



Ab - Initio Calculations of the Electronic, Transport, and Bulk Properties of Cubic Boron Nitride

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ABSTRACT

We present results from ab-initio, self consistent, local density approximation (LDA) calculations of electronic and related properties of cubic boron nitride (zb-BN). We employed the Ceperley and Alder LDA potential and the linear combination of atomic orbitals (LCAO) formalism in our non-relativistic computations. We solved the system of LDA equations self-consistently, through the implementation of the LCAO formalism, following the Bagayoko, Zhao, and Williams (BZW) method as enhanced by Ekuma and Franklin (BZW-EF). The BZW-EF method includes a methodical search for the optimal basis set that yields the absolute minima of the occupied energies. This search entails increasing the size of the basis set and the related modifications of angular symmetry and of radial orbitals. Our calculated, indirect band gap of 6.48 eV, from the Γ to the X points, and bulk modulus of 375 GPa are in excellent agreement with corresponding experimental values at room temperature (RT). The calculated widths of the lowest valence band and that of the entire valence bands of 5.65 eV and 20.26 eV are in excellent agreement with the measured values of 5.5 eV and 20 eV, respectively. We have also calculated electron and hole effective masses for zb-BN, and the total (DOS) and partial (pDOS) densities of states.

Indexing terms/Keywords

Boron Nitride; DFT; electronic structure

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1. INTRODUCTION

BN is a compound semiconductor material with many applications in advanced technologies. The only two stable phases of boron nitride found in nature are the *zb*-BN and hexagonal (*h*-BN) ones. In its zinc-blende (sp^3 bonded) phase, BN is a material that exhibits many properties similar to those of diamond. Owing to its wide band gap (6.2 eV), excellent thermal and chemical stability, high oxidation resistance, and bulk modulus of 372.3 GPa, *zb*-BN is well-suited for many high power and temperature applications as well as abrasives for cutting tools [1].

Experimental studies aimed at the fabrication of *zb*-BN, the first of which dates as far back as 1957 [2], used a high temperature high pressure (HTHP) apparatus, with *h*-BN as a starting material [3]. To the best of our knowledge, Chrenko [4] reported the first measurement of the band gap energy (6.4±0.5 eV), based on ultraviolet and infrared absorption spectra obtained at RT for thin (24 μm) and thick (600 μm) samples. Since then, a number of experimental works have reported band gap values ranging from 6.0±0.5 to 6.27±0.02 eV, measured by various optical characterization techniques including X-ray K-emission spectroscopy [5], soft X-ray emission spectroscopy [6] (SXES), optical absorption edge measurements [7], ultraviolet (UV)-visible reflectance and transmittance spectroscopy [8, 9], and UV luminescence spectroscopy [10]. The range of reported band gap values is presumed to be attributed to differences in growth conditions (i.e. temperature and pressure) and the nature of the sample (i.e. thickness, surface area and morphology, impurities, etc). In addition to the relatively good agreement found amongst the measured band gap values, it is also critical to accurately determine additional parameters associated with the electronic structure of a material such as the bandwidth. The bandwidth can be used to describe the degree of localization in an electron system and is arguably the most important parameter associated the electronic structure of a material. The SXES measurements of Agui *et al* [6] reported upper, lower and total valence bandwidths for *zb*-BN of 13.0 eV, 5.5 eV, and 20 eV, respectively. Another material parameter that can be measured directly and is impacted by the electronic structure is the bulk modulus. Therefore, it is important to note here that the bulk modulus of *zb*-BN has been measured by E. Knittle *et al* [11] to be 369±14 GPa at a lattice constant of 3.615±0.002 Å. In a stark contrast with the relatively good agreement found amongst measured band gaps of *zb*-BN, calculated band gap values vary significantly, depending on the computational approach, the choice for the potential, and various adjustment of fitting procedures.

Theoretical studies of *zb*-BN have had difficulty in reproducing the measured band gap values for *zb*-BN. Accurate, theoretical predictions of band structures and related properties are essential for the development of semiconductor based devices by avoiding the need for expensive and time-consuming experimental trials and errors. Theoretical investigations of the electronic structure of *zb*-BN date as far back as 1967, when D.R. Wiff and R. Keown published results from augmented plane wave calculations (APW), as described by Slater and Wood. They found a band gap energy of 4.5 eV, using the RT lattice constant of 3.615 Å [12]. Tsay *et al.*, employing a nonlocal, empirical-pseudo-potential method, found a band gap of 8.0 eV, with a width of the upper valence sub bands of 14.0 eV [13]. Dovesi *et al.* reported exact-exchange Hartree-Fock (EE-HF) calculations within a linear combination of atomic orbitals (LCAO) formalism. Their self-consistent, ab-initio method, at a lattice constant of 3.59 Å, gave a zero temperature band gap of 11.3 eV and a binding energy of -9.83 eV [14].

