Relativistic effects on the linear optical properties of Au, Pt, Pb and W

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Abstract. We report first-principles calculations of the linear optical properties for the metals gold, platinum, lead and tungsten. The dielectric functions are obtained within the independent particle approximation using Kohn–Sham energies and wavefunctions. We focus on the impact of spin–orbit coupling, but also investigate the role of the scalar-relativistic terms. The latter are crucially important to explain the absorption behavior and hence the color of gold. A detailed analysis of the oscillator strengths allows us to trace back the origin of the optical transitions within a given energy range to certain regions in the Brillouin zone. The four examples highlight the importance of relativistic effects that show up in different energy regimes of the optical spectra. Our results, not relying on any further approximation, allow us to judge the origin of the remaining discrepancies with experiment.
1. Introduction

Density functional theory (DFT) has proven to be successful for more than 30 years for the parameter-free description of solids and molecules. In particular, the properties related to the total energy, such as equilibrium volume, elastic constants and phonon frequencies of any solid, can be predicted with reasonable precision. The capability of dealing with excited states from first principles, on the other hand, opens up new research perspectives. In fact, understanding the optical properties of solids is not only of major interest from a basically scientific point of view but also highly relevant for industrial applications, such as opto-electronic devices. The treatment of excited states is, however, a more involved task. The use of ground state quantities for the interpretation of excited states has been quite successful for a variety of materials and properties, whereas it has failed badly for others. In this context, it is often not clear to what extent errors are due to the over-interpretation of ground state properties or caused by the approximations used in the ground state calculation itself, e.g. by the choice of the exchange-correlation (xc) potential.

The simplest theoretical framework for calculating the dielectric response of solids is the independent particle approximation (IPA), where the Coulomb interaction between the excited electron and the created hole is neglected. Both, standard xc functionals—such as the local density approximation (LDA) or the generalized gradient approximations (GGAs)—and the IPA, impose restrictions on the applicability to semiconductors. The former are responsible for the underestimation of band gaps, while the latter ignores excitonic effects. In contrast, the electron–hole interaction is well screened in metals. Hence, for the materials under consideration, the IPA is expected to work reasonably well.

Most of the experimental data for simple metals stem from the 1960s and 1970s [1]–[6]. In the majority of cases, real and imaginary parts of the dielectric function were obtained from the reflectivity by the Kramers–Kronig transformation. Only recently, a new experimental approach has been proposed to derive these quantities from reflection electron energy-loss spectroscopy (REELS) [7, 8]. It was shown that REELS and DFT results exhibit good consistency for Cu, Ag and Au, while earlier optical data deviate significantly. A more recent review including 16 metals and one semi-metal impressively confirms this trend, thereby providing a new reference database for these materials [9]. In any case, judging the impact of relativistic effects requires insight from the theoretical point of view. Comparison between theory and experiment serves two goals. Firstly, a detailed analysis provides information about the origin
of particular features. Secondly, applying the most accurate computational method for solving the Kohn–Sham equations allows for an assessment of the approximations underlying the computation of optical spectra. These are the aims of the present investigation.

While relativistic effects on the electronic structure of metals have been discussed in the literature extensively, hardly any calculation of optical spectra is available for the materials under investigation or spin–orbit (SO) effects are not explicitly addressed. Even for gold, which is the most widely studied metal, existing data deviate by more than a factor of two in magnitude and several eV in peak positions. In light of the resolution of modern spectroscopic methods, such discrepancies are not acceptable.

In this work, we present highly accurate \textit{ab initio} calculations of the linear optical properties, i.e. the imaginary part of the complex dielectric function and the reflectivity of gold, platinum, lead and tungsten in the energy ranges up to 25, 25, 10 and 60 eV, respectively. They represent examples where relativistic effects become evident in different ways. Relativity not only determines the color of gold but also shows up in the low-energy dielectric function and reflectivity of platinum and lead, as well as in the high-energy spectral range of tungsten. Overall, it is crucial to avoid pronounced discrepancies with experiments. We focus mainly on the influence of SO interaction, but also study scalar-relativistic effects in the case of gold. To illustrate our findings, we provide a detailed analysis of the most important features in terms of oscillator strengths, band characters and their origin in \textbf{k} space.

