Time-dependent density functional theory for periodic systems
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2001

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 6

Relativistic effects in TDDFT calculations


6.1 Abstract

We show how relativistic effects can be included in the time-dependent density-functional theory (DFT) for the optical response properties of nonmetallic crystals. 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. We show that this theory can also be applied to indium antimonide and mercury selenide in the zinc-blende structure, notwithstanding the fact that they turn into semimetals when scalar relativistic effects are included. Results are given for the band structure, the static dielectric constant $\epsilon_\infty$ and the dielectric function $\epsilon(\omega)$, for the various levels on which relativity can be included, i.e., nonrelativistic, only in the ground-state, or also in the response calculation. Comparisons of our calculated results are made with experiment and other theoretical investigations. 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 in good agreement with experiment, although the spectral features are shifted to somewhat lower energies compared to experiment.
CHAPTER 6. RELATIVISTIC EFFECTS IN TDDFT CALCULATIONS

6.2 Introduction

In a recent paper [94] we found that time-dependent density-functional theory (TDDFT) [63] in the adiabatic local density approximation (ALDA) works very well for a large range of nonmetallic crystals, for which we achieved, on average, an accuracy of about 5% compared with experiment. A clear exception, however, was found for InSb in the zinc-blende structure ($a=6.48\,\text{Å}$), for which the predicted static dielectric constant was underestimated by about 40% compared with experiment [77]. Simultaneously we found a considerable overestimation of the experimental bandgap, 0.99 eV DFT-LDA, in comparison with experimental bandgaps of 0.17 eV [92] ($T=300\,\text{K}$) and 0.23 eV [7] ($T=0\,\text{K}$) for this small-gap semiconductor. This overestimation of the bandgap is in clear contrast with the general trend which is observed in LDA band structure calculations, i.e., that the bandgaps are generally underestimated by about 50%. The inclusion of scalar relativistic effects within the zeroth-order regular approximation in our full-potential ground-state DFT-LDA band structure calculation causes the lowest $s$-like conduction band to be stabilized considerably more than the upper $p$-like valence bands. The band order is changed in the centre of the Brillouin Zone (BZ), which results in a vanishing bandgap, and consequently the incorrect prediction of the InSb crystal being a semimetal. A similar result was found in the fully relativistic linear-muffin-tin-orbital method (LMTO) of Cardona et al. [71] and in the full-potential scalar relativistic linear augmented plane-wave (FLAPW) calculation of Guo et al. [72]. Recently, the nature of the material HgSe was also debated, whether it is a small-gap semiconductor or a semimetal in the zinc-blende structure. Experimentally, as determined using photoemission spectroscopy [103], there seemed to be no evidence of a bulk-like conduction band that either crosses or touches the valence-band maximum, hence favoring it to be a small-gap (0.42 eV) semiconductor. On the other hand, conductivity, optical and magneto-optical measurements, compiled in Ref. [104], favored an inverted bandstructure with zero fundamental gap, and thus a semimetallic nature. The seemingly contradicting experimental results have been brought into accordance with an \textit{ab-initio} quasiparticle bandstructure calculation [105]. This GW calculation (like the DFT-LDA calculation on which it was based) predicts an inverted semimetallic bandstructure. The experimentally observed very low photoemission intensity just above the valence band maximum could be attributed to the enhanced dispersion, and hence very light effective mass and low density of states, of the lowest conduction band. We investigate the effects on the optical response properties of InSb and HgSe after including scalar relativistic ZORA in the ground-state DFT, as well as in the time-dependent response calculations. The outline of this paper is as follows. First we show the way in which scalar relativistic ZORA is incorporated in the present TDDFT calculations, and validate the use of the TDDFT equations in this special case of semimetals. This is followed by a section about the method and implementation. Then, in the next sections, we present the results for the band structure, the dielectric constant and function for InSb and HgSe, and compare these with experimental data. Finally, in the last section, we draw the conclusions.
6.3 Theory

