First Principle Band Structure Calculations of Zinc-Blende BN and GaN Compounds

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Abstract— Pseudopotential plane wave method within local density approximation (LDA), generalized gradient approximation (GGA) frameworks and GW approximation (in conjunction with the ABINIT package) is used to investigate lattice constant parameter (a) and band structure for zinc-blende BN and GaN. To be more specific, the Perdew-Wang92 (PW92) and Perdew-Burke-Ernzerhof (PBE) flavors have been employed for exchange-correlation term of LDA and GGA, respectively. Lattice constant (a), band gap energy (E_g) have been calculated using LDA and GGA approximations. The GGA results for (a) are strongly agree with the experimental and much more accurate than LDA values. The values of a in both LDA and GGA methods are well accurate when compared with the other theoretical works. The E_g values obtained are in a good agreement with other theoretical works especially for ZB-BN. On the other hand, the E_g values are not in good agreement with the experimental due to the well known band gap problem of density functional theory (DFT). To improve the E_g value, GW approximation has been used. It was found that the improvement is better for ZB-BN than ZB-GaN.

Index Terms— First Principle, Density functional theory, Electronic structure, Pseudopotential, BN and GaN Compounds

1 INTRODUCTION

THE III-V semiconductors consist of two elements, one is from group III and another is from group V in the periodic table. III-V semiconductors are more important in optoelectronics because of their wide band gap. They have applications in specific areas such as wireless communications. III-Nitrides (III-N) form a specific subgroup of the III-V compounds with basic crystal structures, Hexagonal wurtzite (WT) structure and cubic zinc-blende structure (ZB). III-N semiconductors are characterized by high iconicity, very short bond length, low compressibility and high thermal conductivity [1, 2 and 3]. These properties make the III-N semiconductors interesting and very useful. These materials can therefore be used for short wavelength light-emitting diodes (LED), laser diodes [4], and optical detectors, as well as for high-temperature, high power, and high frequency devices [5 and 6].Among III-N semiconductors, the Boron nitride (BN) and Gallium nitride (GaN) with indirect and direct band gaps have attracted extensive experimental and theoretical interest. BN and GaN, like most III-V compounds, have WZ and ZB structures. The main focus of this project is ZB-BN and ZB-GaN. ZB-BN is formed under high pressure, high temperature treatment of WZ-BN. It is the second hardest material known after diamond. It has high thermal conductivity and excellent wear resistance. It can be used to make cutting tools due to its hardness and to make optoelectronics devices [7].

ZB-GaN used in bright (LED),and recently, it was used as solid-state ultraviolet (UV) detectors in medical diagnostic, chemical and biological analysis, flame detection, andmissile warning, as well as for UV LEDs in food and water treatment, and the hardness and large bulk modulus make it ideal protective coating materials [4].

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2 CALCULATIONS

The calculations were performed using Pseudopotential-Plane wave method within the framework of the density functional theory (DFT) [8 & 9]. The pseudopotentials for all atoms were generated according to the scheme of Troullier and Martins [10].In the density functional formalism, the total electronic energy of the ground state is given as a functional of the total electron charge density $n(\boldsymbol{r})$:

$$E_{ks}[n(\boldsymbol{r})] = T_{ni}[n(\boldsymbol{r})] + \int n(\boldsymbol{r})\, v_{ext}(r) d\boldsymbol{r} + \frac{1}{2}\iint \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r} d\boldsymbol{r}' + E_{xc}[n(\boldsymbol{r})]$$

where$T_{ni}[n(\boldsymbol{r})]$ represents the non-interacting particles kinetic energy, $v_{ext}(r)$ the interaction potential of the ions with the electrons (external potential), $\frac{1}{2}\iint \frac{n(r)n(r')}{|r-r'|} d\boldsymbol{r} d\boldsymbol{r}'$ the electrostatic interaction among the electrons and $E_{xc}[n(\boldsymbol{r})$ the exchange-correlation energy. In the present work, the exchange- correlation energy is treated using both the local density approximation (LDA) with the Perdew and Wang92 flavor [11], and the generalized gradient approximation (GGA) with the Perdew, Burk and Ernzerhof (PBE)flavor [12].The ab initio calculations show the typical underestimate of the band gap with respect to the experimental one, due to the use of the Density Functional Theory (DFT) formalism. Therefore, the Kohn-Sham (KS) eigenvalues are usually corrected by using Hedin's GWapproximation [13] to evaluate the quasiparticle energies instead of the considered fictitious KS particles. The quasiparticle energy E_i^{QP} can be obtained from the so-called quasiparticle equation, which can be written as:

