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Total Energy Calculation of Alas and InAs Binary Semiconductors Using the Projector Augmented Wave Method

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Abstract: *The total energy of an element is the basic energy value from which other properties of the element can be calculated. Aluminum Arsenide (AlAs) and Indium Arsenide (InAs) are III – Arsenic binary semiconductors with indirect and direct energy band gap respectively. The total energy of each of them was calculated using the Projector Augmented Wave (PAW) method with the PBE-GGA for the exchange-correlation functional. The total energy were calculated and from the results gotten, the lattice constants were found to be 5.722Å and 6.176Å, the bulk modulus are 68.8 GPa and 50.5GPa respectively while the pressure derivative of the bulk modulus are 4.24 and 4.61 respectively, also the unit cell volumes were gotten as 316.100a.u^3 and 397.445a.u^3. The computed values are in close agreement with experimental values and that from other methods.*

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I. Introduction

The group III-Arsenide semiconductors are rapidly emerging as the best of semiconducting materials. They are used in the manufacture of devices like microwave frequency integrated circuits, monolithic microwave integrated circuits, infrared emitting diodes, laser diodes, solar cells and optical windows (Moss and Ledwith, 1987). Generally, the III-V compound semiconductors provide good basis for many established commercial and new technological applications in electronic and optoelectronic devices, such as light emitting diodes, photo detectors, lasers, modulators, integrated circuits and filter. The III-Arsenide compounds belong to a family of common-anion III-V semiconductors. These compounds have the widest range of energy gaps apart from the III-nitrides (Vurgaftman, *et al*, 2001). AlAs is an indirect energy band gap semiconductor while InAs is a direct energy band gap semiconductor. AlAs can form a supper-lattice with Gallium Arsenide (GaAs) which results in its semiconductor properties, it has almost the same lattice constant with GaAs (Guo, 2011).

The value of the total energy of a semiconductor may have no direct physical relevance but is very expedient in discovering other physical and structural parameters of the compound such as the lattice constants, bulk modulus, cell volume, band gap energy etc. which are vital and enable us to know which purpose each semiconductor can serve especially those that can serve as photovoltaic cells. This calculation of the total energy of these semiconductors is done using the electronic structure calculations.

There are several electronic structure calculations of AlAs and InAs that have been carried out. Ziane *et al*, carried out an electronic structure calculation of GaAs, InAs, GaN and InN using the full potential Linear Augmented Plane Wave (FP-LAPW) method. From their calculations, they used both the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). Also Luiz *et al* (1991) carried out same calculations using the *ab initio* pseudopotential method. Ahmed et al (2007), carried out same calculations for the III-Binary Arsenide using the ground-state total energy calculation approach.

Thus, in this work the total energies of AlAs and InAs were calculated using the Projector Augmented Wave(PAW) method and the Generalized Gradient Approximation (GGA) was used for the exchange-correlation functional, all within the frame work of the density functional theory. In a recent work (Ugwuagbo et al, 2016). We have carried out a total energy calculation for GaAs using the PAW method and the PBE-GGA was used for the exchange correlation functional and we got a value that agreed with experimental values by 98.12% and 81% for the lattice constant and bulk modulus respectively. All the electronic calculations done in this work were done using the computational package called *Quantum Espresso*.

II. Method Of Calculation

Since most physical problems like those of semiconductors that we try to solve have large numbers of interacting electrons and ions or nuclei. The total number of particles, N is usually too large that an exact solution cannot be found. It is therefore necessary to seek for controlled and well understood approximations to

reduce the complexity of such a system to a tractable level. This is because once the equations are solved; a good number of other properties can be discovered or derived from the wave function equation.
The interaction between the ions and electrons in a system is completely a quantum mechanical phenomenon, so getting the solution involves solving a many-body Schrodinger equation of the form

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_{r_i}^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_{R_I}^2 - \sum_{iI}\frac{Z_I e^2}{|R_I - r_i|} + \frac{1}{2}\sum_{ij\,(j\neq i)}\frac{e^2}{|r_i - r_j|} + \frac{1}{2}\sum_{IJ\,(J\neq I)}\frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (1)$$

