Electronic structures and optical properties of TiO_2: Improved density-functional-theory investigation*

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TiO_2 has been recently used to realize high-temperature ferromagnetic semiconductors. In fact, it has been widely used for a long time as white pigment and sunscreen because of its whiteness, high refractive index, and excellent optical properties. However, its electronic structures and the related properties have not been satisfactorily understood. Here, we use Tran and Blaha's modified Becke-Johnson (TB-mBJ) exchange potential (plus a local density approximation correlation potential) within the density functional theory to investigate electronic structures and optical properties of rutile and anatase TiO_2. Our comparative calculations show that the energy gaps obtained from mBJ method agree better with the experimental results than that obtained from local density approximation (LDA) and generalized gradient approximation (GGA), in contrast with substantially overestimated values from many-body perturbation (GW) calculations. As for optical dielectric functions (both real and imaginary parts), refractive index, and extinction coefficients as functions of photon energy, our mBJ calculated results are in excellent agreement with the experimental curves. Our further analysis reveals that these excellent improvements are achieved because mBJ potential describes accurately the energy levels of Ti 3d states. These results should be helpful to understand the high temperature ferromagnetism in doped TiO_2. This approach can be used as a standard to understand electronic structures and the related properties of such materials as TiO_2.

Keywords: rutile, anatase, electronic structures, optical properties

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1. Introduction

Recently, TiO_2 in the anatase and rutile forms is used to make high-temperature ferromagnetic semiconductors, and Co-doped anatase TiO_2 is used to realize electric manipulation of ferromagnetism in ferromagnetic semiconductors above room temperature.[1−4] These are of huge potential for spintronic applications in the future. In fact, TiO_2 (rutile) has been most widely used for a long time as white pigment and sunscreen because of its whiteness, high refractive index, strong ultraviolet light absorbing capabilities, and resistance to discolouration to ultraviolet light.[5] In addition, it is often used to increase palatability of skimmed milk. TiO_2 in the anatase form can be used as a photocatalyst under ultraviolet light. Therefore, researchers have studied TiO_2 intensively to understand its physical and chemical properties and to explore more important applications in various fields.

The rutile and anatase structures are the most important phases for TiO_2. Their structural, electric, and optical properties have been experimentally measured with various methods[1−14] and their electronic structures and optical properties have been theoretically investigated in terms of popular density-functional-theory (DFT) approaches.[15−24] It is obvious that the electronic structures need to be accurately calculated because they are the starting point for first-principles calculations of other physical and chemical properties. Nevertheless, their energy gaps, like those of other semiconductors and insulators, are underestimated by local density approximation (LDA) and generalized gradient approximation (GGA)[17−19,25,26] in comparison with the experimental values.[6−11] Thus, further approximations, such as scissors approximations, are required to modify the gaps to make the calculated results comparable with the experimental results. On the other hand, many sophisticated methods, such as GW methods, often

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overestimate the energy gaps.[20−24] Therefore, it is highly desirable, or necessary, to understand the electronic structures and physical properties of TiO_2 and similar materials in terms of an atomic-parameters-free reliable DFT approach.

In this paper, we use Tran and Blaha's modified Becke–Johnson (TB-mBJ) exchange potential (plus LDA correlation potential)[27,28] within the density functional theory to investigate the electronic structures and optical properties of rutile and anatase TiO_2. Our comparative calculations show that the mBJ energy gaps are substantially improved over LDA and GGA values toward experimental results, in contrast with overly large values from GW methods.[20−24] Our calculated results for optical dielectric functions (real part and imaginary part), refractive index, and extinction coefficients as functions of photon energy are in excellent agreement with the experimental curves. Our further study reveals that these excellent improvements are achieved because the mBJ potential accurately describes the energy levels of Ti 3d states.

In this study, we will give our computational details, present our calculated electronic structures and optical dielectric functions (or constants), compare them with experimental results, and make discussion on mBJ and its role in improving description of electronic and optical properties.

