First Principle Calculation of Lattice Constants for Generalised Quasirandom Structures of Ingan Alloy

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Abstract: ***This paper presents calculations of ground state total energy of InGaN alloy carried out in a disordered quasirandom structure for a triclinic super cell. This structure replicates the disorder and composition effect in the alloy. First principle calculations within the density functional theory with the local density approximation approach are employed to accurately determine the lattice constants for different concentration ratios of the alloy. We provide precise results of quasirandom structures of the alloy and their lattice constants with the total energy of the system for the entire range of compositions with their respective parameters.***

Keywords: Ground State, DFT, LDA, XC, SCF

1. Introduction

The late 1990s marked the entrance of group-III nitride compounds and their alloys to the physics of optical and electronic devices. Recent technological breakthrough in InGaN epitaxial growth has attracted attention in LED application and fabrication [1]. This material has a wide spectrum of emission frequency, making it highly efficient light emitters in green, blue, white and UV light emitting diodes and laser diodes [2]. The emitted wavelength depending on the material band gap can be controlled by InN/GaN composition ratios; studies based on device simulation have shown that it could be possible to increase InGaN LEDs efficiency using bandgap engineering [3]. Due to their technological importance, an approximate prediction of electronic properties of InGaN alloys is desirable.

To find the ground state energy of any system, a palatable way would be to solve the time independent Schrodinger equation for the system (many body problem) which reads

$$H\Psi(\boldsymbol{r}_i,\boldsymbol{R}_j) = E\Psi(\boldsymbol{r}_i,\boldsymbol{R}_j) \qquad (1)$$

Where $\boldsymbol{r}_i$ and $\boldsymbol{R}_j$ are position vectors of electrons and nuclei.

Although the time independent Schrodinger equation appears comprehensible for a single electron (single body problem) the consideration of nuclei along with electrons in the many body problem increases the computational complexity of the problem. To go about this problem we implement Born-Oppenheimer (BO) approximation [4] which attempts to decouple the dynamics of electrons and nuclei by treating electrons as an inhomogeneous cloud in a static potential field due to fixed set of nuclei.

$$\psi = \psi_{electronic} * \psi_{nuclei} \qquad (2)$$

The many body Schrodinger equation now involves solving the Schrodinger equation to calculate the wave function for electrons in a static potential V(**r**).

$$\left[\sum_{i}^{N}\left(\frac{-\hbar^2\nabla_i^2}{2m}+V(\boldsymbol{r}_i)\right)+\sum_{i}^{N}\sum_{i<j}U(\boldsymbol{r}_i,\boldsymbol{r}_j)\right]\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\dots,\boldsymbol{r}_N) = E\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\dots,\boldsymbol{r}_N) \qquad (3)$$

Where N is the number of electrons and $U(\boldsymbol{r}_i,\boldsymbol{r}_j)$ is the columbic intra electronic interactions. The BO approximation may have reduced the number of variables to simplify the problem to some extent, however this is not an instigative solution to any real materials; for instance, a lead nano cluster of 100 atoms have 8200 electrons and solving the many body Schrodinger equation becomes a 24600 dimensional problem. To overcome this issue, a computational quantum mechanical modeling method called density functional theory (DFT) mainly used in investigating ground state properties of many body systems has been implemented. DFT provides a way to systematically map the many body problem with potential U, onto a single body problem, without U [5]. The key variable here is the electron density $n(\boldsymbol{r})$, and that instead of dealing with a function of 3N variables, we can instead deal with a function of only 3 variables (the density). For N Electron system we define the electronic density

The scheme presented in this paper can be a reasonably reliable method for investigating electronic properties and as a guide for designing new materials, not yet discovered in the laboratory. In the following, we give a brief description of DFT with Local Density Approximation and provide the reader with a complete description of calculations required and identify the approximations involved. Here we have only included steps that are crucial to make approximations and refer the reader to the original works for more detailed derivations.

2. Essential Background Literature

2.1 Hohenberg-Kohn theorem

This theorem establishes the relationship between ground state energy and electron density and also describes the process of calculating it [6].

The first theorem states that the external potential $V_{ext}(\boldsymbol{r})$ (and hence the total energy) is uniquely determined by the corresponding ground state density.

$$E = E[n(\boldsymbol{r})] \qquad (5)$$

For all densities $n(\boldsymbol{r})$ which are ground state densities for some external potential, the functional F$[n(\boldsymbol{r})]$ is unique and well defined. This functional defined as

$$F[n(\boldsymbol{r})] = T[n(\boldsymbol{r})] + U[n(\boldsymbol{r})] \qquad (6)$$

is a universal functional of the density which includes all the quantum mechanical interactions of the system and is explicitly independent of the external potential.

Now a functional for an arbitrary external potential $V(\boldsymbol{r})$ unrelated to the $V_{ext}(\boldsymbol{r})$ determined by $n(\boldsymbol{r})$ can be defined as

$$E_V[n(\boldsymbol{r})] = F[n(\boldsymbol{r})] + \int V(\boldsymbol{r})n(\boldsymbol{r})d^3\boldsymbol{r} \quad (7)$$

The second theorem states that the functional that delivers the ground state energy of the system gives the lowest energy if and only if the input density is the true ground state density.

