Accuracy and Transferability of Ab Initio Electronic Band Structure Calculations for Doped BiFeO₃

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Abstract. BiFeO₃ is a multiferroic material and, therefore, highly interesting with respect to future oxide electronics. In order to realize such devices, pn junctions need to be fabricated, which are currently impeded by the lack of successful p-type doping in this material. In order to guide the numerous research efforts in this field, we recently finished a comprehensive computational study, investigating the influence of many dopants onto the electronic structure of BiFeO₃. In order to allow for this large scale ab initio study, the computational setup had to be accurate and efficient. Here we discuss the details of this assessment, showing that standard density-functional theory (DFT) yields good structural properties. The obtained electronic structure, however, suffers from well-known shortcomings. By comparing the conventional DFT results for alkali and alkaline-earth metal doping with more accurate hybrid-DFT calculations, we show that, in this case, the problems of standard DFT go beyond a simple systematic error. Conventional DFT shows bad transferability and the more reliable hybrid-DFT has to be chosen for a qualitatively correct prediction of doping induced changes in the electronic structure of BiFeO₃.

1. Introduction

BiFeO₃ (BFO) is a ferroelectric material with a polarization of $P_r \approx 100 \mu C cm^{-2}$[1] below a Curie temperature of $T_C = 1123 K$.[2] In addition, the iron centers have a magnetic moment of $\mu_B \approx 3.8 \mu_B$[3], which are arranged in a G-typical antiferromagnetic pattern below the Néel temperature of $T_N = 643 K$.[2] Therefore, BFO is multiferroic at room temperature and a promising material for oxide electronics. Consequently, BFO has been intensively studied in recent years. Especially doping studies are of importance, as they are the foundation of desired pn junctions, which are a vital compound for the envisioned electronics but also photovoltaic devices. While n-type doping is readily available and naturally present in most grown BFO crystals due to oxygen vacancies, no successfully p-type doped modification has been reported so far. We, therefore, recently carried out a comprehensive computational study, investigating the effects of 31 dopants on the electronic structure of BFO.[4] Here, we assess the computational methodology for doping studies in such a complex material.
2. Computational Details

A primitive BFO unit cell was considered for initial tests. These tests are carried out as all-electron (AE) calculation employing the Fritz Haber Institute ab initio molecular simulations package.[5] Total energies and atomic structures are fully relaxed to $10^{-6}$ eV/cell and until forces on ions are below 0.005 eV/Å. The Brillouin zone is sampled by a $3 \times 3 \times 3$ Monkhorst-Pack k-point grid. [6] We test different density-functional theory (DFT) methods, including two parameterizations of the local-density approximation (LDA),[7, 8] as well as the Perdew–Burke–Ernzerhof (PBE)[9] and the PBEsol[10] generalized-gradient approximations (GGA).

Doping experiments are carried out in a larger ($2 \times 2 \times 2$) pseudo-cubic unit cell. Substitution of one cation (bismuth or iron) results in a defect concentration of 12.5%. Structural optimization and initial electronic structure results at the PBE level were carried out using Quantum Espresso.[11] In these calculations, core electrons are treated by different flavors of pseudo potential schemes, compiled in the optimized and tested Standard Solid State Pseudopotential database.[12, 13]

Reference electronic structure results are obtained with a hybrid-DFT scheme that uses a fraction of (screened) exact exchange via the HSE06 functional[14], with 25% Hartree-Fock (HF) exchange and a screening parameter $\omega$ of 0.07 Å$^{-1}$. These calculations were again carried out as AE calculations, using the obtained PBE-optimized geometries.

