The electronic structure and optical response of rutile, anatase and brookite TiO$_2$

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Abstract

In this study, we present a combined density functional theory and many-body perturbation theory study on the electronic and optical properties of TiO$_2$ brookite as well as the tetragonal phases rutile and anatase. The electronic structure and linear optical response have been calculated from the Kohn–Sham band structure applying (semi)local as well as nonlocal screened hybrid exchange–correlation density functionals. Single-particle excitations are treated within the GW approximation for independent quasiparticles. For optical response calculations, two-particle excitations have been included by solving the Bethe–Salpeter equation for Coulomb correlated electron–hole pairs. On this methodological basis, gap data and optical spectra for the three major phases of TiO$_2$ are provided. The common characteristics of brookite with the rutile and anatase phases, which have been discussed more comprehensively in the literature, are highlighted. Furthermore, the comparison of the present calculations with measured optical response data of rutile indicate that discrepancies discussed in numerous earlier studies are due to the measurements rather than related to an insufficient theoretical description.

1. Introduction

Of the manifold of synthesizable crystalline TiO$_2$ polymorphs, mainly the three crystal types rutile [crystal system: tetragonal (4/mmm), space group: $P4_2/mmm–D_{4h}^{14}$], anatase [tetragonal (4/mmm), $I4_1/amd–D_{4h}^{19}$] and brookite [orthorhombic (mmm), $Pbcn–D_{2h}^{15}$] are found in nature. Only the first two play a significant role in industrial applications. Experimental data on TiO$_2$ brookite is limited due to its rareness and difficult preparation [1].

As a semiconductor material with long-term stability, non-toxic environmental acceptability and broadly low cost availability TiO$_2$ has also been taken into account for photovoltaic applications. However, due to optical gaps slightly above 3 eV (rutile: $\sim$3.0 eV [3, 4], anatase: $\sim$3.4 eV [5] and brookite: $\sim$3.3 eV [6]), natural TiO$_2$ is only photoactive in the UV region of the electromagnetic spectrum and an inefficient active solar cell material. Still, the material advantages of TiO$_2$ can be used indirectly in technically and economically viable dye-sensitized solar cells [7–9] where it acts as an electron-transporting substrate for a chemisorbed photoactive dye.

The structure of the three main phases is well characterized by the two complementary Ti$_x$O$_{2x}$ building-block representations pictured in figure 1. The most common representation is the view of the crystal structures as networks of edge- and/or corner-linked distorted TiO$_6$ octahedron building blocks. Rutile and brookite exhibit corner—as well as edge-sharing TiO$_6$ units. In rutile, the O$_h$ symmetry of an ideal octahedron is reduced to $D_{2h}$ symmetry due to different in-plane (equatorial) and out-of-plane (axial) Ti–O bond lengths and two types of Ti–O–Ti in-plane bond angles deviating from 90°. In the anatase phase, additional displacements of the O ions from the equatorial positions generate a local $D_{2h}$ symmetry seen by the Ti ions. Due to stronger distortions in TiO$_2$ brookite, all bond lengths and...
bond angles slightly differ from each other, thus leading to the formal loss of local symmetry and $C_1$ symmetric TiO$_6$ units.

A complementary view of the crystal structure is given by the threefold coordination of O ions in trigonal-planar-type Ti$_3$O$_5$ building blocks. While the Ti$_3$O units exhibit a Y-shaped conformation in rutile, the anatase units are closer to a T-shape. In brookite, both T- and Y-shaped Ti$_3$O units are present.