For N electrons in potential $V(\boldsymbol{r})$, the HK functional $F[n(\boldsymbol{r})]$ obtains its minimal value.

$$E_V[n(\boldsymbol{r})] \geq E_0 \qquad (8)$$

Where E_0 is now the ground state density for potential $V(\boldsymbol{r})$.

The existence of the universal functional $F[n(\boldsymbol{r})]$ independent of the external potential is the remarkable results of DFT since instead of dealing with a function of 3N variables (many body problem) we can instead deal with a function of 3 variables (density). However, the exact form of the universal function $F[n(\boldsymbol{r})]$ is unknown. Remarkably, it is possible to make some approximations for the Exchange-Correlation energy [7], and the simplest approximation adopted in this work is the Local Density Approximation (LDA).

For electron gas, a system of many interacting particles, the effects of exchange and correlation are crucial to an accurate description of its behavior. In such a system, exchange and correlation effects are caused by the repulsion of particles and their motion [8].

2.2 The LDA Concept

In the LDA, the contribution to the exchange-correlation energy from each infinitesimal volume $d\boldsymbol{r}$ is taken to be the value it would have if the whole space were filled with a homogeneous electron gas with the same density found in $d\boldsymbol{r}$. This was originally introduced by Kohn and Sham [9]. i.e:

$$E_{XC}^{LDA}[n(\boldsymbol{r})] = \int n(\boldsymbol{r})E_{XC}[n(\boldsymbol{r})]d\boldsymbol{r} \quad (9)$$

Where $E_{XC}[n(\boldsymbol{r})]$ is the exchange-correlation energy per electron in homogeneous electron cloud of density $n(\boldsymbol{r})$. They also suggested that $E_{XC}[n(\boldsymbol{r})]$ can be written as the sum of exchange and correlation parts. For the details on exchange and correlation energies, we refer reader to the original works.

$$E_{XC}[n(\boldsymbol{r})] = E_X[n(\boldsymbol{r})] + E_C[n(\boldsymbol{r})] \quad (10)$$

Where $E_X[n(\boldsymbol{r})] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}(n(\boldsymbol{r}))^{\frac{1}{3}}$

and $E_C[n(\boldsymbol{r})] = E_C^{VMN}[n(\boldsymbol{r})]$ [10].

The exchange energy in a system where the density is not homogeneous is obtained by applying the homogeneous electron gas results point wise, giving [11].

$$E_X^{LDA}[n(\boldsymbol{r})] = \int nE_X[n(\boldsymbol{r})]d\boldsymbol{r}$$

$$= -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\int (n(\boldsymbol{r}))^{\frac{4}{3}}d\boldsymbol{r} \quad (11)$$

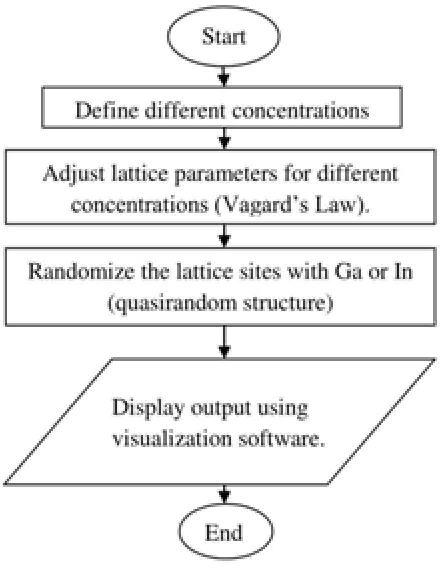
3. Methodology

3.1 Material Modeling

Our choice of material is $In_{1-x}Ga_xN$ alloy which has a hexagonal closed packed structure and is a direct band gap semiconducting material. It has a band gap span from 0.69 eV to 3.4 eV, depending upon the composition ratio of InN and GaN in the alloy [12].

We proceed by generating triclinic supercell structure for the alloy for different concentration ratios of InN and GaN compound (namely seven). Despite ideal periodicity being the most available methods to explore solid-state materials, such periodicity does not exist in this type of materials. The supercell approximation is a way to imply periodicity to a disordered system while still preserving disordered properties at the local level [13]. Alloy Theoretic Automated Toolkit (ATAT) which contains the first principle calculation code was used for the input FORTRAN script to generate the output file for the alloys structure [14], (POSCAR file) which contains the information about the geometry of the cell. From this file 3D visualization for structural models was done by Visualization for Electronic and Structural Analysis (VESTA) from which all the lattice parameters were obtained too. (Fig 1 a-g) and Table 1.

3.2 Computational Algorithm



3.3 Self Consistent Scheme

To calculate the ground state energy, one has to now solve the Kohn-Sham equation for a non-interacting system [9], with interactions explicitly being accounted in the potential.

