# Electronic structure of stoichiometric and reduced ZnO from periodic relativistic all electron hybrid density functional calculations using numeric atom-centered orbitals

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**Abstract**

The atomic and electronic structure of stoichiometric and reduced ZnO wurtzite has been studied using a periodic relativistic all electron hybrid density functional (PBE0) approach and numeric atom-centered orbital basis set with quality equivalent to aug-cc-pVDZ. To assess the importance of relativistic effects calculations were carried out without and with explicit inclusion of relativistic effects through the zero order regular approximation. The calculated band gap is ~0.2 eV smaller than experiment, close to previous PBE0 results including relativistic calculation through the pseudopotential and ~0.25 eV smaller than equivalent non-relativistic all electron PBE0 calculations indicating possible sources of error in non-relativistic all electron density functional calculations for systems containing elements with relatively high atomic number. The oxygen vacancy formation energy converges rather fast with the supercell size, the predicted value agrees with previously hybrid density functional calculations and analysis of the electronic structure evidences the presence of localized electrons at the vacancy site with a concomitant well localized peak in the density of states ~0.5 eV above the top of the valence band and a significant relaxation of the Zn atoms near to the oxygen vacancy. Finally, present work shows that accurate results can be obtained in systems involving large supercells containing up to ~450 atoms using a numeric atomic centered orbital basis set within a full all electron description including scalar relativistic effects at an affordable cost.

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## Introduction

Because of its large optical and chemical stability, natural abundance, and concomitant commercial availability, zinc oxide (ZnO) has received considerable attention for a series of applications, from catalysis[1] and photocatalysis[2,3] to gas sensors,[4] transparent conductors,[5,6] solar devices,5 electronic[7] and optoelectronic properties.[8] The already technologically relevant properties of ZnO can be further improved by suitably modifying the material either by introducing defects,[8] doping8[-10] and/or nanostructuring.[11-13] However, engineering the physical, chemical, and catalytic properties of ZnO, and of similar types of materials, is far from being simple and often involves large doses of intuition and of serendipity.

The situation just described is not restricted to ZnO; on the contrary, it is rather general and affects many different families of materials. Therefore, it is not surprising that materials scientists seek guidance from first principles based computational approaches. This is not as simple as it may seem because of the several approximations which are intrinsic to solutions of the time independent Schrödinger equation. Therefore, it is essential that the accuracy of these computational approaches is well established for the stoichiometric material and also for the most common point defects. In the present work we tackle the case of stoichiometric ZnO and of neutral oxygen vacancy point defects. However, before focusing on ZnO it is worth pointing out that, in the case of properties directly governed by the electronic structure of the material, computational approaches often rely on periodic density functional theory based calculations[14] which, in turn, require choosing a form of the unknown density functional. Methods based on the generalized gradient approach (GGA)[15,16] constitute the usual option. However, GGA based methods fail to properly predict the optical band gap of semiconducting or magnetic transition metal oxides, usually severely underestimating it.[17] In fact, hybrid density functionals[18] mixing a certain amount of non-local Fock exchange are required to reach a more accurate description of the band gap of simple and transition metal oxides[19-21] and of more complicated systems such as antiferromagnetic NiO[22] or $UO_2$.[23] Nevertheless, it is pertinent to remark that the amount of Fock exchange required to accurately predict the properties of oxides and related systems is likely to be defined for each particular case.[24]

Several studies have been reported for ZnO using periodic hybrid density functional calculations which address the electronic structure of the bulk materials

and/or of the oxygen vacancy related properties. As it also holds for most of the theoretical studies on different materials, those dealing for ZnO can be broadly divided in two families: the ones using all electron methods and a linear combination of atomic orbitals (LCAO) with the orbitals expanded in a basis set of Gaussian type orbitals (GTO),[25-27] and those describing the inner cores by means of a pseudopotential and expanding the valence electron density in a plane wave (PW) basis set.[28-2931] Gerosa *et al.* present a comparison of the two approaches for different oxides including ZnO.[32] Here it is important to mention that all electron calculations neglect relativistic effects that may be important for Zn. Scalar relativistic effects are usually included in the pseudopotential based approaches although here the core electrons are not relaxed which may also have an effect on the calculated results, especially if the number of electrons included in the pseudopotential is large, including semicore orbitals. To disentangle relativistic from the approximate description of the core electrons herewith we present scalar relativistic all electron hybrid density functional calculations for bulk ZnO in its wurtzite crystal structure and of oxygen vacancies using the recently developed numeric atom-centered orbitals basis set which allow for efficient parallelization and allow the study of rather large supercells at an affordable computational cost.[21,33,34]