Scalar relativistic (SR) effects can be included in the ground-state DFT calculation as described by van Lenthe et al. in Refs. [95] and [96] and Philipsen et al. in Ref. [97], by replacing the kinetic-energy operator by the ZORA term

\[ T_{\text{ZORA}}^{\text{SR}} = p \cdot \frac{c^2}{2c^2 - v_{\text{eff}}(\mathbf{r})} p, \]

in which \( p = -i\nabla \), \( c \) the velocity of light, and \( v_{\text{eff}}(\mathbf{r}) \) the self-consistent effective potential. This results in a semi-metallic band structure for InSb and HgSe, the bottom \( s \)-like conduction band is lowered in energy, below the top \( p \)-like valence band in the centre of the BZ. The Fermi energy coincides with the three degenerate energy bands of \( p \)-character at \( \Gamma \). Two of these are completely occupied and one is unoccupied, hence there is no Kohn-Sham bandgap. However, the Fermi-surface reduces to a point (\( \Gamma \)), and more importantly, the density of states vanishes at the Fermi energy. In this special case we expect no intraband contributions so we can use our TDDFT formulas [94] as before. The susceptibility of this isotropic material follows as one-third of the trace of the susceptibility tensor according to [63]

\[ \chi_e(\omega) = \frac{1}{3} \sum_i \left\{ \frac{-1}{\omega^2 V} \left[ \delta J_p(\omega) - \delta J_p(0) \right] \right\}_{E=-i\omega,\epsilon_i}, \]

in which the macroscopic paramagnetic current \( \delta J_p(\omega) \) that is induced by a macroscopic electric field \( \mathbf{E}(\omega) \) is obtained from

\[ \delta J_p(\omega) = \int \int \left( \frac{i}{\omega} \chi_{ij}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{E}_{\text{mac}}(\omega) + \chi_{ip}(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\text{eff}}(\mathbf{r}', \omega) \right) d\mathbf{r}' d\mathbf{r}. \]

Here the induced effective potential \( \delta v_{\text{eff}}(\mathbf{r}', \omega) \) is lattice periodic and comprises the induced microscopic part of the Coulomb and exchange-correlation contributions. It is a functional of the induced density and in linear response it can be given in the adiabatic approximation by

\[ \delta v_{\text{eff}}(\mathbf{r}, \omega) = \int \frac{\partial v_{\text{eff}}[\rho](\mathbf{r})}{\partial \rho(\mathbf{r}')} \delta \rho(\mathbf{r}', \omega) d\mathbf{r}', \]

where the ground-state expression is used for the functional dependence of the \( v_{\text{eff}}[\rho](\mathbf{r}). \) The induced density is obtained by solving the following equation self-consistently:

\[ \delta \rho(\mathbf{r}, \omega) = \int \left( \frac{i}{\omega} \chi_{jd}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{E}_{\text{mac}}(\omega) + \chi_{\rho p}(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\text{eff}}(\mathbf{r}', \omega) \right) d\mathbf{r}'. \]

In these equations the various response kernels follow from the expression:

\[ \chi_{ab}(\mathbf{r}, \mathbf{r}', \omega) = \frac{V}{4\pi^3} \sum_{i,a} \int \frac{(\psi_{ik}(\mathbf{r}) \hat{a} \psi_{ak}(\mathbf{r}))(\psi_{ak}^*(\mathbf{r}') \hat{b} \psi_{ik}(\mathbf{r}'))}{\epsilon_{ik} - \epsilon_{ak} + \omega + i\eta} d\mathbf{k} + c.c.(-\omega), \]

in which \( i \) runs over all occupied and \( a \) over all virtual band indices. The operator \( \hat{a} \) and \( \hat{b} \) are either the density or the current operator. The acronym \( c.c.(-\omega) \) denotes the complex
conjugate expression at negative frequency. The Bloch functions \( \psi_{nk}(r) \) are the solutions of the ground-state ZORA equation with eigenvalues \( \epsilon_{nk} \)

\[
\left[-\nabla \cdot \frac{c^2}{2c^2 - v_{\text{eff}}(r)} \nabla + v_{\text{eff}}(r)\right] \psi_{nk}(r) = \epsilon_{nk} \psi_{nk}(r).
\] (6.7)

The four appearing kernels are obtained by substituting for \( a \) and \( b \) either \( \hat{\rho} = 1 \) or the relativistic velocity operator \( \hat{j} \), which is given by,

\[
\hat{j} = -i[r, \hat{H}_{ZORA}] = -i\frac{c^2}{2c^2 - v_{\text{eff}}(r)} \nabla + h.a.,
\] (6.8)

where \( h.a. \) is the hermitian adjoint expression. As can be seen by inspecting Eqs. (6.3) and (6.5), the factors involving the operator \( \hat{j} \) are always integrated, so that only the values of the matrix elements matter. The absence of an energy gap, and the quadratic dispersion of the valence and conduction bands make it necessary to investigate the small-frequency behaviour of the response kernels. In Chapter 6.8 Appendix, we show that all off-diagonal matrix elements are of the order \( O(|k|^2) \), thus falling-off sufficiently fast to smooth any singular behaviour near \( \omega = 0 \), such that the electrical susceptibility has the asymptotic behavior \( \chi_e(\omega) \approx \chi_e(0) + O(\sqrt{\omega}) \).