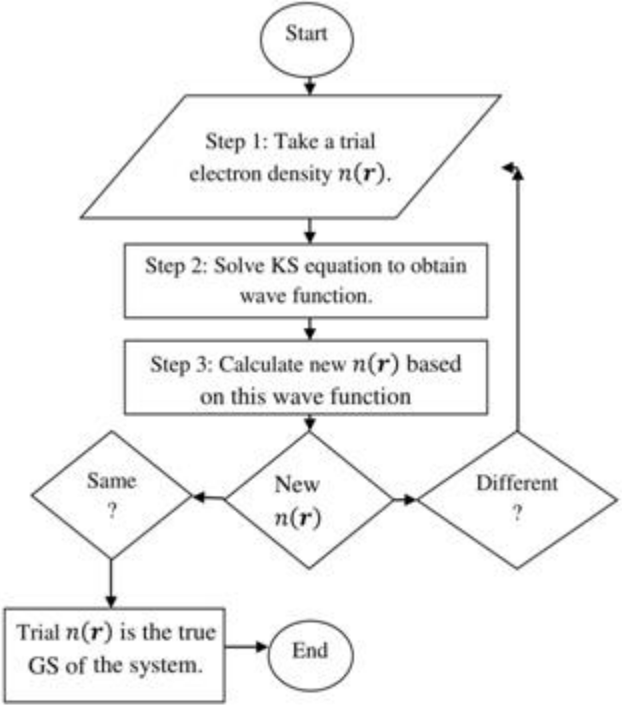
$$\left[\frac{-\hbar^2\nabla_i^2}{2m}+V_s\right]\psi_i=E_i(\boldsymbol{r})\psi_i \qquad (12)$$

$$i.e,\left[\frac{-\hbar^2\nabla_i^2}{2m}+V(\boldsymbol{r})+V_H[n(\boldsymbol{r})]+V_{XC}[n(\boldsymbol{r})]\right]\psi_i=E_i(\boldsymbol{r})\psi_i \qquad (13)$$

Where, the first term is the kinetic energy of the electrons, second term is the effective potential from the BO approximation, third term is the Hartree-Fock potential resulting from approximation from many body to single body, and the fourth term is the Exchange Correlation potential resulting from LDA approximation.

Here since the Hartee term and XC term depends on $n(\boldsymbol{r})$, which depends on ψ_i, which in turn depends on V_s the sum of all three potentials, the Kohn-Sham equation has to be solve in an iterative (self-consistent) way. One starts with an initial trial for $n(\boldsymbol{r})$, then calculates the corresponding V_s and solves the Kohn-Sham equation. From the wave function resulting from the solution, one calculates a new density and starts again. This process is repeated until a convergence is reached. We have used Quantum Espresso, an integrated suite of Open-Source computer codes for electronic structure calculation based on DFT for our Self Consistent Field calculations of our system.

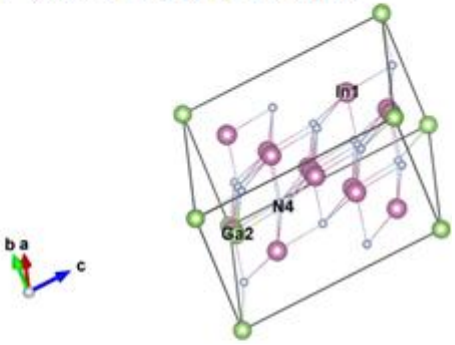
3.4 Computational Algorithm



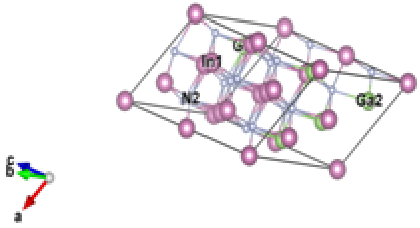
4. Results and Discussion

We were successfully able to generate the quasirandom super cell for seven different concentration ratios of $In_{1-x}Ga_xN$ alloy namely, $In_{0.875}Ga_{0.125}N$, $In_{0.75}Ga_{0.25}N$, $In_{0.625}Ga_{0.375}N$, $In_{0.5}Ga_{0.5}N$, $In_{0.375}Ga_{0.625}N$, $In_{0.25}Ga_{0.75}N$ and $In_{0.125}Ga_{0.875}N$.

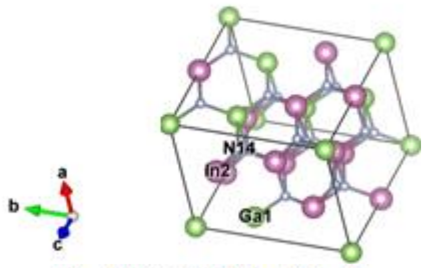
a. For $x=0.125$: $In_{0.875}Ga_{0.125}N$