2. Computational methods

We perform our study by using the full potential linear augmented plane wave (FP-LAPW) method within the DFT,[15,16] as implemented in WIEN2k package.[29] We take the TB-mBJ approximation[27,28] as the exchange potential (plus the LDA correlation potential) to do our main calculations. For comparison, the LDA[25] and GGA (PBE version)[26] are also used. The mBJ potential has been proved to yield quite accurate gaps for numerous semiconductors and insulators,[27,28,30−33] and to improve half-metallic gaps for half-metallic materials.[34] The scalar relativistic approximation without spin-orbit coupling is employed in the calculation of the valence states, whereas the core levels are treated with fully relativistic effects.[35−37] The radii of the Ti and O atomic spheres are set to be 1.94 and 1.72 bohr, respectively. We make harmonic expansion up to $l_{\max} = 10$, and set $R_{\rm mt} \times K_{\max} = 8.0$, where $R_{\rm mt}$ is the smallest atomic sphere radius in the unit cell and $K_{\max}$ is the magnitude of the largest K vector. We use 3000 k-points in the first Brillouin zone for both rutile and anatase structures, which corresponds to meshes $12 \times 12 \times 19$ in the reduced Brillouin zone for rutile and $14 \times 14 \times 14$ for anatase. The self-consistent calculations are considered to be converged only when the integration of absolute charge-density difference per formula unit between the successive loops is less than $0.0001|e|$, where e is the electron charge. The optical dielectric functions are calculated under dipole approximation.[38]

3. Electronic structures

The two phases of TiO_2 are both in a tetragonal structure. The rutile TiO_2 is in the $P4_2/mnm$ space group (No 136) with lattice constants $a = 4.586$ Å and $c = 2.954$ Å; the anatase crystallizes in space group $I4_1/amd$ (No 141) with lattice constants $a = 3.782$ Å and $c = 9.502$ Å, and we adopt the internal atomic position parameters measured at 15 K.[8] We study their electronic structures by using the three exchange-correlation potentials: LDA, GGA (PBE) and mBJ (plus LDA correlation). The calculated band gaps are summarized in Table 1. For comparison, we also present experimental data available[6,8−11] and some previous calculated results.[20−24] It is obvious that the LDA and GGA gap values of the rutile and the anatase are substantially smaller than the experimental results, but the mBJ approximation makes a remarkable improvement over them and describes the experimental results excellently. The mBJ results are comparable with the best of the gap values calculated with the more sophisticated and expensive GW approximation[20−24] with respect to the experimental results, but the mBJ values and GW ones are on different sides of the experimental ones.

Table 1. Calculated energy gaps (eV) of rutile and anatase TiO_2 using LDA, GGA, TB-mBJ, and GW[20−24] in comparison with the corresponding experimental results.[6,8−11]

Structure	LDA	GGA	mBJ	GW	Exp
rutile	1.79	1.89	2.60	3.34, 3.78	3.0
anatase	1.98	2.12	3.01	3.56, 3.79	3.2

Figure 1 presents the band structures of the rutile (a) and anatase (b) TiO_2 between −6 and 8 eV calculated with mBJ. It can be seen that the valence band maximum (VBM) and the conduction band minimum (CBM) of the rutile are both at Γ point, which

then produces a direct band gap. This direct gap is in line with other DFT calculations,[19,23] but is different from the experimental results of indirect gaps.[8] Recently, the indirect gap between Γ and R points is produced using a GW approximation.[24] However, the indirect gap value is just 0.04 eV smaller than the direct one at Γ point. The VBM and CBM of anatase are at Δ and Γ points, respectively, and then our calculations confirm the indirect character of the experimental band gap for the anatase.[9] Calculated values of the widths of valence bands for the rutile and the anatase are approximately equivalent to 5.4 and 4.5 eV, in excellent agreement with the experimental values of 5.4 eV[12] and 4.7 eV[13], respectively.