2. Computational details

DFT calculations were carried out for the experimental lattice constants of 4.08 Å (Au), 3.92 Å (Pt), 4.95 Å (Pb) and 3.16 Å (W) \cite{10}. The full-potential linearized augmented plane wave (LAPW) method, more precisely, the full-potential APW + lo method \cite{11}, was used as implemented in the WIEN2k code \cite{12}. Being an all-electron method, where no shape approximation of the potential is made, it allows for the calculation of arbitrary systems, i.e. irrespective of the atomic species involved.

For the xc potential, we applied the GGA parameterized by Perdew \textit{et al} \cite{13}. (In fact, the optical spectra hardly depend on the choice of the particular (semi)local xc functional.) SO interaction was treated self-consistently in a second variational scheme which is known to yield good agreement with exact results \cite{14, 15}. The Kohn–Sham equations have been solved on a $31 \times 31 \times 31$ \textbf{k} mesh. For all calculations, we used muffin-tin radii of 2.5 a.u. and $RK_{\text{max}}$ values of 11. The latter parameter is given by the product of the muffin-tin radius and the largest wavevector $K_{\text{max}}$ in the expansion of the wavefunctions. The plane-wave cut-off $G_{\text{max}}$ in the Fourier series of the potential and electron density in the interstitial region was chosen to be 24.0\textit{R}$_{y}^{0.5}$. For the 5s (Au, Pt, W), 5p (Au, Pt, Pb) and 4f (Au, Pt, W) semi-core states, local orbitals have been introduced. Additional local orbitals were taken into account to improve the description of unoccupied states. Since the optical properties are usually very sensitive to the Brillouin zone (BZ) sampling, we used the aforementioned grids as a starting point for convergence tests in this respect. The spectra presented here always correspond to the \textbf{k} mesh, which yields the highest precision, i.e. no changes are visible with respect to the next smaller mesh. A Lorentzian broadening of 0.1 eV was used for Pt, Pb and W. In the case of Au, a value of 0.01 eV was adopted to resolve specific details more easily.

The optical spectra were calculated within the IPA. A detailed description of the formalism within the LAPW framework can be found in \cite{16}. Here we give only a brief summary of
the computed expressions. The imaginary part of the interband contribution to the dielectric function is given by

\[
\text{Im} \epsilon_{\text{inter}}(\omega) = \frac{\hbar^2 e^2}{\pi m^2 \omega^2} \sum_{n,n'} \int \left| p_{n',n,k} \right|^2 \left[ f(\epsilon_{n',k}) - f(\epsilon_{n,k}) \right] \delta(\epsilon_{n',k} - \epsilon_{n,k} - \omega) \, d^3k
\]

\[
= \frac{\hbar^2 e^2}{\pi m^2 \omega^2} \sum_{n,n'} \int O_{n,n'}(k, \omega) \left[ f(\epsilon_{n,k}) - f(\epsilon_{n',k}) \right] \, d^3k,
\]

(1)

with

\[
O_{n,n'}(k, \omega) = \left| p_{n',n,k} \right|^2 \delta(\epsilon_{n',k} - \epsilon_{n,k} - \omega)
\]

(2)

representing the oscillator strength for a transition between bands \(n\) and \(n'\) with energy \(\omega\) at a given \(k\) point. The corresponding real part is obtained by Kramers–Kronig transformation. The free electrons are characterized by the plasma frequency \(\omega_{\text{pl}}\)

\[
\omega_{\text{pl}}^2 = \frac{\hbar^2 e^2}{\pi m^2} \sum_n \int \left| p_{n,n,k} \right|^2 \delta(\epsilon_{n,k} - \epsilon_F) \, d^3k.
\]

(3)

For the intraband contribution, \(\epsilon_{\text{intra}}(\omega)\), to the dielectric function, a Drude-like shape is adopted by introducing a lifetime broadening \(\Gamma\),

\[
\text{Im} \epsilon_{\text{intra}}(\omega) = \frac{\Gamma \omega_{\text{pl}}^2}{\omega(\omega^2 + \Gamma^2)}.
\]

(4)

In equations (1)–(3), \(p_{n',n,k}\) represents the momentum matrix element between bands \(n'\) and \(n\) at a certain \(k\) point of the BZ, and \(f(\epsilon_{n,k})\) is the occupation number of the single particle eigenvalue \(\epsilon_{n,k}\) approximated by the corresponding Kohn–Sham eigenstate.