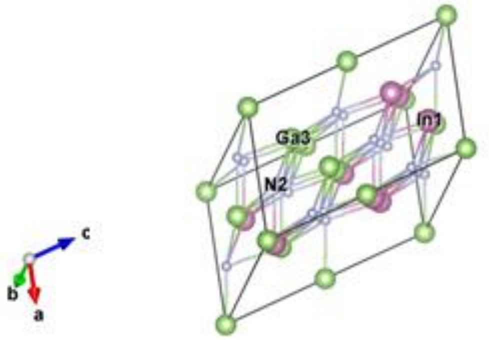
b. For $x=0.25$: $In_{0.75}Ga_{0.25}N$



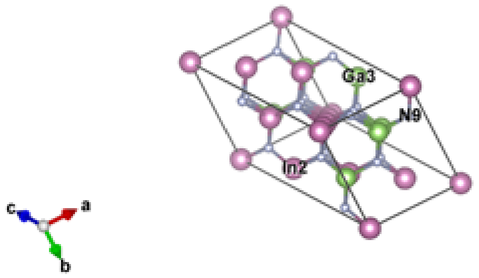
c. For $x=0.375$: $In_{0.625}Ga_{0.375}N$



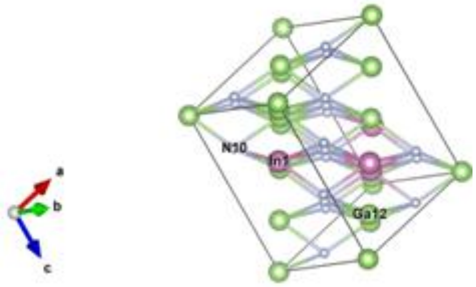
d. For $x=0.5$: $In_{0.5}Ga_{0.5}N$



e. For $x=0.625$: $In_{0.375}Ga_{0.625}N$



f. For $x=0.75$: $In_{0.25}Ga_{0.75}N$



g. For $x=0.875$: $In_{0.125}Ga_{0.875}N$

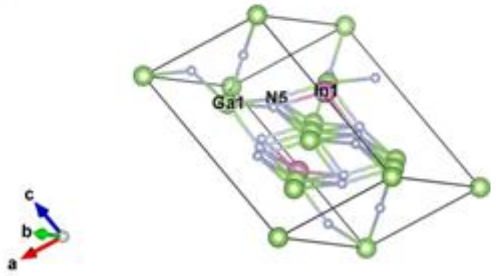


Figure 1: Super cell structure of $In_{1-x}Ga_xN$ as viewed by VESTA

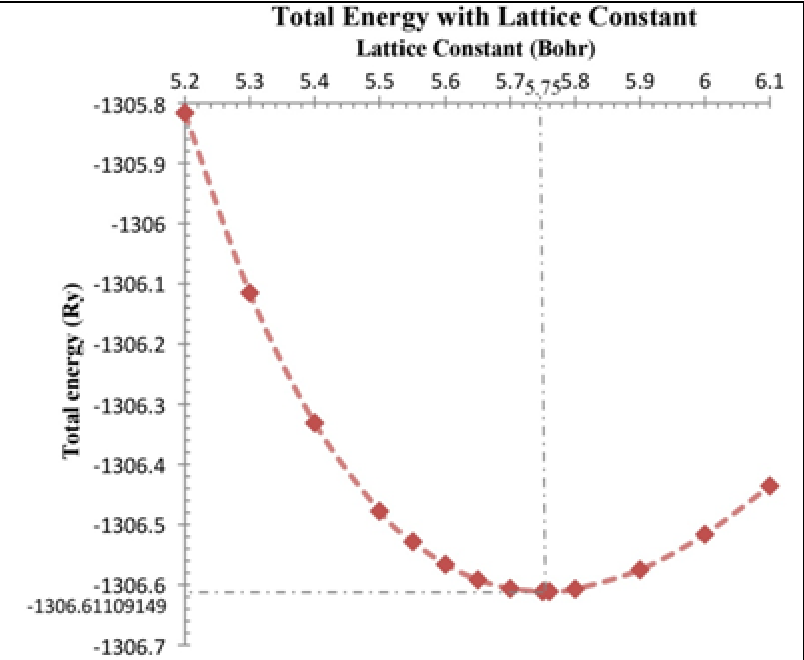
The values of lattice parameters for all the systems were noted from their structural models viewed in VESTA.