Figure 2 shows the total and partial density of states (DOS) of the rutile and anatase TiO_2. The valence bands range from −5.4 to 0 eV for the rutile and from −4.5 to 0 eV for the anatase. The partial DOSs show that the valence bands are dominated by O 2p states with a mixture of Ti 3d states. The mixture is a manifestation of hybridization between O 2p and Ti 3d states. These are in line with the reported covalent character of the Ti–O bonds.[14] The conduction bands of the two phases can be described to have two sub-bands: the lower t_{2g} and the upper e_g. They are split thanks to the O octahedral crystal field. There are some differences in the DOS distributions between the rutile and the anatase, which can be attributed to the different distortions of the O octahedrons. The larger gap of the anatase is correlated with the narrower width of its valence bands and conduction bands in the energy window.

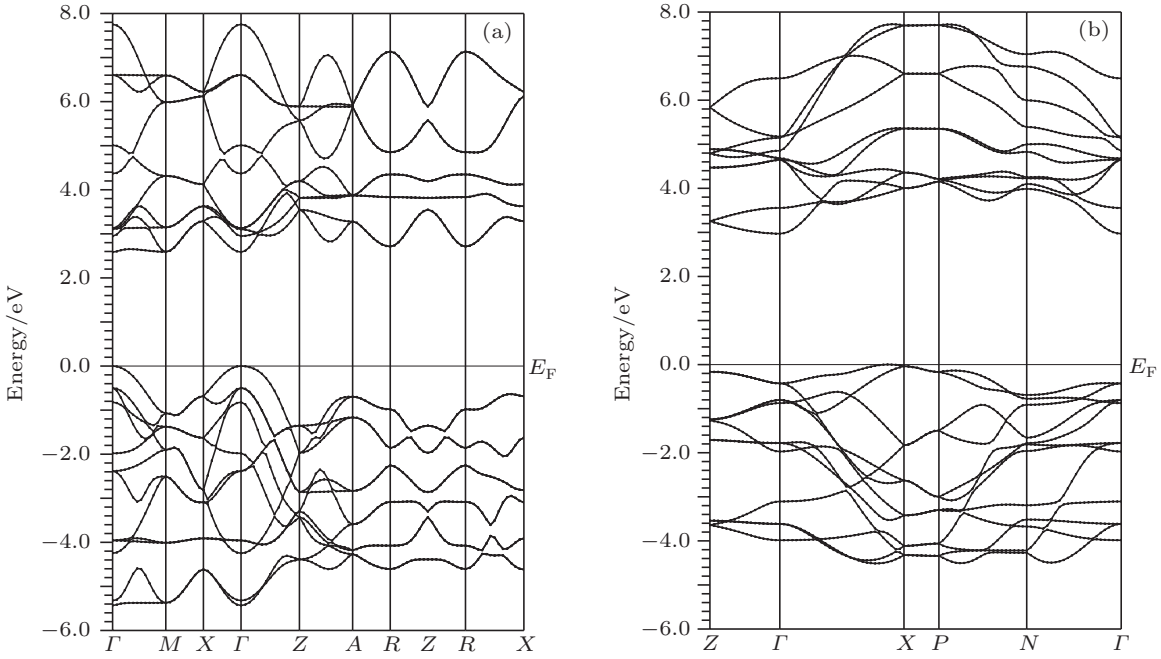


Fig. 1. Calculated band structures of rutile (a) and anatase (b) TiO_2 with the mBJ approximation. The Fermi level E_F (0 eV) is shown by the solid line.

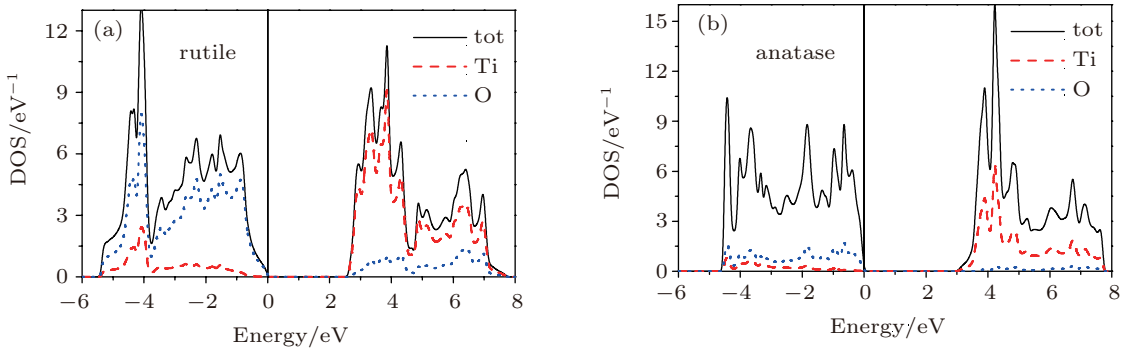


Fig. 2. (color online) The total and partial density of states of rutile (a) and anatase (b) TiO_2 calculated with the mBJ approximation.