### 6.4 Method and Implementation

The ground-state DFT calculations are performed by using the Amsterdam Density Functional BAND-structure program (ADF-BAND) [37, 38]. The general characteristics of this implementation are described in Ref. [94] and more specific details can be found, e.g., about the accurate numerical integration scheme, for evaluating matrix elements between basisfunctions which are either numerical atomic orbitals (NAO) or Slater type exponential functions (STO) in Refs. [37] and [91], the density fitting procedure, for evaluating the Coulomb potential, in Ref. [12], and the quadratic tetrahedron method, for evaluating the integrals over the BZ, in Ref. [48]. In the time-dependent extension [63] on this DFT implementation we employ a lattice periodic (microscopic) effective scalar potential, in combination with a uniform (macroscopic) transverse electric field \( E_{\text{mac}}(r, t) \). For solving the TDDFT equations, an iterative scheme is used, with a fixed macroscopic electric field and in which the microscopic potential is updated in each cycle, until self-consistency in the first order density change \( [\delta \rho(r, \omega)] \) is established. The evaluation of the integrals over the irreducible Brillouin zone (IBZ) in the Kohn-Sham response kernels, \( \chi_{ab}(r, r', \omega) \) (which show up in the first order density change) are done numerically with integration weights as described in Ref. [94], so singularities in the response kernels, at resonance frequencies, are handled analytically. Finally, after establishing self-consistency in the density change, we obtain the electric susceptibility \( \chi_e(\omega) \) and thus the dielectric function \( \epsilon(\omega) \) from the (paramagnetic) induced current \( \delta j_{\rho}(r, \omega) \), hereby using the conductivity sumrule. Results for the dielectric function of various nonmetallic crystals using this TDDFT implementation can be found in Ref. [94].
6.5 Results for Indium Antimonide

6.5.1 Band structure

In Fig. 6.1 we show the band structure of InSb, with and without the inclusion of scalar relativistic effects in the ground-state DFT calculation.

![Band Structure of InSb](image)

Figure 6.1: Band structure of indium antimonide (InSb), the solid line is the scalar relativistic (SR), and the dashed line is the nonrelativistic (NR) ground-state calculation.

In order to facilitate the comparison between the two band structure calculations we made the Fermi energy levels coincide. The calculations were done by using a 3Z2P NAO/STO basis (basis V in the BAND program), which is a triple zeta basis augmented with two polarization functions and frozen core. In the calculations, the 4\(d\) atomic states of In and Sb were included in the valence basis. These states give rise to shallow core bands, which can affect the position of the valence band maximum [71, 72]. As can be seen from the band structure in Fig. 6.1 and the blowup of the band structure around the center (\(\Gamma\)) of the BZ in Fig. 6.2, the inclusion of scalar relativistic effects stabilizes the lowest \(s\)-like conduction band considerably more than the highest valence bands [98, 99]. Consequently the conduction band is lowered in energy below the top valence bands, and this causes an avoided crossing between the \(s\)-like conduction band and one of the valence bands. These bands change in character from \(s\)-like to \(p\)-like near \(\Gamma\) and vice versa, as indicated in Fig. 6.2. The ordering of the energy bands is changed and the bandgap vanishes at the \(\Gamma\) point. Thus LDA-ZORA predicts InSb to be a semimetal, as was also found in Ref. [100] and in the full-potential scalar relativistic LAPW calculations of Ref. [72]. The inclusion of spin-orbit coupling in the relativistic calculation will only cause a splitting of the top \(p\)-like valence bands into an occupied \(p_{1/2}\) band and a half occupied \(p_{3/2}\)
band, thereby leaving InSb to be a semimetal, as was confirmed by earlier fully relativistic LMTO calculations in Ref. [71]. Experimentally InSb is found to be a semiconductor with a narrow bandgap of 0.23 eV [7]. In our SR band structure we find the generally accepted trend for DFT-LDA band structure calculations, that the bandgaps are normally underestimated for semiconductors, and in the case of InSb predicting this crystal even to be a semimetal. Nevertheless the scalar relativistic calculated band structure is in good agreement with experiment [101], e.g. comparing the valence band width of 10.8 eV in our SR band structure with experiment [101] of 11.2 eV [ultraviolet photoemission spectroscopy (UPS)] and 11.7 eV [x-ray photoemission spectroscopy (XPS)]. The valence band energies for L\textsubscript{3}, X\textsubscript{3}, and X\textsubscript{1} [see Fig. 6.1] are -1.0, -6.0, and -8.8 eV, respectively, which is also in good agreement with the UPS experimental values of -1.1, -6.5, and -9.0 eV respectively.