Table 1: Lattice Parameters retrieved from VESTA

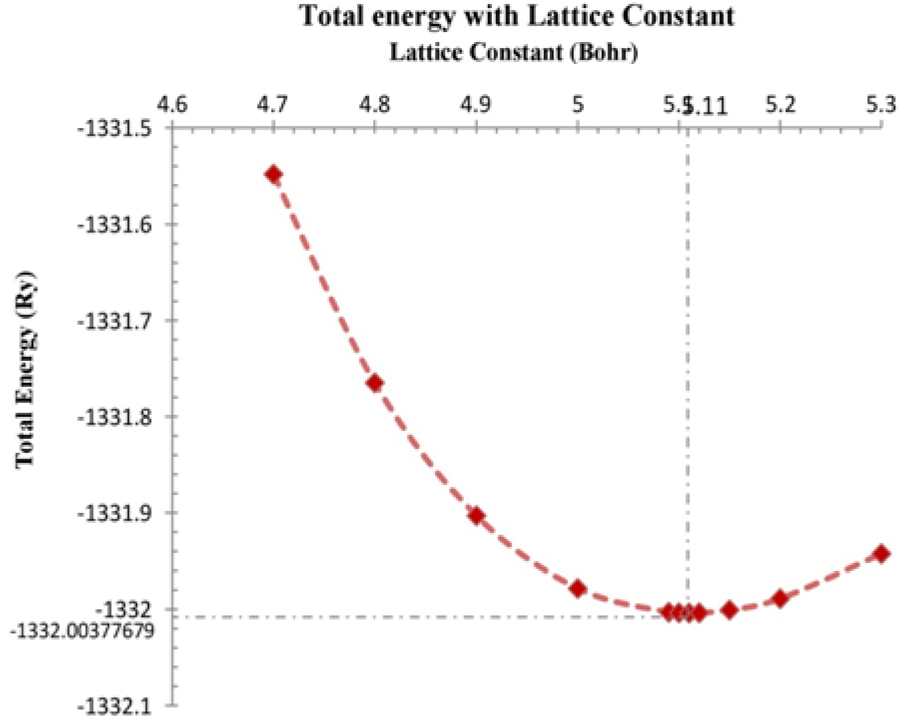
Materials	*a(Å)*	*b (Å)*	*c (Å)*	*alpha (α)*	*beta (β)*	*gamma (γ)*	*Unit-cell volume (Å³)*
$In_{0.125}Ga_{0.875}N$	7.65229	8.30376	13.50018	83.2557	76.8172	64.4834	753.583952
$In_{0.250}Ga_{0.750}N$	8.41380	8.41380	11.14447	92.4316	92.4316	84.5666	784.102245
$In_{0.375}Ga_{0.625}N$	7.85391	8.52384	13.85196	83.3615	76.9197	64.5496	815.432563
$In_{0.500}Ga_{0.500}N$	8.63388	8.63388	12.76645	109.2979	109.2979	84.6524	847.585791
$In_{0.625}Ga_{0.375}N$	8.99721	8.99721	12.92492	84.2928	75.706	76.1527	880.573247
$In_{0.750}Ga_{0.250}N$	8.85397	8.85397	13.08340	109.2139	109.2139	84.7340	914. 04721
$In_{0.875}Ga_{0.125}N$	8.25720	8.96401	14.55554	83.5575	77.1096	64.6721	949.091073

Lattice Constant Optimization

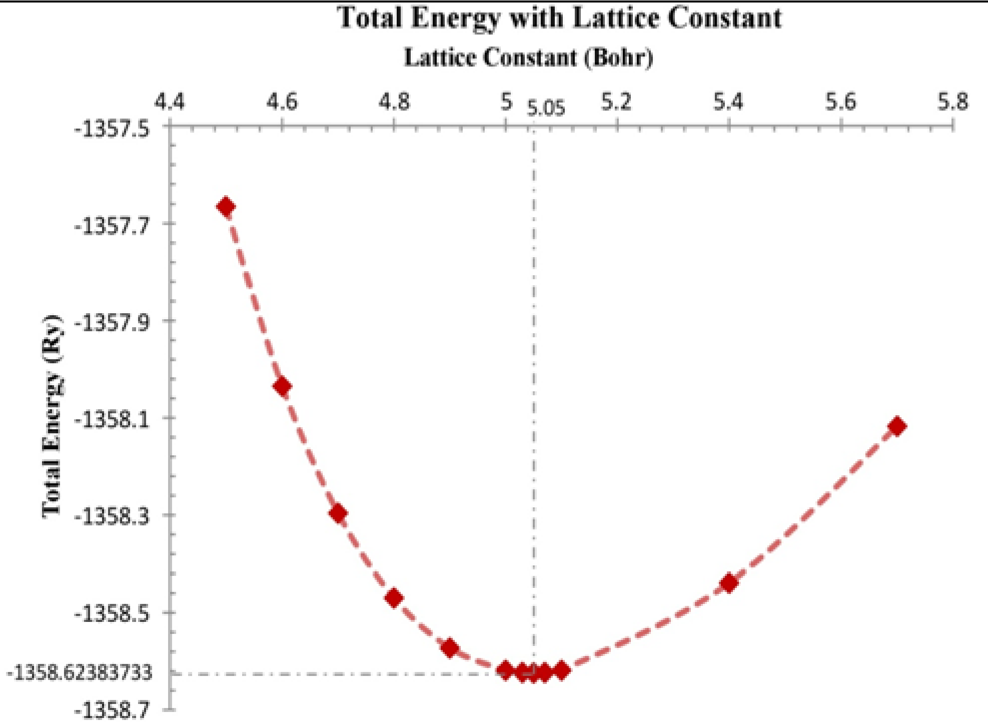
We have calculated the total energy for seven different concentration ratios of $In_{1-x}Ga_xN$. The lattice constants were chosen around the value that was predicted by Vegard's Law [15], which is an empirical formula that roughly estimates the lattice constant for an alloy. The optimized lattice constant for each system are noted for which the total energy of the system was minimum (Ground State).