In recent decades, a number of LDA and generalized gradient approximation (GGA) calculations [15-17] have mostly underestimated the band gap of *zb*-BN. Li and coworkers employed a scissor operation of 1.9 eV to correct their theoretical band gap. Their calculations found band gap values of 4.39 eV, using a lattice parameter of 3.588 Å, and of 4.44 eV, using a lattice parameter of 3.638 Å for LDA and GGA, respectively [18]. Ahmed and coworkers found calculated band gaps of 4.35 eV, 4.47eV, 5.43 eV for LDA, GGA-PBE, and GGA-EV, respectively [19]. They used lattice parameters of 3.585 Å for the full potential-LDA calculations and 3.629 Å for the full potential-GGA calculations. The orthogonalized LCAO (OLCAO) method and the LDA potential employed by Xu *et al* [20]. led to an indirect band gap of 5.18 eV for *zb*-BN, along with upper, lower, and total valence bandwidths of 3.28 eV, 10.94 eV, and 21.1 eV, respectively. Chkhartishvili used a new version of the quasi-classical parameterization based on the screened Coulomb-like atomic potentials to calculate a band gap value of 7.1 eV, using a lattice parameter of 3.588 Å [21]. Various other theoretical calculations reported values ranging from 8.6 eV up to 11.3 eV [13, 14, 22]. Table 1 summarizes several of the above computational approaches, potentials, and resulting band gaps for *zb*-BN.

Table I. Previous, computational results for the indirect band gap of *zb*-BN, along with other experimental findings. Emphasis is placed on ab initio DFT calculations.

Formalism	Computational Method	E_g (eV)
APW	method described by Slater and Wood	4.5 [11]
LMTO	LDA-ASA (atomic sphere approximation)	4.42 [15]
Full Potential APW	LDA	4.4 [16]



Non-local Pseudo potential	LDA	4.20 [17]
Full Potential-APW	LDA	4.35 [19]
Exchange-Correlation Functional	LDA	4.39 [18]
OLCAO	LDA	5.18[20]
	GGA	4.44 [18]
Full Potential-APW + LO	GGA – PBE	4.47 [19]
	GGA-EV	5.43 [19]
Quasi-classical approach	Quasi classical limit	7.1 [21]
Non-local Pseudo potential	Empirical Pseudo potential	8.0 [13]
Composite wave variational version of APW	Tight-binding interpolation with iconicity	8.6 [22]
	Tight-binding interpolation without iconicity	9.16 [22]
LCAO	Exact Exchange Hartree Frock (HF)	11.3 [14]
Experiment	Measured by ultraviolet absorption spectra	6.4 ± 0.05 [4]

While experimental results for the band gap and other properties of *zb*-BN are in basic agreement, taking temperature, pressure, and film thickness into account, that is not the case for the findings from calculations, with emphasis on ab-initio density functional theory (DFT) ones. The calculated band gaps, for LDA and GGA potentials, mostly underestimate the measured band gap by 1 to 2 eV or more. This situation is a key motivation for our work. Specifically, we aim to aid in the removal of the significant discrepancy between measured and calculated band gaps for *zb*-BN. Previous successful applications of the distinctive feature of our calculations have accurately described [23-27] and predicted [27, 28] properties of over 25 semiconductors [29, 30]. Hence, we presume that the application of this method portends a likely success in describing *zb*-BN, with its particularly large band gap. In this paper, we present results from ab-initio calculations of electronic and related properties of *zb*-BN. Our method and computational details needed for a replication of our work are described in section II. The main results are presented in Section III and discussed in Section IV. A summary of our results and the conclusion are given in section IV

2. COMPUTATIONAL METHOD

Our calculations have features that are common to most others, i.e., the use of a DFT potential and of the LCAO formalism to construct the wave functions for the materials using those of atomic or ionic species that appear in them. The Ceperley and Alder [31] local density potential is one of the most accurate [i.e., exact], due to the extensive Monte Carlo calculations that led to it. The specific parameterization we selected is that of Vosko, Wilk, and Nausair (VWN) [32]. The feature that drastically sets apart our calculations consists of their strict application of the BZW [23, 25-27] method and its enhancement known as BZW-EF[24, 29, 30]. We trace differences between our findings and those from other calculations to the use of this method. For that reason, we briefly describe it below.