The linear optical absorption properties of rutile have been investigated, among other studies, in reflection measurements by Cardona and Harbeke [13] and in a more recent reflection-generalized ellipsometry study by Tiwald and Schubert [14]. Their results have demonstrated the characteristic anisotropy in the optical absorption for $E \parallel c$ (extraordinary polarization) and $E \perp c$ (ordinary polarization). However, the reported dielectric functions show significant deviations. In the Cardona–Harbeke data the spectral weight on the first main peak at $\sim$4 eV is much more pronounced for $E \parallel c$ than for $E \perp c$. In contrast, more recently published data by Tiwald and Schubert indicate a less intense peak for $E \parallel c$ at $\sim$4 eV. Also, the existence of distinct second main peaks above 6.5 eV in both polarizations, observed in the newer data, is not resolved in the Cardona–Harbeke data either. The anisotropies in the optical functions of anatase for $E \parallel c$ and $E \perp c$ have been characterized, among others, by Hosaka et al [15]. The optical properties of brookite TiO$_2$ have been investigated in the last few years by several experimental studies [17–21, 6], predominantly focusing on the absorption edge.

Several density functional theory (DFT)-based studies on various TiO$_2$ phases (mainly rutile and anatase) have been published so far [22–31]. The improved description of the electronic structure by hybrid-functional schemes has been discussed in the literature [32–37]. Recently, some studies have investigated many-body effects (self-energy corrections and excitonic effects) on the optical absorption [38–40] of rutile and anatase. Lawler et al investigated the birefringence of the oxides TiO$_2$ including excitonic effects from the solution of the Bethe–Salpeter equation (BSE). Kang and Hybertson [40] as well as Chiando et al [39] both applied many-body perturbation theory (MBPT) methods (i.e. GW approximation and BSE) to calculate optical properties. Their results have clearly demonstrated the necessity of quasiparticle corrections to reproduce experimental photoemission bandgap data as well as the importance of including electron–hole interaction in the simulation of the optical response of the two tetragonal polytypes rutile and anatase. So far, a similar investigation for the more complex brookite phase, whose symmetry-reduced structure might indicate how optical characteristics in TiO$_2$ are affected by increasing disorder, is still missing.

Several authors [39, 40] have attributed the observed differences between the theoretical dielectric function and the experimental data of Cardona and Harbeke [13], among other reasons, to possible deficiencies of the BSE formalism in describing all spectral features of the TiO$_2$ rutile phase. However, as we will demonstrate in light of our numerical results and the comparison with the data published by Tiwald and Schubert [14], there is strong evidence for an insufficient description of the optical properties of rutile by the Cardona–Harbeke data.

2. Methodology

We have performed DFT calculations [41, 42] using the projector-augmented wave (PAW) method [43, 44] as implemented in the Vienna ab initio simulation package (VASP) [45]. An energy cutoff of 400 eV was used to expand the Kohn–Sham orbitals into plane wave basis sets. In addition to the 3d and 4s valence states, the 3s and 3p semicore states of Ti have been explicitly treated as valence states throughout this work. We applied both the standard generalized gradient approximation (GGA) exchange–correlation (XC) functional according to Perdew–Burke–Ernzerhof (PBE) [46] as well as a modern nonlocal, range-separated, screened Coulomb potential hybrid density functional proposed by Heyd,
Scuseria and Ernzerhof (HSE06) [47–50] that corrects, to a large part, the bandgap underestimation in standard DFT.

Quasiparticle (QP) corrections due to self-energy effects within the GW approximation have been included perturbatively in a full-frequency-dependent \(G_0W_0\) scheme (for details on VASP implementation see [51–54]) on top of DFT–PBE and DFT–HSE06 calculations.

In order to account for excitonic contributions and local field effects, the Coulomb correlation of (quasi-)electrons and (quasi-)holes is included by solution of the Bethe–Salpeter equation [55–60] in the Tamm–Dancoff approximation. Instead of an unfavorable \(O(N^3)\) scaling diagonalization of the electron–hole pair Hamiltonian, the calculation of the frequency-dependent dielectric function is performed by an \(O(N^2)\) scaling time-evolution scheme proposed by Schmidt et al [61].