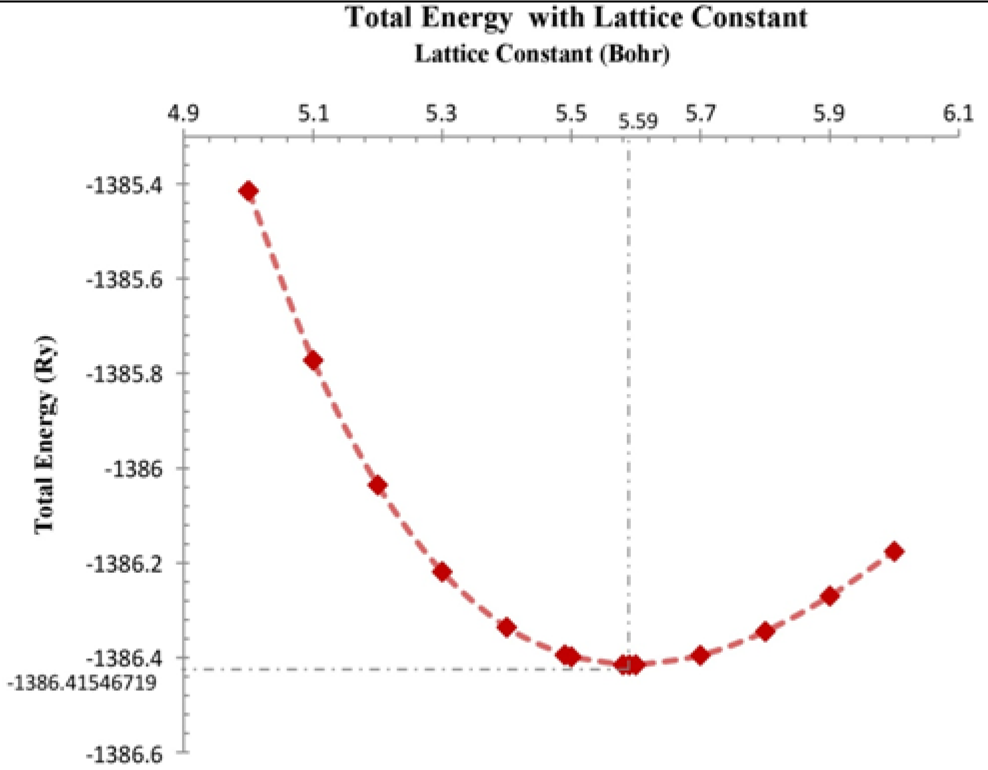
(a). Total energy for $In_{0.875}Ga_{0.125}N$



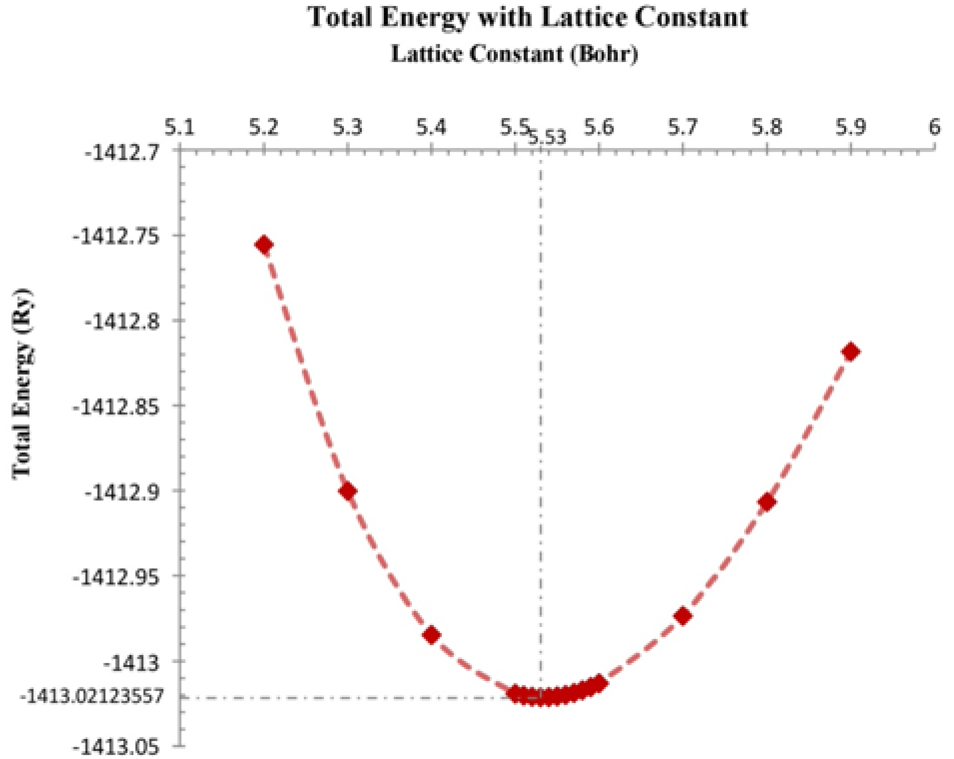
(b) Total energy for $In_{0.75}Ga_{0.25}N$.



