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Rutile, anatase, brookite and titania thin film from Hubbard corrected and hybrid DFT

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Abstract

As a benchmark, the structural, electronic and optical properties of the three main phases of TiO₂ crystals have been calculated using Hubbard U correction and hybrid functional methods in density-functional theory. These calculations are compared concerning the available experimental observations on pristine TiO₂ crystals. Modified hybrid functionals, particularly the PBE0 functional with 11.4% fraction of exact exchange, are shown to provide highly accurate atomic structures and also accurate electronic structure data, including optical excitation energies. With DFT + U, accurate optical spectra are also possible, but only if the Hubbard U is applied on the O 2p electrons exclusively. Furthermore, both methods, the 11.4%-PBE0 hybrid functional and the DFT + U_p scheme have been used to study TiO₂ amorphous ultra-thin films, confirming the agreement of the two methods even with respect to small details of the optical spectra. Our results show that the proposed DFT + U_p methodology is computationally efficient, but still accurate. It can be applied to well-ordered TiO₂ polymorphs as well as to amorphous TiO₂ and will allow for the calculations of complex titania-based structures.

1. Introduction

Titania, TiO₂, has an extremely wide range of applications, including the utilisation of solar energy for photocatalysis [1–10] and photovoltaics [10–12], as well as in electronic devices [13–15]. It exists in numerous polymorphs, the most common ones being rutile (R), anatase (A), and brookite (B) (see figure 1), found in natural minerals [16–19].

The electronic band gaps determined by photoemission for R- and A-TiO₂ amount to 3.30 eV [20] and 3.47 eV [21], respectively. Furthermore, as concluded from work function measurements, the conduction band of R-TiO₂ is about 0.2 eV above the one of A-TiO₂ [22]. We are not aware of any photoemission measurements on B-TiO₂. However, there are optical gap measurements for all three polymorphs: They are reported to be ~3.0 [23–26], 3.4 [25–27], and 3.3 [28, 29] eV for R-, A-, and B-TiO₂, respectively.

These gap sizes require additional efforts to sensitise TiO₂-based materials for sunlight below the UV region of the electromagnetic spectrum [21, 30–34]. Corresponding experimental work is increasingly supported and guided by computational studies [33–38]. In particular, *first-principles* simulations provide valuable insight into the excitation processes in TiO₂-based systems [21, 30, 31, 33, 35, 36]. However, the predictive power of density-functional theory (DFT), the methodology most frequently used in this context, is severely limited with respect to the accurate description of the electronic structure, e.g., the band gap [39–42]. While there are numerous approaches with superior predictive power, such as quantum chemistry methods [16], many-body perturbation theory [18, 39], or dynamical mean-field theory [43, 44], these methods are computationally too demanding for routine applications to complex titania-based systems. Therefore, there is a need for a versatile, computationally efficient and accurate methodology to address the titania electronic properties.

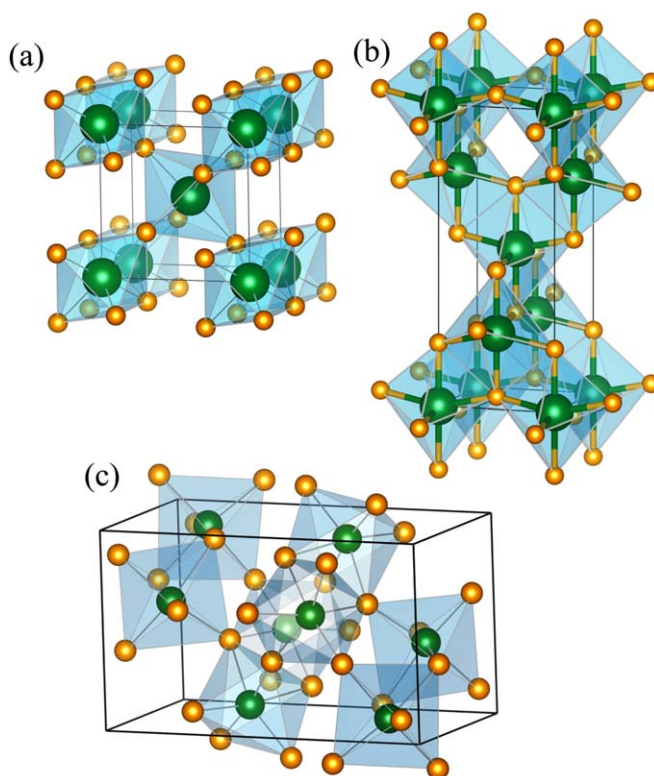


Figure 1. Atomic structures of the (a) rutile, (b) anatase, and (c) brookite polymorph of titania. Green and orange spheres represent Ti and O atoms, respectively. Polyhedra indicate the direct neighbourhood of each Ti atom defined by the nearest O atoms.