### 6.5.2 Static dielectric constant

In Table 6.1 we give the values for the calculated static dielectric constant ($\epsilon_\infty$) for InSb with and without including scalar relativistic effects in the ground-state and also the time-dependent DFT calculation.

For the integration in reciprocal space we used several accuracies, in which we varied the number of \textit{k}-points in the irreducible part of the Brillouin zone (IBZ). The improvement upon the static value for the dielectric constant with the inclusion of SR effects in the ground-state DFT calculation is very clear from Table 6.1. Looking at the relative errors compared to the experimental value ($\epsilon_\infty = 15.7$) of Ref. [77], it can be seen that the error is 42% in the non-relativistic calculation, and 8% when scalar relativistic effects were considered.
6.5. RESULTS FOR INDIUM ANTIMONIDE

Table 6.1: Static dielectric constant of InSb including non/scalar relativistic (NR/SR) effects in the ground-state/time-dependent DFT calculation, and error compared to the experimental value of 15.7 [77].

<table>
<thead>
<tr>
<th>k-space / # k-points</th>
<th>NR/NR Error (%)</th>
<th>SR/NR Error (%)</th>
<th>SR/SR Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/15</td>
<td>11.91</td>
<td>18.13</td>
<td>18.12</td>
</tr>
<tr>
<td>4/34</td>
<td>11.22</td>
<td>16.63</td>
<td>16.61</td>
</tr>
<tr>
<td>5/65</td>
<td>9.15</td>
<td>16.91</td>
<td>16.42</td>
</tr>
</tbody>
</table>

included in the ground-state calculation. From Table 6.1 it can be seen that for the value of \( \varepsilon_\infty \) the inclusion of SR effects in the ground-state DFT calculation is most significant, and that the improvement becomes even more evident when SR effects are also included in the response calculation. Now, after including SR effects for InSb, we find the same accuracy for \( \varepsilon_\infty \), about 5\% deviation from experiment, as we found earlier for the III-V compounds in the zinc-blende structure of Ref. [94]. Other theoretical calculations for the \( \varepsilon_\infty \) of InSb by Huang et al. [51] were less accurate, their value of 13.51 underestimates experiment [77] by 14\%. This nonrelativistic value was obtained from an uncoupled response calculation in which the \( \chi_0 \) response is directly calculated from the ground-state DFT solutions, and therefore, this value does not include the Coulomb or exchange-correlation contributions.

6.5.3 Dielectric function

In Fig. 6.3 we show the dielectric function \( \varepsilon(\omega) \) of InSb, with and without the inclusion of scalar relativistic effects in the ground-state DFT calculation, in comparison with the experimental data of Ref. [46].

The result for \( \varepsilon(\omega) \) with SR effects also included in the response calculation did not deviate by more than a few percent from the one in which SR effects were only included in the ground-state calculation. The calculated spectra for \( \varepsilon(\omega) \) were shifted to higher energies in order to facilitate the comparison with experiment in such a way that the zero crossings in the calculated Re[\( \varepsilon(\omega) \)] coincided with the experimental zero crossings. The shifts needed to accomplish this were 0.15 eV for the NR and 0.3 eV for the SR spectra. LDA calculated the bandgaps to be 0.99 and \( \approx 0 \) eV in the NR and SR case, respectively, and these values should be compared to the experimental gap of 0.23 eV [7]. Therefore, we find, in agreement with earlier findings [94], that there is no direct relation between the necessary shifts of the spectra, and the error in the calculated LDA bandgaps. The improvement upon the calculated (shifted) dielectric function \( \varepsilon(\omega) \) after the inclusion of scalar relativistic effects in the ground-state DFT calculation is clear from Fig. 6.3. The overall agreement of the \( \varepsilon(\omega) \) with the inclusion of SR effects and experiment [46] is very good, even though there are still some features to be improved. E.g., the position of the \( E_2 \) peak [93] (high-energy peak in Im[\( \varepsilon(\omega) \)]) coincides with experiment, but it is too sharp and the magnitude is overestimated compared to experiment. Althought we do find the right magnitude for the \( E_1 \) peak (low-energy peak in Im[\( \varepsilon(\omega) \)]), the double peak structure found in experiment is not reproduced.
Figure 6.3: Plots of the real and imaginary part of the calculated dielectric function of InSb including non/scalar relativistic (NR/SR) effects in the ground-state/time-dependent DFT calculation, in comparison with the experimental data [46]. The calculated spectra are shifted 0.15 eV NR, and 0.3 eV in the SR case.
6.6 Results for Mercury Selenide

