifts needed were 0.68 eV, 0.77 eV, and 0.79 eV in the nonrelativistic, scalar ZORA, and ZORA calculations of ZnTe, and 0.61 eV, 0.80 eV, and 0.89 in the nonrelativistic, scalar ZORA, and ZORA calculations of CdTe. The nonrelativistic, scalar ZORA, and ZORA spectra of ZnTe and CdTe are red-shifted by about 0.6-0.9 eV with respect to the experimental curves. Note that there is not a direct relation

![Figure 8.8: Real (upper graph) and imaginary (lower graph) parts of the dielectric function of HgTe. In the left panel we compare nonrelativistic calculations (thin lines), scalar ZORA relativistic calculations (dashed lines), and ZORA relativistic calculations (bold lines). To facilitate the comparison we have rigidly shifed upwards nonrelativistic ($\epsilon(\omega) + 10$) and scalar relativistic ($\epsilon(\omega) + 5$) curves. In the right panel we compare the ZORA relativistic calculations with the experiments (dotted-dashed lines) from Ref. [149].](image)
between the shift of the optical spectra and the error in the calculated band gaps, in line with previous findings \[30,93\]. In particular the ZORA spectra of CdTe show a low-frequency peak, whose high intensity is due to the too low frequencies at which it occurs. The spectra of HgTe reflect the strong impact of relativity on the electronic-structure: in particular, the relativistic absorption spectra show the onset at \( h\omega = 0 \) eV, while the nonrelativistic one shows the onset at a finite frequency and is quite different from the experiments. In the ZORA spectra all the main spectral features are present and well described in intensity, although they are red-shifted with respect to the experimental curves by \( \sim 1 \) eV. The same red-shift is also present in the scalar ZORA spectra. A striking feature common to the ZORA spectra is the doublet at about 2.7 eV for ZnTe, 2.5 eV for CdTe, and 1.7 eV for HgTe. This is mainly due to transitions between bands \( 5, 6 \rightarrow 7, 8 \) and \( 3, 4 \rightarrow 7, 8 \), expected to occur at the L point and along the \( \Gamma-L \) line \[148-150\]. Transitions \( 5, 6 \rightarrow 9, 10 \) and \( 3, 4 \rightarrow 9, 10 \) are responsible for the absorptions around 6 eV. The remaining main peak at about 4-5 eV is mainly due to transitions \( 5, 6 \rightarrow 7, 8 \), which are expected to occur at or close the X point \[148-150\]. The calculated and measured \[164\] dielectric constants are reported in table 8.2. We find that in the two semiconductors the nonrelativistic results are in better agreement with the experiments than the relativistic ones. Scalar-ZORA and ZORA calculations overestimate the dielectric constants. For HgTe, instead, we find a strong improvement of the calculated dielectric constant if the relativity is included.

Table 8.2: Nonrelativistic, scalar ZORA relativistic, and ZORA relativistic dielectric constants (eV) calculated for ZnTe, CdTe, and HgTe. The experiments are taken from Ref. \[164\].

<table>
<thead>
<tr>
<th></th>
<th>ZnTe</th>
<th>CdTe</th>
<th>HgTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>7.71</td>
<td>6.62</td>
<td>6.90</td>
</tr>
<tr>
<td>SR</td>
<td>9.21</td>
<td>9.48</td>
<td>24.80</td>
</tr>
<tr>
<td>SR+SO</td>
<td>9.49</td>
<td>12.04</td>
<td>21.60</td>
</tr>
<tr>
<td>Exp (^a)</td>
<td>7.3</td>
<td>7.2</td>
<td>21.0</td>
</tr>
</tbody>
</table>

\(^a\) dielectric constants taken from Ref. \[164\]

### 8.4 Conclusions

In this chapter we have proposed a spin-dependent version of the formulation of the linear response of solids within TDCDFT. The final goal of this extension is a future...
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treatment of magnetic response as well. Here we have used the method to include the spin-orbit coupling, beside the dominant scalar relativistic effects, within the zeroth-order regular approximation in linear response calculations. We have shown that our method performs well for both metallic and nonmetallic systems. The calculated ZORA spectra of Au and W show the predicted spectral features which were missing in the scalar ZORA calculations discussed in chapter 5 and 6: a smooth onset of the interband transitions and a more visible second peak in the absorption spectrum of Au, and a sharp onset with peak at about 0.46 eV in the absorption spectrum of W, in agreement with the experiments. We further analyzed the impact of the relativity in the ground-state and response calculations, in particular the additional changes induced by the spin-orbit coupling with respect to the scalar relativistic results, of the semiconductors ZnTe, CdTe, and the semimetal HgTe. The main splittings of states in the band structures and in the spectral features are very well described. The local density approximation used in the ground-state calculations underestimates the band gap due to s- and p-like bands in ZnTe and CdTe. Scalar-relativistic corrections make this worse, which becomes evident in the bad results for the static dielectric constants. Relativity is, instead, essential in the case of HgTe, where the ZORA results are in good agreement with experiments.