By correcting the on-site Coulomb and exchange energies of specific orbitals, the DFT+U method [45–47] is frequently considered to be a meaningful compromise between accuracy and computational expense. In recent years, this theory has been expanded to correct inter-site electronic hybridisations by DFT+U+V [48] and to account for the over-delocalisation of the electrons in the localised Hubbard manifold within density-functional perturbation theory [49]. A number of DFT+U studies were performed, where the U value was chosen such as to reproduce a specific TiO_2 property known from either experiment or high-level theory [50–63]. Nevertheless, this approach is somewhat unsatisfactory. The accurate description of one specific property does not necessarily guarantee the accurate description of others. For example, the optimisation of U_d with respect to the energy of reduction of TiO_2 to Ti_2O_3 fails to result in the correct band gap [50]. Similar results were also observed in [61]. Combining separate U parameters for Ti 3d and O 2p electrons can improve the description of the atomic structure and in particular the electronic band gap [62]. However, it gives rise to additional complexity and inconsistencies, particularly with respect to the calculated optical response [55, 56]. Very recently, Kirchner-Hall *et al* [63] performed an extensive benchmarking of DFT+U for various compounds, including R- TiO_2 and noted that the calculated band gaps are extremely sensitive to the type of projector functions.

Hybrid DFT, which incorporates a fraction of the exact exchange (EEX) from Hartree–Fock theory, is another scheme, numerically more comprehensive than DFT+U, to address the shortcomings of DFT in describing titania, particularly concerning the prediction of single-particle excitation energies [18, 64–70]. Ko *et al* [71] examined the effect of the EEX fraction on the electronic structure of R- and A- TiO_2 . Landmann *et al* [18] calculated HSE-based optical absorption spectra for R-, A- and B- TiO_2 . Here, excitonic effects were included by solving the Bethe–Salpeter equation, and it was concluded that discrepancies between theory and experiment discussed in numerous earlier studies are due to the measurements rather than related to an insufficient theoretical description. Recently, hybrid DFT was also used to determine optical transitions and Franck Condon shifts in titania [70].

Here, we compare the accuracy of hybrid DFT with varying EXX-admixture with different Hubbard U correction schemes in describing TiO_2 bulk crystals. We find that hybrid functionals with considerably reduced EXX fraction describe the optical absorption spectra of all TiO_2 polymorphs best. In addition, we find that DFT + U_p , (i.e., if the U values is applied on the O 2p electrons exclusively,) nearly perfectly reproduces the gold standard of the best hybrid functional. We also use DFT + U_p and the optimized hybrid functional methods to study a TiO_2 amorphous thin film structure. Here, we confirm that both methods give essentially the same results also in case of disordered TiO_2 material. The structural, electronic and optical results of our calculations

for titania crystals and amorphous thin films are presented and discussed in section 3. The remainder of this study covers the computational methodology described in section 2 and some concluding remarks stated in section 4.

2. Computational methodology

DFT within the generalised gradient approximation using the Perdew–Burke–Ernzerhof functionals (PBE [72] and PBE_{sol} [73]) in conjunction with Grimme’s D2 correction [74, 75] to account for dispersion interactions is the starting point of the present calculations. Here, the QUANTUM ESPRESSO implementation [76, 77] with norm-conserving pseudopotentials is used. The electron orbitals are expanded in a plane-wave basis with an energy cutoff of 150 Ry. Energy and force convergence criteria of 10^{-10} Ry and 10^{-6} Ry/bohr are applied to determine the structurally relaxed ground state. The Brillouin zone (BZ) sampling is performed using $8 \times 8 \times 12$, $10 \times 10 \times 4$, and $3 \times 5 \times 5$ Monkhorst–Pack k -point meshes for R-, A-, and B-TiO₂ unit cells, respectively.

The valence band (VB) and conduction band (CB) edges of titania are dominated by O 2p and Ti 3d states, respectively [18]. Therefore, a Hubbard correction is applied to these states. Here, we use the Dudarev rotationally invariant Hubbard U/J correction scheme [47].

$$E_{\text{DFT}+U} = E_{\text{DFT}} + E_U, \quad (1)$$

where E_{DFT} is the approximate DFT energy, while E_U contains the additional Hubbard. It is given as

$$E_U = \frac{1}{2} \sum_{I,m,m',\sigma} (U^I - J^I) (\delta_{mm'} - n_{mm'}^{I\sigma}) n_{m'm}^{I\sigma}, \quad (2)$$

where $U_{\text{eff}}^I = U^I - J^I$ the effective Hubbard parameter, $n^I = \sum_{m,\sigma} n_{mm}^{I\sigma}$ the total occupation of localised states σ at site I , and m and m' are magnetic quantum numbers. In the DFT+ $U_{p,d}$ (DFT+ U_p + U_d) scheme, U_d parameter represents the screened on-site Coulomb interaction of Ti 3d electrons and U_p parameter accounts for the O 2p electrons.

Furthermore, we account for exchange and correlation (XC) effects beyond (semi-)local DFT by using hybrid functionals, specifically PBE0 [78, 79] and HSE [80, 81], which contain a fraction α of EXX from the Hartree–Fock (HF) theory

$$E_{\text{xc}}^{\text{PBEO}} = \alpha E_{\text{x}}^{\text{HF}} + (1 - \alpha) E_{\text{x}}^{\text{PBE}} + E_{\text{c}}^{\text{PBE}} \quad (3)$$

and

$$E_{\text{xc}}^{\text{HSE}} = \alpha E_{\text{x}}^{\text{HF,SR}}(\mu) + (1 - \alpha) E_{\text{x}}^{\text{PBE,SR}}(\mu) + E_{\text{x}}^{\text{PBE,LR}}(\mu) + E_{\text{c}}^{\text{PBE}}. \quad (4)$$

Here the adjustable parameter μ controls the short-ranginess of the interaction in HSE. Note that HSE degenerates to the PBE0 hybrid functional for $\mu = 0$. In the following, a value of 0.106 Bohr^{-1} is used.