$$\left[-\frac{\nabla^2}{2} + v_H + v_{ext}\right]\psi_i^{QP}(\boldsymbol{r}) + \int \sum(\boldsymbol{r}, \boldsymbol{r}'; E_i{}^{QP})\psi_i^{QP}(\boldsymbol{r}')d\boldsymbol{r}' = E_i{}^{QP}\psi_i^{QP}(\boldsymbol{r})$$

where v_H and v_{ext} are Hartree potential and external potential, respectively,$\sum$ is called self-energy, and$\psi_i^{QP}(\boldsymbol{r})$is the quasiparticle wave function.

Boron Nitride (BN) and Gallium Nitride (GaN) in ZB structure are such that B (and Ga) atom is located at 000 coordinates while N atom is located at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ coordinates. It is well known that the atomic numbers of B, Ga and N are 5, 7 and 31, respectively. So, the electronic configuration for B is$1s^2 2s^2 2p^1$, for N is $1s^2\ 2s^2 2p^3$ and for Ga is $1s^2\ 2s^2\ 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$. In the present work, the pseudopotentials have been used which treats B: $2s^2\ 2p^1$, N: $2s^2 2\ p^3$ and Ga: $4s^2$, $4p^1$ as the valence states. In the present work, first, convergence tests to E_{TOT} were performed in order to determine the cut-off energy (E_{cut}) and the number of **k**-point grids (ngkp).The E_{TOT} convergence was obtained forE_{cut}being equal to 828.381(eV) for ZB-BN, while for ZB-GaN compound E_{cut} is830.084 (eV). The other convergence test corresponds to the sampling of the BZ. One should examine different grids for increasing resolution. TheE_{TOT}has been converged for the 6×6×6 grid. The Symmetries are used to decrease the number of **k**-points needed to sample the BZ, so that only the irreducible part of it can be sampled. The number of **k**-points that has been generated automatically by the code and used in the lattice constant (a) calculations is 28 **k**-points, while the number of **k**-points used in LDA and GGA present calculations of band structure was set to 40. Finally, the number of **k**-points used in GW corrections to band gap was restricted in 4 points for ZB-BN, due to its indirect band gap(Γ_{15v},Γ_{1c},$X_{15v}$and X_{1c}), and 2 points for ZB-GaN (Γ_{15v} and Γ_{1c}).