4. Optical dielectric functions

The long-wavelength dielectric constants of rutile and anatase TiO_2 (ε_a^∞ in the ab plane and ε_c^∞ along the c axis) calculated with LDA, GGA, mBJ are presented in Table 2. It can be seen that the GGA results of ε_a^∞ and ε_c^∞ are slightly smaller than those of LDA, but they are both too large with respect to the experimentally measured data.[6,7] Fortunately, the mBJ values are in satisfactory agreement with the experimental values.

Table 2. Calculated long-wave optical dielectric constants (ε_a^∞ and ε_c^∞) of rutile and anatase TiO_2 using LDA, GGA, and TB-mBJ in comparison with the corresponding experimental results.[6,7]

Structure	Dielectric	LDA	GGA	mBJ	Exp.
rutile	ε_a^∞	7.61	7.34	5.75	5.7[6]
	ε_c^∞	9.01	8.68	6.70	7.0[6]
anatase	ε_a^∞	6.99	6.75	5.35	5.8[7]
	ε_c^∞	6.66	6.44	5.21	5.4[7]

For the rutile, the whole mBJ and GGA dielectric functions (ε_1 for the real part and ε_2 for the imaginary part) within the photon energy window of 0–12 eV are presented in Fig. 3. Because of the anisotropy, we present our calculated results in terms of the ab plane and c axis. There are substantial differences between mBJ and GGA at the lower energy (0–6 eV), but the differences become small at the higher energy end (8–12 eV). When the photon energy is smaller than 3 eV, the GGA results of ε_1 are substantially larger than the mBJ ones. For ε_2 between 2 and 5 eV, the rightward shift of the mBJ results with respect to the GGA ones are caused by the improved energy gap versus GGA. In order to directly compare with experimental results available, we calculate the refractive indexes (n) and extinction coefficients (κ) in the ab plane and along the c axis. They are presented and compared with the corresponding experimental curves in Fig. 4. It is obvious that the mBJ results at lower energy (0–6 eV) are in excellent agreement with the experimental curves,[6] in contrast with the GGA ones; and when the photon energy is larger than 7 eV, there is no substantial difference between mBJ and GGA results. For the long-wave refractive index $n(0)$ along the c axis, mBJ value, 2.59, is in excellent agreement with the experimental one 2.61, much better than GGA result of 2.95; for that in the ab plane, mBJ value, 2.4, is equivalent to the experimental one, in contrast with GGA result of 2.72. Therefore, mBJ is better than GGA in describing the electronic structure and optical properties of the rutile TiO_2.