### 3. Results and discussion

#### 3.1. Electronic properties

The electronic band structures of the three \(\text{TiO}_2\) modifications rutile, anatase and brookite are shown in figure 2. Besides HSE06 and \(G_0W_0\) results, the DFT–PBE band edge positions are included to demonstrate the DFT–PBE underestimate of the electronic bandgap. The fundamental bandgaps have been summarized in table 1. The rutile and brookite PBE gaps of 1.88 and 1.86 eV are direct (d) at \(\Gamma\). However, the \(\Gamma\)-point conduction band minimum in rutile is almost degenerate with the local R and minima M (0.03 and 0.05 eV higher in energy). For anatase, an indirect (id) energy gap of 1.94 eV is observed between the conduction band minimum at \(\Gamma\) and the valence band maximum along the \(\Sigma\) path (0.88\(\Gamma\) → M), that is marginally smaller than the direct \(\Gamma\)-point gap of 2.07 eV. Using the HSE06 hybrid functional, the bandgaps of rutile, anatase and brookite are increased to 3.39 eV (d), 3.60 eV (id) and 3.30 eV (d), which follows the trends in previous hybrid-functional studies [27, 32, 33, 35, 37].

Our full-frequency-dependent \(G_0W_0\) calculations predict QP gaps of 3.46 eV (d) for rutile, 3.73 eV (id) for anatase and 3.45 eV (d) for brookite. These results are slightly (0.1–0.15 eV) above the HSE06 values, thus demonstrating that the QP characteristics of \(\text{TiO}_2\) are well approximated by the HSE06 functional. The rutile and anatase bandgaps are comparable to the \(G_0W_0\) QP gaps of 3.34 eV (\(\Gamma\) → R)/3.38 eV (\(\Gamma\) → \(\Gamma\)) and 3.56 eV (id) recently reported by Kang and Hybertson [40] as well as close to the 3.59 eV (d) and 3.83 eV (id) reported by Chiado et al [39].

The HSE06 functional reproduces the \(G_0W_0\) QP bands close to the band edges with high accuracy (cf figure 2). This conformity becomes significantly worse further away from the band edges as demonstrated by HSE06 \(O\Sigma\) states ~0.7 eV below the \(G_0W_0\) QP energies.

We also tested the influence of different initial wavefunctions by calculating \(G_0W_0\) QP shifts for HSE06 wavefunctions which increases the QP gaps by 0.40 ± 0.05 eV.

<table>
<thead>
<tr>
<th>Method</th>
<th>Rutile</th>
<th>Anatase</th>
<th>Brookite</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT–PBE</td>
<td>1.88 ((\Gamma) → (\Gamma))</td>
<td>1.94 (0.88(\Sigma) → (\Gamma))</td>
<td>1.86 ((\Gamma) → (\Gamma))</td>
</tr>
<tr>
<td>DFT–HSE06</td>
<td>3.39 ((\Gamma) → (\Gamma))</td>
<td>3.60 (0.89(\Sigma) → (\Gamma))</td>
<td>3.30 ((\Gamma) → (\Gamma))</td>
</tr>
<tr>
<td>PBE–(G_0W_0)\</td>
<td>3.46 ((\Gamma) → (\Gamma))</td>
<td>3.73 ((\Sigma) → (\Gamma))</td>
<td>3.45 ((\Gamma) → (\Gamma))</td>
</tr>
<tr>
<td>HSE06–(G_0W_0)\</td>
<td>3.73 ((\Gamma) → (\Gamma))</td>
<td>4.05 ((\Sigma) → (\Gamma))</td>
<td>3.68 ((\Gamma) → (\Gamma))</td>
</tr>
</tbody>
</table>
and brookite. The O is recognizable for rutile and much less prominent for anatase. Figure 3, shows predominantly O
threefold-degenerate t
structures, the broad Ti
for all three major phases. As indicated in the DOS and band
and Ti
crystalline TiO
and PBE–G
similar trends as obtained for rutile. Consequently, the HSE06
sp
are split into the twofold-degenerate e
field, the five unoccupied d-states of the central Ti ion
(di)oxide complexes [64]. In an octahedral-type crystal
order described in the introductory section and descriptively
derivable from the crystal-field theory of transition-metal
complexes. In an octahedral crystal field, the five unoccupied d-states of the central Ti ion
are split into the twofold-degenerate e_g-like states with
d_{x^2−y^2} and d_{z^2} character and the energetically lower lying threefold-degenerate t_{2g}-like d_{xy}, d_{xz} and d_{yz}
type states.

