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Empirical optimization of DFT + U and HSE for the band structure of ZnO

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Abstract

ZnO is a well-known wide band gap semiconductor with promising potential for applications in optoelectronics, transparent electronics, and spintronics. Computational simulations based on the density functional theory (DFT) play an important role in the research of ZnO, but the standard functionals, like Perdew–Burke–Erzenhof, result in largely underestimated values of the band gap and the binding energies of the Zn_{3d} electrons. Methods like DFT + U and hybrid functionals are meant to remedy the weaknesses of plain DFT. However, both methods are not parameter-free. Direct comparison with experimental data is the best way to optimize the computational parameters. X-ray photoemission spectroscopy (XPS) is commonly considered as a benchmark for the computed electronic densities of states. In this work, both DFT + U and HSE methods were parametrized to fit almost exactly the binding energies of electrons in ZnO obtained by XPS. The optimized parameterizations of DFT + U and HSE lead to significantly worse results in reproducing the ion-clamped static dielectric tensor, compared to standard high-level calculations, including GW, which in turn yield a perfect match for the dielectric tensor. The failure of our XPS-based optimization reveals the fact that XPS does not report the ground state electronic structure for ZnO and should not be used for benchmarking ground state electronic structure calculations.

Keywords: ZnO, band gap, DFT + U, hybrid functionals, HSE, XPS

(Some figures may appear in colour only in the online journal)

1. Introduction

ZnO is one of the most studied semiconductors, which promises important technological advances in the area of optoelectronic devices [1–3]. A number of physical properties make ZnO superior to other materials, both in terms of device functionalities and chemical processing [4]. However, a widespread adoption of this material in device engineering is limited by the difficulty of achieving the p-type doping in ZnO, which naturally displays the n-type behavior [1, 5]. Understanding the behavior of defects in ZnO is the fundamental problem for developing ZnO-based applications [5]. However, finding experimental identification and characterization of defects are quite challenging [6]. In this situation, theoretical and computational support has been making an important contribution to the understanding of defects and their impact on the electronic and optical properties of ZnO [4].

On the computational side, density functional theory (DFT), based on functionals like Perdew–Burke–Erzenhof (PBE) [7], presents a practical tool capable of simulating reasonably large systems with adequate chemical accuracy. However, the standard DFT approach is known to significantly underestimate band gap values for some semiconductors [8, 9]. For ZnO, DFT calculations report a band gap of less than 1 eV, while the experimental value is 3.4 eV [4]. Such a small calculated band gap results from the approximations made in the exchange-correlation (XC) functionals like LDA or GGA, using the idea of the homogeneous electron gas. However, in ZnO, electrons exhibit more localized behavior, which is not captured by the standard semilocal XC functionals [10]. This problem impacts the ability of electronic structure calculations to correctly predict formation energies and energy level positions of defects in ZnO [11, 12].

To remedy this situation, a popular approach is to use the hybrid functionals, which mix the exact exchange from Hartree–Fock with the exchange calculated from some standard density-based approach, yielding authoritative methods like PBE0, B3LYP or HSE [7, 13]. The HSE approach reduces the cost of computations by introducing the range-separation in the $1/r$ dependence of the Coulomb potential:

$$\frac{1}{r} = \mathrm{SR}_\omega(r) + \mathrm{LR}_\omega(r) = \frac{1 - erf(\omega r)}{r} + \frac{erf(\omega r)}{r}. \quad (1)$$

The exact Hartree–Fock exchange is considered to be short-range, which is determined by the empirical range parameter ω [14]:

$$E_{\mathrm{XC}}^{\mathrm{HSE}} = \alpha E_X^{\mathrm{HF,SR}}(\omega) + (1-\alpha)E_X^{\mathrm{PBE,SR}}(\omega) + E_X^{\mathrm{PBE,LR}}(\omega) + E_C^{\mathrm{PBE}}. \quad (2)$$

In equation (1), the ranges of the HSE parameters are $0 \leqslant \omega \leqslant \infty$ and $0 \leqslant \alpha \leqslant 1$. By setting $\omega = 0$ Å^{-1}, we recover the PBE0 method, setting $\omega = \infty$ Å^{-1} recovers the standard PBE behavior, while using $\omega = 0.2$ Å^{-1} corresponds to HSE06, and $\omega = 0.3$ Å^{-1} to HSE03 [7, 14, 15]. The second empirical parameter α is the mixing fraction of the non-local exact exchange with the PBE exchange. Typically, α is assumed to be $\alpha = 0.25$, which is, however, not well justified. Recent studies have been 'playing' with the approach of a self-consistent adjustment of α based on the computed static dielectric tensor, which results in marginal changes for ZnO compared to the standard $\alpha = 0.25$, but suggests an important idea that by tuning α one can achieve a better agreement with experiment, like XPS data [16, 17].