**Models and methods**

Wurtzite, the most stable polymorph of ZnO with space group 186 ($P6_3mc$), has been considered through all the present work. In an initial step, the crystal structure of bulk wurtzite has been optimized using the GGA type PBE exchange-correlation functional[15] and further refined with the PBE0 hybrid scheme[35] containing a 25% of Hartree-Fock (HF) exchange. Calculations reported by Oba *et al.*,[28] carried out within a plane wave basis set and a projected augmented wave (PAW) description of the core electrons, have shown that the PBE0 functional provides a reliable prediction of the band gap and formation energy of ZnO whereas, with the standard parameters, the Heyd-Scuseria-Ernzerhof (HSE06) range separated functional underestimates it. For comparison, present calculations aiming at obtaining the crystal and electronic structure of wurtzite have also been carried out using the HSE06 functional. It is worth pointing out that the band gap of oxides, as defined from the band structure without taking many body effects into account, is very sensitive to the amount of Fock exchange included in the hybrid functional and/or to the magnitude of the screening parameters. In fact,

recent calculations have shown that a 12.5% of Fock exchange is necessary to reproduce the band gap of stoichiometric $TiO_2$ rutile and anatase polymorphs,[24] whereas within the HSE type of functional it is necessary to reduce it to 20%.[36] Similar findings have been also recently reported for ZnO including very accurate diffusion quantum Monte Carlo calculations.[37] This fact seems to be a consequence of the different dielectric constant of each material and, in fact, several authors[38,39] suggested to use this property to define the amount of Fock exchange required to properly describe a given solid, although one needs to realize that such approach includes, in an empirical way, a macroscopic parameter external to theory, even if this can be done in a self-consistent manner.[40]

The PBE0 and HSE06 calculations for bulk wurtzite have been carried out explicitly including all electrons and taking into account scalar-relativistic effects at the zero order regular approximation (ZORA) level,[41] which is largely based on the work of Chang *et al.* on regular 2-component effective-Hamiltonians in Dirac theory.[42] The electron density has been described with a basis set of numeric atom-centered orbital (NAO) using the seamless parallel *ab initio* simulation package (AIMS).[33,34] The Tier-1 basis set together with the light grid options has been chosen. Since the numerical accuracy of the NOA basis sets is not yet broadly known, in the next section we provide evidence that the quality of this basis set is of (or higher than) double-ζ plus polarization with results comparable to those obtained with Dunning[43,44] GTO aug-cc-pVDZ basis set optimized for providing accurate results in calculation explicitly including electron correlation. Integration in the reciprocal space was carried out using a 17×17×17 Monkhorst-Pack grid of special **k**-points.[45] This setting ensures convergence in the total energy below 0.04 eV. Atomic positions and cell dimensions were allowed to fully relax until forces acting on atoms were below 0.001 eV $Å^{-1}$. Calculations were carried in a non spin-polarized fashion. A gaussian smearing of 0.01 eV width was used to speed up convergence of the calculations, although final energies were all extrapolated to 0 K. Finally, to further investigate the role of relativistic effects some selected calculations have also been carried out at the non-relativistic level yet using the same basis set and crystal structure.

To further inspect the accuracy of the present relativistic all electron calculations we consider the atomic and electronic structure of oxygen vacancies ($V_O$) in wurtzite bulk ZnO. To this end three different supercells of increasing size containing up to 432 atoms have been built: 2×2×1, 4×4×2, and 6×6×3, with the latter one featuring a $V_O$

concentration below 0.5%. Different **k**-points meshes— 9×9×17, 5×5×3, and 1×1×1, respectively— were used in each case with the maximum grid size limited by the stringent memory requirements of the AIMS code. For each supercell, all atomic positions have been optimized at PBE0 level. Next a single $V_O$ has been created and all atomic positions in the cell allowed to further relax. The $V_O$ formation energy, $E_f$, is obtained by the difference in between the system with no vacancies and the sum of that with one $V_O$ and the energy of one isolated oxygen atom calculated spin-polarized in its triplet ground state.

