The effects of including the Hubbard on-site Coulombic correction to the structural parameters and valence energy states of wurtzite ZnO was explored. Due to the changes in the structural parameters caused by correction of hybridization between Zn d states and O p states, suitable parameters of Hubbard terms have to be determined for an accurate prediction of ZnO properties. Using the LDA+U method by applying Hubbard corrections $U_p$ to Zn 3d states and $U_p$ to O 2p states, the lattice constants were underestimated for all tested Hubbard parameters. The combination of both $U_d$ and $U_p$ correction terms managed to widen the band gap of wurtzite ZnO to the experimental value. Pairs of $U_p$ and $U_p$ parameters with the correct positioning of d-band and accurate bandwidths were selected, in addition to predicting an accurate band gap value. Inspection of vibrational properties, however, revealed mismatches between the estimated gamma phonon frequencies and experimental values. The selection of Hubbard terms based on electronic band properties alone cannot ensure an accurate vibrational description in LDA+U calculation.
1 Introduction

Zinc oxide had been known as a relatively low cost and readily synthesized material. It has the properties of a polar semiconductor with a wide band gap of 3.44 eV with potential applications in the optoelectronic industries [1]. Numerous theoretical calculation on the properties of ZnO had been carried out using density functional theory (DFT). However, it is widely known that a standard DFT calculation typically suffers from a band gap problem, where the band gap of a material is grossly underestimated [2]. This could lead to an inaccurate estimation of the electronic properties of a material such as ZnO, which is a potential material for the optoelectronic industry.

The band gap problem of DFT calculation can be addressed by including the GW approximation in which the self-energy of a many-body system of electrons is taken into account [3]. Zhang et al. estimated that the band gap of wurtzite ZnO to be within the range of 2.82 eV to 4.54 eV by using various types of GW approximations [4]. An alternative way to improve the band gap is to employ the hybrid exchange correlation functionals in a DFT calculation. Using the HSE06 functional, Zhou predicted the band gap of wurtzite ZnO to be 2.79 eV [5]. While both GW approximation and hybrid functional have proved to be effective in mitigating the band gap in a standard DFT calculation, a major downside is the requirement of a computational power much higher than that required by a standard DFT computation. This has limited the feasibility of conducting a realistic prediction of properties of a material via DFT.

DFT+U calculation has emerged as a means to improve the electronic properties prediction at a computational cost comparable to that required by a standard DFT calculation. In a DFT+U calculation, Hubbard-type interactions are included in the standard exchange correlation functional of local density approximation (LDA) or generalized-gradient approximation (GGA) through the Hubbard parameters $U$ and $J$ [6, 7]. A method of estimating the values for the Hubbard parameters $U$ and $J$ had been provided by Cococcioni et al. through the linear response approach [8]. However, the linear response approach, which has been widely used for the open shell system, is less than ideal in the case of a closed-shell system such as ZnO with a full electronic shell of d orbitals. Numerical reliability is an issue of concern in the case of completely full localized bands which exhibit a very small response to linear perturbation [9].

In this work, the dependence of structural parameters and electronic properties of wurtzite ZnO on the different values of Hubbard parameters $U$ and $J$ is investigated. A series of DFT+U calculation is carried out with different values of both Hubbard parameters associated with Zn and O. While the Hubbard parameters are introduced to improve
electronic properties, the structural parameters of a material are modified alongside with the electronic properties; the selection of suitable values of Hubbard parameters depends on the both structural and electronic properties. A similar work on the LDA+U and GGA+U calculation of wurtzite ZnO had been carried out by Huang et al. [10] by using the electronic calculation package VASP. However, different results are obtained in this work through the use of different pseudopotentials.

2 Computational Methods

The experimental structural parameters of wurtzite ZnO at $a=3.2427$ Å and $c=5.1948$ Å with wurtzite parameter $z=0.3826$ as discovered by Sabine and Hogg [11] using X-ray crystallography method is used as the reference structural data in this work. A standard DFT geometrical optimization is first performed on the primitive wurtzite ZnO unit cell, followed by a self-consistent DFT calculation to study its electronic properties. Hubbard term $U_d$ is then added to the d-orbitals of the Zn atoms, ranging from 2 eV to 14 eV in the interval of 2 eV. The second part of this research studies the effect of including both Hubbard term $U_d$ to Zn d-orbitals and $U_p$ to O p-orbitals, where the $U_p$ values ranges from 5 eV to 9 eV. The changes to lattice constants and wurtzite parameter $z$ as well as the band gap and valence band width are investigated.