Results from PBE0 lead to the energy band gap for ZnO of 3.32 eV, which is very close to the experimental value of 3.4 eV [18]. On the other hand, HSE predicts the band gap of 2.4–2.9 eV [19, 20]; still it is also a significant improvement with respect to the standard PBE result. Specifically for ZnO, it was reported that increasing of the exact exchange weight to $\alpha = 0.375$ brings HSE06 into a perfect agreement with the desired for ZnO band gap of 3.42 eV [21]. This trend is not surprising, because the increase of the fraction of the exact exchange in HSE naturally leads to a larger band gap. For example, by setting $\alpha = 1.0$ and $\omega = 0$ Å^{-1} we would reproduce the Hartree–Fock limit for ZnO with the energy gap of 11.4 eV [22].

Even with the increased α, all hybrid functionals still underestimate the binding energies of the Zn_{3d} band [23]. Surprisingly, results based on the many-body perturbation theory underestimate the binding energies for the Zn_{3d} electrons of ZnO [24–26]. A single known approach that fully recovered the band gap of ZnO and the position of the Zn_{3d} band was offered by Pollmann *et al*. That approach was based on the self-interaction and relaxation correction (SIRC) scheme [27]; however, the SIRC method does not provide a straightforward evaluation of total energies, limiting its applicability [28]. Thus, even the more computationally demanding methods, like scGW, do not provide the desirable agreement for the ZnO, which is almost entirely based on XPS data [23, 29].

Another alternative would be to use the DFT + U approach, which corrects empirically the problem of the over-delocalization of electrons [10, 30]. Some earlier studies focused on the idea of applying the +U correction to the *3d*-electrons of Zn only, showing that increasing the $\mathrm{U}_{\mathrm{Zn}-3d}$ parameter for Zn *3d*-electrons gradually opens the gap up to $E_g \approx 2.1$ eV for $\mathrm{U}_{\mathrm{Zn}-3d} = 8$ eV [31, 32]. It was also shown that in addition to correcting the Zn- *3d* electrons, further applying +U to Zn- *s* with $\mathrm{U}_{\mathrm{Zn}-s} = 43.5$ eV opens the gap of ZnO to the near experimental value of 3.4 eV [33]. However, such a large value of U for Zn- *s* electrons led to nonphysical effects [12]. Recent studies have demonstrated the importance of correcting localization of not only the Zn *3d*, but also simultaneously the O *2p*-states, described by parameters $\mathrm{U}_{\mathrm{Zn}-3d}$ and $\mathrm{U}_{\mathrm{O}-2p}$, respectively [34, 35]. Such DFT + $\mathrm{U}_{\mathrm{Zn}-3d}$ + $\mathrm{U}_{\mathrm{O}-2p}$ approach allows for tunability of the band gap of ZnO, achieving the experimental value of 3.4 eV [34, 35]. Appropriate combinations of $\mathrm{U}_{\mathrm{Zn}-3d}$ and $\mathrm{U}_{\mathrm{O}-2p}$ values have been shown to fit the calculated electronic structure to experimental data with respect to both energy band gap of 3.4 eV and the position of the Zn_{3d} band of ≈8.0 eV (with ≈7.5 eV reported in experiments) [27, 36, 37].

Overall, both DFT + U and hybrid functionals seem to be practical choices. They provide significant improvement over the standard functionals, but unfortunately both have empirical parameters. In this manuscript, we attempt to uniquely determine the empirical parameters, by fitting the calculated electronic structure (DOS) to the available experimental XPS data. This work presents a thorough investigation of the ($\mathrm{U}_{\mathrm{Zn}-3d}$, $\mathrm{U}_{\mathrm{O}-2p}$) parameter space for the DFT + U approach, and the (ω, α) parameter space for the HSE hybrid functional with a single purpose of fitting the calculation to the XPS data. The fitting procedures in both DFT + U and HSE parameterizations establish a close match with experimental XPS data for the electronic structure of ZnO. However, the resulting optimized for XPS parameterizations of both DFT + U and HSE lead to disappointing accuracy in terms of the static dielectric tensor. Supporting self-consisten GW calculations rase a question whether the XPS experiments can be trusted to reveal the actual ground state of the material.

2. Methods

The calculations in this work were performed using the Vienna *ab initio* simulations package (VASP) [38, 39], with the PBE parametrization of the local spin-density approximation and projector-augmented wave potentials [9, 40, 41], with PBE0 and Heyd–Scuseria–Ernzerhof (HSE) [7, 14], and GW approach: single-shot $\mathrm{G_0W_0}$ and self-consistent GW [24, 42]. Two types of VASP pseudopotentials (PP) were used: (1) standard Zn (12 valence electrons) and O (6 valence electrons); (2)

GW-type PP Zn_sv_GW (20 valence electrons) and O_GW (6 valence electrons). The latter were used only in the 'DFT + U' section for comparison with the standard PP. HSE calculations were carried out using the standard PP. The calculations with the standard PP were performed using the 'Accurate' setting in VASP, which corresponds to a plane-wave energy cutoff of 400 eV. For the GW-type PP, we used 500 eV cutoff. For all calculations we used a $10 \times 10 \times 10$ Monkhorst–Pack *k*-point sampling of the Brillouin zone. In the calculations with the onsite correction, we used Dudarev's approach, which uses only one effective U-parameter, instead of the original formulation with two parameters, U and J [30, 43]. For GW calculations, we used the PBE results as the starting point. A total of 240 bands were used for the primitive wurtzite cell, which is the same as reported previously [26]. It is sufficient to reproduce earlier GW results for ZnO [24].