In order to analyze the features in the optical spectra in terms of their strongest contributions in \(k\) space and possible changes due to the presence/absence of SO coupling, we can evaluate the oscillator strength for transitions contributing to a chosen energy range at a given \(k\) point according to

\[
O_E(k) = \sum_{n,n'} \int_{E_{\min}}^{E_{\max}} O_{n,n'}(k, \omega) \, d\omega,
\]

(5)

where the sum can be restricted to all \(n'\) and \(n\) for which the corresponding transition energy lies within the selected energy range, i.e.

\[
E_{\min} \leq \epsilon_{n',k} - \epsilon_{n,k} \leq E_{\max}.
\]

(6)

The results of equation (5) can be visualized as a function of \(k\), as will be seen below. This procedure allows for scanning the BZ for regions that are mainly responsible for a particular feature in the optical spectra. A similar analysis was applied by Sexton et al [17] studying the interband optical conductivity of iron.

3. Results

3.1. Gold

Gold is the classical example to study relativistic effects on the electronic structure and optical properties. Its color is correctly predicted only in relativistic calculations [18]–[22]. A large
number of theoretical studies are available in the literature [18], [22]–[28], [31]. Most of the theoretical works, however, are dedicated to the band structure with various underlying approximations. Early pioneering calculations by Christensen and Seraphin [23]–[26] were performed within the relativistic augmented plane-wave method, constructing a potential that guaranteed the best possible agreement with experiment. A model band structure was obtained by Smith [29] by a fitting procedure to non-relativistic and relativistic APW data and adding SO effects by introducing a parameter. More recent results obtained by Dal Corso and Mosca Conte [30] and by Theileis and Bross [31] are based on fully relativistic ultrasoft pseudopotentials and on the relativistic modified augmented plane wave method, respectively.

*Ab initio* calculations of the complex dielectric function have only recently been reported [8, 22]. Whereas in [22] the ZORA approximation has been applied to account for scalar relativity and the effect of SO coupling has only been estimated, in [8] the impact of relativistic effects has not been studied explicitly. Previous calculations by Antonov et al [28] were performed with the relativistic LMTO method relying on the atomic sphere approximation, including but not discussing relativistic effects.

Here, we present a more detailed analysis of the optical spectra in the energy range up to 25 eV in terms of oscillator strengths, as described in the previous section. We first focus on a non-relativistic calculation. Figure 1(a) shows in the upper panel the imaginary part of the complex dielectric function for the three types of calculations. The inclusion of scalar-relativistic effects, i.e. the mass–velocity and the Darwin terms, has the greatest effect. It lowers the interband onset by as much as 1.65 eV from 3.5 to 1.85 eV. By accounting for SO interaction, it further shifts downwards by 0.5 eV. Around 7 eV, a double-peak structure is observed that is absent in the non-relativistic spectrum. Also, the position of the structure around 20 eV differs by 0.5 eV between the non- and scalar-relativistic results. Our results compare reasonably well with the calculations of Romaniello and de Boeij [22] for the energy range 0–10 eV. They are in overall agreement with the results of Antonov et al [28] up to 20 eV. In the 20–25 eV range, however, the peak positions differ by a few eV compared with ours and thereby fail to reproduce recent experimental data [9]. One should note that local-field effects could slightly reduce the magnitude in this energy range, however, without affecting the peak structure.

The impact of the interband onset clearly shows up in the reflectivity, as demonstrated in the lower panel of figure 1(a). The sharp absorption edge observed at 3.5 eV in the non-relativistic case goes hand in hand with a drop in the reflectivity to almost 0%. Since the reflectivity is 100% up to this energy, gold would reflect the whole spectrum of visible light, thus appearing white in contrast to reality. As the absorption edge is lower in energy when relativity is accounted for, the reflectivity is diminished to roughly 40% in the energy range above 1.9 eV. As a consequence, red light is reflected almost perfectly, whereas the intensity of the remaining colors in the reflected light is reduced. This results, in principle, in the characteristic color of gold. Still the underestimated interband onset, arising from an improper d-band position, diminishes the yellow contribution. (Similarly, in silver, the rapid drop in the reflectivity moves to lower energies, i.e. from 3.5 to 3 eV, when including scalar-relativistic effects [9].)