The optical response calculations on HgSe were performed using the full-potential ADF-BAND package [37, 38]. For both the ground state and the response calculations we used the free-atom core and valence orbitals, which were supplemented with Slater-type functions to form a triple-zeta valence basis. The free atom orbitals were obtained numerically using a Herman-Skillman type program [43] employing the same ZORA approximation in the relativistic case. We kept the deepest core levels frozen and orthogonalized the valence basis to these cores, but the shallow 5d quasi-core states of Hg were included in the valence set. This basis was then further augmented using a double-zeta polarization set. All matrix elements were evaluated numerically with a relative accuracy of 1e-3. For the numerical evaluation of k-space integrals, 175 symmetry-unique points were used to sample the irreducible wedge of the Brillouin zone. As lattice parameter of the HgSe zinc-blende structure we used \( a = 6.08 \) Å.

6.6.1 Bandstructure, static dielectric constant and the dielectric function

The experimental optical data compiled in Ref. [104] have been used to derive the low frequency behavior for the dielectric function of HgSe. The room temperature refractive index data, which show a large scatter, were used in the frequency range above 0.2 eV to fit a quadratic polynomial in a least squares procedure (Fig. 6.5). In this range both the temperature dependence and the intraband contributions due to impurity carriers are small [104]. This refractive index measurements together with the absorption coefficients obtained at 5K [104], provided the data to derive the experimental dielectric function in the infrared frequency range from 0.2 to 0.55 eV. We thus find an extrapolated value of 11.7 for the dielectric constant \( \epsilon_\infty \). For the optical and ultraviolet frequencies we used ellipsometric data [106] in the range from 1.75 to 5.35 eV.

In Fig. 6.4 we have depicted the energy dispersion of the highest valence and lowest conduction bands of HgSe. These bandstructures are shown for the two cases where we either included or excluded the relativistic effects. We can clearly see that the small direct gap at the center of the Brillouin zone \( \Gamma \) is reduced, and even inverted, upon inclusion of the scalar relativistic effects. The s-like (6s Hg) states at the conduction band minimum are stabilized with respect to the p-like (4p Se) states at the valence band maximum mainly due to the relativistic mass-velocity effect near the nucleus of Hg. This inversion of the typical band order [71] of zinc-blende type semiconductors results in an avoided crossing, even at high symmetry directions, since the s-like band hybridizes with one of these p-like bands into \( \Gamma_{6v} \). This results in an inverted gap of about -1.16 eV, which overestimates the experimental value of -0.45 eV by about 0.8 eV [104]. A further inclusion of spin-orbit coupling will split the p-like Se bands into an occupied \( p_{1\frac{1}{2}} \) band (\( \Gamma_{7v} \)) about 0.3 eV [105] below a half-occupied \( p_{2\frac{1}{2}} \) degenerate pair of bands (\( \Gamma_{8cv} \)), hence preserving the semimetallic nature of the bandstructure.
Figure 6.4: The inverted band structure of HgSe. The solid line is the result with scalar relativistic effects included. The dashed line is the nonrelativistic ground-state calculation. Critical points $E_0$ and $E_1$ and the band character ($s$ or $p$) are indicated near the zone center $\Gamma$.