The electronic structures calculated with PBE_{sol}, PBE_{sol}+ U_d , PBE_{sol}+ $U_{d,p}$, and PBE0 are used to calculate the dielectric function within the independent-particle approximation [82], i.e., local field effects and electron-hole attraction are not considered [83]. Specifically, the tensor elements in the long-wavelength limit are calculated as

$$\varepsilon_{\beta\beta}(\omega) = 1 + \frac{16\pi}{\Omega} \sum_{v,c} \sum_{\mathbf{k}} \frac{1}{\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}} \frac{|\langle v\mathbf{k} | p_{\beta} + i[V^{nl}, r_{\beta}] | c\mathbf{k} \rangle|^2}{(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}})^2 - (\omega + i\gamma)^2}, \quad (5)$$

where β denotes the spatial direction. We follow the usual convention where the three-fold symmetry axis is identified with the z -direction, while the x -direction is perpendicular to the z -direction and lies in the plane spanned by the three-fold symmetry axis and one of the three equivalent basis vectors of the primitive orthorhombic unit cell. The sum runs over all valence and conduction band states and the wave vectors in the BZ. The transition dipole moments include the commutator with the nonlocal part of the pseudopotentials, Ω is the cell volume, and γ is the broadening. The Yambo package [84, 85] is used for the numerical calculations.

3. Results and discussion

3.1. Parametrization

First, the hybrid functionals, PBE0 and HSE, are used to account for XC effects beyond conventional DFT. As expected [71], the EXX fraction α has a strong influence on the band gap. As shown in figure 2, it increases nearly linearly with α . The strongest and weakest slopes are observed for A- and B-TiO₂, respectively. The EXX fractions α of 11.4% and 16.3% in PBE0 and HSE, respectively, lead to the best simultaneous reproduction of the experimental band gaps of all titania polymorphs studied here.

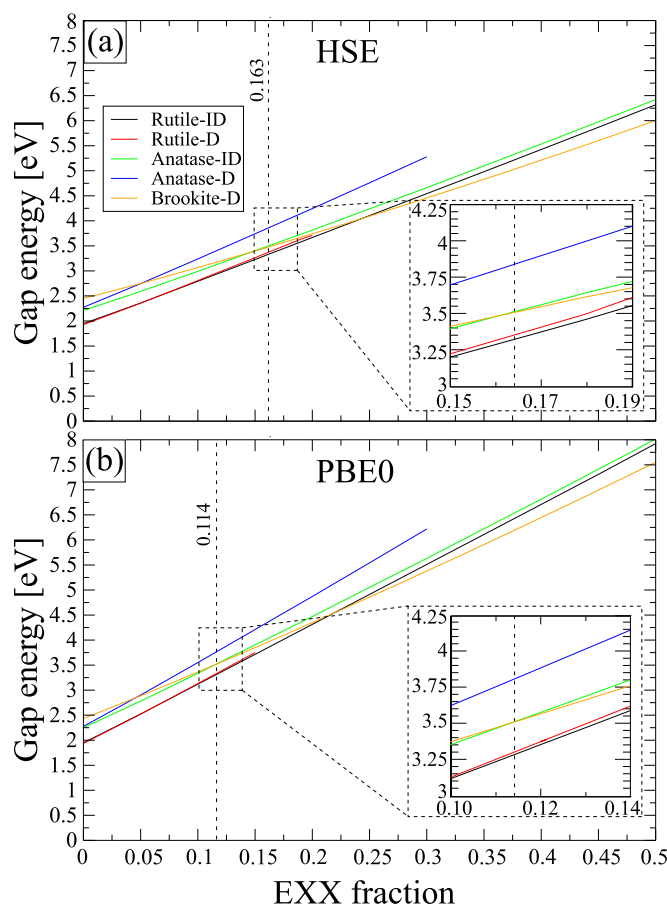


Figure 2. Calculated fundamental lowest direct (D) and indirect (ID) band gaps for R-, A-, B-TiO₂ as a function of the EXX fraction α used in the respective hybrid DFT.

Alternatively, we parametrise the U value for a sufficiently representative XC effect in TiO₂ materials. Therefore, we start to find the U_d and U_p values self-consistently for R-, A-, and B-TiO₂ crystals by using the linear response method [86]. We found U_d values of 5.91, 5.97, and 5.95 eV for the respective Ti 3d states. However, the self-consistent determination of U_p using linear-response theory leads to rather large (>18 eV) values unsuitable for calculating realistic band structures. This finding has already been reported earlier [87] and was attributed to the fact that linear-response theory is unsuitable for light elements application. On the other hand, U_d values alone are insufficient to reproduce the band gap of titania structures correctly. If U_d is increased to improve the band gap of titania structures, the band gap surprisingly decreases again for $U_d > 7.5$ eV. This behaviour is due to the partial hybridisation of $\text{Ti}^{3d} \leftrightarrow \text{O}^{2s}$ and $\text{Ti}^{3d} \leftrightarrow \text{O}^{2p}$ states; see also the projected density of states (PDOS) in figure 3(c). In addition, U_d alone causes the extension of bond length and lattice parameters; see table 1, figures 3(a), and S2(a).² Most importantly, a gradual deterioration of the optical spectrum is observed as U_d increases; see figure S2(c), (d) in (See footnote 3).