In the O_{2p}-like valence band, a weak two-peak separation is recognizable for rutile and much less prominent for anatase
and brookite. The O_{2p} band splitting in rutile results from the
sp^2-like hybridization in the planar (Y-shaped) OTi_3 building
blocks. The p_x and p_y states of the O ion form bonding
σ-hybrid states with the central Ti ion. These σ states form
the lower edge of the O_{2p}-like valence band and extend
almost through the whole band. The uppermost valence band
edge consists of p_z-type states which form the lone pair
(out-of-plane) π states that are higher in energy than the
sp^2-like hybrid states. The slightly different characteristics
in anatase are due to the more T-like shape of the OTi_3
building blocks that lead to stronger deviations from the ideal
sp^2 hybrid states than in rutile. In brookite, both rutile-like
(Y-shape) and anatase-like (T-shape) OTi_3 building blocks
are present, which is why the O_{2p} valence band shows
characteristics from both tetragonal phases.

3.2. Optical properties

In figure 4, the dielectric functions including electron–hole
interaction from solution of the BSE are shown for all three
major phases in ordinary and extraordinary polarization. The
overall line shape of the dielectric functions is characterized
by an absorption onset above 3 eV and two distinct broad
peaks below and above ∼6.5 eV. This characteristic spectral
weight distribution directly reflects the octahedron-type
crystal-field splitting of the Ti_{3d}-like valence states. The
first main peak can be identified with interband transitions
from the O_{2p}-like valence band into the t_{2g}-like sub-band.
The high-energy main peak arises from transitions into the
e_g-like sub-band. Even for the symmetry-reduced TiO_6 units
of brookite, the formal sixfold coordination leads to identical
qualitative properties.

For rutile, the imaginary part of ε(ω) shows a sharp
excitonic feature for E ∥ c (cf figure 4(a)) at the adsorption
onset, which is missing in the independent (quasi-)particle
spectra on the PBE and G_0W_0 levels of theory. This first main
peak is in excellent agreement with the experimental data
of Tiwald and Schubert [14]. Also for E ∥ c, the position of the
first main peak agrees with the experiment. Nevertheless,
the peak height is underestimated in our calculation and the
predicted doublet structure of this peak is not resolved in
the experiment. The second major spectral features present
above 6.5 eV in the calculated spectra for both polarizations
are clearly resolved in the Tiwald–Schubert data. Even the
single-peak characteristic for E ⊥ c and the double-peak
characteristic for E ∥ c is seen experimentally. Further
evidence for notable spectral features above 6.5 eV is also
given by electron energy loss spectroscopy measurements of
Rocquefelte et al [65].

In light of the newer experimental data and our calculated
spectra, it appears reasonable to argue that the experimental
data of Cardona and Harbeke [13], commonly used as
experimental reference on TiO_2 rutile but not indicating a
second main peak neither for E ⊥ c nor for E ∥ c, do not
properly reflect the absorption characteristics.
Figure 4. Polarization-dependent real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) parts of the complex dielectric function for TiO$_2$ rutile (a), anatase (b) and brookite (c). The dielectric functions have been calculated on the BSE level of theory using 72, 144 and 288 electronic bands, 539, 243 and 75 regularly distributed irreducible $k$-points, and QP energies obtained from $G_0W_0$ calculations. The included experimental reference data were extracted from [14] for rutile and from [15] for anatase.