**Results and discussion**

This section starts with a brief assessment of the quality of the NOA basis set used along this work and next describes the results obtained for bulk wurtzite and for the supercells containing one $V_O$.

*a) Establishing the quality of the light-Tier 1 NAO basis set*

To provide reliable information about the quality of the basis set used in this work, Table 1 reports the non-relativistic total energy of O and Zn atoms in their triplet and singlet ground state as well as the corresponding value for the $O_2$ and ZnO diatomic molecules, again in triplet and singlet ground states and at the geometry optimized at the PBE0/light Tier-1 level: 1.70004 Å for ZnO and 1.19800 Å for $O_2$. For comparison, HF, PBE, and PBE0 values are reported as obtained using the light Tier-1 NAO basis set and the aug-cc-pVDZ, the latter values have been obtained using the Gaussian09 code.[46] Results in Table 1 show that for all systems and for the three different methods, the total energy obtained with the NAO light Tier-1 basis is significantly lower than that corresponding to the already high quality aug-cc-pVDZ basis indicating that, as far as variational arguments are used, the NAO light Tier-1 basis set is closer to the complete basis set limit. This is in line with the systematic study of Zhang et al. regarding the quality of these NAO basis sets.[47]

The effect of the basis in the total energy is, not unexpectedly, larger than on dissociation energy. In fact, for the $O_2$ molecule at the PBE0 level and using the light Tier-1 basis set. Neglecting the zero point energy correction, the dissociation energy obtained with the NAO basis set is 5.22 eV whereas the corresponding aug-cc-pVDZ value, at the same geometry, is 5.33 eV. In a similar way the PBE0 dissociation energy of ZnO computed with the NAO basis set is 1.25 eV whereas that obtained with the

aug-cc-pVDZ basis is 1.27. Comparison to experiment is not provided purposely since the aim of this section is to establish the quality of the light Tier-1 NAO basis set by comparing to calculations using GTO basis sets and different methods.

From the preceding discussion one can safely conclude that values reported in the present work with the NAO light Tier-1 basis set are of quality comparable to those which would be obtained using a GTO basis set of aug-cc-pVDZ quality.

*b) Atomic and electronic structure of bulk wurtzite*

The wurtzite ZnO crystal structure has a lattice with two equal vectors ($a = b$), and a third different one, $c$, with a given $c/a$ ratio. Table 1 lists the experimental data listed in Table III in the work of Santana et al.[37] and PBE0 optimized values obtained in the present work with previous values obtained with the same functional but different basis sets or treatment of core electrons included for comparison. Comparing the results from all electron calculations either using NAO or GTO basis set in Table 1 (second and third columns) it is clear that the relativistic effects included explicitly in the present work have a small but noticeable effect. Moreover, comparing the all electron NAO results to those corresponding to calculations with the cores described through the PAW approach show that the latter efficiently captures the scalar relativistic effects. In any case, the three approaches are relatively good in predicting the structure, with deviations of $a$, $c$, and $c/a$ ratio of ~1%.

The accurate theoretical calculation of the optical band gap of materials requires relying on many body theories such as those based in the GW approaches due to the seminal work of Hedin.[48] However, these are by no means simple, imply exceedingly large computational resources and, in addition, depend on the starting density functionals.[17,49] Hence, we focus in the optical band gap as obtained from the band structure calculations which is a common and broadly used approach as recently illustrated by Garza and Scuseria.[50] This is, as mentioned above, a quantity which is also very sensitive to the choice of the exchange-correlation functional with hybrid functionals performing much better that those of GGA family but with a strong dependence on the amount of Fock exchange included (see Refs 22, 24, and 36 and references therein). The experimental band gap of ZnO has been measured by several authors with reported values in a rather close agreement. Hence, a value of 3.44 eV has been reported earlier by Hümmer[51] which is fully consistent with the value reported later on by Reynolds *et al.*[52] at 2 K. The PBE0 value calculated in the present work is