Therefore, while using the U_d values determined via linear response for the Ti 3d electrons, the U_p values are empirically determined such that a satisfactory direct band gap for the titania structures is obtained. This results in corrections of 4.20 eV for the O 2p electrons in R-, A- and B-TiO₂, respectively. We briefly note here, that a value of 8 eV in an U_p -only scheme will allow us to produce accurate dielectric optical spectra (for more details see below).

3.2. The pristine TiO₂ crystals.

R-TiO₂ and A-TiO₂ belong to the tetragonal space groups $P4_2/mmm$ (136) and $I4_1/amd$ (141), respectively. B-TiO₂ is orthorhombic with space group $Pbca$ (61). R-, A- and B-TiO₂ unit cell contain 6, 12, and 24 atoms, respectively. In all these titania polymorphs, TiO₆ octahedra chains are formed (see figure 1) that consist of Ti^{4+} cations coordinated to six O^{2-} anions. These octahedra are uniquely aligned in R- and A-TiO₂, whereby varying orientation is responsible for the reduced symmetry in B-TiO₂. At ambient conditions, R-TiO₂ is the most stable

² See Supplementary information, which includes [86, 88–93, 95], for additional details to accompany this study.

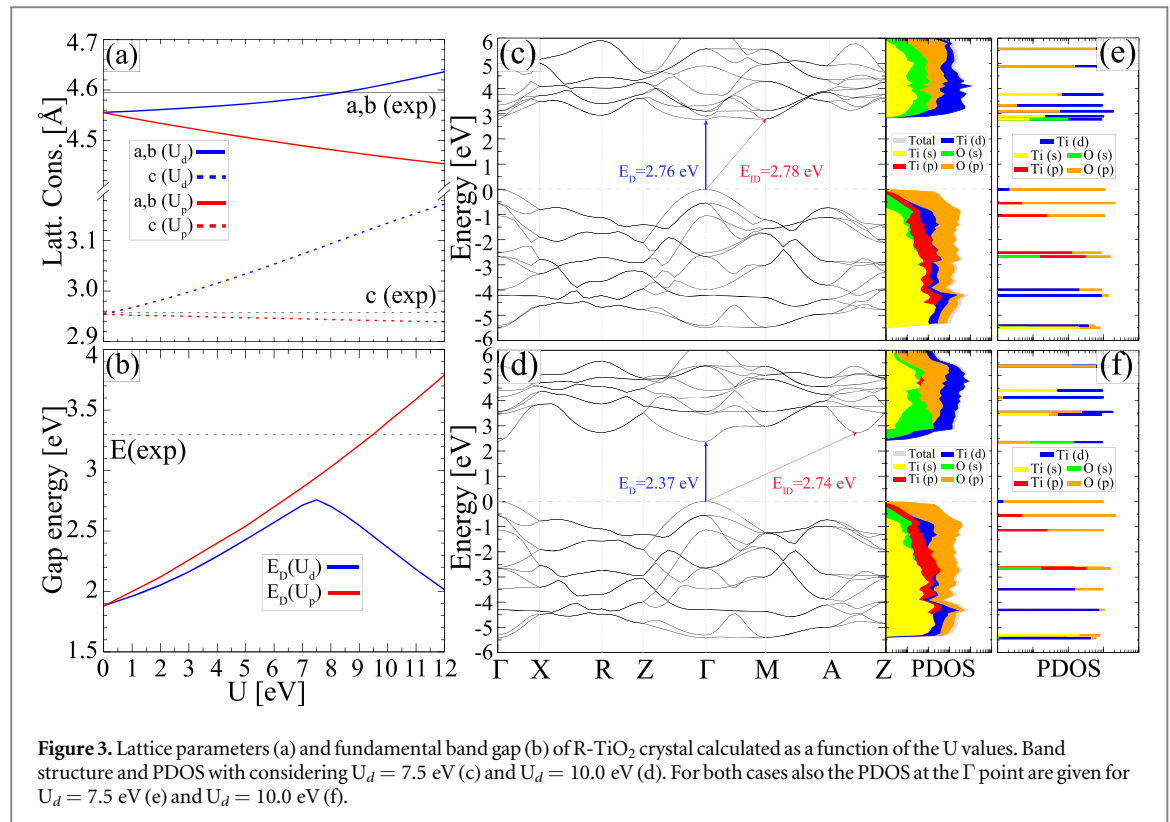


Table 1. Calculated unit cell parameters a , b , c (in Å) and volume V (in Å³) of R-, A- B-TiO₂ in comparison to experiment. U_d values are equal to 5.91, 5.97, and 5.95 eV for the respective Ti 3d states of R-, A- B-TiO₂; U_p is equal to 4.2 eV for the respective O 2p states. Relative deviations are given with respect to the mean of experimental data.