All calculations in this work are completed using the ABINIT electronic package [12] within the framework of projector-augmented-wave (PAW) potentials [13] and LDA exchange correlation functionals. The PAW potentials used are from the datasets provided by Jollet et al. [14]. The plane wave basis sets are expanded to kinetic energy cutoff of 34 Hartree whereas the Monkhorst-Pack k-point mesh is set to an array of $8 \times 8 \times 6$ at gamma centred grid.

The LDA+U calculations are performed using full localized limit (FLL) double-counting correction [6]. The double-counting correction is necessary in a LDA+U calculation to avoid double counting of correlation part in localized electrons. The Hubbard term $J$ is set to zero for all calculations; the rotationally invariant LDA+U form proposed by Dudarev et al. [7] is equivalent to the FLL method with $J=0$ and $U$ in place of $\bar{U} - \bar{J}$ [15].

3 Results and Discussion

3.1 Standard DFT result

Wurtzite ZnO possesses a space group number of 186 with hexagonal symmetry and the following Wyckoff positions (see Table 1). $z$ is the wurtzite parameter to be determined using
Table 1Wyckoff positions of atoms in the primitive unit cell of wurtzite ZnO

| Atom | Wyckoff letter | Wyckoff positions                  |
|------|----------------|-----------------------------------|
| Zn   | 2b             | (1/3,2/3,0), (2/3,1/3,1/2)        |
| O    | 2b             | (1/3, 2/3, z),(2/3,1/3, z+1/2)     |

DFT geometrical optimization. The result obtained from a DFT geometrical optimization followed by a self-consistent calculation is compared with the corresponding experimental results in Table 2. The primitive unit cell volume is underestimated by 4.45% compared to the experimental volume, which is typical of a LDA calculation due to overbinding in estimation for solids [17]. While both $a$ and $c$ lattice constants are estimated to be lower than the experimental values, the hexagonal unit cell is noticed to have experienced elongation of approximately 1% in the $c$ axis by comparing the $c/a$ ratios. Regarding the atomic positions within the unit cell, the heights of the two oxygen atoms are predicted to be lower by about 0.0113 Å, due to the lower value of wurtzite parameter $z$ found by LDA. On the other hand, the electronic band gap value is predicted to be only approximately a quarter of the experimental value, which is a serious underestimation known the “DFT band gap problem” as alluded to earlier.

Table 2Comparison between the experimental result of wurtzite ZnO and the result from standard DFT LDA calculation.

| $a$ (Å) | $c$ (Å) | $c/a$ | $z$     | Volume (Å$^3$) | Band gap (eV) |
|---------|---------|-------|---------|---------------|---------------|
| Experiment* | 3.2427  | 5.1948 | 1.6020  | 0.3826        | 47.3056       | 3.44          |
| LDA     | 3.1836  | 5.1497 | 1.6175  | 0.3804        | 45.2022       | 0.7965        |

* The values for $a$, $c$, $c/a$ and $z$ are taken from Ref [11], whereas the band gap value is from Ref [16].
Figure 1  Variation of (a) lattice constant $a$ and $c$, (b) $c/a$ ratio and wurtzite parameter $z$ with respect to $U_d$.

3.2 Inclusion of Hubbard parameter $U_d$ to Zn

The dependence of the lattice constant $a$ and $c$ and the $c/a$ ratio on $U_d$ is shown in Figure 1. It shows that lattice constant $a$ increases whereas the lattice constant $c$ decreases monotonically with the increment in the value of Hubbard term $U_d$ applied to the Zn d-orbitals. However, the trend lines of the figures never reach the point of experimental values, which are 3.2427 Å for $a$ and 5.1948 Å for $c$. While the values of lattice constant $a$ do increase with $U_d$, the rate of increment is not high enough to reach the experimental value even at $U_d=14$ eV. The increasing trend of lattice constant $a$ is also in contrast to the decreasing trend found by Huang et al. [10] in a similar study using VASP within the PAW framework. Despite the mismatch of $a$ and $c$ values, the $c/a$ ratio does approaches the experimental value of 1.6020 between $U_d$ values of 10 eV and 12 eV in its decreasing trend. The wurtzite parameter $z$ increases with the value of $U_d$, approaching but not reaching the experimental value of 0.3826.