The original BZW method is thoroughly described in the literature [23, 33] while the enhancement is expounded upon by Ekuma *et al* [29] and Franklin *et al* [30] Upon performing self consistent calculations of electronic properties of the atomic or ionic species present in a material, the method begins by selecting a small basis set to construct the solid state wave functions in the LCAO formalism. This initial basis set is not to be smaller than the minimum basis set, i.e., the one just large enough to account for all the electrons in the atomic or ionic species in the material. Completely self consistent calculations are performed with this small basis set. It is understood that this basis set does not provide a correct description of the material. Its small size enables a methodical increase of the basis set in subsequent, self consistent calculations. So, Calculation I is followed by Calculation II that uses the basis set of Calculation I augmented by one atomic (ionic) orbital. For s, p, d, and f orbital, augmentation means the increase of the size of the basis set by 2, 6, 10, or 14, respectively, taking spin into account. The occupied energies from Calculations I and II are graphically and numerically compared. This comparison requires setting the Fermi energy to zero in both sets of eigenvalues. As expected, some occupied energies from Calculation II are always found to be lower than corresponding ones from Calculation I. The variational principle of DFT says that Calculation II is closer to a DFT description of the material as compared to Calculation I. Naturally, the question then arises whether or not Calculation III, upon augmenting the basis set of Calculation II, is going to give occupied eigenvalues that are even lower. So, Calculation III is always carried out and the resulting occupied energies are compared to those of Calculation II.

The above process of augmenting the basis set and of performing completely self consistent calculations continues until three consecutive calculations lead to the same occupied energies within our computational uncertainty of 5 meV.



The first of these three calculations (i.e., with the smallest of the three basis sets) is the one providing the DFT description of the material. The corresponding basis set is referred to as the optimal basis set. In DFT language, it is the one that yield the correct ground state charge density of the system, the pivotal “variable.” In the original BZW method, only two consecutive calculations were required to yield the same occupied energies. Upon stumbling on local minima in our studies of GaP and ZnS, the requirement extended to three consecutive calculations. Much larger basis sets obtained by augmenting the basis set of the last of the three Calculations do not change the occupied energies; they do lower some unoccupied energies on account of the Rayleigh theorem [34]. This extra lowering of unoccupied energies, while the charge density and the occupied energies do not change from their values obtained with the optimal basis set, is not a manifestation of a physical interaction. Rather, it straightforwardly follows from the Rayleigh theorem that states the following. Let the same eigenvalue equation be solved with N and $(N+1)$ basis functions, with the N functions entirely including in the $(N+1)$, then, the eigenvalues from the two solutions, ordered from the lowest to the highest, follow the relation $\lambda_i^{(N+1)} \leq \lambda_i^N$ for $i \leq N$. We ascribe the lowering of occupied and unoccupied energies to physical interaction embedded in the Hamiltonian up to the attainment of the absolute minima of the occupied energies. Upon reaching their absolute minima with the optimal basis set, the occupied energies no longer change upon an augmentation of the basis set. Then, given that the charge density does not change, successive calculations now solve the same eigenvalue equation and the Rayleigh theorem explains the lowering of some unoccupied energies.

The only remaining clarification relative to our method consists of the way in which the basis set is augmented. In the original BZW, we added orbitals to the basis set in the increasing order of the corresponding, excited energies in the atomic or ionic species in the material. Some extensive computations by Ekuma and Franklin led Bagayoko to the realization that the above way of augmenting the basis set was not necessarily the best. Indeed, for valence electrons in any multi-atom systems, the polarization of the p, d, and f orbitals clearly has primacy over the spherical symmetry of s orbitals. Hence, for a given principal quantum number and a given atomic site, BZW-EF adds the p, d, and f orbitals, if applicable, before the corresponding s orbital. In fact, this counter-intuitive approach should have been obvious to us before, given the role of the valence orbitals in the formation of the materials (in bonding) and their related “belonging” to more than one atomic site! With the above understanding of the distinctive feature of our calculations, we present our key results below.