This splitting will cause the $\Gamma_{8cv}$ bands to be raised by about 0.1 eV (and the $\Gamma_{7v}$ band to be lowered by about 0.2 eV), thus further increasing the inverted LDA gap to about -1.26 eV. This is in good agreement with the relativistic pseudopotential/LDA result (-1.27 eV) of Rohlfing and Louie [105], in which spin-orbit splitting was included. They found that quasiparticle (QP) corrections (within the GW approximation) mainly affect the $s$-like states, moving them upward rigidly by about 0.8 eV, thus reducing the gap $\Gamma_{6v} - \Gamma_{8cv}$ to about -0.51 eV. In the experimental optical spectra of HgSe, shown in Fig. 6.5, this inverted gap appears as the critical point labelled $E_0$ at about 0.5 eV [104]. However, the absorption edge visible in the experiment at about 0.3 eV is most likely due to the transition between the bands connecting to $\Gamma_{8v}$ and $\Gamma_{8c}$, which is symmetry forbidden at $\Gamma$, but becomes allowed outside this point since there $\Gamma_{8c}$ changes character rapidly from $p$- to $s$-like. Simultaneous with the changing of $\Gamma_{8c}$ the band connecting to $\Gamma_{6v}$ changes from $s$- to $p$-character, while the bands connecting to $\Gamma_{8v}$ and $\Gamma_{7v}$ remain of $p$-character. The quasiparticle shift of the $s$-like states will bring the $s$- and $p$-like bands closer together at $\Gamma$ which will further enhance the steepness of the transition in character. This will allow for optical transitions of lower frequency, with a steeper edge in the absorption spectrum. The gap of about 1.95 eV between the nearly parallel top valence and lowest conduction band along the line $\Lambda$ and at the point $L$ at the zone boundary gives rise to the critical point $E_1$. This gap is again increased by about 0.80 eV when QP corrections are included. The top valence states $\Lambda_{4,5}$ along this line $\Lambda$ will split by about 0.8 eV upon inclusion of spin-orbit coupling [71], but the bottom conduction band $\Lambda_6$ will not. This will give rise to a doublet structure in the dielectric function [104], which is however not clearly resolved.
6.6. RESULTS FOR MERCURY SELENIDE

The TDDFT result for the dielectric function, depicted in Fig. 6.5, shows a drastic change with the inclusion of the scalar relativistic corrections. We observe an almost fourfold increase in the absorption in the range from 1 to 3 ev, with a prominent $E_1$-feature just above 2.2 eV. The experimental $E_1$-peak appears around 3 eV. This shift is consistent with the underestimation of the energy gap along the line $\Lambda$ in our ground state DFT-LDA calculation. Due to the Kramers-Kronig relation, the too low position of this peak will give rise to a too high calculated value for the dielectric constant $\epsilon_\infty = 14.4$, vs. 11.7 experimentally.

It is clear that with the removal of the energy gap, also the absorption onset has disappeared, although we do not reproduce the steep increase at the absorption edge $\Gamma_{8v} \rightarrow \Gamma_{8c}$. The $E_0$ critical point shows up as a knee in the calculation at around 1.25 eV (experimentally 0.45 eV), where again the relative shift of about 0.8 eV is in agreement with the overestimation of the $\Gamma_{6v} - \Gamma_{8c}$ gap in the ground-state calculation.

These findings are quite similar to the results we obtained previously for the InSb crystal [102]. For comparison, the relativistic and non-relativistic bandstructures of InSb are shown in Fig. 6.1. Here again the order of the energy bands is inverted at the point $\Gamma$ within the local density approximation upon inclusion of relativistic effects. The interchanged $s$- and $p$-like character of the upper valence bands and the lowest conduction band switches back to the usual ordering just outside the zone center, along the same lines as in the analyses given above for HgSe. The inverted bandgap is much smaller than in HgSe, in InSb it is -0.42 eV, whereas in HgSe it is -1.26 eV. Experimentally, however, InSb is not found to be a semimetal but a narrow-gap semiconductor, with a direct gap of 0.23 eV [7].