3.18 eV, still slightly underestimating the experimental value. Exactly the same value has been reported by Oba *et al.*[28] using a plane waves basis set and with the cores described through the PAW approach and a slightly larger value of 3.26 eV has been reported by Marques *et al.*[38] using exactly the same approach but at the experimental structure. However, a rather large value of 3.93 eV is predicted by the non-relativistic all electron calculations of Labat *et al.*[27] using a GTO basis set. Since all the calculations commented above have been obtained with the PBE0 functional and since no differences were found in the equilibrium geometry one can safely conclude that the differences observed must arise mainly from the relativistic effects explicitly included in the present work, implicitly included in the PAW in the calculations of Oba *et al.*[28] and not accounted for in the all electron calculations of Labat *et al.*[27] To further confirm this finding we carried out the PBE0 calculations at the same geometry and same basis set but removing the ZORA relativistic correction. The calculated band gap thus obtained is larger than that predicted from the relativistic calculations, 3.43 versus 3.18 eV thus verifying, at least in part, the hypothesis above. The remaining discrepancy with respect to the PBE0 all electron calculations of Labat *et al.*[27] being attributed to differences in the quality of the basis set and, to a lesser extent, to slight differences in the optimized atomic structure. This is an important conclusion that should warn computational materials scientists on the potential errors in non-relativistic all electron calculations.

To conclude this section, it is worth commenting on the effect of the exchange correlation functional in the description of the ground state properties of ZnO. Since the differences in the equilibrium geometry are minor, we will concentrate just on the band gap. The band gap of 3.43 eV predicted by the present PBE0 calculations at the non-relativistic, all electron, level of theory almost matches the B3LYP results —3.46 or 3.38 depending on the authors.[25,27] Note, that the B3LYP band gap reported by Labat *et al.* is smaller than their PBE0 value. This is not unexpected since B3LYP contains 20% of Fock exchange whereas PBE0 contains a 25% and, as found for $TiO_2$,[24] the magnitude of the band gap goes linear with the percent of non-local Fock exchange as shown in Figure 1. Including, the scalar relativistic effects on these B3LYP calculations will surely lead to even smaller values indicating that the agreement with experiment is somehow fortuitous, coming largely from cancellation of errors.

Finally, we comment on the results obtained with the broadly used range-separate HSE functional. Using the two standard parameters (25% of Fock exchange and a screening parameter of 0.2 $Å^{-1}$) the present HSE calculations —at the HSE equilibrium structure— predict a band gap of 2.43 eV, significantly smaller than the PBE0 and rather severely underestimating the experimental value. A similar value (2.57 eV) has been reported by Marques *et al.*[38] for the experimental structure using the HSE (HSE06) functional, a plane wave basis set and a PAW description of the cores. However, a rather larger value of 2.90 eV, hence closer to experiment, has been reported by Labat *et al.*[27] using the HSE functional within an all electron framework but not accounting for relativistic effects. Assuming that relativistic effects on PBE0 and HSE are similar (*i.e.* 0.26 eV), one would expect a non-relativistic HSE band gap of 2.69 eV to be obtained with the NAO light tier1 basis set, very close to the value of Labat *et al.*[27] This is an additional confirmation of the importance of including scalar relativistic effects in all electron density functional theory based calculations when including elements with Z>19.

*c) Atomic and electronic structure of oxygen vacancies in wurtzite*

The oxygen vacancy in ZnO has been the subject of several studies and of some controversy as well as discussed by Gallino *et al.*[25] For the $V_O$ in ZnO we discuss first the calculated values of the energy formation ($E_f$) calculated as indicated in the preceding section. Previous studies have determined $E_f$ for ~ 1% concentration but using a GGA functional, a PW basis set and describing the cores through the PAW method.[53] This type of calculations found a contraction of Zn atoms surrounding the $V_O$, plus little dependency on the number of neighbouring cells relaxed. The same situation is found here for all considered supercells when carrying out the calculations at the PBE level. However, present and previous calculations at the PBE level find that the electrons left on the material upon removal of a neutral O atom are loosely localized. This is not unexpected from previous GGA calculations for F centers on different systems.[17] Table 3 reports $E_f$ values for different supercells obtained at the PBE and PBE0 level. For a supercell size similar to that used in previous work (4×4×2 *versus* 4×4×3) the present and previous $E_f$ values predicted from GGA calculation are very similar with the 0.18 eV difference attributed to different basis set and **k**-points density. Note, however, that extending the supercell size from 4×4×2 (1.56% $V_O$) to 6×6×3 (0.46% $V_O$) results in an unexpected significant lowering of $E_f$ from 7.19 to 6.61 eV, the