3. Results

3.1. Standard calculations

Figure 1(a) shows the electronic density of states (DOS) of ZnO calculated using PBE functional. The value 0.8 eV is significantly lower than the experimental value (3.4 eV), but agrees with the overall picture of how standard PBE calculations perform for ZnO [4, 46]. With the goal of getting a comparative picture of all available mainstream methods, we repeated the basic relaxations and the DOS calculations using HSE03, HSE06, PBE0 and self-consistent GW, with the latter using the PBE results as the starting point. Fully optimized (except for GW) lattice parameters for all listed method are summarized in table 1. The GW calculations are not the goal of this work, and included only as a reference. Nevertheless, the scGW results agree with the previos reports both in terms of the band gap and the position of the Zn_{3d} band [24]. In all these calculations, we see that ehile the experimental XPS band gap is mostly recovered, the calculated Zn_{3d} electrons are bound weaker than shown by the comparison with XPS data from [23]. This situation brings us to an idea that an empirical approach based on DFT + U would not be such a bad idea if we employ a reliable method for determining the optimal U-values.

3.2. DFT + U

Due to the need for a meaningful way to optimize the Hubbard on-site corrections applied to Zn *3d* and O *2p*-states, we performed a thorough study of 325 combinations of $\mathrm{U}_{\mathrm{Zn}-3d}$ and $\mathrm{U}_{\mathrm{O}-2p}$, uniformly mapping the ranges of ($0 \leqslant \mathrm{U}_{\mathrm{Zn}-3d} \leqslant 12$) and ($0 \leqslant \mathrm{U}_{\mathrm{O}-2p} \leqslant 24$). For all 325 combinations, we performed full relaxations of the crystal structure and consequent DOS calculations.

At first, we focus on the U-values that yield the correct band gap of 3.4 eV. Figures 2(a) and (b) show all values for the energy gap of ZnO obtained by varying the two U-parameters: $\mathrm{U}_{\mathrm{Zn}-3d}$ and $\mathrm{U}_{\mathrm{O}-2p}$. Overall, the band gap increases with increasing values of those parameters. The band gap of 3.4 eV is achieved at a broad range of $\mathrm{U}_{\mathrm{Zn}-3d}$ and $\mathrm{U}_{\mathrm{O}-2p}$, indicated by a curve in figures 2(a) and (b), showing us that the combination of the U-parameters that yields the correct band gap is not unique. This uncertainty makes sense; we are fitting two U-parameters to just one physical observable, meaning that the problem is underdetermined.

The infinite number of $\mathrm{U}_{\mathrm{Zn}-3d}$ and $\mathrm{U}_{\mathrm{O}-2p}$ combinations with the correct band gap presents unresolved uncertainty. Fortunately, available in the literature experimental x-ray photoemission spectroscopy (XPS) data helps to resolve this ambiguity [23]. A direct comparison of the DOS calculated for a representative number of points lying on the '3.4 eV—band gap line' with the XPS data, shown in figure 2(b), reveals a monotonic trend for the binding energies of the Zn *3d*-states moving across the corresponding experimental Zn *3d*-band, see figure 2(c). From this comparison one can identify the best fit to be around $\mathrm{U}_{\mathrm{Zn}-3d} = 9.3$ eV and $\mathrm{U}_{\mathrm{O}-2p} = 18.4$ eV. Having such a good match to the XPS data is quite encouraging, especially considering the low computational costs of the DFT + U approach. However, the structure of ZnO in this case has lattice parameters $a_{\mathrm{DFT+U}} = 3.08$ Å, $c_{\mathrm{DFT+U}} = 4.96$ Å, significantly smaller then the experimental values listed in table 1. This contraction of the structure is expected, because of the stronger electron localization enforced on the system.

A note should be taken that switching to the so-called GW-pseudopotentials from VASP: Zn_sv_GW (with 20 valence electrons) and O_GW, leads to different optimal U-parameters: $\mathrm{U}_{\mathrm{GW-PP:Zn}-3d} = 13$ eV and $\mathrm{U}_{\mathrm{GW-PP:O}-2p} = 20$ eV, and different lattice constants: $a_{\mathrm{GW-PP:DFT+U}} = 3.16$ Å, $c_{\mathrm{GW-PP:DFT+U}} = 5.067$ Å, which are in a better agreement with the experimental data. The density of states shown in figure 3 allow to compare the results obtained with the two different sets of pseudopotentials. In the case of GW-type pseudopotentials, the Zn_{3d} band is narrower, which may correlate with the better lattice parameters. In the DOS calculated with DFT + U using the standard PP (figure 2(c)) we see that we have the control over the position of the Zn_{3d} band, but its width is significantly greater than the we see in HSE and scGW calculations (figure 1). Thus, using the GW-type PP for DFT + U calculations seems more reasonable. We also should mention another combination of U parameter that was optimized in a recent study for the LDA—based calculations: $\mathrm{U}_{\mathrm{Zn}-3d} = 9.5$ eV and $\mathrm{U}_{\mathrm{O}-2p} = 7.86$ eV [36]. Overall, these variations in the U values remind us that such optimizations are not transferable.