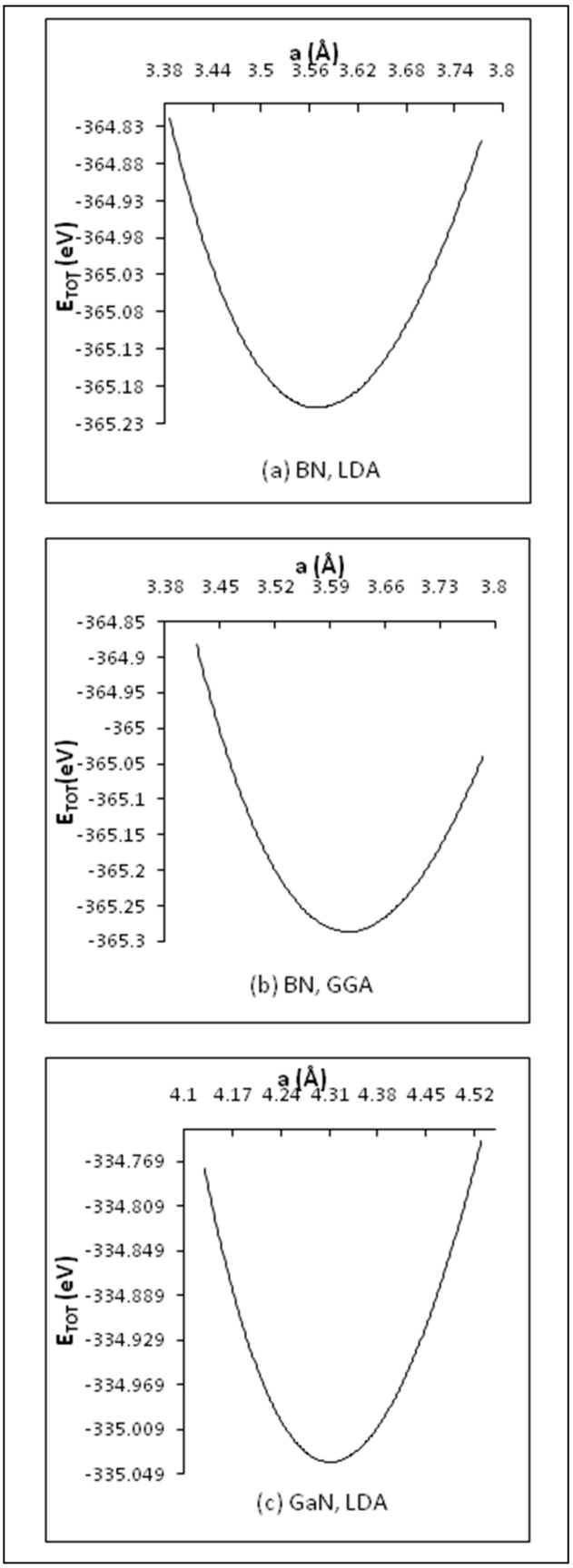
3 Results and Discussion

3.1 Lattice Constant Parameter(a)

The lattice constant (a) of ZB-BN and ZB-GaN has been determined using LDA and GGA by calculating the total energy (E_{TOT}) for many different values of (a). The E_{TOT}has been plotted against the corresponding (a) values (Figure 1), and the value of (a) (the equilibrium value) has been chosen, which corresponds to the least minimum energy.

3.1.1 BN

The equilibrium value of a for ZB-BN in LDA calculations was obtained to be 3.57 (Å), while in GGA calculationsit was 3.61(Å). The results of (a) is given in table (1) with the experimental and results of other theoretical works. The present values of a in GGA (with PP-PW) calculations for ZB-BN were found to be exactly agreeable with the experimental value of reference [14], while the a value in LDA (with PP-PW) calculations is by (1.1%) smaller than the experimental value. On the other hand, the value of a in LDA calculations has the exact value when compared with the value of the full potential linear augmented plane waves method (FP-LAPW) presented by the reference [15], while a value in GGA calculations (with PP-PW) is 0.2% and 0.5% smaller than other work values of references [6 and16]whereFP-LAPW have been used. In general, the $a$value in GGA calculations has been found to be much better than $a$value in LDA calculation.



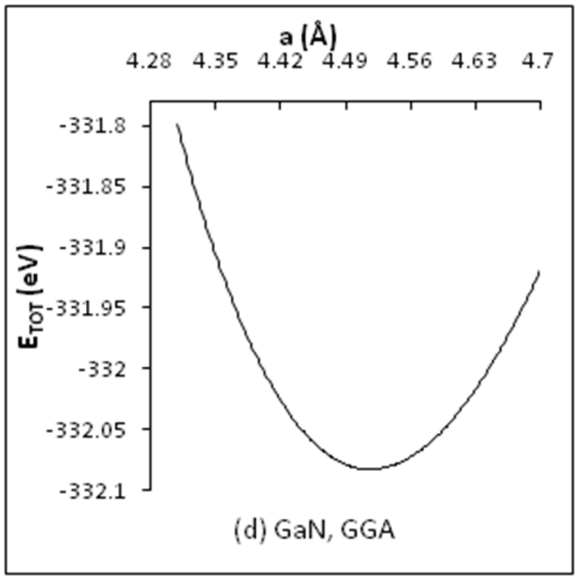


Fig.(1) The total energy ETOT plot sversus lattice constant (a) for ZB-BN and ZB-GaN in LDA and GGA calculations.

3.1.2 GaN

The present value for(a) in GGA calculations for ZB-GaN was found to be 4.5 (Å), which agrees exactlywith the experimental and theoretical valuesevaluated by reference [17], while a value in LDA calculationswas found to be smaller by 4.2% than the experimental value. Thea value in GGA calculation is 0.5% larger than that of reference[18] calculated in FP-LAPW method and its value is smaller by 1.3% than the values computed by references[16 and 19] using FP-LAPW method. The value ofain LDAwas found to be smaller by 2.4% and 3.5 % than other theoretical values [20 and 15]using PP-PW, which is the same method used here. In general, the a valuein GGA was found to be much better thanthe a valueusing LDA.