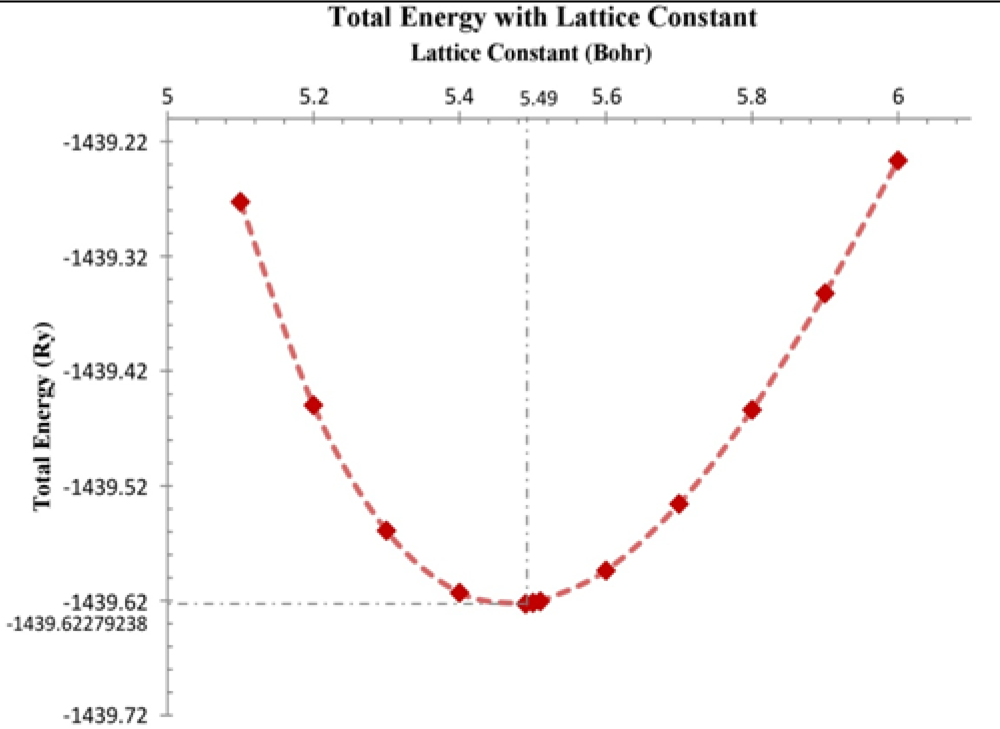
(c) Total energy for $In_{0.625}Ga_{0.375}N$



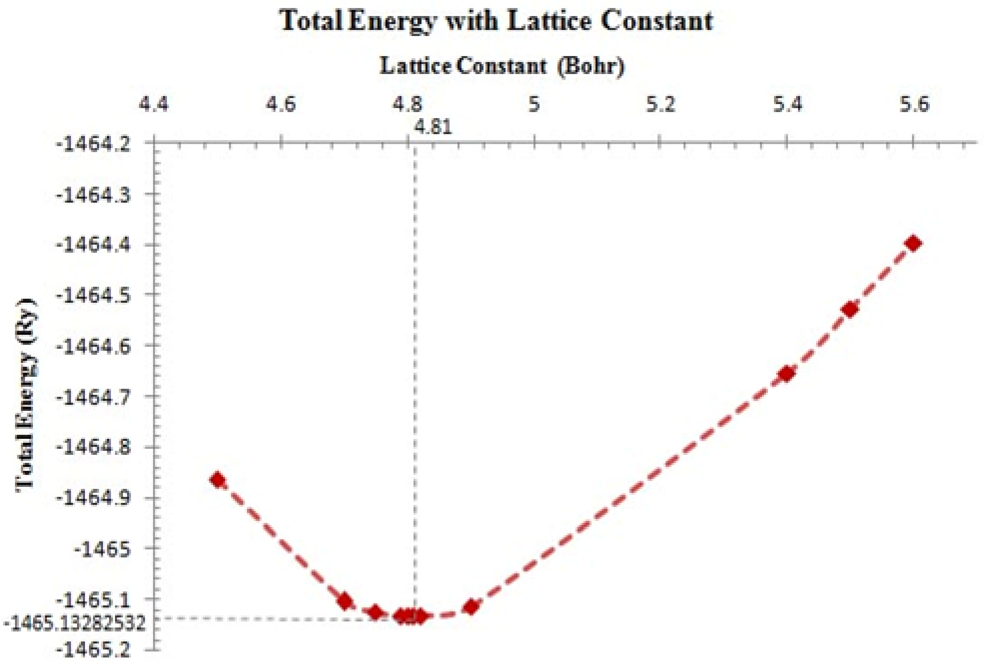
(d) Total energy for $In_{0.5}Ga_{0.5}N$.



(e) Total energy for $In_{0.375}Ga_{0.625}N$.



(f) Total energy for $In_{0.25}Ga_{0.75}N$.