3.3. Revisiting hybrid functionals

Now, since we have shown that DFT + U can be carefully tuned to reproduce the electronic structure of ZnOfit the XPS data, we would like to revisit the hybrid functionals, HSE03 and HSE06, and see if we can optimize them in the same way. It was discussed earlier by Mousa *et al* that both parameters (α and ω) are adjustable and can be fitted to achieve the best agreement with experiment at acceptable computational cost [47]. In this work, we suggest that those parameters should

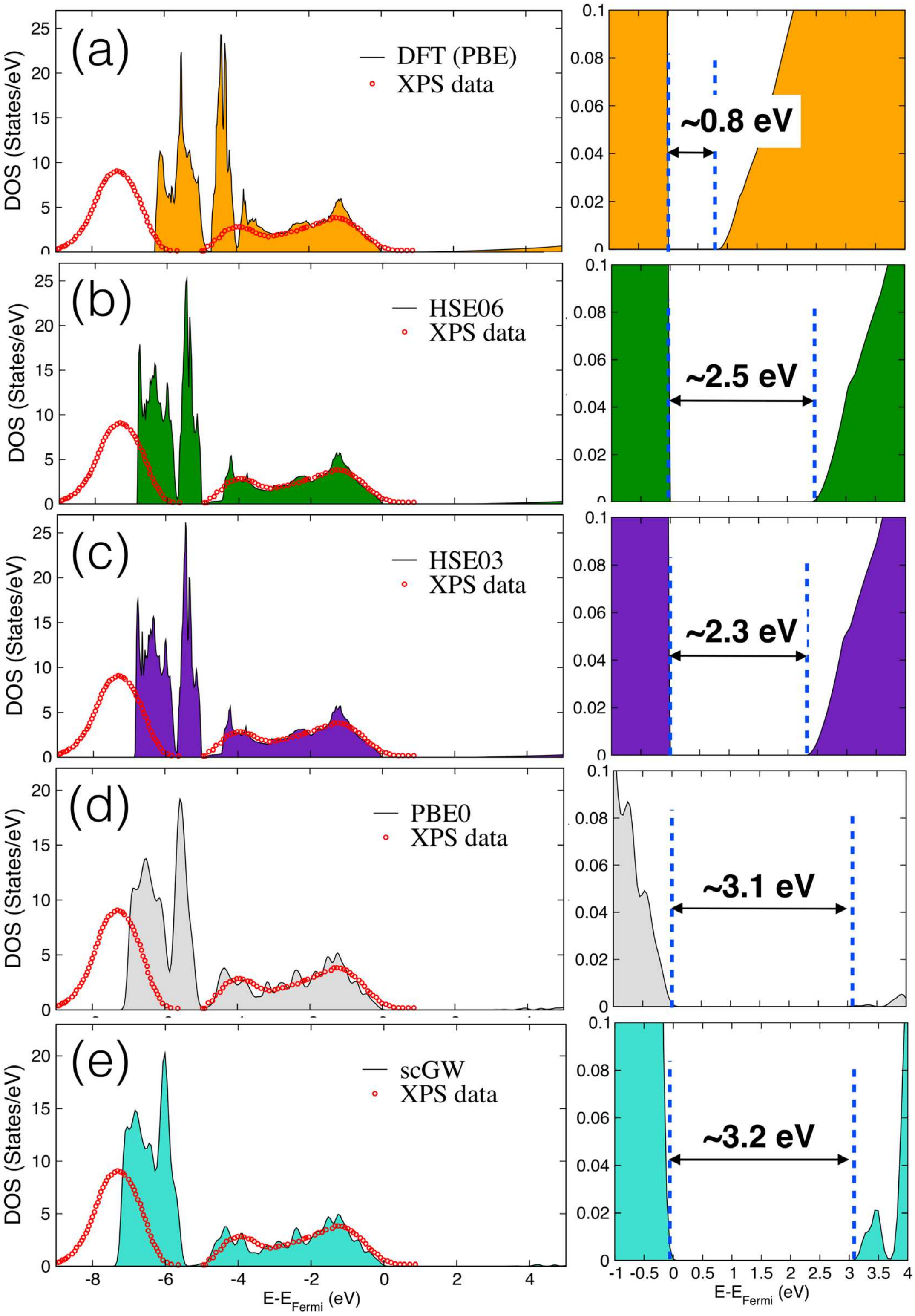

Figure 1. Total density of states (TDOS) of ZnO wurtzite structure calculated with: (a) PBE functional; (b) HSE06; (c) HSE03; (d) PBE0; (e) self-consistent GW. The XPS data was adopted from [23].

be fitted for each specific material, based on available experimental data.