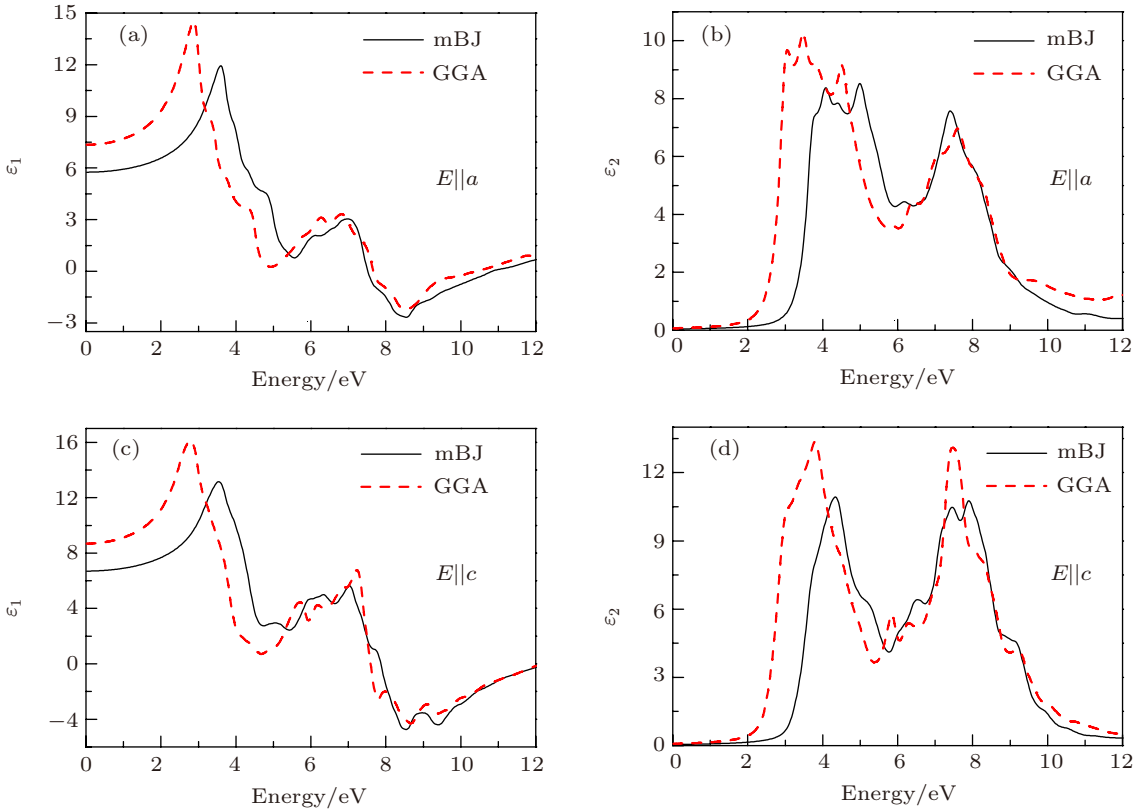


Fig. 3. (color online) The real (ε_1) and imaginary (ε_2) parts of dielectric functions versus photon energy (eV) of rutile TiO_2 in the ab plane ($E||a$, (a), (b)) and along the c axis ($E||c$, (c), (d)). Solid lines show the mBJ results, and dashed lines the GGA ones.