(g) Total energy for $In_{0.125}Ga_{0.875}N$

5. Acknowledgement

This work was supported by Arkansas High Performance Computing Center (AHPCC), University of Arkansas by making the supercomputer “razor” accessible to us for the SCF calculations. We also thank Kathmandu University, Department of Natural Sciences for providing the working environment and support for this work.

Appendix

Table 2: Total energy of the $In_{1-x}Ga_xN$ system at different lattice constants.

Lattice Constant (Bohr)	*Total Energy (Ry)*
5.20	-1305.81634853
5.30	-1306.11509488
5.40	-1306.33107282
5.50	-1306.47757037
5.55	-1306.52834074
5.60	-1306.56599577
5.65	-1306.59164874
5.70	-1306.60626934
5.75	**-1306.61109149**
5.76	-1306.61096278
5.80	-1306.60692208
5.90	-1306.57486012
6.00	-1306.51611902
6.10	-1306.43571896
6.20	-1306.22661666

a. For x=0.125: $In_{0.875}Ga_{0.125}N$

Lattice Constant (Bohr)	*Total Energy (Ry)*
4.70	-1331.54835884
4.80	-1331.76486688
4.90	-1331.90312640
5.00	-1331.97831725
5.09	-1332.00297792
5.10	-1332.00356025
5.11	**-1332.00377683**
5.12	-1332.00358413
5.15	-1332.00064715
5.20	-1331.98883471
5.30	-1331.94264863

b. For x=0.25: $In_{0.75}Ga_{0.25}N$

Lattice Constant (Bohr)	*Total Energy (Ry)*
4.50	-1357.66520100
4.60	-1358.03475448
4.70	-1358.29611057
4.80	-1358.46965917
4.90	-1358.57260107
5.00	-1358.61854456
5.03	-1358.62299333
5.05	**-1358.62383733**
5.07	-1358.62304886
5.10	-1358.61854456
5.40	-1358.43909492
5.70	-1358.11726351

c. For x=0.375: $In_{0.625}Ga_{0.375}N$

Lattice Constant (Bohr)	*Total Energy (Ry)*
5.00	-1385.41462230
5.10	-1385.77254575
5.20	-1386.03522057
5.30	-1386.21862521
5.40	-1386.33587554
5.49	-1386.39424872
5.50	-1386.39830831
5.58	-1386.41517779
5.59	**-1386.41546719**
5.60	-1386.41537505
5.70	-1386.39520019
5.80	-1386.34476333
5.90	-1386.26990572
6.00	-1386.17547296

d. For x=0.5: $In_{0.5}Ga_{0.5}N$

Lattice Constant (Bohr)	*Total Energy (Ry)*
5.20	-1412.75538721
5.30	-1412.90027609
5.40	-1412.98456599
5.50	-1413.01915874
5.51	-1413.02023994
5.52	-1413.02092793
5.53	**-1413.02123557**
5.54	-1413.02114715
5.55	-1413.02068585
5.56	-1413.01987354
5.57	-1413.01868241
5.58	-1413.01713690
5.59	-1413.01524835
5.60	-1413.01303163
5.70	-1412.97341673
5.80	-1412.90667495
5.90	-1412.81834489

e. For x=0.625: $In_{0.375}Ga_{0.625}N$

Lattice Constant (Bohr)	*Total Energy (Ry)*
5.10	-1439.27268663
5.20	-1439.44950661
5.30	-1439.55892739
5.40	-1439.61310527
5.49	**-1439.62279238**
5.50	-1439.62187777
5.51	-1439.62059417
5.60	-1439.59374888
5.70	-1439.53565445
5.80	-1439.45357048
5.90	-1439.35244248
6.00	-1439.23658640

f. For x=0.75: $In_{0.25}Ga_{0.75}N$

Lattice Constant (Bohr)	*Total Energy (Ry)*
4.50	*-1464.86345126*
4.70	-1465.10543057
4.75	-1465.12537410
4.79	-1465.13221489
4.80	-1465.13273434
4.81	**-1465.13282532**
4.82	-1465.13245351
4.90	-1465.11512106
5.40	-1464.65516857
5.50	-1464.52771866
5.60	-1464.39688741

g. For x=0.875: $In_{0.125}Ga_{0.875}N$

6. Discussion

The use of DFT in LDA approximation to theoretically calculate the ground state total energy of the system has made remarkable progress in the past few decades. One can go even further to calculate the band gaps by taking the values of optimized lattice constants and number of Kohn-Sham orbitals however, the problem of accurate calculation of band gap for semiconductors by LDA approach remains a major theoretical challenge.

The imprecision of DFT/LDA approach in accounting electronic excitation properties can be addressed by Hedin's GW approximation [16]. This has been proven very successful. Nevertheless, the GW method requires significant additional computational effort as it involves computation of Green's function and dielectric function, and relies on the solution of Dyson equation. This is computationally more demanding than the single particle Kohn-Sham equation in DFT/LDA approach.

Consequently from practical view point, it is desirable to have a simple, efficient and reasonably accurate scheme for calculating lattice constants and ground state energies without extensive computational rigor beyond that required for DFT/LDA calculations.

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