Figure 1 shows that both HSE03 and HSE06 underestimate the band gap for ZnO and the binding energies of the Zn_{3d} electrons, but we also know that increasing α improves the agreement with experiment for the band gap [22]. In this section we reproduce that trend in HSE06 (figure 4) with increasing α in order to observe the effect not only on the band gap, but also on the position of the Zn_{3d} band. Indeed, one can see in figure 4 that at $\alpha = 0.375$ the band gap corresponds to the experimental value of about 3.4 eV [22]. It is also seen that greater α increases the binding energy for the

Table 1. Lattice parameters of ZnO calculated using different methods. For the parameter $E_{\mathrm{Zn}-3d}$ we used the middle of the band. The second from the bottom raw showing the LDA + A-1/2 data represents another approach for fitting DFT calculations to XPS data [44].

Method	a	c	u	E_g (eV)	$E_{\mathrm{Zn}-3d}$	$\varepsilon_{\infty\|}$	$\varepsilon_{\infty\perp}$
PBE	3.254	5.239	0.3808	0.8	−5.1	4.98	4.97
HSE03$_{(\omega=0.3;\alpha=0.25)}$	3.233	5.166	0.3822	2.3	−5.81	3.69	3.75
HSE06$_{(\omega=0.2;\alpha=0.25)}$	3.236	5.17	0.3820	2.5	−5.87	3.64	3.70
PBE0$_{(\omega=0.0;\alpha=0.25)}$	3.233	5.166	0.3823	3.1	−6.1	3.62	3.67
PBE + scGW	PBE	PBE	PBE	3.2	−6.45	3.73	3.73
scGW [24]	—	—	—	3.2	−6.4	—	—
LDA + A-1/2 [44]	—	—	—	3.49	−7.45	—	—
Expt. [27, 45]	3.242	5.188	0.3819	3.44	≈−7.5	3.72	3.68

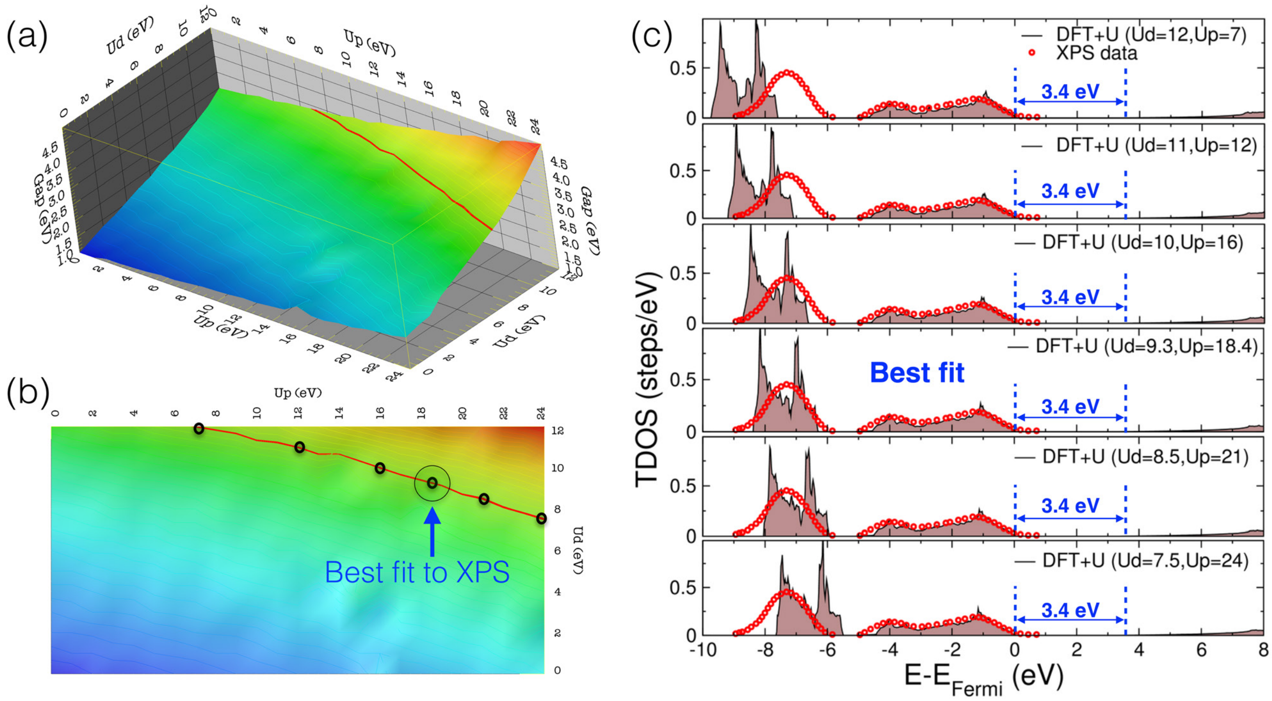

Figure 2. (a) The angle view on the surface plot of the energy gap of ZnO computed for various combinations of $U_{\mathrm{Zn}-3d}$ and $U_{\mathrm{O}-2p}$. The line indicates all combinations that yield the right band gap of 3.4 eV. (b) The top view of the same surface plot of the energy gap. (c) TDOS for several combinations of $U_{\mathrm{Zn}-3d}$ and $U_{\mathrm{O}-2p}$ that yield the correct band gap of 3.4 eV, shown by circles in panel (b). The XPS data is taken from [23].