Relativistic effects also influence the plasma frequency changing from 9.44 to 8.96 eV when taking scalar-relativistic terms into account. The inclusion of SO interaction leads to

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4 The local-field effects significantly reduce the loss function for energies larger than 15 eV as recently shown for silver [32], while the effect on the dielectric function is much smaller. Similar findings hold for gold.
Figure 1. (a) Imaginary part of the dielectric function (top) and reflectivity (bottom) of gold from a non-relativistic (gray), a scalar-relativistic (black) and a relativistic (red) calculation. (b) Analysis of oscillator strengths for selected energy ranges and planes inside the BZ. From top to bottom: $E = 2.5–4 \text{ eV}$, $E = 6.4–7.4 \text{ eV}$ and $E = 18.2–21.2 \text{ eV}$; from left to right: $k_z = 1/34$, $17/34$ and $33/34$ (in units of $2\pi/a$). Regions with high oscillator strengths are in dark red.

(c) fcc BZ with the selected plane highlighted. (d) Band structures of gold for the non-relativistic (left panel), scalar-relativistic (middle panel) and relativistic (right panel) calculations. The predominant band characters are shown by the corresponding symbols and colors displayed in the legend. The gray boxes highlight the most active regions for the creation of different optical features.

an additional decrease to 8.81 eV. It now agrees well with a value of 8.83 eV extracted from experimental data by Cooper et al [18].

In the following, we want to trace back the differences in the optical spectra of the three cases to their origin in k space. For this purpose, we analyze selected peaks in terms of their oscillator strengths by highlighting the most important contributions in k space according to equation (5). The results are displayed in figure 1(b) for the energy ranges 2.5–4, 6.4–7.4 and 18.2–21.2 eV (from top to bottom). The selected planes are shown in figure 1(c). The data are displayed for the SO case only. One should note that, by inclusion of relativistic effects, it is
mainly the joint density of states rather than the matrix elements that is altered. Summing up
the squared matrix elements contributing to a particular transition does not reveal significant
changes, as has also been found by Benbow and Smith [33].

To facilitate the interpretation of the oscillator strengths, the corresponding band structures
are depicted in figure 1(d). Therein the respective band characters are highlighted by different
symbols and colors, allowing for an explanation of the momentum matrix elements in terms of
atomic-like selection rules. A comparison of the energy eigenvalues including SO interaction
at high-symmetry points with the results of Dal Corso and Mosca Conte [30] yields reasonable
agreement, with deviations smaller than 0.2 eV. Similarly, the band structure of Theileis and
Bross [31] differs from ours by up to 0.3 eV, while an earlier calculation by Christensen and
Seraphin [24] exhibits deviations up to even 1.25 eV.

In the valence-band region, the inclusion of mass–velocity and Darwin corrections results
in an increased band width of the low-lying parabolic s-like band, where the minimum at the
\( \Gamma \) point is shifted from \(-8.3 \) to \(-10 \) eV. At the same time, the d bands are shifted towards the
Fermi level by approximately 1.6 eV. For the conduction bands, the major effects are an upward
shift of the f bands in the energy region between 12.9 and 14.6 eV along \( L-\Gamma \) by roughly 1 eV,
and a downward shift of the lowest sd bands around 5 eV along \( W-L \) and around 8 eV along \( X-W-K \). The former is then located 3 eV above \( E_F \), whereas the latter changes its character
to predominantly s-like and increases in band width (located at 5.8 eV at \( X \), 4.7 eV at \( W \) and
3.8 eV at \( K \) in the scalar-relativistic case). The impact of SO coupling is less dramatic, mainly
leading to some splittings of the valence and conduction bands, as will be discussed in terms of
the spectral features below.

A closer look reveals that transitions from the uppermost valence band of d character to
the Fermi level in a V-shaped region close to the \( X \) point (also visible in the upper left image
of figure 1(b)) determine the threshold for interband transitions. The first maximum, at \( 5 \) eV in
the non-relativistic case and around \( 3 \) eV in the relativistic case, is mainly created by transitions
around the \( X \) and \( L \) points.

The double-peak structure around \( 7 \) eV, which is only present in the relativistic cases, is
produced by \( d \to s \) and \( d \to p \) transitions from the highest valence bands to conduction bands
of s and pd character along \( W-K \). Moreover, \( k \) points close to the boundaries of the BZ are
involved (middle row of figure 1(b)).