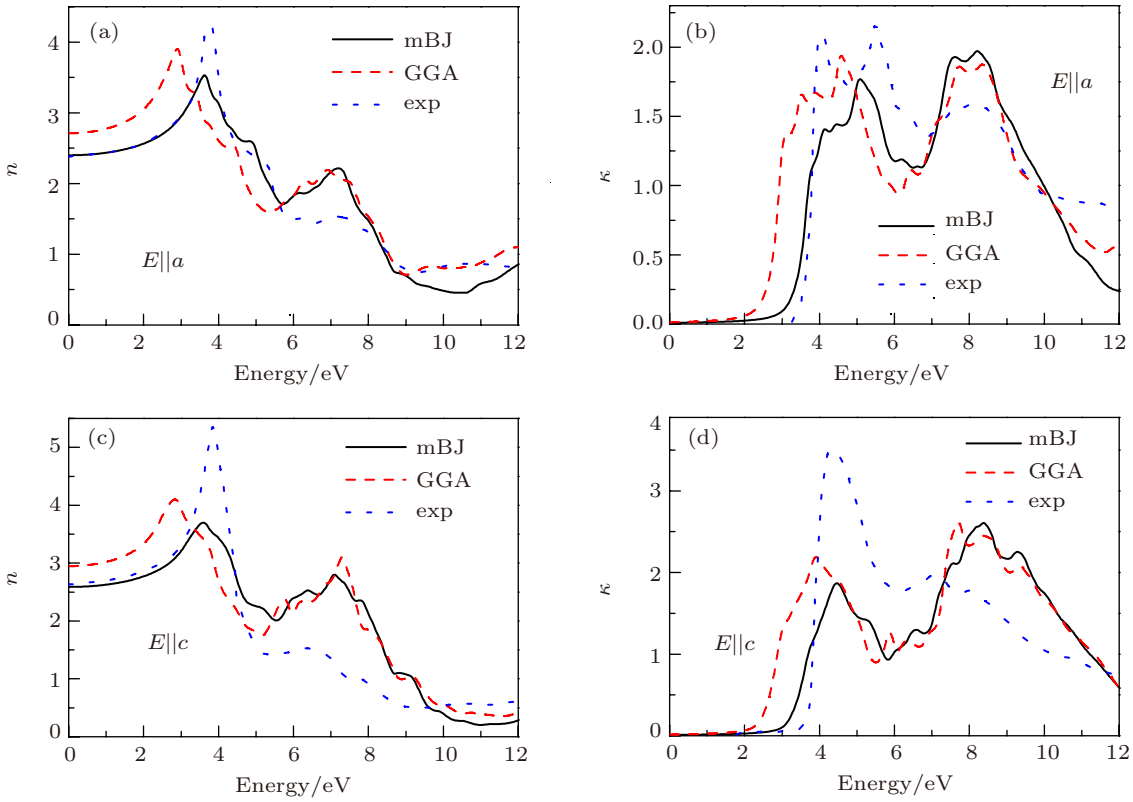


Fig. 4. (color online) The refractive indexes (n) and extinction coefficients (κ) versus photon energy (eV) of rutile TiO_2 in the ab plane ($E||a$, (a), (b)) and along the c axis ($E||c$, (c), (d)). Solid lines denote the mBJ results, dashed lines GGA ones, and dotted lines are the experimental (exp) curves.[6]