3. RESULTS

The successive calculations we performed are shown in Table II, along with the orbitals utilized to construct the wave functions of the valence states and the resulting band gaps. We present the electronic band structure, the DOS, and pDOS in Figures 1, 2A, and 2B, respectively. The electronic energies at high symmetry points are given in Table III. Finally, the total energy curve is discussed using Figure 3.

3.1 Electronic Energy Bands, Band Gap, and Effective Masses of zb-BN

The content of Table II shows the steps in our implementation of the LCAO formalism following the BZW-EF method. Namely, the initial charge density for zb-BN was calculated using the atomic orbitals of B ($1s^2, 2s^2, 2p^0$) and N ($1s^2, 2s^2, 2p^4$). We then repeated the self-consistent calculation using the above basis set augmented by an orbital describing the applicable, excited state of an ionic species. Hence, N ($3p^0$) orbital was added to the basis set. The superscript index (0) indicates that an orbital is unoccupied. Other calculations followed, with the order of addition of orbitals shown in Table II. We performed a total of six (6) self consistent calculations. *The absolute minima of the occupied energies were reached by calculation IV*, as was determined by the perfect superposition of these energies with corresponding, occupied ones from Calculations V and VI. *The basis set of Calculation IV was therefore the optimal one, i.e., the one leading to the DFT description of zb-BN.* With the (EF) enhancement of the BZW method, we added 3p orbitals before the 3s ones, given that the initial ions had both s and p orbitals. However, the 3d orbital on N^{1-} was added after the 3s, due to the fact that these ions had no d orbitals.

As can be seen in Figure 1, the top of the valence band is at the Γ point. The bottom of the conduction band is at the X point. Our BZW-EF calculated, indirect band gap is 6.48 eV, from Γ to X. This result is in good agreement with the experimental one of Chrenko [4]. Table III contains the calculated, electronic energies at the high symmetry points in the Brillouin zone, for values between -24 and +18 eV. The total width of the valence band of 20.26 eV (corresponding to a binding energy of -20.26 eV) is in agreement with the experimental value of 20 eV [6]. The width of the lowest valence band is 5.649 eV, in excellent agreement with the 5.5 eV from experiment [6]. The width of the group of upper valence bands is 10.917 eV. This value is smaller by 2 eV than the 13. eV reported in Reference 6. In their extensive studies of X-ray photoemission spectra of III-V and II-VI compounds, Ley *et al* [35] reported data that show similarities and differences between characteristic features of valence band spectra obtained with XPS and UPS. For instance, in the case of GaP, the S_1 , P_{II} and P_{III} data from XPS and UPS are practically identical. The labels are as defined in Fig. 14 in the article by Ley *et al*. On the other hand, the -13.4 eV XPS binding energy for GaP is 1.1 eV lower than the -12.2 eV obtained with UPS. While we do not know if the -13 eV XPS binding for the upper group of valence band of zb-BN could be around -12 eV in UPS measurement, the point may be examined with additional and experimental data from both XPS and UPS for