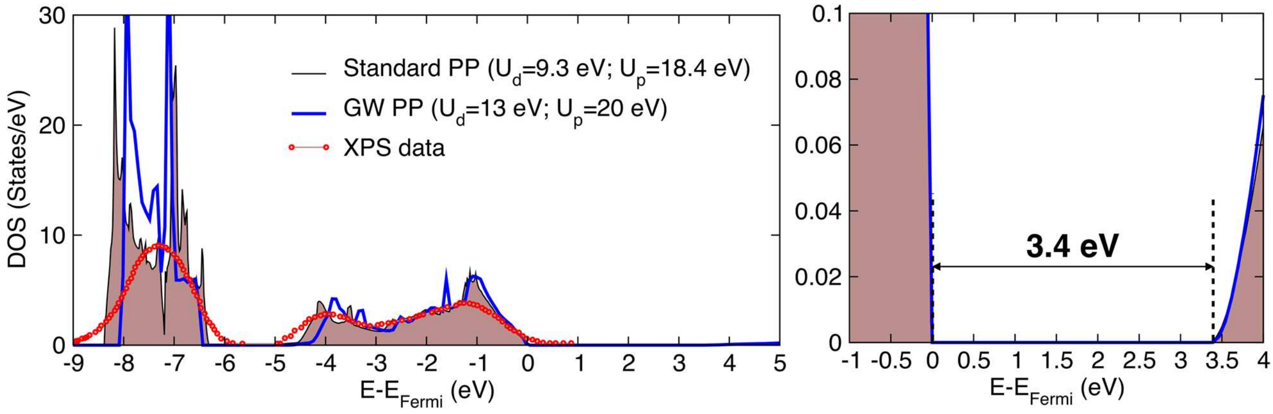

Figure 3. Total density of states of ZnO computed with optimized U-parameters for two sets of VASP pseudopotentials (PP): the standard PP $U_{\mathrm{Zn}-3d} = 9.3$ eV and $U_{\mathrm{O}-2p} = 18.4$ eV, and the GW-type PP $U_{\mathrm{GW-PP:Zn}-3d} = 13$eV and $U_{\mathrm{GW-PP:O}-2p} = 20$ eV.

Zn_{3d} electrons. However, at $\alpha > 0.5$ where we could expect the calculated Zn_{3d} band to overlap with the experimental XPS data, the band gap would be significantly overestimated. Thus, while pushing the Zn_{3d} band to lower energies, we need to reduce the effect of α on the band gap. The solution came from the analysis of HSE03 calculations, which yield the same as HSE06 positions of the Zn_{3d} band, but smaller band gaps. It seems that by increasing both ω and α we can optimize our HSE calculations to fit the XPS experiment.

Figures 5(a) and (b) show the band gap values of ZnO computed with HSE method using various combinations of ω and α. In all cases the structures were fully relaxed. The red line indicates combinations of ω and α that yield the correct band gap of 3.4 eV. Figures 5(c) and (d) show the positions of the middle of the Zn_{3d} band as a function of ω and α. The blue line indicates the experimental position obtained from the XPS data from [23], which we set at −7.3 eV. We note that in the literature the position of the Zn_{3d} band is usually referred to be at −7.5 eV, but the XPS data that we use as a reference has the peak maximum for the Zn_{3d} band around −7.3 eV [23]. To find the combination of ω and α that satisfies both search criteria, for the band gap and for the binding energies of the Zn_{3d} electrons, we overlay the two curves to find their crossing, as shown in figure 6(a). Finally, figure 6(b) shows an exact alignment of the calculated DOS with the XPS data.

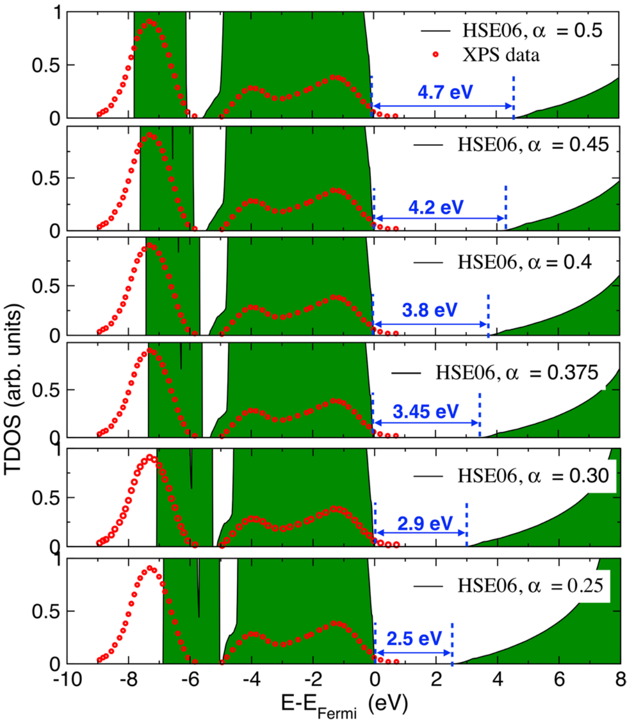

Figure 4. The DOS of ZnO computed with HSE06 ($\omega = 0.2$) with different weights for the exact exchange α. The XPS data is included for comparison [23].