Method	Rutile			Anatase			Brookite			
	$a = b$	c	V	$a = b$	c	V	a	b	c	V
PBE _{sol}	4.556	2.954	61.32	3.761	9.579	135.50	9.154	5.424	5.107	253.57
	-0.8%	-0.1%	-1.8%	-0.6%	+0.7%	-0.6%	-0.3%	-0.5%	-0.8%	-1.7%
PBE _{sol} + U_d	4.578	3.052	63.96	3.834	9.657	141.95	9.240	5.488	5.239	265.67
	-0.4%	+3.2%	+2.5%	+1.3%	+1.5%	+4.1%	+0.6%	+0.7%	+1.7%	+3.0%
PBE _{sol} + $U_{d,p}$	4.542	3.038	62.67	3.803	9.653	139.61	9.184	5.448	5.215	260.93
	-1.1%	+2.7%	+0.4%	+0.5%	+1.4%	+2.4%	+0.0%	-0.1%	+1.3%	+1.2%
HSE	4.563	2.953	61.48	3.707	9.949	136.72	9.202	5.418	5.109	254.72
	-0.7%	-0.1%	-1.5%	-2.1%	+4.6%	+0.3%	+0.2%	-0.6%	-0.8%	-1.2%
PBE0	4.573	2.960	61.90	3.738	9.783	136.69	9.175	5.441	5.133	256.25
	-0.5%	+0.1%	-0.8%	-1.2%	+2.8%	+0.3%	-0.1%	-0.2%	-0.3%	-0.6%
Experiments	4.604	2.959	62.72 [88]	3.787	9.518	136.50 [88]	9.184	5.454	5.146	257.76 [88]
	4.587	2.954	62.15 [89]	3.784	9.515	136.24 [90]	9.180	5.457	5.158	258.39 [91]
	4.593	2.959	62.42 [92]	3.785	9.514	136.30 [92]	9.184	5.447	5.145	257.38 [93]

phase while A- and B-TiO₂ are metastable and transform to R-TiO₂ when heated. However, A- and B-TiO₂ are thermodynamically stable in titania nanoparticles with diameters below 11 nm, and in the range from 35 to 11 nm, respectively [96].

The lattice parameters of R-, A- and B-TiO₂ are determined within PBE_{sol}, PBE_{sol}+ U_d , PBE_{sol}+ $U_{d,p}$, HSE, and PBE0; see table 1. It can be seen that PBE0 provides structural data in excellent agreement with experiment for all three titania polymorphs, while the HSE data are only of similar quality as the PBE_{sol} calculations, suggesting that the short range feature of the HSE hybrid functional is of limited benefit in this case. The PBE_{sol}+ U_d calculations lead to a systematic overestimation of the lattice parameters by 1-4 %, which is improved by considering Hubbard corrections for the O 2p states. Based on the above evaluation, we refer to the PBE0 atomic geometries for band structure and optical response calculations as the 'gold standard' in the following.

Table 2. Calculated direct (D) and indirect (ID) fundamental band gap (in eV) of titania in comparison to experimental data. U_d values are equal to 5.91, 5.97, and 5.95 eV for the respective Ti 3d states of R-, A-, and B-TiO₂ in PBE_{sol}+ U_d and PBE_{sol}+ $U_{p,d}$, where the U_p value for the respective O 2p states is equal to 4.2 eV. In PBE_{sol}+ U_p , U_p is chosen equal to 8.0 eV so that the calculated optical absorption spectra reproduce the experimental ones.

Method	Rutile	Anatase	Brookite	Amorphous thin-film
PBE _{sol}	1.88 (D) 1.93 (ID)	2.27 (D) 2.16 (ID)	2.40 (D)	2.43 (D)
PBE _{sol} + U_d	2.60 (D) 2.55 (ID)	3.08 (D) 2.91 (ID)	2.90 (D)	2.98 (D)
PBE _{sol} + $U_{d,p}$	3.29 (D) 3.29 (ID)	3.87 (D) 3.76 (ID)	3.69 (D)	3.37 (D)
PBE _{sol} + U_p	2.91 (D) 2.95 (ID)	3.39 (D) 3.32 (ID)	3.50 (D)	3.15 (D)
HSE	3.34 (D) 3.31 (ID)	3.84 (D) 3.52 (ID)	3.50 (D)	3.43 (D)
PBE0	3.31 (D) 3.29 (ID)	3.83 (D) 3.51 (ID)	3.49 (D)	3.43 (D)
Experiment	3.30 (D) [35] —	3.97 (D) [36] 3.47 (ID)	—	—

In table 2, we compare the band gaps calculated for R-, A- and B-TiO₂ with the experimental data. As expected, the DFT values underestimate the measured data considerably. A band gap widening by about 0.5–0.8 eV occurs upon including Hubbard corrections for the Ti 3d states. This widening results mainly from an upward shift of the conduction band. However, it is not sufficient to reproduce the experimental data. Moreover, in contrast to the experiment [23, 24], an indirect rather than a direct band gap is calculated for R-TiO₂. The correct character of the rutile band gap is recovered, and excellent band gap values for all three polymorphs are obtained if Hubbard correction is considered for both the Ti 3d and O 2p states. The band gaps calculated within hybrid DFT agree with the PBE_{sol}+ $U_{p,d}$ values and the experiment within 0.05 eV. However, both types of hybrid functional, PBE0 as well as HSE, predict an indirect rather than a direct band gap for R-TiO₂, in contrast to the PBE_{sol}+ $U_{p,d}$ (and + U_p) schemes, which are able to reproduce the experimental finding of a direct gap; see also figure S1 in (See footnote 3).