change being much larger than when going from 12.5% $V_O$ concentration to 1.56%. This is a clear indication that the GGA functional is introducing an artifact in the description of F centers in ZnO which is confirmed by the PBE0 values also reported in Table 3 displaying almost converged values with $V_O$ concentration. The present PBE0 values are relative to the energy of the supercell with and without the O vacancy and the energy of atomic oxygen in its triplet ground state. This choice is unambiguous and provides a clear cut value. Note, that this is different from the definition of Van de Walle and Neugebauer,[54] which makes use of the oxygen chemical potential as reference and is better suited to investigate the variation of $E_f$ with experimental conditions as in subsequent work by Clark *et al.*[55] using a screened exchange DFT approach.

In order to compare to previous work it is, however, necessary to use yet another different reference. Thus, the non relativistic all electron B3LYP calculations of Gallino *et al.*,[25] carried out using a GTO basis set lead to an $E_f$ value of 3.5 eV with respect to one half the energy of the $O_2$ molecule, which corresponds to oxygen rich conditions.[56] This value is in fair agreement with the one reported by Alkauskas and Pasquarello[56] (3.6 eV) using a modified hybrid functional including 32% of Fock exchange, a plane wave basis set, and norm conserving pseudopotentials. However, using the same reference, a somewhat higher value of 4.1 eV is obtained from present scalar relativistic PBE0 all electron calculations (3.8 eV at the PBE level) with the differences necessarily attributed to the limited basis set, the different amount of Fock exchange, the lack of relativistic effects in the B3LYP calculations, and to the different amount of Fock exchange and computational setup used by Alkauskas and Pasquarello.[56] It is also necessary to point out that Janotti and Van de Walle[57] reported a larger value (4 eV) using the same reference and the LDA+U method, which nevertheless severely underestimates the ZnO band gap. Finally, we note that Oba *et al.*[28] reported a very low $E_f$ value (0.9 eV at the PBE0) level using plane wave basis set and the PAW description of the atomic cores. A low $E_f \sim 1.0$ eV value was also reported by Lany and Zunger using a GGA method.[58] On the basis of the results discussed above, such a low value is hard to understand. Here it is worth commenting that $E_f$ decreases by decreasing the oxygen chemical potential, although extremely low, almost unphysical, oxygen partial pressures are required to reach such low values.[25] Clearly, the $E_f$ value represents a difficult quantity very sensitive to the computational method, a feature that can

confirmed by inspecting the recent review by Oba *et al.*[59] Below we will argue that, in part, this may be understood from the different degree of localization predicted by the different functionals with a concomitant difference in the relaxation of the atoms in the supercell in response to the presence of the point defect. Henceforth, from the available literature and present results, a physically reasonable value for the oxygen vacancy formation, relative to half the energy of the oxygen molecule, on oxygen rich conditions, can proposed as 3.6 ± 0.5 eV.

Previous quantum mechanical studies beyond the LDA or GGA approximations carried out using periodic[25,28,60] or embedded cluster[61] models have presented strong evidence that the creation of an O vacancy in ZnO results in the appearance of well localized state in the gap. In order to analyze in some detail the degree of localization we first briefly discuss the atomic relaxation introduced by the removal of one oxygen atom from the 4×4×2 supercell. In the wurtzite structure each O anion is surrounded by four Zn cations forming a tetrahedron. At the relativistic, all electron, PBE0 level of theory the Zn-Zn distance in bulk is 3.232 Å (3.276 Å at the PBE level) which, upon O removal becomes 2.942 Å (2.980 Å at PBE level), implying an inwards relaxation of 9.03% (8.96% at the PBE level), in agreement with the results reported by Gallino *et al.*[25] The slightly larger contraction predicted by the PBE is consistent with a larger delocalization of the two electrons lefts on the crystal upon removal of one neutral oxygen atom. At the PBE0 these electrons are localized around the cavity (Figure 2, bottom panel) resulting in a clear and well defined state in the band gap located ~0.5 eV above the top of the valence band (Figure 3), fully consistent with the description provided by Gallino *et al.*[25] Note also that at the PBE level this state is barely a continuation of the valence band (Figure 3) with an artificial delocalization which is clearly seen in the top panel of Figure 2, implying a decrease of the Pauli repulsion between the Zn cations that are surrounding the cavity. The increased Pauli repulsion with the localized electron density at the cavity is precisely the reason for a slightly smaller atomic relaxation. This degree of localization depends strongly on the type of exchange-correlation functional used and is at the heart of the problems encountered when aiming at describing this point defect.