3. Electronic Structure of Pristine BiFeO$_3$

3.1. Structural Properties

BFO can be described in different unit cells. The primitive unit cell of the R3cH structure is rhombohedral ($r$). It is related to a hexagonal ($h$) unit cell with lattice vectors $a_1^h = a_0^h(\sqrt{3}/2, 1/2, 0)$, $a_2^h = a_0^h(\sqrt{3}/2, -1/2, 0)$, and $a_3^h = c_0^h(0, 0, 1)$. Accurate low temperature (5 K) structural data of BFO can be found in the literature,[15] giving lattice vectors for the hexagonal unit cell of $a_0^h = 5.57$ Å and $c_0^h = 13.84$ Å. The deviation of other experimental reports (ICSD:[16] 15299, 75324, 51664, 97591, 157424, 163687, 188396, 191940) is small and errors are within ±0.01 Å and 0.04 Å for $a_0^h$ and $c_0^h$, respectively, with averaged values of 5.58 Å and 13.87 Å. Thus, the low temperature experimental structure of Palewicz et al. appears to be of good quality and will serve as reference. The primitive unit cell can be constructed from the lattice parameters of the hexagonal cell with lattice vectors $a_1^r = (-a_0^h/\sqrt{3}, 0, c_0^h/3)$, $a_2^r = (\sqrt{3}a_0^h/6, a_0^h/2, c_0^h/3)$, and $a_3^r = (\sqrt{3}a_0^h/6, -a_0^h/2, c_0^h/3)$.

The experimental structure is compared to various computed structures in table 1. In order to exclude influences of pseudopotentials, we first compare the experimental structure with DFT results using AE calculations. Different flavors of the LDA give similar results, underestimating the lattice constant $a_0^h$ by -2.9 to -3.1%. PBEsol improves this, with a smaller underestimation of -1.17%. As it has been observed for many materials, PBE results in an opposite trend, overestimating the lattice constant by 1.12%. Hence, from the tested standard DFT functionals, PBE performs best, with both PBE and PBEsol yielding structures within reasonable errors from experiment. From this point, two strategies seem to be valid, besides testing for other functionals that are differently or higher parameterized (e.g., meta-GGAs): On the one hand, one could employ one of the functionals that underestimates the lattice constant, supplementing it with a semi-empirical Hubbard correction.[17] The latter usually leads to a linear expansion of the lattice for oxide materials and also improves the electronic structure by opening the band gap. On the other hand, one may continue with the method that yields the best structural properties at this level of theory, relying on a different scheme for electronic structure properties. We chose the latter (see below), since Hubbard U (and J) corrections can not always be employed in a straightforward way. While it is, in principle, possible to determine a parameter set for a given system from first principles,[18] in practice this does not always provide the best correction to a
quantity of interest. In addition, different parameters are often desirable if different quantities are investigated. In fact, for BFO, a variety of different parameters has been applied in the past, with $U_{\text{eff}}$ ranging typically from 0 eV to 4 eV\cite{19–21}. In addition, calculations employing $U = 7$ eV and $J = 0.9$ eV have been proposed.\cite{22} In conjunction with the variety of dopants that should be described equally well, this strategy seems disadvantageous.

Table 1. BFO lattice parameter comparing all-electron (AE) and pseudopotential (SSSP) calculations with experimental results.

| Method          | $a_0^r$/Å | $a_0^r - a_0^r(\text{exp.})$/\% |
|-----------------|----------|---------------------------------|
| Experiment\cite{15} | 5.63   |                                 |
| AE-PBE          | 5.69    | 1.12                            |
| AE-PBEsol       | 5.56    | -1.17                           |
| AE-LDA(PZ)      | 5.45    | -3.07                           |
| AE-LDA(VWN)     | 5.46    | -2.89                           |
| SSSP-PBE(65 Ry) | 5.67    | 0.72                            |
| SSSP-PBE(80 Ry) | 5.73    | 1.80                            |
| SSSP-PBE(100 Ry)| 5.70    | 1.36                            |
| SSSP-PBE(200 Ry)| 5.70    | 1.35                            |

Therefore, we choose the second approach, i.e., we rely on the PBE functional, but only for structural relaxations, whereas electronic structure results are determined in a second step by a different method. For a trade-off between accuracy and computational feasibility, we choose the so called hybrid-DFT, specifically the HSE functional, over more expensive alternatives (see below).