The change in band gap with respect to $U_d$ value is portrayed in Figure 2. The band gap is shown to steadily increase to the highest value of 1.81 eV at $U_d=14$ eV. Despite the role of the Hubbard term $U_d$ in interaction between localized electrons, the estimated band gap is still too small with respect to the ZnO experiment value of 3.44 eV at low temperature; the estimated value is only approximately one half of the real value. Nevertheless, our estimation of the structural parameters and band gap is in good agreement with the LDA+$U$ results found by Kaczkowski [18].
3.3 Inclusion of Hubbard parameter $U_d$ to Zn and $U_p$ to O

The dependence of the structural parameters upon the application of on-site Coulomb correction $U_p$ on the O $p$-orbitals is shown in Figure 3. In contrast to the reduction of lattice constant $a$ with increasing $U_d$, the lattice constant drops monotonically with increasing $U_p$ at all fixed values of $U_d$ due to stronger localization of the electron states, in agreement with the results produced by Huang et al. [10] and Ma et al. [19]. The same trend is observed for lattice constant $c$, in which the height of the hexagonal unit cell deviates from the experimental value of 5.1948 Å with increasing $U_p$. On the contrary, the correlation between $c/a$ ratio and estimated wurtzite parameter $z$ with $U_p$ is weak; the changes in the said parameters are insignificant. The reduction in the volume of unit cell is revealed to be isotropic along both $a$ and $c$ axis directions.

The influence of $U_p$ on the p-d hybridization is evident by inspecting the band gap as shown in Figure 4. There is a huge enhancement in the magnitude of the electronic band gap with the increment with value of $U_p$. The rate of band gap widening is high enough that the estimated band gaps have exceeded the corresponding experimental value; the higher the $U_d$ value, the lower the magnitude of $U_p$ needed to widen the band gap to match the experimental gap of 3.44 eV. Further investigations on the electronic band properties are needed for the selection of suitable values of $U_d$ and $U_p$. Our result here is in contrast to that found by Ma et al. [19], in which the increment of $U_d$ to 12.5 eV in GGA+U method is sufficient to obtain a band gap that matches with that of experiment.

Analysis of projected density of states (PDOS) is done to ascertain the modification of the electronic band due to addition of Hubbard terms. A few sets of $U_d$ and $U_p$ values are selected.
Figure 3  Variation of (a) lattice constant $a$, (b) lattice constant $c$, (c) $c/a$ ratio and (d) wurtzite parameter $z$ with the Hubbard term $U_p$ applied to O p-orbitals with fixed $U_d$ values. The dash line corresponds to the corresponding experimental values.

for their capability to reproduce band gap value close to the corresponding experimental value of 3.44 eV. The PDOS diagrams in Figure 5 with the corresponding analysis tabulated in Table 3 show that the position of the cationic Zn d-band is heavily dependent on the selection of the values of Hubbard terms. The addition of Hubbard terms effectively lowers the position of the Zn 3d states to mitigate the artificially strong hybridization with O p states provided by inadequate description in LDA. $U_d=10$ eV is shown to be able to produce the d-band energy in good agreement with experiment whereas $U_d=9$ eV produces a shallower d-band energy level and $U_d=12$ eV overestimates the magnitude of the d-band energy by 1 eV. All test cases produced narrower cation d-band bandwidth and anion p valence bandwidth compared to experiments, particularly for the d-band bandwidth. The internal band gap
Figure 4  Variation of band gap with respect to Hubbard parameter $U_p$ applied to O p-orbitals with fixed $U_d$ values.

Table 3  Estimated structural parameters and electronic band properties based on selected $U_d$ and $U_p$ values (in eV) matched to the experimental band gap of 3.44eV. $E_d$: cation d-band positions. $W_d$: cation d-band bandwidth. $W_p$: anion p valence bandwidth (in eV). The experimental values are referred from Ref [20-22].

| $U_d$ | $U_p$ | a (Å) | c (Å) | c/a | z    | $E_d$ | $W_d$ | Internal gap | $W_p$ | Valence bandwidth |
|------|------|------|------|-----|-----|------|------|--------------|------|------------------|
| 9.0  | 7.99 | 3.110| 4.985| 1.603| 0.3812| 7.495| 1.968| 0.946        | 5.161| 8.075           |
| 9.5  | 7.86 | 3.113| 4.987| 1.602| 0.3813| 7.685| 1.931| 1.208        | 5.102| 8.242           |
| 10.0 | 7.74 | 3.115| 4.988| 1.601| 0.3815| 7.875| 1.888| 1.387        | 5.137| 8.412           |
| 12.0 | 7.30 | 3.124| 4.995| 1.600| 0.3820| 8.740| 1.837| 2.369        | 4.998| 9.204           |
| Experiment | 3.2427 | 5.1948 | 1.602 | 0.3826 | 7.8 | 2.5 | 1.2 | 5.3 | 9 |