In addition, the electronic states below the VB edge (see band structures in figure S1 in (See footnote 3)) are accurately depicted using PBE_{sol}+ $U_{p,d}$ or hybrid DFT. For R-TiO₂, an upper valence bandwidth in the range of 5–6 eV was measured [97–100]. This is well reproduced by the present PBE_{sol}+ $U_{p,d}$ calculations, which determine a value of 5.90 eV in agreement with 5.93 eV determined with PBE0. Similarly, PBE_{sol}+ $U_{p,d}$ predicts a bandwidth of 4.81 eV for the upper valence band in A-TiO₂, close to the measured 4.75 eV [101] and the PBE0 value of 4.93 eV. Previous quasiparticle and HSE calculations (with standard EXX fraction of 25%) resulted in bandwidths exceeding 6.5 and 5.5 eV, respectively [18, 21, 60, 102, 103]. For B-TiO₂, a bandwidth of 5.05 and 5.09 eV is predicted within PBE_{sol}+ $U_{p,d}$ and PBE0, respectively. We are not aware of relevant experimental data. PBE_{sol}+ U_d calculations provide only slightly smaller bandwidths, with values of 5.42, 4.74 and 4.74 eV for R-, A-, and B-TiO₂, which also fit to the experimental values, suggesting that the + U procedure at all does not alter this property considerably.

It also improves significantly (albeit not as much as the PBE_{sol}+ $U_{p,d}$ and PBE0) the band gap of titania structures, see table 2. Surprisingly, the bandgap of B-TiO₂ is found to be almost identical (3.50 eV) with the corresponding value obtained by PBE0. The most notable difference is found in the remaining range of –7.0 to –4.5 eV, where the PBE_{sol}+ U_p bands are over-downshifted in comparison to the PBE0 results, see figure 4.

The surprising agreement of the + U_p -only approach motivates us to apply this approach also to optical absorption spectra. In figure 5, the calculated imaginary parts of the dielectric functions of R-, A-, and B-TiO₂ in ordinary and extraordinary polarisation are compared to the experiment. All calculations, apart from those based on PBE_{sol}, account well for the onset energy of the optical absorption caused by O^{2p} → Ti^{3d} t_{2g} inter-band transitions. PBE_{sol}+ $U_{p,d}$ fails also in the sense that the characteristic valley in the prominent two-peak structure tends to disappear or to become at least strongly underestimated.

However, PBE0 provides the best description of the line shape of the dielectric function, at least for low photon energies. PBE_{sol}+ U_p resembles shifted PBE_{sol} results. Interestingly, even some small peaks for E⊥c and E||c are found in agreement with the PBE0 hybrid and the experiment. Furthermore, the calculated line shape for photon energies between 9–12 eV matches the measured optical spectra of A-TiO₂ quite well. A similar behavior is also observed in the real parts of the dielectric functions, reflectivity and absorption results of R-, A-, and B-TiO₂, see figures S3–S5 in (See footnote 3) [88].

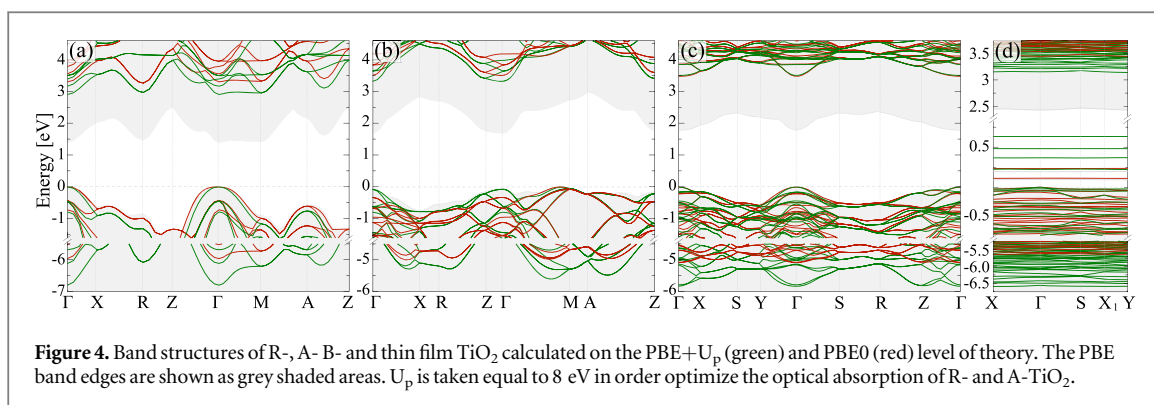


Figure 4. Band structures of R-, A- B- and thin film TiO_2 calculated on the PBE+ U_p (green) and PBE0 (red) level of theory. The PBE band edges are shown as grey shaded areas. U_p is taken equal to 8 eV in order to optimize the optical absorption of R- and A- TiO_2 .