Where **H** is the Hamiltonian of the system

The problem obtained after the first level approximation (Born-Oppenheimer) is much simpler than the original one, but it is still far too difficult to solve. Several methods exist to reduce equation (1) to an approximate but tractable form. A very important approximation is the Hartree-Fork method (HF).
For this work, we will be using the density functional theory by Sham and Kohn(Kohn and Sham, 1965), where they discovered that there is a one-to-one correspondence between the ground-state density n(**r**) of a many-electron system and the external potential V_{ext} which can be used to find other parameters of the semiconductor.
From this theory, we have that the total energy of the system is a functional of the density, and is given by

$$E[n(r)] = \langle\Psi|H|\Psi\rangle = F[n(r)] + \int V(r)\,n(r)dr \quad (2)$$

From the variational principle we can deduce that this functional attains its minimum for the correct density *n*(**r**) corresponding to *V*(**r**), since for a given *V*(**r**) and any other density *n* (**r**) we would have

$$E[n'(r)] = \langle\Psi'|H|\Psi'\rangle = F[n'(r)] + \int V(r)\,n'(r)dr > \langle\Psi|H|\Psi\rangle = E[n(r)] \quad (3)$$

Using the expressions for the one-particle and the two-particle density matrices, we can obtain explicit expressions for *E*[*n*] and *F*[*n*]:

$$E[n(\mathbf{r})] = \langle\Psi|\mathcal{H}|\Psi\rangle = -\frac{\hbar^2}{2m_e}\int \nabla_{\mathbf{r}'}^2\gamma(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}d\mathbf{r} + \int\int \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\Gamma(\mathbf{r},\mathbf{r}'|\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}' + \int V(\mathbf{r})\gamma(\mathbf{r},\mathbf{r})d\mathbf{r} \quad (4)$$

$$F[n(\mathbf{r})] = T^S[n(\mathbf{r})] + \frac{e^2}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E^{XC}[n(\mathbf{r})] \quad (5)$$

We can now consider a variation in the density, which we choose to be

$$\delta n(\mathbf{r}) = \delta\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) \quad (6)$$

with the restriction that

$$\int \delta n(\mathbf{r})d\mathbf{r} = \int \delta\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})d\mathbf{r} = 0 \quad (7)$$

so that the total number of particles does not change; note that $\emptyset_i(\mathbf{r})$ and $\emptyset_i$ (**r**) are treated as independent, as far as their variation is concerned. With this choice, and taking the restriction into account through a Lagrange multiplier $\in_i$, we arrive at the following single-particle equations, through a variational argument:

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{\mathbf{r}}^2 + V^{eff}(\mathbf{r}, n(\mathbf{r}))\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \quad (8)$$

where the effective potential is given by

$$V^{eff}(\mathbf{r}, n(\mathbf{r})) = V(\mathbf{r}) + e^2\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E^{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (9)$$

The single particle equations Eq. (8) are referred to as Kohn–Sham equations and the single particle orbitals $\emptyset_i(\mathbf{r})$ that are their solutions are called Kohn–Sham orbitals.
In this work, the Generalized Gradient Approximation was used. The generalized gradient approximation (GGA) is a semi-local approach that includes the gradient of the density in the determination of the exchange correlation potential. This is an approach which includes gradient corrections, by making a functional of the density and its gradient as seen in the relation below:

$$E_{XC}^{GGA}[n(r)] = \int \epsilon_{XC}\big(n(r)\big)n(r)dr + \int Fxc[n(r), |\nabla n(r)|]dr \quad (10)$$

The projector augmented wave (PAW) method is described as an approach that combines the versatility of the LAPW method with the formal simplicity of the traditional plane waves pseudo-potential approach.

The PAW method is a linear transformation between smooth valence pseudo (PS) wave functions, $\tilde{\Psi}_n$(n is the state index) and all-electron (AE) wave functions,Ψ_n. The core states of the atoms, φ^a_i,core, are fixed to the reference shape for the isolated atom. Here a,is an atomic index and i,is a combination index for the principal, angular momentum, and magnetic quantum numbers respectively (n, ℓ and m)(Cottenier, 2013).
Given a smooth PS wave function, the corresponding AE wave function, which is orthogonal to the set of φ^a_i,coreorbitals, can be obtained through a linear transformation

$$\psi_n(\mathbf{r}) = \hat{T}\tilde{\psi}_n(\mathbf{r}). \tag{11}$$

The transformation operator, $\hat{T}$, is given in terms of atom-centered AE partial waves, $\emptyset_i^a(r)$, the corresponding smooth partial waves, $\tilde{\emptyset}_i^a(r)$, and projector functions $\tilde{P}_i^a(r)$, as

$$\hat{T} = 1 + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle)\langle\tilde{p}_i^a|, \tag{12}$$

For a complete set of partial waves, we have

$$\psi_n = \psi_n^a \text{ and } \tilde{\psi}_n = \tilde{\psi}_n^a \text{ for } |\mathbf{r} - \mathbf{R}^a| < r_c^a \tag{13}$$