To increase computational efficiency in the first step, the structural optimization at the PBE level, we chose a pseudopotential method employing a plane wave basis set instead of AE calculations. Since our goal is to study a large variety of elements in form of BFO dopants, we choose the highly tested SSSP database.\cite{12} The latter ensures accurate results for the entire periodic table, although with the caveat of being tested for a very costly setup, employing an over-converged plane-wave cutoff of 200 Ry. We tested the respective pseudopotential calculations and its convergence with respect to the plane-wave cutoff (see Table 1). It shows that converged structures are obtained for a plane-wave cutoff of 100 Ry. This is, although being reduced by a factor of two compared to the benchmark results of the SSSP,\cite{13} still an unusually extensive basis. In order to ensure accurate results for a wide range of elements, however, we employ this setup in our PBE calculations. Calculations for this setup are in very good agreement with the AE results, indicating the quality of the employed pseudopotentials.

3.2. Electronic Structure

We now turn our discussion to the electronic structure of BFO. The band structure of BFO at the PBE level for our plane wave calculations is shown in figure 1 (a). It is in very good agreement with the AE result and both band gaps agree within 0.01 eV (see Table 2), i.e., the chosen pseudopotentials also do not introduce errors on the electronic structure. It is known, however, that GGA as well as LDA have a band gap problem that leads to the underestimation of computed band gaps.\cite{23} Thus, experimentally observed optical gaps are significantly larger (2.1 eV to 2.8 eV). In order to improve this shortcoming of standard DFT methods, one has
to (i) improve the form of the employed density functional or (ii) apply perturbative many-body corrections.[24, 25] We chose the first option, by adding a (fraction) of exact Hartree-Fock exchange to the approximate treatment of exchange and correlation, as implemented in the HSE hybrid-functional. Such a correction is somewhat ad hoc, as the fraction of exact exchange is not defined and likely to be system dependent, similar to Hubbard corrections. Therefore, more accurate treatments that go even beyond this hybrid method are desirable. Besides the above mentioned many-body treatment (ii), this is also possible in the spirit of option (i), by employing full exact exchange[26, 27] together with good approximations to the exact correlation contribution.[28] Such methods are, however, computationally very expensive and still under development, hence, not suitable for a broad computational study. Therefore, we have to choose a sensitive parameterization, judging the employed methodology by its performance against reference results. We do so by computing the band structure with the HSE functional. AE calculations at the HSE level give a band gap of 3.17 eV. This is in reasonable agreement with the upper end of the spectrum of experimental optical gaps, overestimating the latter by 0.37 eV. However, we must keep in mind that optical gaps are a lower bond to energy band gaps, which indicates the accuracy of the HSE band gap. This is further validated by comparing to a reported GW band gap of 3.6 eV.[29] The HSE result is in the middle of experimental optical gaps and reference many-body calculations. Despite a quantitatively exact treatment of the gap states in BFO seems to require special care in order to reproduce the observed optical band gaps computationally, the applied hybrid-DFT method seems to provide a band gap description that is qualitatively correct and quantitatively reasonable. We, therefore, choose the hybrid-DFT treatment as reference.

The resulting HSE band structure and density of states (DOS) are shown in figure. 1 (c and d). Besides the changed band gap, significant differences arise in the DOS comparing the HSE to the PBE results. The valence band (VB) region is comprised by hybridized iron (3d) and oxygen (2p) states that are fully mixed in the PBE case. In contrast, HSE attributes only some iron character to the oxygen dominated VBs, whereas the majority of the iron 3d orbitals are located slightly below this set of bands, forming a localized set of d states, with only little oxygen contribution. This is in line with previous observations for transition metal d states and the reason for the success of Hubbard corrections in these kind of materials. GGA (and LDA) delocalize transition metal d states. This is not correct for systems like transition metal oxides such as BFO.[19] Thus, in addition to the commonly observed underestimation of band gaps, standard DFT is additionally problematic whenever a partly filled d state is present in the valence region. We will see that this has further important consequences on the results of doped systems, making this level of theory unreliable to even give qualitative trends. This is important, since a mere under- or overestimation of the band gap could be corrected by a simple scissor operation if a more accurate reference (independent of its origin) is known.[30, 31]

Table 2. Comparison between optical gaps and computed band gaps for different computational models.

| Method          | $E_g$/eV |
|-----------------|----------|
| Experiment[32–38]| 2.1 – 2.8|
| AE-PBE          | 1.06     |
| SSSP-PBE        | 1.07     |
| AE-HSE          | 3.17     |
4. Alkali Metal Doping

With a scheme in hand that is computationally feasible and accurate enough to provide electronic structures quantitatively correct within reasonable error margins and that gives qualitatively correct trends to a high degree of confidence, we can turn to the discussion of doped systems.