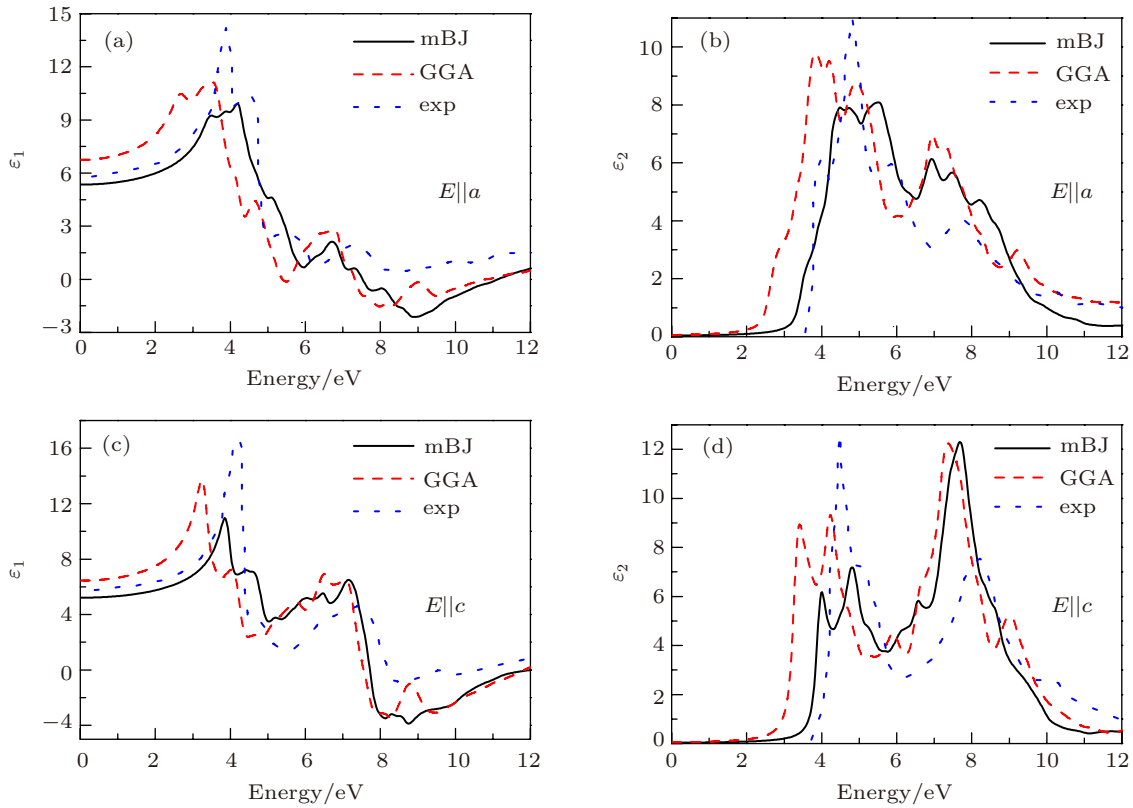


Fig. 5. (color online) The real (ε_1) and imaginary (ε_2) parts of dielectric functions versus photon energy (eV) of anatase TiO_2 in the ab plane ($E||a$, upper panels) and along the c axis ($E||c$, lower panels). Solid lines denote the mBJ results, dashed lines GGA ones, and dotted lines are the experimental (exp) curves.[7]

For the anatase TiO_2, there exist experimental data of optical dielectric functions.[7] We present the real and imaginary parts of the dielectric functions of the anatase and compare them with the experimental results in Fig. 5. It is obvious that below 5 eV, the mBJ results of the real parts ε_1 and the imaginary part ε_2, both in the *ab* plane and along the *c* axis, are much better than the corresponding GGA results with respect to the experimental curves,[7] but the difference between the mBJ and GGA results becomes small for higher photon energy. The rightward shift of the mBJ ε_2 results between 2 and 5 eV with respect to the GGA ones reflects the fact that the mBJ energy gap is substantially improved over the GGA one. The main features of the optical dielectric functions are similar to those of the rutile. For the long-wave real dielectric constants in the *ab* plane and along the *c* axis, LDA produces 6.99 and 6.66 and GGA 6.75 and 6.44, but the mBJ results are 5.35 and 5.21, in much better agreement with the experimental values, 5.8 and 5.4.[7]

5. Discussion and conclusion

For the rutile and anatase TiO_2, the energy gaps are underestimated only 13% and 6% by mBJ, but at least 37% and 34% by GGA and LDA, respectively. On the other hand, the two gaps are overestimated 11%–26% and 11%–18% by GW methods, as shown in Table 1. Therefore, mBJ is best in describing the energy gaps. As for the long-wave optical dielectric constants, the errors of the mBJ results range from 1% to 8%, but those of GGA and LDA are larger than 16%, as shown in Table 2. For dielectric functions and refractive indexes and extinction coefficients as functions of photon energy, our mBJ results are in excellent agreement with experimental curves, especially for low photon energy (0–5 eV), as shown in Figs. 3–5. Some further improvements can be achieved in some narrow energy regions by considering many-body effects, such as exciton effects and electron–hole interaction.[23] However, it should be pointed out that here we do not make any further approximation (such as scissors approximation), so we can conclude that the dielectric functions calculated with mBJ are very satisfactory.

The mBJ valence band widths of the rutile and anatase, 5.4 and 4.5 eV, are in excellent agreement with the experimental values of 5.4 and 4.7 eV.[12,13] The mBJ gaps are much better than LDA and GGA results and even the GW ones available, as shown in Table 1. The conduction bands within the energy windows shown in Figs. 1 and 2 are mainly of Ti 3d states. Thus, the energy levels of the Ti d bands with respect to the valence band maximum are accurately described by the mBJ potential. These explain the substantial improvement of the energy gaps and the dielectric functions calculated with mBJ.

In summary, we have used TB-mBJ exchange potential (plus LDA correlation potential) within the density functional theory to investigate the electronic structures and optical properties of rutile and anatase TiO_2. Our calculated results show that the energy gaps are substantially improved by mBJ over LDA and GGA values toward experimental results, in contrast with substantially overestimated values from GW methods. Our calculated results for optical dielectric functions (both real and imaginary parts) and refractive index and extinction coefficients as functions of photon energy agree well with the experimental curves. Our further study reveals that these excellent improvements are achieved because mBJ potential describes accurately the energy levels of Ti 3d states and the hybridization between the Ti d and O p states. These results should be helpful to understand the high temperature ferromagnetism in doped TiO_2. This approach should be applicable to similar materials and can be taken as a standard to understand their electronic structures and related properties.

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