TABLE (1)

THE PRESENTLY CALCULATED AND OTHER THEORETICAL AND EXPERIMENTAL LATTICE CONSTANTS IN Å FOR BN AND GaN IN ZB STRUCTURE.

Compound	a (Å)			
	LDA	GGA		Experimental
	PP-PW	PP-PW	FP-LAPW	
BN	3.57[a,c] 4.31[a]	3.61[a]	3.63[b],3.623[b]	3.61[b,j]
GaN	4.47[c] 4.428[d]	4.5[a], 4.5[i]	4.562[b,g] 4.475[e]	4.5[f,j]

[a]*Present work*, [b]*Reference[16]*, [c]*Reference[15]*, [d]*Reference[20]*, [e]*Reference[18]*, [f]*Reference[21]*,[g]*Reference[19]*, [h]*Reference[14]*, [i]*Reference[17]*, [j]*Reference [6]*.

3.2 Band Structure and Band Gap Energy (E_g)

The band structures and band gap energies have been computed for ZB-BN and ZB-GaN compounds using both LDA and GGA calculations with and without GW approximation employing the a values that were obtained from GGA calculations.

3.2.1 BN

Fig. (2) shows that GGA results for band energies are higher than the LDA results, and that the difference in the conduction band are larger than the difference in the valence band energies.

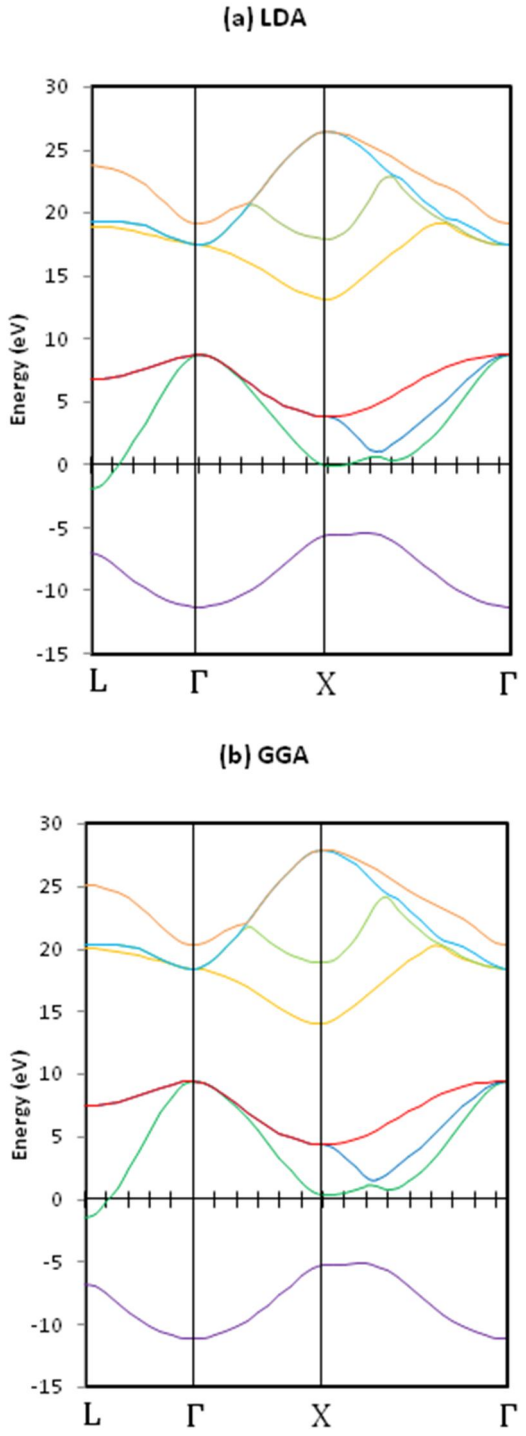


Fig.(2)Band structure of ZB-BNin (a) LDA calculations and (b) GGA calculations, the (a) value obtained from GGA calculations was employed.

Table (2) contains the energies of the most important high symmetry points, including Γ_{15v} and X_{1c} points, calculated in LDA and GGA calculations with and without GW approximation for avalue obtained from GGA.

The energies computed here using LDA are in good agreement when compared with the energies obtained by the reference [15] because in both works the PP-PW method has been used, while the energies computed here using GGA are higher than the energies presented by the reference [16] where FP-LAPW method has been used.