**Conclusions**

The atomic and electronic structure of stoichiometric and reduced ZnO wurtzite has been studied using a periodic relativistic all electron hybrid density functional

(PBE0) approach and numeric atom-centered orbital of light Tier-1 quality. Results have been presented evidencing that, from a variational point of view, the basis set chosen has a completeness comparable to that of the aug-cc-pVDZ broadly used in accurate molecular quantum chemical calculations.

The equilibrium atomic structure predicted from this computational approach is in very good agreement experiment and with previous calculations,[25-30] especially with those including relativistic effects indirectly through the pseudopotential with some small difference with respect to values predicted from non relativistic all electron calculations using the same PBE0 functional. The calculated band gap is ~0.2 eV smaller than experiment but, again, in very good agreement with previous calculations including relativistic calculation through the pseudopotential and ~0.25 eV smaller than the value predicted from non-relativistic all electron calculations using the same PBE0 hybrid functional. This is a clear indication of possible sources of error in non-relativistic all electron density functional calculations for systems containing elements with relatively high atomic number.

Regarding oxygen vacancies in ZnO, the present work shows that formation energy converges rather fast with the size of the supercell but only when using a hybrid functional, which is a consequence of the artificial delocalization of the electron density arising from the removed oxygen atoms when using a GGA type functional. The formation energy relative to one half the energy of the oxygen molecule is in agreement with previous hybrid DFT results although somewhat higher which might be related to the effect of scalar relativistic effects.

The electronic structure of the oxygen vacancy predicted from the present relativistic all electron hybrid density functional calculations evidences the presence of localized electrons in the cavity left by the removed oxygen atom with a concomitant well localized peak in the density of states ~0.5 eV above the top of the valence band and a significant relaxation of the Zn atoms near to the oxygen vacancy. Qualitatively, the description emerging from the present work is in full agreement with previous hybrid density functional calculations.[25]

From a computational point of view, it is important to highlight that the present work shows that accurate results can be obtained in systems involving large supercells containing up to 432 atoms using a numeric atomic centered orbital basis set within a full all electron description including scalar relativistic effects at an affordable cost.

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**Table 1.-** Total energy (eV) of the O and Zn atoms and of the diatomic $O_2$ and ZnO molecules at different levels of theory and using the light Tier-1 NAO and aug-cc-pVDZ basis sets. The internuclear distances are 1.70004 Å for ZnO and 1.19800 Å for $O_2$, and correspond to the PBE0 optimized value using the NAO basis set. For comparison all calculations are non relativistic.

| Species | Method | light-tier1 | aug-cc-pvdz |
|---|---|---|---|
| O | HF | -2035.632661 | -2035.320222 |
| | PBE | -2041.220977 | -2040.613346 |
| | PBE0 | -2041.423202 | -2040.860771 |
| $O_2$ | HF | -4072.509541 | -4072.018779 |
| | PBE | -4088.496175 | -4087.401852 |
| | PBE0 | -4088.067839 | -4087.057286 |
| Zn | HF | -48376.513582 | -48377.698958 |
| | PBE | -48413.990504 | -48413.641224 |
| | PBE0 | -48414.165884 | -48414.047656 |
| ZnO | HF | -50410.354949 | -50411.222025 |
| | PBE | -50457.204294 | -50456.271778 |
| | PBE0 | -50456.844396 | -50456.198592 |

**Table 2.-** Structural parameters (*a* and *c* in Å, and α and γ angles in degrees) of bulk ZnO wurtzite as predicted by the density functional theory based calculations with the PBE0 exchange-correlation potential and different basis sets and treatment of core electrons. AE stands for all electron, PAW for projected augmented wave description of cores, NAO for numeric atom-center orbital (light Tier-1 quality), PW for plane wave basis sets, and GTO for Gaussian type orbitals. Experimental values are given for comparison. Experimental values are taken from. Ref. 37.