between the d states and p states is another quantity sensitive to the change in the Hubbard terms values, directly affecting the position of the adjacent d-bands and hence p-d coupling strength. The test case corresponding to $U_d=9.5$ eV and $U_p=7.86$ eV produces an accurate internal band gap comparable to the experimental value 1.2 eV. The valence bandwidths have increased with the values of $U_d$, even though the cation d-band bandwidth and anion p
valence bandwidth both decrease. This is explained by noticing that the internal band gap expands with a much higher rate compared to the narrowing of both d and p bandwidth as $U_d$ increases. Taking the d-band energy position and the sensitive internal band gap as a benchmark, either the pair of $U_d=9.5$ eV and $U_p=7.86$ eV or $U_d=10.0$ eV and $U_p=7.74$ eV is the optimum choice for estimation of accurate band gap, which is close to the choice of Huang et al. [10].

Figure 6 shows the overlap between the band structures obtained using both the standard LDA and LDA+$U$ with selected $U_d=10.0$ eV and $U_p=7.74$ eV, aligned to the fermi energy level. The conduction band minimum (CBM) is exactly similar in terms of width and dispersion for both calculations, differing only by a translation of energy in LDA+$U$ due to widening of band gap. The two curves almost overlap at the valence band maximum (VBM), but slight deviation starts to appear at 4 eV below the fermi energy level. The similar dispersions observed for both calculations at CBM and VBM indicate the effective mass of electrons and holes at each region is not affected by the application of the Hubbard terms. Narrowing of the lower valence bands is observed for the LDA+$U$ results compared
Comparisons between the band structures obtained from a standard LDA calculation and a LDA+U calculation with $U_d=10$ eV and $U_p=7.74$ eV. To that of LDA, which is consistent with the reduction in cation d-band bandwidth in the PDOS in Figure 5.

The investigation is finalized by extending our work to vibrational properties of wurtzite ZnO at the center of Brillouin zone with the optimum $U_d=10.0$ eV and $U_p=7.74$ eV pair. An analysis of the gamma phonon mode Table 4 reveals mismatch between experiment phonon frequencies estimated by LDA+U using linear response method. Compared to LDA, LDA+U overestimates the gamma point frequencies by about 10% for the higher lying modes. It is noticed that gamma phonon modes frequencies in good agreement with experiment is reproduced by PBE+U calculations [23, 24]. The choice of change correlation functional plays a huge role in the accurate description of the underlying electrostatics and vibrational properties of a system. On the other hand, LDA+U correctly reproduces the correct order of gamma centered phonon mode, in contrast to the higher frequency B1 mode estimated by LDA.

4 Conclusion

This study attempts to identify suitable values of Hubbard parameters in order to produce an accurate band gap estimate for wurtzite ZnO. It is noticed that the predicted lattice constant $a$ and $c$ and wurtzite parameter $z$ is low compared to experiment with the addition of $U_d$ alone. The same is true for the band gap which is still very low. The addition of Hubbard term $U_p$ serves to increase the band gap on par with the magnitude of experimental value, but with the same underestimation of lattice constants. By constraining the band gap
Table 4  Phonon mode frequencies (in cm\(^{-1}\)) at Gamma point of Brillouin zone.

| Mode   | LDA  | LDA+U | Experiment [25] |
|--------|------|-------|-----------------|
| E\(_2\) | 92.5 | 112.1 | 98.4           |
| B\(_1\) | 258.4| 299.4 | 258.9          |
| A\(_1\)(TO) | 376.5| 433.5 | 378.3          |
| E\(_1\)(TO) | 415.8| 466.5 | 412.1          |
| E\(_2\) | 447.9| 495.9 | 438.8          |
| B\(_1\) | 544.7| 623.4 | 551.7          |
| A\(_1\)(LO) | 513.6| 638.4 | 573.5          |
| E\(_1\)(LO) | 532.6| 646.9 | 592.8          |

to that of experiment, the d-band energy value and the bandwidths for cationic d states and anion p valence states appear to approximate that of experiment with the pairs of \(U_d=9.5\) eV and \(U_p=7.86\) eV as well as \(U_d=10.0\) eV and \(U_p=7.74\) eV, depending on the benchmarking parameters. The internal band gap is very sensitive to the changes in Hubbard terms, directly affecting the d-band level and the hybridization between d and p orbitals. However, the mismatch between predicted gamma point phonon frequencies and the corresponding experiment values illustrates the need of caution of applying LDA+\(U\) calculation to wurtzite ZnO in describing its vibrational properties.

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