TABLE (2)
THE ENERGIES (IN eV) AT HIGH SYMMETRY POINTS OF ZB-BN CALCULATED IN LDA AND GGA METHODS WITH AND WITHOUT GW APPROXIMATION EMPLOYING (A)OBTAINED FROM GGA.

	Energy (eV)					
	LDA[a]	LDA[b]	GW[a]	GGA[a]	GGA[c]	GW[a]
Γ_{15v}	8.73545	10.8	8.363	8.91605	0	8.711
Γ_{1c}	17.43254	19.6	19.275	17.73106	8.79	19.539
X_{15v}	3.84835	5.59	2.881	4.0478	-4.78	3.119
X_{1c}	13.12771	15.19	14.403	13.43241	4.45	14.49

[a]Presentwork,[b]Reference[15], [c]Reference[16].

The theoretical E_g values calculated in LDA and GGA methods with and without GW approximation with the experimental E_g values are listed intable (3). The present work results of E_g in LDA and GGA do not agree with the experimental value. On the other hand, there is fair agreement when the calculated E_g values using GW approximation are compared with the experimental. The value of E_g using LDA is smaller than E_g value given in reference [15], and the value of E_g using GGA is close to the E_g value obtained by the references [16 and 22] where FP-LAPW method and PP-PW method have been used, respectively.

TABLE (3)
THE EXPERIMENTAL BAND GAP VALUES (IN eV) AND THEORETICAL BAND GAP VALUES FOR ZB-BN CALCULATED IN LDA AND GGA METHODS WITH AND WITHOUT GW APPROXIMATION EMPLOYING (**a**)VALUE OBTAINED FROM GGA.

	E_g (eV)		
	KS	GW	Experimental
LDA	4.39[a], 4.61[b]	6.04[a]	(6.1- 6.4)[d]
GGA	4.51[a],4.459[c],4.45[d]	5.77[a]	

[a]Presentwork,[b]Reference[15],[c]Reference[16],[d]Reference[22]

3.2.2 GaN

The band structure and E_g of GaN were also computed in LDA and GGA with and without GW approximation employing thea value obtained from GGA.The band structure in LDA and GGA methods illustrated in the figure (3).