Which leads to

$$\psi_n = \tilde{\psi}_n + \sum_a (\psi_n^a - \tilde{\psi}_n^a). \tag{14}$$

Here, the term in the parenthesis is a correction inside the augmentation spheres only.
We define a PS electron density

$$\tilde{n}(\mathbf{r}) = \sum_n f_n |\tilde{\psi}_n(\mathbf{r})|^2 + \sum_a \tilde{n}_c^a(\mathbf{r}), \tag{15}$$

we define one-center expansions of the AE and PS densities,

$$n^a(\mathbf{r}) = \sum_{i_1,i_2} D_{i_1 i_2}^a \phi_{i_1}^a(\mathbf{r})\phi_{i_2}^a(\mathbf{r}) + n_c^a(\mathbf{r}), \tag{16}$$

and

$$\tilde{n}^a(\mathbf{r}) = \sum_{i_1,i_2} D_{i_1 i_2}^a \tilde{\phi}_{i_1}^a(\mathbf{r})\tilde{\phi}_{i_2}^a(\mathbf{r}) + \tilde{n}_c^a(\mathbf{r}), \tag{17}$$

respectively.

These calculations were done using the *Quantum espresso* computation codes, which basically solves the equation (8) stated earlier.
As a first step, the set of calculated total energies (cell energies) at various energy cut-offs (E-cut) was calculated starting from a value of 5Ry with a constant value for the lattice constant of the semiconductors and constant k-point grids.The value of the energy cut-off where convergence was gotten was kept constant with the k-point grid size varying. Next, a set of total energy calculation versus unit cell volume (E-V), which for cubic cells implies energy versus lattice parameter (E-a_0), for AlAs and InAs were carried out to determine their structural parameter.

III. Result And Discussion

The total energies of AlAs and InAs were calculated, from which some of the structural properties were calculated using the PAW with the PBE-GGA as the exchange and correlation function. A set of total energy calculation versus unit cell volume (E-V), which for cubic cells implies energy versus lattice parameter (E-a_0), for AlAs was carried out to determine its structural parameter.

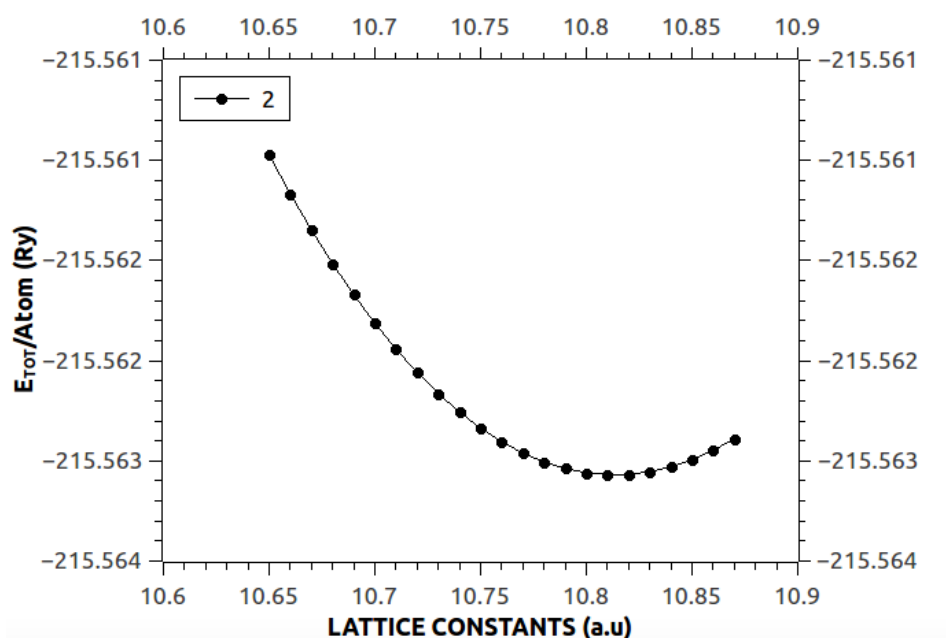

Fig. 1: *A graph of total energies against Lattice constants for AlAs*

Also, the results obtained by fitting Murnaghan's equation of state (Murnaghan, 1944) to the calculated total energies are reported, exactly as obtained from QE, which gave a lattice constant of 5.722Ǻ and a bulk modulus of 68.8GPa also, pressure derivative of the bulk modulus of 4.24 and a cell volume 316.100a.u^3.
For the InAs, a set of total energy calculation versus unit cell volume (E-V), which for cubic cells implies energy versus lattice parameter (E-a_0), for InAs was carried out to determine its structural parameter. The graph can be seen in Figure 2.0.