The hump around \( 12 \) eV in the scalar-relativistic calculation can be traced back
to transitions from a d band 2.1 eV below the Fermi level to a conduction band of
p character at 10 eV above \( E_F \) close to the \( X \) point. Inclusion of SO results in a splitting of
the latter p band, the branches of which then appear at \( 9.5 \) and \( 10.6 \) eV, producing the observed
double-peak structure.

The features around \( 20 \) eV are produced by \( d \to f \) transitions from \( k \) points close to the
center of the BZ, as well as from a region around the \( L \) point, as shown in the bottom row
of figure 1(b). Moreover, \( k \) points along the lines \( \Gamma-L \) and \( K-L \) (closer to \( L \)) contribute. The
aforementioned decrease in transition energy by approximately 0.5 eV in the scalar-relativistic
case compared to the non-relativistic one results from the upward shift of flat valence bands
of d character around \( -6.2 \) eV by roughly 1.5 eV along \( \Gamma-L \), accompanied by an upward
movement of the f bands appearing at 12.9 eV at \( L \) and 13.5 eV at \( \Gamma \) (figure 1(d), left panel)
by approximately 1 eV (figure 1(d), middle panel). The inclusion of SO interaction leads to
splittings of the d bands involved in the transitions. For example, the valence band around
\(-4.8 \) eV splits into branches around \(-4.4 \) and \(-5.6 \) eV at \( L \) and \(-4.3 \) and \(-5.5 \) eV at \( \Gamma \). The
corresponding transitions give rise to the observed multi-peak structure. Apart from a moderate downward shift by roughly 0.1 eV, the conduction bands of f character remain almost unaffected (figure 1(d), right panel).

3.2. Platinum

The upper panel of figure 2(a) depicts the imaginary part of the dielectric function up to 25 eV. Overall, our results compare reasonably well with an earlier calculation of Krasovskii and Schattke [34]. However, their observation that the inclusion of SO coupling has no tangible effect on the optical spectra below 40 eV contradicts our findings, as will be seen below. A comparison with the results of Antonov et al [28] also yields generally good agreement, but the first interband peak is found to be approximately twice as high in our calculation. The relativistic band structure used in the discussion of the optical spectra, as shown in figure 2(d) (red curve), is similar to the results of Dal Corso and Mosca Conte [30], as well as of Theileis and Bross [31]. Deviations are less than 0.3 eV and up to 0.4 eV, respectively.

The low-energy range is dominated by free electrons, with a plasma frequency of 7.54 eV, but there are also strong interband transitions highlighted by the inset in the upper panel of figure 2(a). This part of the spectrum, together with the plasma frequency, is strongly affected by SO interaction, the latter being considerably larger in the scalar-relativistic case, i.e. 8.82 eV. The lowest-energy peak of the interband spectrum shifts by 0.6 eV to higher energies when SO coupling is invoked. Although this absorption feature around 0.8 eV is masked by the Drude-like term in the dielectric function, it gives rise to a reduction in the reflectivity by roughly 12%, and is crucial to meet the experimental spectra in this range (see insets of figure 2(a)). We can trace back the contributions of individual bands by a similar analysis to that described above. The top row of figure 2(b) demonstrates that the transitions within this energy range originate from small pockets around the high symmetry points L and X. While the main peak comes from a region along the Γ–X line, distinctly closer to X, the two shoulders to the left and right can be related to small areas around X and L. Although all of the matrix elements are moderate, they significantly contribute to the optical response through the $1/\omega^2$ behavior in the imaginary part of the dielectric function. The impact of SO coupling is due to the change in band structure around the X and L points (see figure 2(d)), where band splittings at the Fermi level lead to an increase in the interband transition energy, as displayed in figure 2(a).

The energy range between 6 and 12 eV shows a triple-peak structure originating from transitions between d-like valence states with s and p admixtures and conduction bands of sd or pd character. The second row of figure 2(b) demonstrates them to be located at the BZ boundary. Further analysis reveals that the matrix elements responsible for the three sub-peaks are similarly distributed in k space. The first subpeak is mainly created by transitions from an area around the L point, as well as from a region in the $k_z = 11/34$ plane at half the distance of the $k_z = 1$ plane and the $k_z$-axis (all k vectors in units of $2\pi/a$). The corresponding bands are basically unaffected by SO interaction. The double peak in the 8–9 eV range can be ascribed to regions close to X and along the line K–L close to K, as well as at about half the distance from K. While in the latter case the conduction band at 5.6 eV above $E_F$ is not altered by SO coupling, two almost degenerate valence bands at 3 eV below $E_F$ now appear at 2.7 and 3.4 eV below $E_F$, respectively (figure 2(d), along K–L).