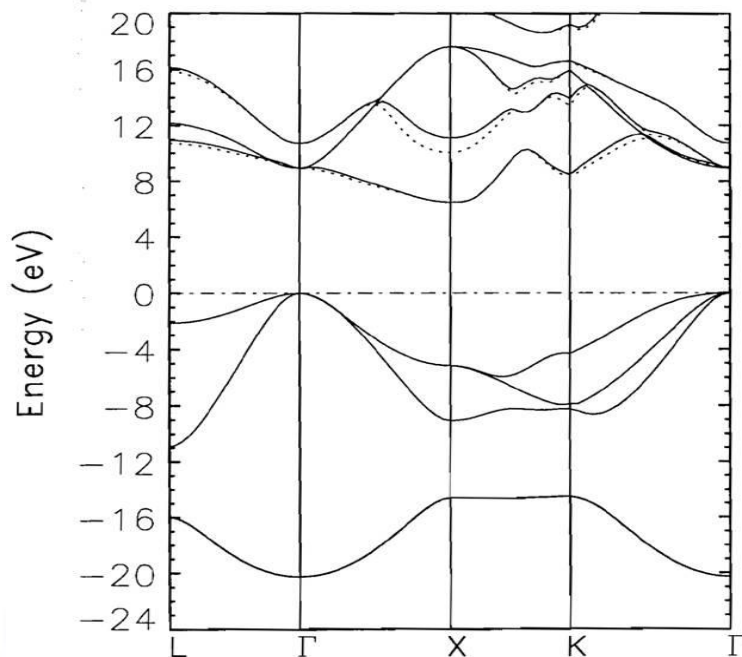


Figure 1. Calculated band structures of *zb*-BN, as obtained from Calculations IV (solid line) and V (dashed line) of the BZW-EF method, at the RT lattice constant of 3.616 Å. The Fermi Energy (E_F) has been set equal to zero. The perfect superposition of the occupied energies from the two verifies the attainment of minima of these energies. The horizontal dashed-dotted line indicates the position of the Fermi energy set equal to zero.

Table II. Successive calculations of the BZW-EF method for *zb*-BN (Calculations I-V). In these calculations, for the description of the valence states, the experimental lattice constant used was 3.616 Å at RT. Calculation IV led to the absolute minima of the occupied energies; Calculations V and VI did not modify any occupied energy. The superscript zero (0) indicates added orbitals representing unoccupied levels

Calculation Number	Orbitals for B^{1+}	Orbitals for N^{1-}	No. of Valence Functions	Band Gap (indirect from Γ to X, in eV)
I	$2s^2 2p^0$	$2s^2 2p^4$	32	7.82
II	$2s^2 2p^0$	$2s^2 2p^4 3p^0$	38	7.53
III	$2s^2 2p^0 3p^0$	$2s^2 2p^4 3p^0$	44	6.50
IV	$2s^2 2p^0 3p^0$	$2s^2 2p^4 3p^0 3s^0$	46	6.48
V	$2s^2 2p^0 3p^0 3s^0$	$2s^2 2p^4 3p^0 3s^0$	48	6.48
VI	$2s^2 2p^0 3p^0 3s^0$	$2s^2 2p^4 3p^0 3s^0 3d^0$	58	4.63

zb-BN. We should note that the content of Table III is intended to enable further comparison with future, experimental, optical transition and X-ray and ultraviolet spectroscopy data.

Effective masses are used in determining transport properties of a system, such as the transport of electrons under the influence of external fields or carrier density gradients. At the X point, close to the minimum of the lowest conduction band, the calculated electron effective masses in units of free electron mass, m_0 , along X – Γ (longitudinal), X-U (transverse), and X –W (transverse) directions, are 1.328, 0.380, 0.384 m_0 , respectively.



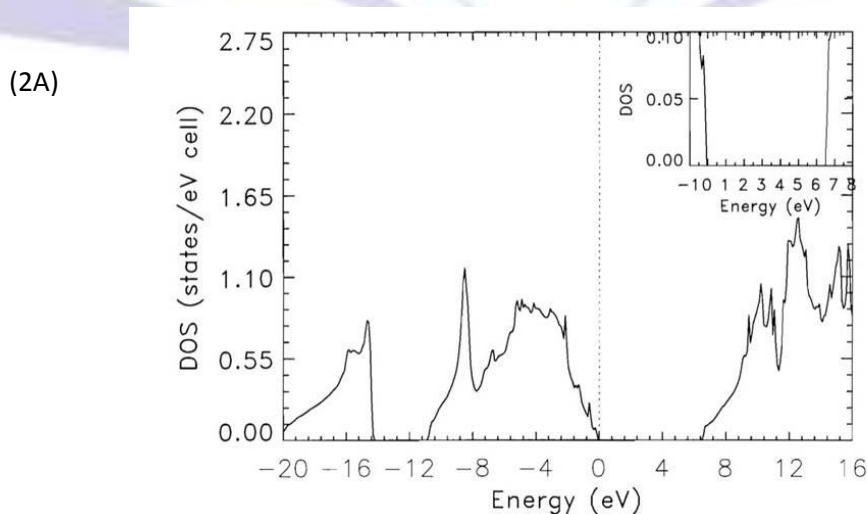
Table III. Electronic energies (eV) at high symmetry points, with the top of the valence band set to 0 eV. Data are from Calculation IV for a RT lattice constant of 3.616 Å.