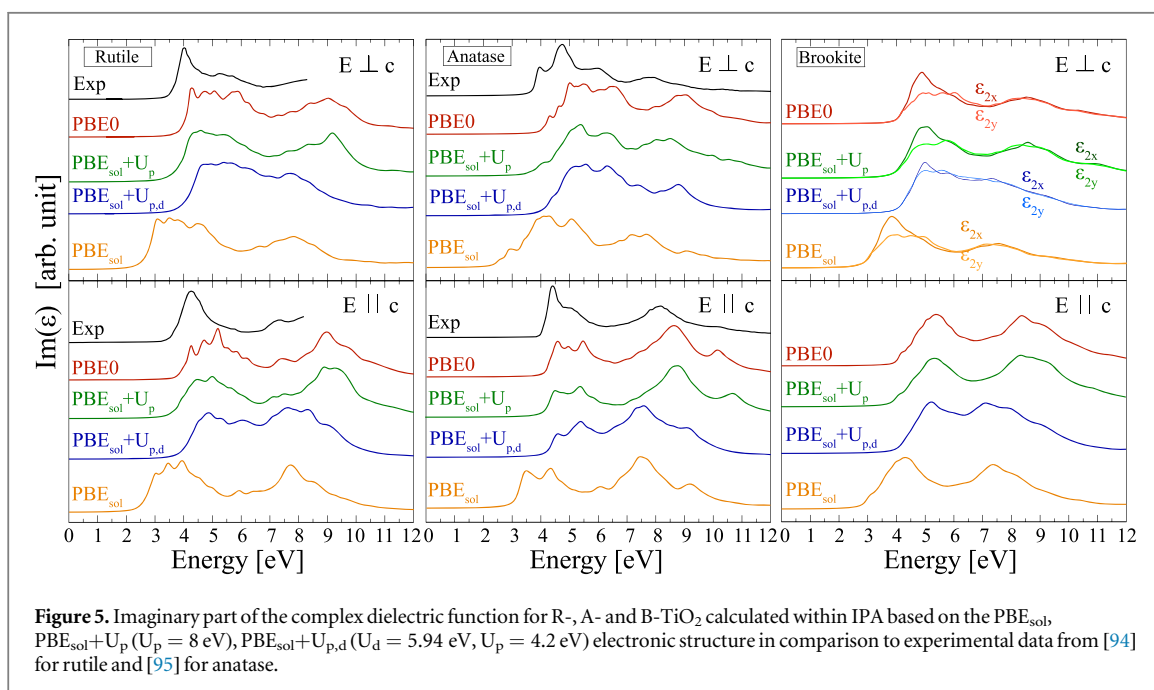


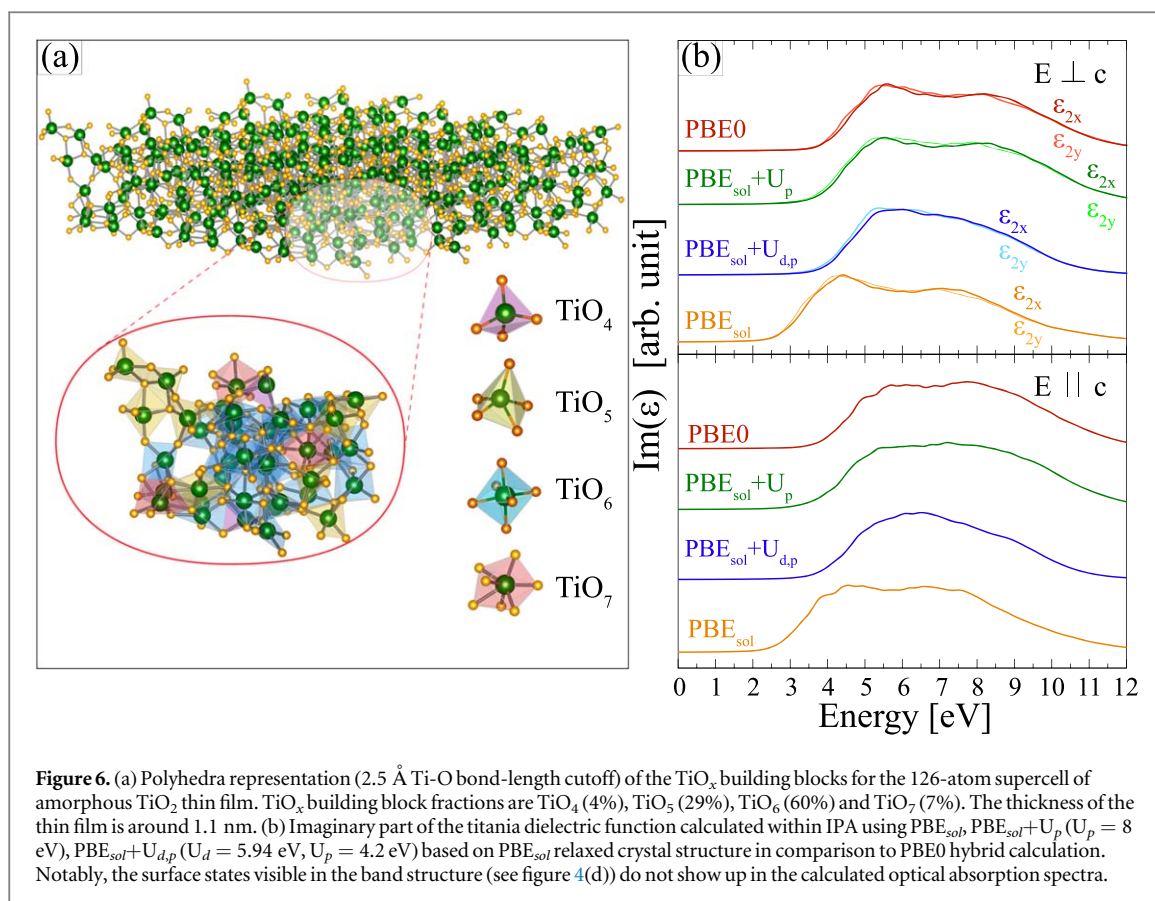
Figure 5. Imaginary part of the complex dielectric function for R-, A- and B- TiO_2 calculated within IPA based on the PBE_{sol}, PBE_{sol}+ U_p ($U_p = 8$ eV), PBE_{sol}+ $U_{p,d}$ ($U_d = 5.94$ eV, $U_p = 4.2$ eV) electronic structure in comparison to experimental data from [94] for rutile and [95] for anatase.