A QP-correction of 0.65 eV for the $s$-like band, similar to the rigid 0.8 eV energy shift for the $s$-like band in HgSe would revert the LDA-band ordering in InSb again, resulting in a semiconducting bandstructure. In our LDA calculation for InSb, unlike the dispersion of the HgSe bands, both the lowest conduction band and the band connecting to $\Gamma_{6c}$ have very strong dispersions, which hence corresponds to very low densities of states. We can therefore expect a very small contribution to the absorption at the $E_0$ critical point. We get a good overall agreement in the low energy range, with a value of 16.4 for $\epsilon_\infty$ (15.7 experimentally [77]), which can be inferred by comparing the calculated dielectric function with the available experimental data [46] as depicted in Fig. 6.3. To facilitate the comparison, the calculated spectra have been shifted 0.30 eV to higher energy in the relativistic case and 0.15 eV for the nonrelativistic case. These shifts have been determined, such that the frequencies at which the respective real parts become negative coincide, effectively fixing the position of the very sharp $E_2$ at the experimental value. We do not reproduce the double peak feature at the critical point $E_1$ which requires inclusion of spin-orbit effects in the calculation. The spin-orbit splitting of the upper valence bands along the line $\Lambda$ varies from about 0.8 eV at $\Gamma$ [71, 107] to about 0.5 eV at the zone boundary L [71]. This results in the experimentally clearly resolved doublet structure at about 2 and 2.5 eV.
Figure 6.5: Plots of the real (top) and imaginary part (bottom) of the calculated dielectric function of HgSe with (SR, dash-dotted line) or without (NR, dotted line) including scalar relativistic effects. The experimental data have been compiled from the Refs. [104] and [106] (dots and solid line, for discussion see text).

6.7 Conclusions

We show how to include scalar relativistic effect within the zeroth-order regular approximation in time-dependent density-functional theory for the optical response properties of nonmetallic crystals. These TDDFT equations can also be applied to calculate the optical response properties of semimetals, because they do not show any singular behavior even though the Kohn-Sham bandgap vanishes. The band structure of InSb and HgSe show a considerable stabilization of the $s$-like conduction band minimum with the inclusion of SR effects in the ground-state DFT calculation. LDA predicts the bandgap in the $\Gamma$ point even to vanish, and therefore predicting them to be a semimetals. The relative error in the static
value of the dielectric constant for InSb becomes 5% compared to experiment when SR effects are included in the ground-state DFT calculation as well as in the time-dependent response calculation. The same accuracy as was found earlier with our TDDFT implementation for the III-V compounds in the zinc-blende structure. The dielectric functions for InSb and HgSe, with inclusion of SR effects are clearly improved over the NR ones, and are quite good compared to experiment, although the spectral features are still somewhat shifted to too low energies compared to experiment.

6.8 Appendix: Small-Frequency Response

As we argued before, it is instructive to investigate the \( \mathbf{k} \)-dependence of the off-diagonal \( \hat{\mathbf{j}} \)-matrix elements for the critical bands and region around \( \Gamma \). Therefore, let us consider the following \( \mathbf{k} \cdot \mathbf{p} \) analytic continuation of the Bloch, respectively, eigenfunctions near a special \( \mathbf{k} \)-point. The Bloch theorem allows for the following expansion:

\[
\psi_{n\mathbf{k}+\mathbf{h}}(\mathbf{r}) = \exp(i\mathbf{h} \cdot \mathbf{r}) \sum_s c^s_{n\mathbf{k}}(\mathbf{h}) \phi_s(\mathbf{r}), \tag{6.9}
\]

where the particular choice of eigenfunctions \( \phi_s(\mathbf{r}) \) constitutes a complete orthogonal basis at \( \mathbf{k} \). In order to establish the orthogonality also for the \( \psi_{n\mathbf{k}+\mathbf{h}}(\mathbf{r}) \) functions the expansion coefficients have to satisfy

\[
\sum_s c^s_{n\mathbf{k}}(\mathbf{h}) c^*_s(\mathbf{h}) = \delta_{nm}. \tag{6.10}
\]

These coefficients can be found by substituting the expansion in the scalar relativistic Kohn-Sham equation and by calculating the inner products with respect to \( \exp(i\mathbf{h} \cdot \mathbf{r}) \psi_s(\mathbf{r}) \). This yields the set of equations

\[
\sum_t \left[ \hbar \cdot \langle \phi_s | \hat{\mathbf{j}} | \phi_t \rangle + \left( \gamma_s h^2 - \epsilon_{n\mathbf{k}+\mathbf{h}} + \epsilon_s \right) \delta_{st} \right] c^t_{n\mathbf{k}}(\mathbf{h}) = 0, \tag{6.11}
\]