For TiO$_2$ anatase (cf figure 4(b)) the calculated line shape of the $G_0W_0$–BSE dielectric function is in good agreement with the experimental data published by Hosaka et al [15] for both polarizations. The perhaps most characteristic difference from rutile is the low-energy shoulder at $\sim$4 eV and the resulting main peak triplet structure in $\varepsilon_2(\omega)$ for $E \perp c$. It should be noted that this triplet structure exists already in the PBE and $G_0W_0$ spectra. For $E \parallel c$ no low-energy shoulder is observable. The lowest energy feature is a very sharp exciton peak at $\sim$4.5 eV which is slightly blueshifted and slightly overestimated compared to position and intensity in the experiment. Since the absorption onset for $E \parallel c$ is found at significantly higher energies, our results indicate a more pronounced optical dichroism for anatase than for rutile.

In contrast to the dielectric tensor of the uniaxial materials rutile and anatase, the orthorhombic brookite phase is a biaxial material with three independent components. Similar to anatase, the absorption edge of brookite is found to be dichroic due to low-energy features in the two in-plane components $\varepsilon_{2x}(\omega)$ and $\varepsilon_{2y}(\omega)$ (cf figure 4(c)). In contrast to $\varepsilon_{2x}(\omega)$, the low-energy feature in $\varepsilon_{2y}(\omega)$ exists already in the independent-particle spectra at the PBE and $G_0W_0$ levels of theory, whereas this feature in $\varepsilon_{2x}(\omega)$ arises from excitonic contributions. As observed for anatase, the first main peak exhibits a triplet structure. In contrast, the first peak for $E \parallel c$ is almost structureless, more similar to rutile. The overall influence of electron–hole interaction on the spectral weight distribution is less pronounced in brookite than in the tetragonal phases. This suggests that less local symmetry, which corresponds to smaller spatial anisotropies, diminishes the formation of sharp exciton features.

Since it is difficult to extract the adsorption onset from the dielectric functions in figure 4, we have determined the lowest eigenvalues of the electron–hole pair Hamiltonian for the three TiO$_2$ materials by a recursive approach [67, 68, 66]. For TiO$_2$ rutile, the lowest $G_0W_0$–BSE pair-excitation energy is 3.28 eV. This value is larger than the fundamental optical bandgap of 3.03 eV determined in absorption/photoluminescence spectroscopy measurements [2–5]. A similar result is obtained for TiO$_2$ anatase. While photoluminescence spectroscopy yields a fundamental gap of 3.2 eV, the lowest calculated pair-excitation energy in the $G_0W_0$–BSE approach is 3.57 eV. Our calculated pair-excitation energies of rutile and anatase agree well with the bandgaps of 3.37 and 3.53 eV that were reported by Coronado et al [20] from direct Tauc analysis of UV–visible reflectance spectra. However, the lowest pair-excitation energy of 3.56 eV for brookite in the just mentioned study is found to be larger than the calculated lowest pair-excitation energy of 3.13 eV.

4. Concluding remarks

In this study, we have investigated the electronic and optical properties of the three naturally occurring TiO$_2$ polymorphs rutile, anatase and brookite. The more complex orthorhombic brookite phase has, for the first time, been treated systematically with the same accuracy as the two tetragonal phases. Thus, this work provides TiO$_2$ brookite HSE06 hybrid functional and $G_0W_0$ QP reference data for further studies as well as optical spectra from solution of the BSE. Our results indicate that the inclusion of electron–hole pair excitations on the BSE level of theory allows an accurate modeling of the polarization-dependent optical properties. This is especially true for TiO$_2$ rutile, where, in light of the more recent data of Tiwald and Schubert [14], the
reported discrepancies between the calculated and measured dielectric functions seem to be primarily caused by improper experimental reference data used in the preceding studies.

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References