The absorption around 20 eV is dominated by d → f excitations with some admixture of d → p transitions. In contrast to the previous case, they mainly arise from regions around Γ.
Figure 2. (a) Imaginary part of the complex dielectric function (upper panel) and reflectivity (lower panel) of platinum from a scalar relativistic (black) and a relativistic (red) calculation. Experimental data are taken from Yu [1] (green), Weaver [5] (light blue) and Werner [9] (dark blue). (b) Analysis of oscillator strengths of platinum for selected energy ranges and planes inside the BZ. From top to bottom: $E = 0.4-1.2$ eV, $E = 6-12$ eV and $E = 17.5-22$ eV; from left to right: $k_z = 0, 0.5$ and 1.0 (in units of $2\pi/a$). (c) fcc BZ with the selected plane. (d) Band structure of platinum along high symmetry lines. The bands including SO interaction are given in red, whereas black indicates the scalar-relativistic results. The gray boxes highlight the most active regions for the creation of different optical features.
3.3. Lead

The upper part of figure 3 depicts the imaginary part of the complex dielectric function up to 10 eV in comparison with the experimental data of Lemonnier et al [4]. An approximately 0.5 eV broad dip centered at 1.3 eV is followed by a double-peak structure with maxima appearing at 2.0 and 2.7 eV, respectively. In addition, a shoulder is observed around 3.8 eV for the relativistic calculation. As can be seen more clearly in the inset, excellent agreement with experiment is revealed only when accounting for SO coupling. The improvement over the scalar-relativistic results also shows up in the reflectivity presented in the lower panel of figure 3. In this case, two experimental curves are included. The data taken under ultrahigh vacuum (UHV) clearly exhibit higher reflectivity values in the measured energy range and underline the evidence that surface contamination may be a general reason for the often observed smaller magnitudes compared to calculated data.
SO interaction widens the dip at 1.3 eV. This can be traced back to the effect that the contributions from free electrons and interband transitions overlap in this energy range. Inclusion of SO coupling not only shifts a shoulder appearing in the interband spectrum from 1.3 to 1.5 eV, thereby increasing in magnitude, but also reduces the plasma frequency from 9.4 to 9.0 eV. As a result, a broader well is formed, as is visible in the figure.

In the double peak structure, only the first peak at 1.85 eV is influenced by SO coupling. It moves to a higher energy of 2.0 eV and decreases in magnitude by roughly 10%. Analysis of the matrix elements (not shown here) reveals that major contributions appear for \( k_z \approx 0 \) in a region parallel to the zone boundary \( W-K \) at half the distance \( \Gamma-K \) and for \( 0.3 < k_z < 0.7 \) along a line parallel to the \( k_z \)-axis. The increased transition energy is due to the fact that the sp-like valence bands are lowered, while the p-like conduction bands become higher in energy.

The most important SO effect is shown in the inset of figure 3. The shoulder observed at 3.4 eV in the scalar-relativistic case shifts to 3.8 eV, even getting more prominent. Like the already discussed double-peak structure around 2 eV, it originates from s → p transitions between valence bands of mixed sp character to p-like conduction bands. In figure 4(b), this feature is further analyzed by depicting the oscillator strengths (bottom) for the energy range from 3.5 to 4.5 eV for the selected planes indicated in figure 4(a). In addition, the bare matrix elements (top) are shown to visualize the impact of the joint density of states. (In the following, all \( k \) values are given in units of \( 2\pi/a \)). These images reveal that transitions predominantly take place in regions around the \( X \) and \( W \) points. For \( k_z \) almost equal to zero (bottom left), the dominating oscillator strengths can be localized along a line parallel to \( X-W \) close to the BZ boundary. As \( k_z \) increases (the second image from the left), this region moves closer to a line parallel to \( \Gamma-X \). Between \( k_z = 0.3 \) and \( k_z = 0.6 \) (not explicitly shown in the figure), the oscillator strength decreases, while for even larger \( k_z \) values, new strong contributions appear close to the \( k_z \)-axis and along a line parallel to \( \Gamma-X \) (see the two images on the right side). Note that due to the high symmetry of the fcc BZ, the patterns produced in the regions between \( k_z = 0.6 \) and \( k_z = 0.9 \) also represent the oscillator strengths in planes parallel to the \((k_y, k_z)\) plane for \( k_x \) values between 0.6 and 0.9.