4. Discussions

The presented results demonstrate that DOS computed via both DFT + U and HSE can be tuned to match closely the experimental XPS data. One would expect that such a nice alignment as demonstrated by figures 3 and 6 should lead to improved accuracy of both methods in reproducing the key physical properties of ZnO. However, careful calculations of the ion-clamped static dielectric tensor, listed in table 2, reveal that the optimized parameterizations lead to worse results, as compared to the standard HSE03 and HSE06 parameterizations, listed in table 1. The standard hybrid methods HSE03 and HSE06 are also much closer to PBE0 and to scGW results, which fit almost exactly the experimental values [45].

This poor performance of the optimized methods turns out to be not so surprising. We have made a naive mistake by assuming that XPS measurements should yield the correct picture of the electronic ground state, which is directly comparable to the computed DOS data. Apparently, that is not the case. XPS measurements involve the creation of a hole, which determines the final state of the system and in effect changes the binding energies of the emitted electrons [48]. This fact is more important for the emission from the core states. Theoretical calculations of such processes require insertion of a hole in the corresponding electronic states [49]. In the case of valence band structure, one may assume that the creation of a hole can be well screened, which probably leads to the assumption that XPS data can be used as a benchmark for computed ground state DOS. From our results, it seems that the screening works quite well for the *p*-band of ZnO. All hybrid and DFT + U, as well as GW, calculations reproduce the profile of the *p*-band reasonably well. However, the screening of the hole does not seem to work for the Zn_{3d}-band. XPS yields stronger binding for the Zn_{3d} electrons even compared to the scGW results. And it makes sense because the 3*d* state wave function becomes more localized due to the presence of the hole, created via the x-ray absorption and consequent electron emission. The presence of a hole in XPS data may be the season for the discrepancy regarding the position of the Zn_{3d}-band between the experiment and the ground state calculations.

We should also discuss the spread of the values that XPS measurements yielded for the position of the Zn_{3d}-band. Literature on XPS data for ZnO's Zn_{3d}-band reports a range of values between −8.81 eV in [29] and −7.3 eV in [23]. On average, 7.5–8.0 is the most commonly used range for benchmarking computational results [24, 44]. The experimental value of −8.81 from [29] is especially interesting, as it raises the question regarding the reproducibility of XPS measurements. A closer look at that data shows that the value of −8.81 eV was given relative to the Fermi level of the system, not VBM. If the zero energy is adjusted to the onset of the VBM slope, then the XPS data from [29] matches almost exactly the data from [23]. By making that adjustment one obtains the same −7.3 eV from [29] instead of the −8.81 eV, which is frequently mentioned in the literature. Therefore, we would argue that the spread of values from different XPS measurements is not big, averaging around −7.5 eV. The problem may be intrinsic to the whole process of the photoemission from the Zn_{3d}-band, which is not well screened and should not be compared to ground state electronic calculations.