3.3. Amorphous TiO_2 thin film

R-, A-, and B- TiO_2 are well-defined by their octahedral building blocks; nevertheless, the disorder-induced creation of under- and over-coordinated Ti atoms characterise the amorphous phase, defined by the truncation of Ti-O octahedral coordination. The crystalline phases' exceptional optical and catalytic capabilities have also sparked interest in amorphous TiO_2 as a low-cost material for technological applications [104, 105]. Furthermore, amorphous titania serves as a generic forerunner in the hydrothermal treatment of different single-crystalline phases [106–109]. Amorphous titania thin film can be easily prepared using various experimental techniques [109–116].

For modeling an amorphous TiO_2 thin film, we apply the following procedure: Starting from a structure built up by 6 unit cells B- TiO_2 , a 2×3 thin film is built up, periodically repeated in the lateral direction and separated by 15 Å vacuum in z-direction. In the first step, all atoms in the TiO_2 thin film were allowed to relax freely, allowing expansion in the direction of the thin film's normal. Afterwards, 12 additional, stochastically distributed O atoms are inserted, and a molecular dynamics simulation is performed by heating up the structure to 500 K, whereby as-built O_2 molecules are taken out until the structure is stabilised within a disordered quasi-amorphous structure. Single Ti atoms at the surface are removed to minimise the number of surface states. In the final step, the resulting structure containing 126 atoms (40 Ti and 86 O) is again fully relaxed. A geometric analysis of the resulting 1.1 nm thick, thin film structure confirms its amorphous character: Ti-O bond lengths between 1.83 and 2.13 Å. Standard TiO_6 -polyhedron building blocks occur with a fraction of about 60%, whereas fourfold, fivefold, and sevenfold coordinated units occur with a ratio of 4%, 29% and 7%, respectively (see also figure 6(a)). By the quite high percentage of under-coordinated Ti^{4+} ions, our model qualitatively matches the experimental synthesised 'glassy' ultra-thin film (~ 2 nm) amorphous TiO_2 [116].

A few (in our model *two*) under-coordinated surface oxygens also cause the almost flat (non-dispersive) bands in the lower half of the gap, reflecting strongly localized dangling bond (db) states. Besides these db-related



gap states and other rather non-dispersive valence bands, reflecting the amorphous character of the structure, also some energy dispersive bands have been observed along the high-symmetry lines of the BZ, as seen in figure 4(d). This means that the loss of momentum conservation does not induce a HOMO-LUMO type energy gap in the disordered amorphous titania thin film. When analysing the band gap of amorphous titania thin film, its band gap is found to be close to the band gap in the B- TiO_2 phase, see table 2. Furthermore, the optical anisotropy has been observed in the amorphous titania ultra-thin film, and its complex dielectric function acts as almost similar behaviour to the biaxial B- TiO_2 phase, see figures 6(c) and (b). Based on the electronic band gaps and optical spectra, it can be concluded that there is a close relation between B- TiO_2 and the amorphous titania. This observation confirms the significant results about the considerable resemblance of the atomic arrangement in amorphous samples with crystalline B- TiO_2 [25, 117].

It is important to note that the characteristic valley in the prominent two-peak structure tends to disappear as soon as a U value (U_d) is applied to the Ti 3d electrons. In $\text{PBE}_{\text{sol}}+U_{p,d}$, e.g., it keeps similarity with the PBE0 result, but in the spectral region below 7 eV exclusively. Only pure $\text{PBE}_{\text{sol}}+U_p$ coincides with the PBE0 gold standard. In that case, even the tiny peak for $E \perp c$ and $E \parallel c$ at around 8.0 eV is in good agreement with the PBE0 hybrid. Notably and independently of the XC functional used, the optical properties of the amorphous titania thin film are not affected by surface defect states, i.e., the db-related gap states are not visible in optical spectra.

4. Conclusions

The structural, electrical, and optical characteristics of the three primary phases of TiO_2 crystals were computed using Hubbard U correction and hybrid functional methods in density-functional theory. In light of the available experimental findings, these calculations were compared. It was demonstrated that modified hybrid functionals with reduced EXX fraction, especially the 11.4%-PBE0 functional, yield correct electronic structure data and highly accurate atomic structures. Furthermore, the optical spectra nicely agree with the available experimental spectra; i.e., even details such as the small peaks around 7 eV for R- and A- TiO_2 are also accurately described in both energetic position and intensity. By carefully evaluating the DFT+ U method, we were able to show that DFT+ U_p , where the U -value is applied on the O 2p electrons exclusively, yields much more precise titania optical excitation energies than the standard DFT+ U_d or the gap-correcting DFT+ $U_{p,d}$ approach.

The ultra-thin amorphous layer of TiO_2 was then studied with the same methods. Again, PBE0 is the gold standard for examining geometrical structures, electrical characteristics, and optical spectra. However,

PBE_{sol}+U_p describes optical spectra very well, particularly if this is applied on PBE0 (or at least PBE_{sol}) relaxed structures. The resulting still accurate but numerically less demanding approach can be thus generally applied, even for large disordered systems at much more efficient computational cost or for the calculation of nonlinear optical properties, which require a substantially increased numerical effort.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest

The authors declare no competing interests. All research has been carried out within an appropriate ethical framework.

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