In the \( k_z = 4/34 \) plane (the second column of figure 4(b)), the matrix elements are strongest close to the \( W \) and \( X \) points, forming half-moon-shaped areas in the vicinity of \( X \) (top). By taking into account the influence of the band structure, an additional ring appears, which is almost parallel to the BZ boundary in this plane (bottom). It can be ascribed to the high joint density of states between the almost horizontal valence and conduction bands along the line \( B_2-C_2 \), depicted in figure 4(c).

A different situation occurs in the \( k_z = 23/34 \) plane (the third column). Strong transitions now appear in a star-shaped region, where the oscillator strength exhibits roughly the same pattern as the bare matrix elements. Nevertheless, oscillator strengths close to the \( k_z \) (\( k_z \))-axis are weakened by phase space effects. When SO interaction is omitted, only the edges of the star contribute (not shown in the figure). The band structure for the line \( G_3-A_3 \) shown in the bottom panel reveals that SO interaction is responsible for a splitting of the two lowest conduction bands at \( G_3 \), leading to higher transition energies for excitations to the second conduction band.

Finally, the major matrix elements and oscillator strengths for the \( k_z = 27/34 \) plane are depicted in the last column of figure 4(b). Here, a blossom-shaped region is observed with strong contributions arising along the diagonal of the indicated square (parallel to \( \Gamma-X \)). As in the case before, SO splitting of the lowest conduction bands of p character shifts the transition energy upwards (figure 4(c), bottom, outermost right image).
Figure 4. (a) fcc BZ highlighting selected planes, i.e. $k_z = 0$, 4/34, 23/34 and 27/34 (from left to right). (b) Analysis of optical transitions in lead, including SO coupling for the energy range of 3.5–4.5 eV. Top: transition matrix elements only. Bottom: oscillator strength according to equation (5). (c) The band structure along $X_1(1,0)\rightarrow A_1(27/34,0)\rightarrow B_1(27/34,7/34)\rightarrow C_1(1,7/34)$ in the $k_z = 0$ plane, $X_2(1,0)\rightarrow A_2(24/34,0)\rightarrow B_2(24/34,4/34)\rightarrow C_2(6/34,27/34)\rightarrow D_2(13/34,1)$ in the $k_z = 4/34$ plane, $G_3(0,0)\rightarrow A_3(28/34,0)$ in the $k_z = 23/34$ plane and $G_4(0,0)\rightarrow A_4(24/34,0)$ in the $k_z = 27/34$ plane (all coordinates in units of $2\pi/a$).

3.4. Tungsten

Concerning tungsten, experimental spectra cover the range up to 30 eV [6] and 80 eV [9], respectively. Recent theoretical work [35] was carried out within the ZORA approximation to account for scalar-relativistic effects, while SO coupling was neglected in the calculation of the optical properties. Previous calculations by Christensen and Feuerbacher [36] were based on relativistic APW calculations relying on a constructed potential, similar to what has been described for gold before.
Figure 5. (a) From top to bottom: joint density of states per energy squared, imaginary part of the complex dielectric function and reflectivity of tungsten for a scalar-relativistic (black) and a relativistic (red) calculation. The optical spectra are compared to the experimental data (green) of Weaver et al [6] and to the REELS data (blue) of Werner et al (2009) [9]. (b) Band structure of tungsten along high-symmetry lines, as indicated in the bcc BZ (c). The bands including SO interaction are given in red, whereas black indicates the scalar-relativistic results. The gray boxes highlight the most active regions for the creation of different optical features.