| | **AE/NAO (this work)** | **AE/GTO[27]** | **PAW/PW[28]** | **Experiment** |
|---|---|---|---|---|
| *a* | 3.252 | 3.263 | 3.257 | 3.242 |
| *c* | 5.223 | 5.195 | 5.223 | 5.188 |
| $\alpha$ | 90 | 90 | 90 | 90 |
| $\gamma$ | 120 | 120 | 120 | 120 |

**Table 3.-** Supercells employed to model $V_O$ vacancies in ZnO, **k**-points meshes used, concentration of $V_O$ in %, and formation energies with respect to the reference of atomic oxygen as indicated in the text ($E_f$, in eV) as predicted by DFT calculations using the PBE and PBE0 functionals.

| Supercell | k-points | % $V_O$ | $E_f$ (PBE) | $E_f$ (PBE0) |
|---|---|---|---|---|
| 2×2×1 | 9×9×17 | 12.50 | 7.31 | 7.33 |
| 4×4×2 | 5×5×3 | 1.56 | 7.19 | 7.30 |
| 6×6×3 | 1×1×1 | 0.46 | 6.61 | 7.26 |
| 4×4×3[a] | 2×2×2 | 1.04 | 7.01 | — |

[a] (Ref. 53)

**Figure 1.-** Trend of Kohn-Sham band gap ($E_g$, in eV) *versus* the percentage of Fock exchange (%HF) at the experimental ZnO wurtzite crystal structure.

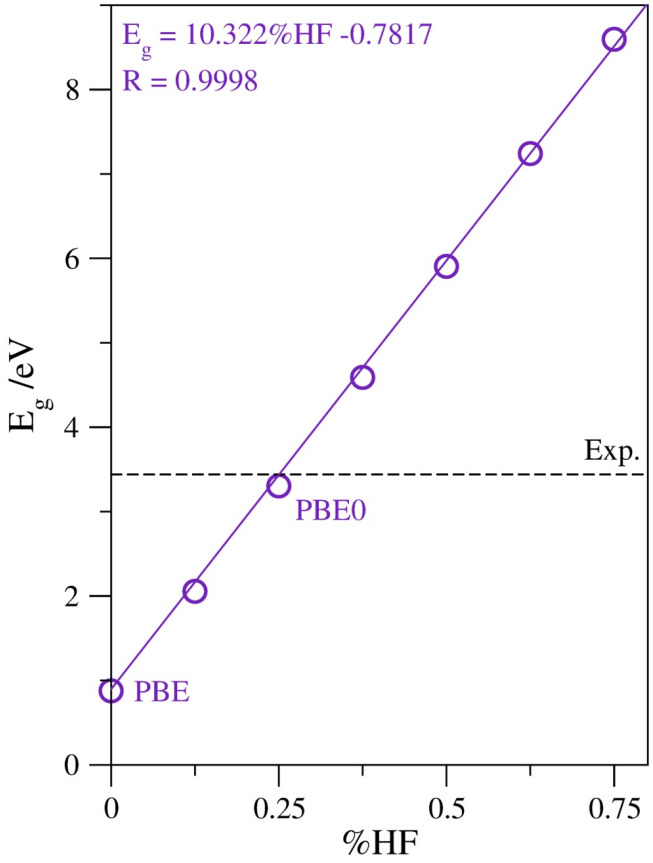


**Figure 2.-** Plot of the electron density corresponding to highest occupied level for a single $V_O$ using 4×4×2 supercell at relativistic all electron PBE (top) and PBE0 (bottom) levels. Yellow isosurfaces belong to isovalues of 0.0005 e/Å$^3$. Iceblue and pink spheres denote Zn and O atoms, respectively.