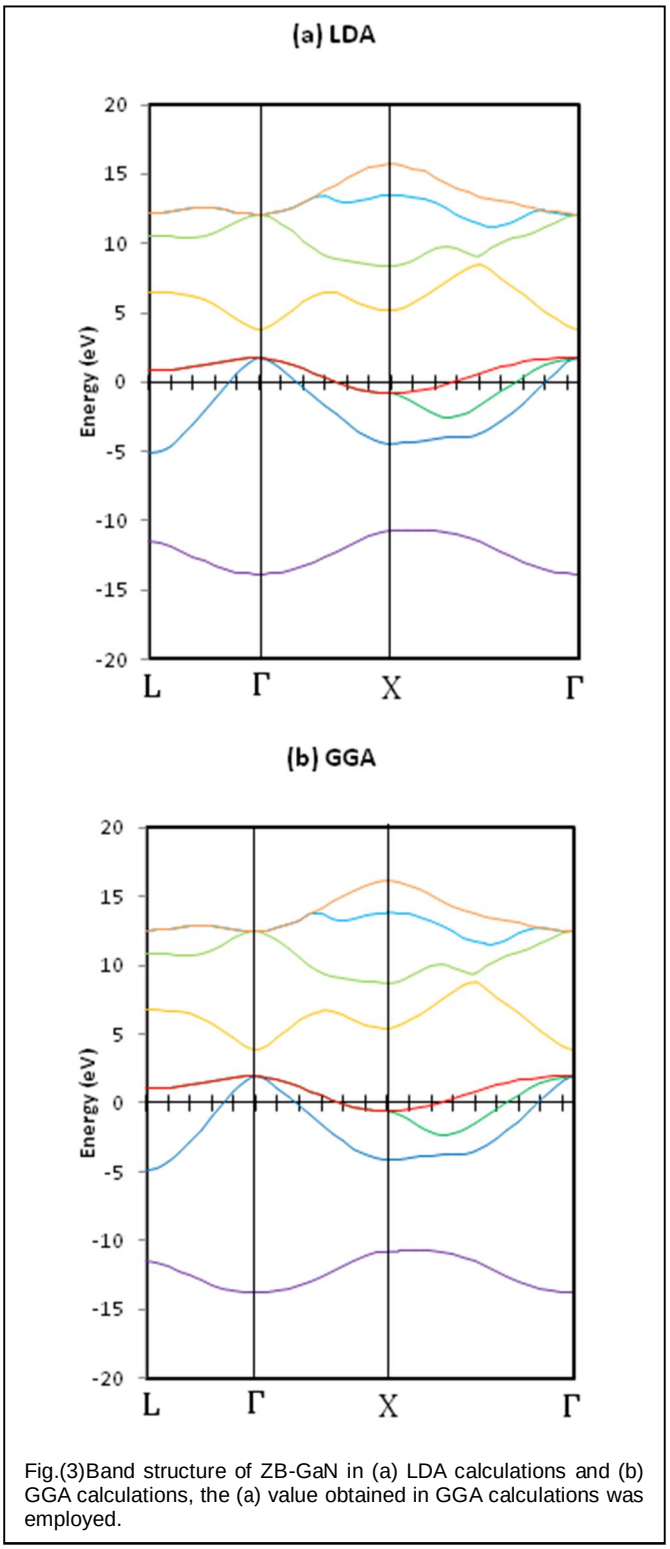


Fig.(3)Band structure of ZB-GaN in (a) LDA calculations and (b) GGA calculations, the (a) value obtained in GGA calculations was employed.

The Γ_{15v} and Γ_{1c} calculated here and by other works in LDA and GGA calculations with and without GW approximation are listed in table (4). The Γ_{15v} and Γ_{1c} energies are higher than the results obtained in the reference [5]. On the other hand, the GGA values for Γ_{15v} and Γ_{1c} energies are higher than LDA values and the difference in the Γ_{15v} is more than the difference in Γ_{1c}, this leads to the smaller E_g for ZB-GaN in GGA than LDA.

TABLE(4)
THE ENERGIES (IN eV) AT HIGH SYMMETRY POINTS OF ZB-GaN CALCULATED IN LDA AND GGA METHODS WITH AND WITHOUT GW APPROXIMATION EMPLOYING (**a**)OBTAINED FROM GGA.

	Energy (eV)					
	LDA[a]	LDA[b]	GW[a]	GGA[a]	GGA[b]	GW[a]
Γ_{15v}	1.74121	0	1.668	1.93045	0	2.033
Γ_{1c}	3.73097	1.76	4.701	3.85829	1.45	4.76

[a]*Present work,* [b]*Reference[5]*

The values of the E_g for ZB-GaN in LDA and GGA calculations with and without GW approximation of the present work with experimental and other theoretical works are listed in the table (5). The E_g value in LDA and GGA are smaller than experimental by 39.7% and 41.5%, respectively, this shows that the band gap problem of DFT. The E_g values in LDA and GGA are in difference with the other LDA and GGA values by (5-23) % presented by the other works. The GW update on LDA and GGA for E_g values are in fair agreement with the experimental one,the value of E_g obtained from GW update on the LDA value has found to be 3.03 (eV) while on the GGA has found to be 2.72 (eV) and the error with the experimental reduced to be 7 % and 17%, respectively.

TABLE(4)
THE ENERGIES (IN eV) AT HIGH SYMMETRY POINTS OF ZB-GaN CALCULATED IN LDA AND GGA METHODS WITH AND WITHOUT GW APPROXIMATION EMPLOYING (**a**)OBTAINED FROM GGA.

	E_g (eV)		
	KS	GW	Experimental
LDA	1.98[a], 1.88[b],1.6[c],2.09[d]	3.03[a]	3.3[f,g]
GGA	1.92[a],1.68[d]	2.72[a],3.32[e]	

[a]*Present work,* [b]*Reference[20],* [c]*Reference[5],* [d]*Reference[23],* [e]*Reference[22],*[f]*Reference[24],*[g]*Reference[25]*

4 CONCLUSIONS

The present study concludes the following:

1- Lattice constant parameter values (a) calculated in GGA method for both ZB-BN and ZB-GaN agree with the experimental values and are much better than (a) values in LDA method.

2- The present calculations have shown (proved) indirect and direct band gaps for each ZB-BN and ZB-GaN, respectively.
3- Band gap energies (E_g) in LDA and GGA calculations are not accurate when compared with the experimental band gap values and that is due to the band gap problem of DFT, while it is in fair agreement when they have been calculated using GW approximation with both LDA and GGA methods.

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