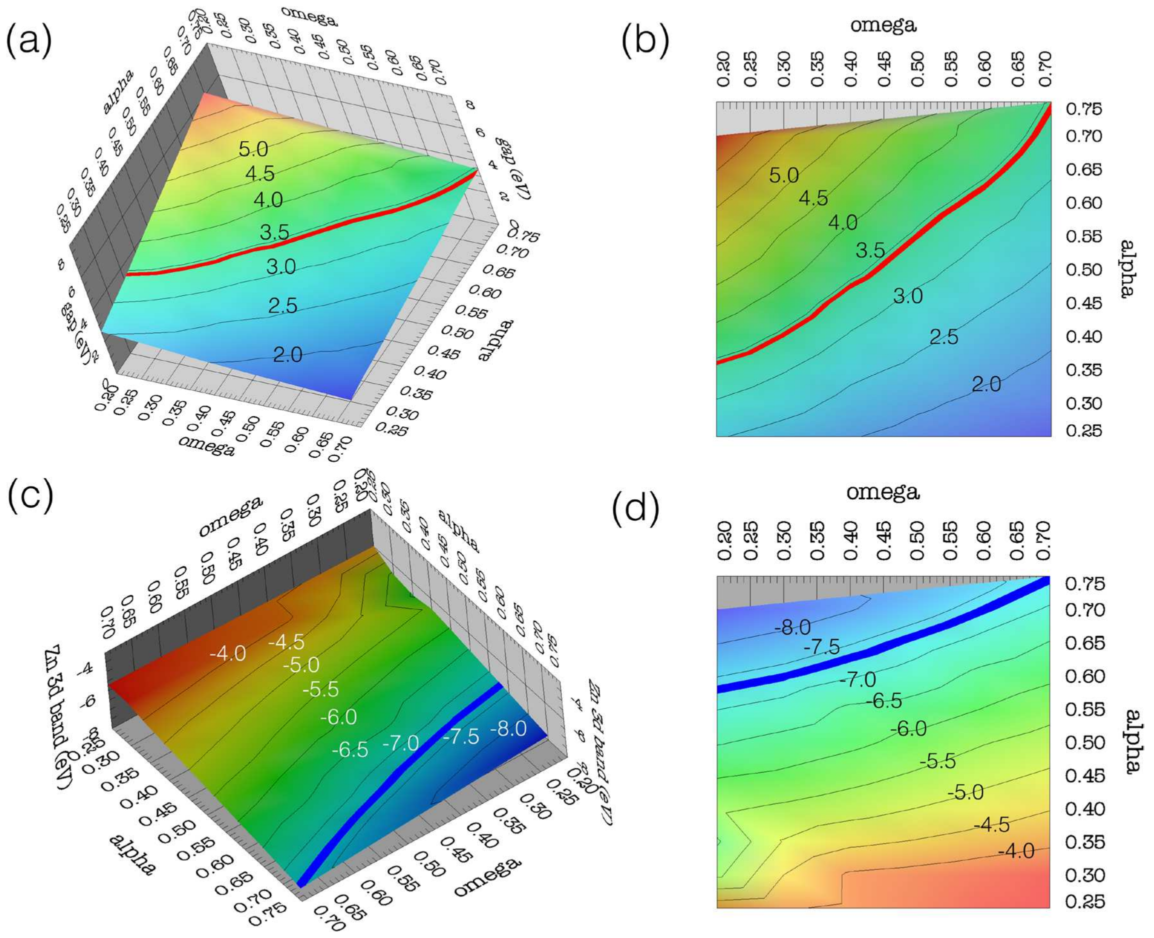

Figure 5. (a) and (b) ZnO band gap as a function of the HSE parameters ω and α: angle view and top view. The red line indicates combinations that yield the correct band gap. (c) and (d) Zn_{3d} band position mapped on the (ω, α) parameter-space. The blue line indicates the experimental value of -7.3 eV, estimated from the XPS data [23].

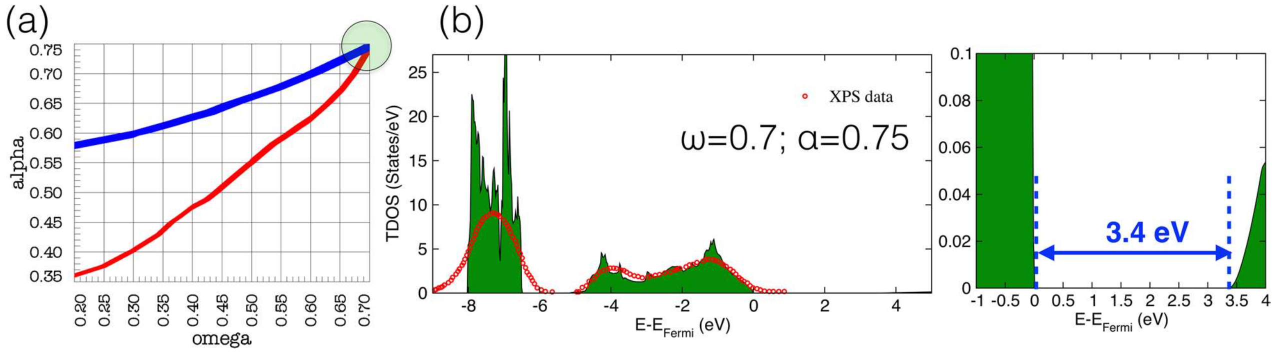

Figure 6. (a) Crossing of the two lines in the (ω,α) parameter space that satisfy the two criteria: ZnO band gap and the position of the Zn_{3d} band. The crossing shows the combination where both criteria are met. (b) The DOS calculated with the optimized HSE ($\omega = 0.7; \alpha = 0.75$), compared with the experimental XPS data. [23].

Table 2. Lattice parameters, energy gap, position of the Zn_{3d} band, and the Bader charge transfer from Zn to O, calculated using the optimized DFT + U and HSE methods.

Method	a (Å)	c (Å)	E_g (eV)	E_{Zn-3d} (eV)	$\varepsilon_{\infty\parallel}$	$\varepsilon_{\infty\perp}$
DFT + U (Standard PP, $U_d = 9.3$, $U_p = 18.4$)	3.08	4.96	3.4	-7.3	3.26	3.29
DFT + U (GW-type PP, $U_d = 13$, $U_p = 20$)	3.16	5.07	3.4	-7.3	3.10	3.13
HSE ($\omega = 0.7; \alpha = 0.75$)	3.23	5.12	3.4	-7.3	3.19	3.24
Expt. [27, 45]	3.242	5.188	3.44	≈ -7.5	3.72	3.68

5. Conclusions

In summary, we hope that the failure of this study creates an important example. When this project started, we did not doubt the reliability of the XPS data for benchmarking calculated ground state electronic structures. It has become a common trend in the literature to consider XPS data as a ‘golden’ standard for the binding energies of electrons and newly developed computational methods are routinely tested against that standard. So far, most practically available methods have failed to reproduce the binding energies of the Zn_{3d} electrons derived from XPS data. We hope that this paper provides sufficient evidence to recognize the fact that the common belief that the existing computational methods fail to reproduce the binding energies of Zn_{3d} electrons may not be correct [23]. The calculations, especially on the level of GW, might be the most accurate reference, and it may be incorrect to compare them to the XPS data.

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