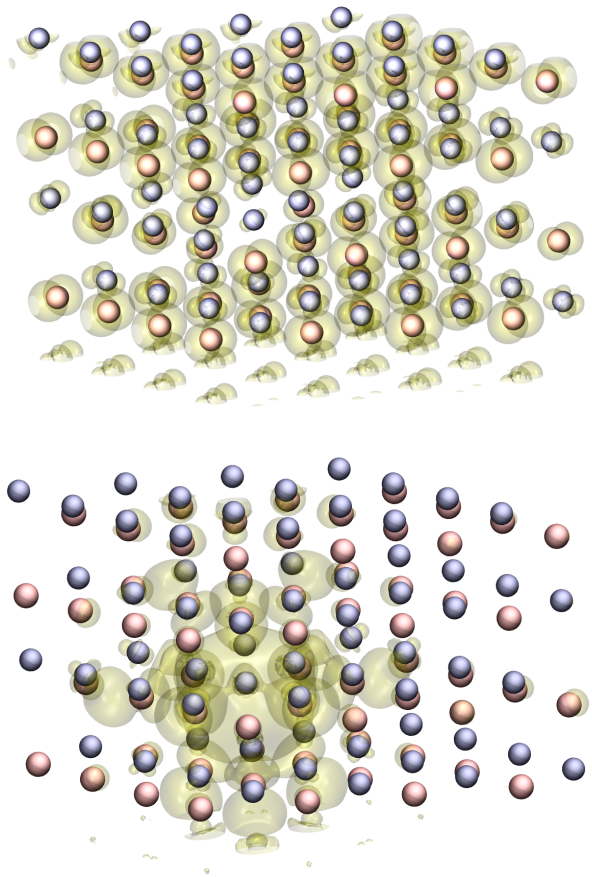
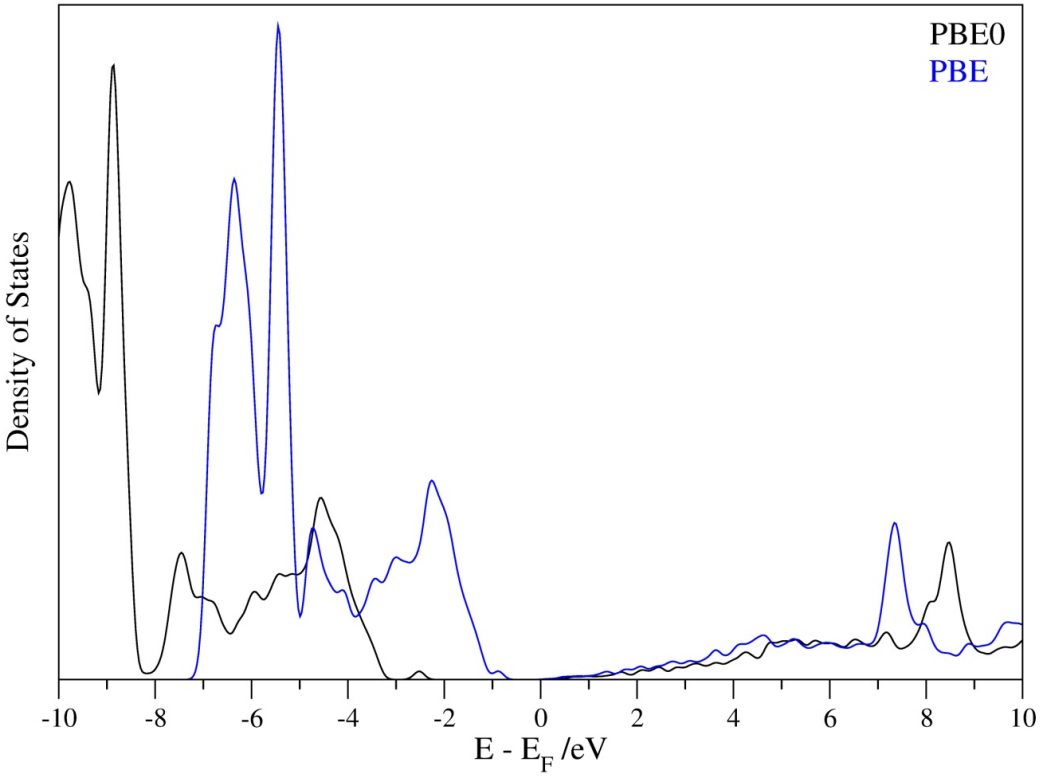


**Figure 3.-** Total density of states of the ZnO 4×4×2 supercell containing one oxygen vacancy as obtained from relativistic all electron PBE0 (black) and PBE (blue) density functional theory based calculations. The different densities of states have been leveled equaling the bottom of the conduction band to the Fermi level, $E_F$.



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## Graphical Abstract

All electron periodic density functional theory calculations carried out using a numerical atomic centered orbital basis set and hybrid functionals highlight the role of relativistic effects on band gap estimations of semiconductors. This is illustrated on stoichiometric and reduced ZnO where explicit inclusion of relativistic effects through the ZORA approach reduce the band gap by 0.25 eV.