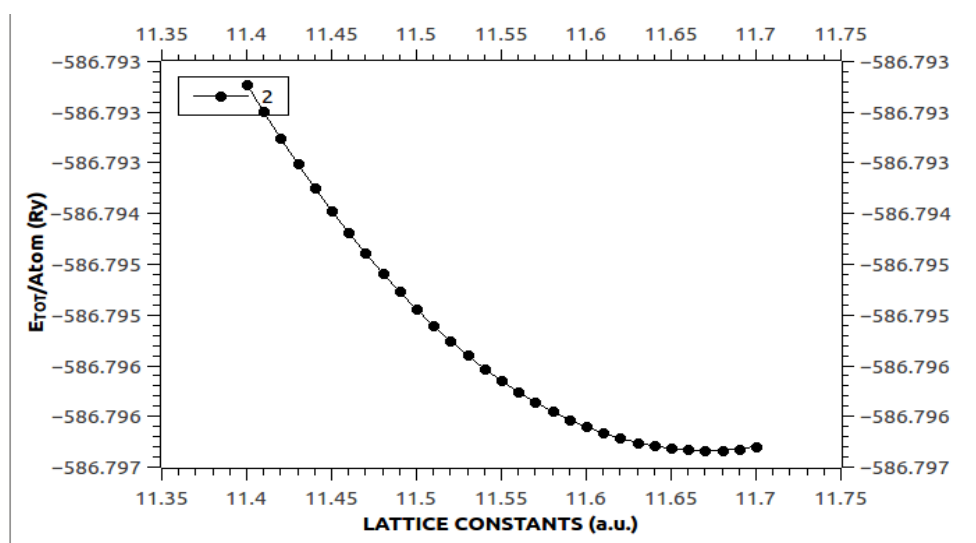

Fig.2.0 *A graph of total energies against Lattice constants for InAs*

Also, the results obtained by fitting Murnaghan's equation of state (Murnaghan, 1944) to the calculated total energies are reported, exactly as obtained from QE, gave a lattice constant of 6.176Ǻ and a bulk modulus of 50.5GPa also, pressure derivative of the bulk modulus of 4.61 and a cell volume of 397.445a.u^3.
The table below gives a comparison of the values gotten from this calculation and that derived from other works and experiment.

Table 1: Structural parameters for GaAs

Semi-conductor	Structural parameter	Present Work	Experiment	Other Works			
				FP-GGA	FP-LDA	RHF-LUC	RUF-LUC
AlAs	a (Å)	5.722	5.661 (a)	5.734 (d)	5.633 (d)	5.45 (e)	5.5 (f)
	B (Gpa)	68.8	77.3 (b)	66.5 (d)	75.1 (d)	81.39 (e)	
	B'	4.24	4.182 (c)	4.184 (d)	4.512 (d)		
	$V(a.u)^3$	316.100		317.988 (d)	301.526 (d)		
						FP-LAPW+lo	FP-GGA
InAs	a (Å)	6.176	6.036 (d)	6.0911 (g)	6.0267 (g)	6.191 (h)	6.195 (d)
	B (GPa)	50.5	58.00 (d)	55.1203 (g)	59.8387 (g)	48.68 (h)	48.1 (d)
	B'	4.61		4.7349 (g)	4.5114 (g)	4.04 (h)	4.683 (d)
	V ($Å^3$)	397.445		381.2687(g)	369.2939(g)		401.104(d)

[a]Ref. (Adachi, 2005)
[b]Ref. (Vurgaftman *et al*, 2001)
[c]Ref. (Hellwege*et al*, 1982)
[d]Ref. (Ahmed *et al*, 2007)
[e]Ref. (Jappor *et al*, 2013)
[f]Ref. (Isa *et al*, 2012)
[g]Ref (Ziane *et al*, 2014)
[h]Ref (Zhenbao *et al*, 2009)

From the result, above, the value of the lattice constant obtained from this work only varied by 1.08% from the experimental value as seen in the table above while the bulk modulus varied by 11% for AlAs; while for InAS, the lattice parameter varies by 2.32% and the bulk modulus 12.93%. This shows that the results in this work are in close agreement with the results from experimental values and that from other methods as seen in the table above.

IV. Conclusion

From the results obtained in this work, it is obvious that the value of the total energy calculated using the Projector Augmented Wave (PAW) method and the PBE-GGA for the exchange-correlation functional; from where other structural parameters were calculated is in close agreement with experimental results and the results obtained from methods. This therefore means that the PAW method, is a reliable method for the calculation of total energy of semiconductor compounds.

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