Γ	X	L	K
10.712	17.615	16.144	16.396
8.946	17.615	12.170	15.469
8.946	11.090	12.170	14.542
8.946	6.488	10.926	8.920
0	-5.160	-2.118	-4.056
0	-5.160	-2.118	-7.895
0	-9.070	-10.917	-8.371
-20.262	-14.613	-15.971	-14.591

The calculated, first heavy hole effective masses at the top of the valence band are the following: $M_{hh1}(\Gamma-L)_{[111]} = 1.137 m_0$, $M_{hh1}(\Gamma-X)_{[100]} = 0.543 m_0$, and $M_{hh1}(\Gamma-K)_{[110]} = 0.998 m_0$ (hh1 –stands for heavy hole one). The second set of heavy hole masses in the same directions as the first one are: $M_{hh2}(\Gamma-L)_{[111]} = 1.137 m_0$, $M_{hh2}(\Gamma-X)_{[100]} = 0.506 m_0$, and $M_{hh2}(\Gamma-K)_{[110]} = 0.563 m_0$. The calculated, light hole effective masses are $M_{lh}(\Gamma-L)_{[111]} = 0.236 m_0$, $M_{lh}(\Gamma-X)_{[100]} = 0.473 m_0$, $M_{lh}(\Gamma-K)_{[110]} = 0.327 m_0$. While we do not know of any experimental data for effective masses for BN, the calculated, heavy and light hole effective masses obtained by Huang and Ching [1, 36] are $M_{hh}(\Gamma-L)_{[111]} = 0.926 m_0$, $M_{hh}(\Gamma-X)_{[100]} = 0.375 m_0$, $M_{lh}(\Gamma-L)_{[111]} = 0.108 m_0$, $M_{lh}(\Gamma-X)_{[100]} = 0.152 m_0$.

3.2 Total and Partial Densities of States (DOS and pDOS)

Figures 2A and 2B show the DOS and pDOS, respectively. The indirect gap, from K to L, between the two parts of the valence band is 3.675 eV. As per the pDOS in Figure 2B, the low lying group of conduction bands is mostly dominated by B-p and B-s bands with moderate contributions from N-s and N-p. On the other hand, the uppermost valence bands seem to be dominated by N-s and N-p bands with smaller contributions from B-p and B-s bands. From our calculated DOS (see Fig. 2A), it can be inferred that the onset of absorption is quite sharp and it starts at about 6.23 eV, as is apparent in the inset. In the low lying conduction bands, sharp peaks appear at 10.54 eV, 12.74 eV, and 14.84 eV. For the uppermost group of valence bands, there is a broad DOS peak between two shoulder features at -2 and -6 eV. We estimate the location of the sharp peak below this broad one to be around -9 eV. Even though it is far from being dominant, N-2s is located at about -16 eV. Again, the above picture is consistent with the experimental measurements of Agui *et al* [6], as their resonant SXES measurements placed peaks associated with the N-2p, B-2p, and N-2s bands at -3.0 eV, -5.4 eV, and -16.5 eV, respectively.





(2B)

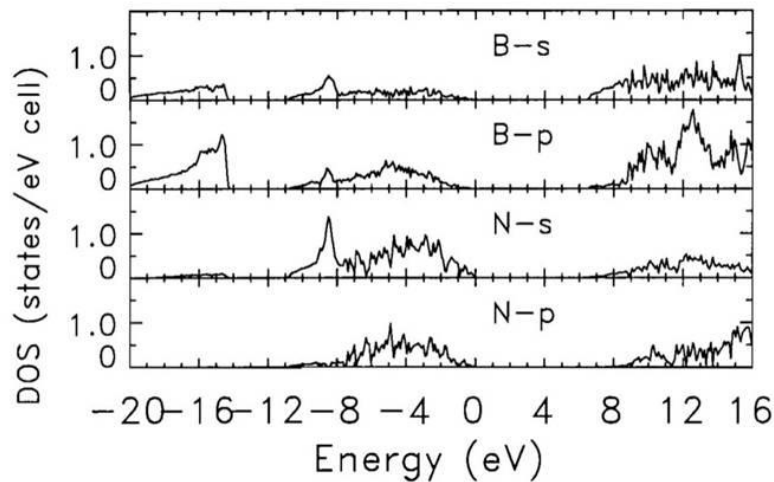


Figure 2. (A) Calculated DOS of *zb*-BN at the lattice constant of 3.616 Å, as obtained with the bands from Calculation IV. (B) Calculated, pDOS of *zb*-BN at the lattice constant of 3.616 Å, as obtained with the bands referenced above.