We start by investigating the influence of an alkali metal defect on the electronic structure of BFO. The band structure and DOS of sodium doped BFO in the A-site is shown in figure 2. Compared to the pristine case, introducing any alkali metal at A- or B-sites introduces a $M^{+}$ defect at a $M^{+3}$ site (here Na$^{+}$ and Bi$^{+3}$). This means that two electron holes are created. In the band structure we observe this generation of charge carriers by the emergence of two acceptor levels in the band gap. By analyzing the DOS, we find that these acceptor states have mixed iron and oxygen character. In addition with structural changes and the depletion of charge at one iron center, this suggests the localization of both electron holes at one FeO$_{6}$ octahedron, i.e., the oxidation of Fe$^{+3}$ towards Fe$^{+5}$, as it is discussed in detail in [4]. This process also changes the conduction band (CB) region. In the spin channel opposite to the doping effect, bands are shifted downwards below the CB edge (CBE). In agreement with the oxidation of iron and by analyzing the DOS, it shows that these bands are the unoccupied $d$ states of the reduced iron center, which can be explained by the larger attraction of states by a higher oxidized, i.e., less shielded, atomic core. Figure 2 (a-b) shows the respective band structure and DOS at the PBE level. Hole doping might be concluded by comparing the band dispersion of the VBE and the CBs around 2 eV with the pristine case, identifying bands between the Fermi level and 1 eV as acceptor bands. This however, gives a spurious number of acceptor bands and, comparing the DOS with the HSE results, a physically wrong picture. The lowest acceptor bands are dominated by iron 3$d$ states, whereas oxygen contribution is found dominantly in the upper bands. Comparing this with the reference HSE result, we observe several differences. Due to the smaller band gap and the wrong description of $d$ orbitals, the two effects that are introduced because of hole doping are overlapping in the PBE case. The acceptor bands (from the iron center oxidation) are observed in the same spin channel as for HSE. In addition, the down-shift of the iron bands from the CBE in the other spin channel is observed. However, instead of two isolated groups of bands with the acceptor bands located below the shifted CBs, both types of bands are close in energy and the acceptor bands are located closer to the CBE, i.e., the bands appear in the wrong order. This complicates the interpretation of the PBE result, which
could lead to miss interpretations. This effect depends on the size of the chosen alkali metal. For lithium doping, both bands are fully overlapping. For larger alkali metals, the acceptor bands are raised, leading to an increasing separation to the downshifted iron CBs. The spurious stabilization of the unoccupied iron conduction bands can be attributed to the reduced splitting of iron $d$ states by standard DFT, i.e., it is in line with the occupied $d$ states hybridizing with the oxygen VBs instead of being localized below them. In summary, this means that correct qualitative trends from the PBE results can only be concluded with special care, knowing about the over stabilization of unoccupied iron states.

![Figure 2. Band structure and DOS of BFO with a Na$^+$ impurity at the PBE (a and b) and the HSE (c and d) level, respectively. Bands are colored blue (spin up) and red (spin down) in the band structures (a, c). Contributions to bands are drawn blue (oxygen), orange (iron), and red (bismuth), respectively. In the PBE case, we differentiate between contributions from spin up polarized iron centers (orange) and spin down polarized iron centers (yellow).](image)

5. Alkaline-earth Metal Doping

Next we discuss the effects of alkaline-earth metal defects. For this we show the band structure and DOS for beryllium in the B-site in figure 3. Similar to the alkali metal dopants, we expect a $M^{+2}$ dopant, resulting in one electron hole generating one acceptor band and, thus, $p$ doping. In fact, we observe great similarities to the effects introduced by $M^+$ alkali metal dopants at the HSE level. An acceptor level is observed, containing once again iron and oxygen character. Analyzing the DOS in detail reveals that the electron hole is located at a neighboring iron center, in line with a decreasing octahedron volume and charge depletion. Thus, oxidation of iron to Fe$^{+4}$ is observed. In addition to the doping effect, the reduced charge at the oxidized iron center leads to a stabilization of its empty $d$ orbitals below the CBE, see [4] for details. Looking at the results at the PBE level figure 3 (a-b), however, acceptor bands are seemingly introduced in both spin channels. Analogously to the alkali metals, this can be attributed to a wrong description of transition metal $d$ states by standard DFT and the too small band gap. The empty iron bands are again stabilized to a degree that they overlap with the actual acceptor band, complicating the interpretation of the observed results.