in which the factor \( \gamma_s = \langle \phi_s | \gamma(\mathbf{r}) | \phi_s \rangle \), where we introduced the shorthand notation \( \gamma(\mathbf{r}) = c^2/(2c^2 - v_{\text{eff}}(\mathbf{r})) \). In the limit of \( \hbar \to 0 \) the expression reduces to the simple relation \( (\epsilon_s - \epsilon_{n\mathbf{k}}) c^s_{n\mathbf{k}}(0) = 0 \). Thus the coefficients \( c^s_{n\mathbf{k}}(\mathbf{h}) \) have to vanish asymptotically unless \( \epsilon_s = \epsilon_{n\mathbf{k}} \) and hence they constitute an ordinary unitary transformation that mixes merely degenerate states. Using these relations we can now evaluate the analytic continuation of the (vertical) \( \hat{\mathbf{j}} \)-matrix elements near \( \mathbf{k} \). First consider

\[
\langle \psi_{n\mathbf{k}+\mathbf{h}} | -i\gamma(\mathbf{r}) \nabla | \psi_{m\mathbf{k}+\mathbf{h}} \rangle = \sum_{s,t} c^s_{n\mathbf{k}}(\mathbf{h}) \langle \phi_s | \gamma(\mathbf{r}) (\mathbf{h} - i\nabla) | \phi_t \rangle c^t_{m\mathbf{k}}(\mathbf{h}). \tag{6.12}
\]

The current matrices follow directly by adding the hermitian adjoint to this expression. Note that \( \gamma(\mathbf{r}) = c^2/(2c^2 - v_{\text{eff}}(\mathbf{r})) \) involves only the fully symmetric ground-state potential. The orthogonality of degenerate \( \phi_{n\mathbf{k}}(\mathbf{r}) \) eigenfunctions is due to symmetry, which is not affected by this totally symmetric factor. The orthogonality involving nondegenerate states with \( \epsilon_s \neq \epsilon_{n\mathbf{k}} \) can be affected, but here the expansion coefficients behave asymptotically
where $\Omega$ is a small sphere surrounding $\Gamma$ and $\nabla$ of $a$ are related due to time-reversal symmetry, which has been made explicit in the combination

$$84$$

CHAPTER 6. RELATIVISTIC EFFECTS IN TDDFT CALCULATIONS

A general structure given by

$$a$$

$$c_n^s$$

so we get a quadratic leading order in the off-diagonal $\hat j$-matrix elements in the case of $\epsilon_{nk} = \epsilon_{mk} = \epsilon_{\text{Fermi}}$ with $n \neq m$.

In the subsequent analysis we can neglect any anisotropy in the energy dispersion, as well as the angular dependence of the $\hat j$-matrix elements, without invalidating the arguments. In the evaluation of the small frequency behaviour of the critical contributions to the various response kernels $\chi_{ab}(\omega)$, we encounter integrals of the following general form:

$$\Delta \chi_{ab}(\omega) \propto \int_\Omega \frac{(a_n(k) + (-1)^n a_n^*(k)) k^{2n}}{k^2 - \omega + i\eta} dk + c.c.(-\omega),$$

where $\Omega$ is a small sphere surrounding $\Gamma$ and $n$ is the number of times the off-diagonal $\hat j$-matrix elements appear in the numerator, i.e., $n=0$ for $\chi_{\rho\rho}(\omega)$, $n=1$ for $\chi_{\rho j}, \chi_{j\rho}(\omega)$, and $n=2$ for $\chi_{jj}(\omega)$. Note that the diagonal elements do not contribute at all. The functions $a_n(k) \approx a_n(0) + \mathcal{O}(k)$ are regular functions of $k$. The contributions of $\psi_{nk}$ and $\psi_{n-k} = \psi_{nk}^*$ are related due to time-reversal symmetry, which has been made explicit in the combination of $a_n(k)$ and $a_n^*(k)$ in the numerator. These integrals can be evaluated directly, with a general structure given by

$$\Delta \chi_{ab}(\omega) \propto p_n(\omega) + \omega^n \sqrt{\omega} \cdot [q(\omega) - 2i\pi^2\theta(\omega)] + \mathcal{O}(h^{n+2}),$$

in which the polynomial part $p_n(\omega)$ of order $n$ contains only even(odd) powers of $\omega$ for even(odd) $n$, just like the regular contributions to the response functions which result from
the nondegenerate bands. The additional terms [in which \( \theta(\omega) \) is the unit stepfunction and \( q(\omega) \) a regular function of \( \omega \)] scale like \( \omega^n \sqrt{\left| \omega \right|} \) which is just one-half an order higher. We can conclude that the absence of a band gap does not lead to irregular contributions to the response functions, and that we can expect a small frequency behaviour of \( \chi_e(\omega) \approx \chi_e(0) + \mathcal{O}(\sqrt{\omega}) \).