In figure 5(a), the joint density of states per energy squared (top panel), the imaginary part of the complex dielectric function (middle panel) and the reflectivity (bottom panel) of tungsten are shown for a scalar-relativistic calculation and a calculation including SO coupling together with experimental data of Weaver et al [6] and Werner et al [9]. A comparison of the top and middle panels reveals that the joint density of states compares well with the imaginary part of the complex dielectric function in terms of peak positions. The peak heights, however, are influenced by the momentum matrix elements of the corresponding transitions. Around 11 and 17 eV, the matrix elements create two wells, and the structures centered at 38 and 47 eV, respectively, are strengthened, leading to excellent agreement with experiment (see the inset in the middle panel of figure 5(a)). Moreover, the little peaks at 30.5 and 32.8 eV are suppressed. SO interaction has a negligible effect on the optical spectra in the energy region up to 30 eV. Only the plasma frequency increases from 7.17 eV in the fully relativistic case to 7.65 eV in the scalar-relativistic case. For higher energies, however, neglecting the SO interaction
leads to significant deviation from experimental data, since only one triple-peak structure is present around 41 eV. Furthermore, the splitting of the peak at approximately 31.4 eV into the two peaks at 30.5 and 32.8 eV is removed. Our results agree reasonably well with previous calculations [28, 35] for energies up to 30 eV. The 30–40 eV range, where SO effects are crucial to meet experimental data, was not studied in [28], whereas in [35] it does not exhibit any appreciable structure.

In order to discuss the origin of the peak positions, figure 5(b) displays the band structure of tungsten for the scalar-relativistic (black) and the relativistic (red) case. In the latter case, the energy eigenvalues at high symmetry points deviate from early results of Christensen and Feuerbacher [36] by up to 0.8 eV.

Apart from some band splittings at the high-symmetry points $\Gamma$ and $H$, the conduction bands up to 40 eV above the Fermi energy remain almost unaffected by SO. The same is true for the highest lying valence bands of d character with slight admixtures of s and p type. The greatest impact of SO coupling is the band splitting of f- and p-like valence bands with energies of $-28.2$ and $-37.6$ eV at $\Gamma$, respectively. A closer look at the band structure reveals that the triple-peak structure situated around 41 eV is created by $p \rightarrow d$ transitions around $N$, whereas the little peak at 31.4 eV stems from $f \rightarrow d$ transitions around $N$ and along $\Gamma-H$. SO interaction splits these bands, resulting in the observed structure.

4. Summary and conclusions

In this work, we have focused on the influences of relativistic effects on the optical excitation spectra of gold, platinum, lead and tungsten. They turn out to be important in all of these cases, the details strongly depending on the energy range and physical quantity.

In gold, the inclusion of scalar-relativistic effects shifts the uppermost valence bands of d character closer to the Fermi level, thus lowering the interband threshold energy by as much as 1.6 eV down to 1.85 eV. The corresponding transitions are localized to arise from a V-shaped region close to the X point. As a consequence, a dramatic drop in the reflectivity from 100% to approximately 40% is observed. In contrast to the non-relativistic calculation, which determines the reflectivity to be high up to 3.5 eV, only a relativistic calculation can predict the golden color. It should, however, be noted that SO effects are small compared to the influence of Darwin and mass-enhancement terms.

In the optical spectra of platinum, SO interaction significantly reduces the reflectivity in the infrared region, leading to a dip at about 0.7 eV, in excellent agreement with experiment.

In the case of lead, the discrepancy with experiment can be lifted by accounting for SO coupling, which concerns a shoulder at 3.4 eV. A detailed analysis of the oscillator strengths in this energy range reveals that major contributions to this feature stem from a region close to the BZ boundary parallel to $X-W$. Due to SO splitting of the lowest conduction bands of p character, this shoulder moves up to 3.8 eV in accordance with experiment.

Finally, the inclusion of SO interaction is crucial to obtain agreement with experimental data in the case of tungsten. Whereas the spectra up to 30 eV are almost unaffected by SO interaction, its impact on the valence bands below $-25$ eV is dramatic. In particular, splitting of the p-like valence bands around $-37.6$ eV at the $N$ point leads to splitting of a structure around 41 eV in the dielectric function into two features around 38 and 47 eV, respectively.

To conclude, our results offer insights with respect to two very complementary aspects. Firstly, being based on the most accurate way of solving the Kohn–Sham equations, they do not
rely on approximations for the wave functions and matrix elements. Hence, they can be seen as a benchmark for what the IPA with Kohn–Sham wave functions as the starting point is capable of. The remaining discrepancies can be traced back to many-body effects. Secondly, they can help in the future to tune novel materials, such as alloys or nano-structures, in terms of their optical properties. Here, understanding the origin of spectral features of simple materials is a prerequisite for designing more complex ones.

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