In figure 4 we also show the obtained electronic structure of magnesium doped BFO. Here, the application of PBE has even more drastic consequences, resulting in qualitatively wrong predictions from the computed band structure. While the HSE result shows that Mg$^{+2}$ doping affects the band structure analogously to Be$^{+2}$ doping, for PBE we observe partly filled bands at the Fermi level instead. Investigating the DOS shows that the partly filled bands have mixed iron and oxygen character. The iron character is dominantly attributed to spin up polarized iron centers. This suggests a fractional reduction of more than one iron center. This is in line
Figure 3. Band structure and DOS of BFO with a $\text{Be}^{\text{+2}}_B$ impurity at the PBE (a and b) and HSE (c and d) level, respectively. Bands are colored blue (spin up) and red (spin down) in the band structures (a, c). Contributions to bands are drawn blue (oxygen), orange (iron), and red (bismuth), respectively. In the PBE case, we differentiate between contributions from spin up polarized iron centers (orange) and spin down polarized iron centers (yellow).

with the tendency of delocalizing charge by standard DFT methods. HSE corrects this behavior, despite using the GGA geometry. This is interesting, as the oxidation of iron centers influences the geometric structure by reducing the oxidized FeO$_6$ octahedra. Partly filled bands at the Fermi level are observed for all alkaline-earth metal dopants besides beryllium at the PBE level, whereas a single acceptor band and a $p$-type doped semiconductor is obtained in each case for HSE. Therefore, standard DFT seems unsuitable to describe the electronic structure of $M^{\text{+2}}$ doped BFO. Although structural relaxations with the more accurate hybrid-DFT method seem desirable, qualitatively correct trends are retained using the GGA structures. Therefore, for a large scale study, the chosen two step procedure using the GGA for crystal structures and hybrid-DFT to describe the electronic structure seems required.

Figure 4. Band structure and DOS of BFO with a $\text{Mg}^{\text{+2}}_B$ impurity at the PBE (a and b) and the HSE (c and d) level, respectively. Bands are colored blue (spin up) and red (spin down) in the band structures (a, c). Contributions to bands are drawn blue (oxygen), orange (iron), and red (bismuth), respectively. In the PBE case, we differentiate between contributions from spin up polarized iron centers (orange) and spin down polarized iron centers (yellow).
6. Summary
We assess the accuracy of DFT for the description of BFO. While structural properties seem to be described reasonably well within the GGA, the band gap is underestimated by a large factor. In addition to the well-known band gap underestimation of the GGA, the problematic description of transition metal $d$ shells, which are predicted to be delocalized by standard DFT, intensifies the errors of GGA results. We find that the application of a hybrid-functional provides a corrected electronic structure description and that it provides a good trade-off between computational affordability and sufficient accuracy for a large scale computational study.

We then test our electronic structure treatment by assessing the influences of various impurities, comparing alkali and alkaline-earth metal doping with the undoped case. Doping with metals in oxidation states smaller than three introduces two major effects in the electronic structure: (i) acceptor bands localized on FeO$_6$ octahedra in the vicinity of the dopant and (ii) a downshift of the unoccupied iron $d$ states of the respective iron centers. The ordering of these emerging new bands turns out to be wrong at the PBE level. The problems of electronic structures obtained from the GGA are more pronounced for the case of $M^{+2}$ alkaline-earth metal dopants. Doping with all elements of this group besides beryllium leads to partly filled bands at the GGA level instead of the $p$-doped semiconductors that are predicted by the hybrid-DFT reference method. Thus, qualitatively wrong trends that go beyond a mere underestimation of the band gap are observed using GGA functionals. We, therefore, use a two step procedure, employing GGA calculations only for structural relaxations, whereas the electronic structure is obtained by hybrid-DFT.

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