3.3 Total Energy and Bulk Modulus

We have calculated the total energy (E) of *zb*-BN as a function of the lattice constant (a), as can be seen in Figure 3. Total energy values were obtained for values of a ranging from 3.2544 Å to 3.9053 Å. The minimum of this curve was determined to be at 3.611 Å, smaller by 0.1 % than the experimental value. The bulk modulus was calculated using the energy vs. lattice constant curve and was determined to be 375 GPa. Our calculated bulk modulus is in good agreement with the experimental value of 369 ± 14 GPa with a corresponding lattice parameter of 3.615 ± 0.002 , as obtained by E. Knittle *et al.*[11] This bulk modulus clearly shows that *zb*-BN is a very hard material.

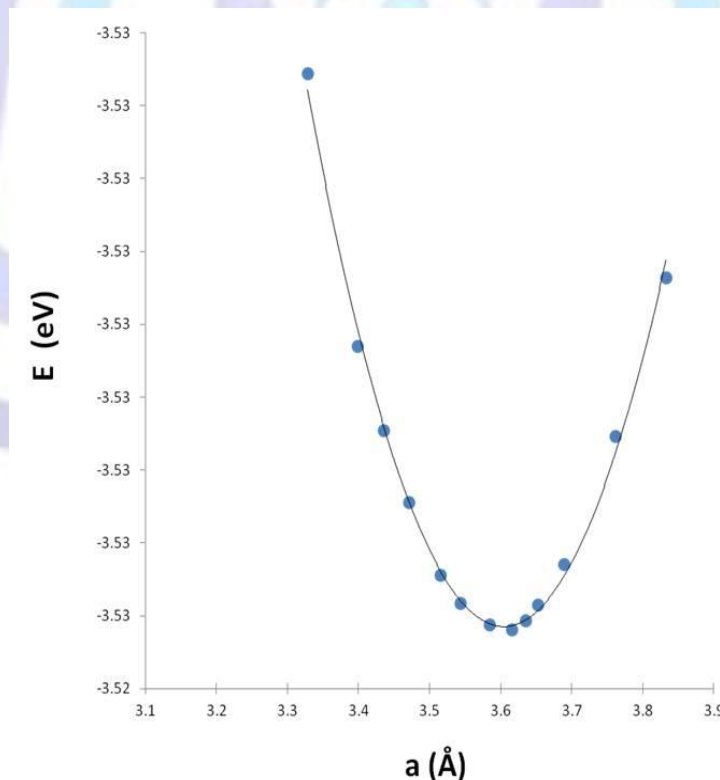


Figure 3. Calculated, total unit cell energy vs. lattice constant, as obtained from calculations with the optimal basis set at lattice constants varying from 3.2544 Å to 3.9053 Å. The calculated bulk modulus is 375 GPa.



4. DISCUSSIONS

The previous LDA and GGA calculations in Table 1 produced band gaps of 4.2 – 5.18 eV and 4.4 - 4.47 eV, respectively. The 5.43 eV gap in Table 1 is from a quasiparticle calculation. Our calculated, indirect gap of 6.48 eV is in excellent agreement with experimental values of 6.0 – 6.4 ± 0.5 eV. The spread of the experimental values is explained by sample quality, thickness, measurement temperature and pressure (i.e., lattice constant), and carrier concentration among other factors.

Using the predicted equilibrium lattice constant of 3.611Å, we performed self consistent calculations of the band structure of *zb*-BN using the above LDA and the GGA potential of Perdew and Wang [37]. The predicted band gaps are 6.50 and 6.74 eV for the LDA and GGA potentials, respectively. These values are a little larger than the above 6.48 eV obtained with our LDA potential, with a RT lattice constant, as expected. With the equilibrium lattice constant, the widths of the lowest valence band, the group of upper valence bands, and the entire valence band are 5.79, 10.96 and 20.31 eV for LDA and 5.65, 10.85, and 20.39 for GGA. The indirect gap, from K to L, between the lowest and upper valence bands is 3.56 eV and 3.89 eV for LDA and GGA, respectively. We recall that this value is 3.74 for the LDA result at RT. Despite some differences, i.e., more binding at zero temperature than at RT, these results are consistent with the ones obtained at RT.

Our accurate description of electronic properties of *zb*-BN, as attested to by comparisons with experimental data, affects the following discussions. Indeed, the discussions center around explaining the mathematical and physical conditions DFT (i.e., LDA) calculations have to meet in order to produce eigenvalues and related wave functions that represent the physical content of DFT. This explanation may be needed in light of the prevailing or preponderant belief in the literature that DFT eigenvalues do not have a physical content, in general, and that DFT calculations cannot obtain the correct band gaps of semiconductors and insulators, in particular.

Our calculated electronic properties of *zb*-BN are mostly in agreement with corresponding, experimental results. In addition to the band gap addressed above, several calculated band widths and the bulk modulus are in excellent agreement with corresponding experimental ones. This success is due to our strict implementation of the BZW-EF method that adheres to conditions that are inherent to the derivation (and hence validity) of DFT. Specifically, we verifiably obtained the absolute minima of the occupied energies, as required by DFT for all calculations that do not, à priori, have the ground state charge density of the material as input [37].

The above excellent agreements signify that DFT (i.e., LDA in this work) can correctly describe electronic and related properties. Specifically, the eigenvalues resulting from the calculation with the optimal basis set have a physical content. This content is preserved for the *occupied energies* when calculations are done with basis sets much larger than the optimal one and that contain it; such calculations, however, often destroy the physical content of some unoccupied energies, including the lowest ones, due to the artificial lowering stemming from the Rayleigh theorem and not from a physical interaction in the Hamiltonian. A typical single basis set calculation cannot ensure the attainment of the referenced minima for the occupied energies or the physical content of the unoccupied ones. Hence, the resulting eigenvalues may not have much physical content.

The confounding seems to have been the confusion [38] between self-consistent results obtained for the Kohn Sham equation, with a single trial basis set, and self consistent results for the system of equations consisting of the Kohn Sham equation and that giving the ground state charge density in terms of the wave functions of the occupied energies – as obtained by the BZW-EF method. Changes only to “linear expansion” coefficients, as done in the iterations with a single basis set, lead to *self-consistent results for the KS equation for that basis set*. Changes to the basis sets, as done by the BZW-EF method described above, coupled with changes to “linear expansion” coefficients through the iterations – for each of the affected basis sets (each choice of orbitals) - solve the system of equations when they lead to the absolute minima of the occupied energies, as required by DFT. For this reason, results of calculations with the optimal basis sets of the BZW-EF method provide the DFT description of materials. This description has a full physical content for occupied and low lying unoccupied energies.

5. SUMMARY AND CONCLUSIONS

We have performed ab-initio, self-consistent calculations of electronic energy bands, DOS, pDOS, and of the bulk modulus of *zb*-BN, using an LDA potential and the LCAO formalism implemented following the BZW-EF method. Our calculated results for the band gap, bandwidths, and the binding energies are mostly in excellent agreement with corresponding experimental ones. The above LDA BZW-EF results point to the capability of DFT to describe and to predict accurately electronic and related properties of semiconductors and other materials. As such, DFT BZW-EF calculations are expected to play a singularly important role in the Materials Genome Initiative (MGI) related work, with emphasis on reliable predictions of properties of materials and of novel materials. Of course, they offer the capability to inform and to guide the design and fabrication of semiconductor and nanostructure based devices.

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Author's Biography



Anthony Duane Stewart is currently an assistant professor in the Mathematics & Computer Science Department at Allen University located in Columbia, South Carolina. In addition to teaching courses in general physics, college algebra, and introductory engineering, Anthony serves on various university committees and organizations aimed at promoting STEM disciplines. Before joining the faculty at Allen University, Anthony was an adjunct professor in the Physics Department at Southern University in Baton Rouge, Louisiana. In addition to Density Functional Theory (DFT) calculations of materials' properties, Anthony's research interests include the electrochemical characteristics of carbon-supported platinum catalysts for Proton Exchange Membrane (PEM) fuel cells.

Anthony received a BS in Physics from Southern University & A&M College in 1999. He then pursued PhD in Materials Science & Engineering at the University of Florida in 2000. He was awarded an MS ('03) and PhD ('08) degree in Materials Science & Engineering with a concentration in electronic materials. His dissertation work focused on the MBE growth and characterization of novel oxide thin films for diode applications. While an adjunct professor at Southern University & A&M College teaching courses in general physics and thermodynamics, he completed the requirements for and was awarded an MS ('14) degree in Physics.

Anthony is from Baton Rouge, Louisiana and is the son of Jackie S. Barrett and Ronald W. Stewart.