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Calculation of the Electronic Properties of Gallium Arsenide (GaAs) Semiconductors for Photovoltaic Cells

Ugwuagbo Kingsley

Student, Department of Physics, Federal University of Technology, Owerri, Nigeria

C. A. Madu

Reader, Department of Physics, Federal University of Technology, Owerri, Nigeria

E. C. Mbamala

Senior Lecturer, Department of Physics, Federal University of Technology, Owerri, Nigeria

N. I. Achuko

Assistant Lecturer, Department of Physics, Federal University of Technology, Owerri, Nigeria

Abstract:

Gallium Arsenide is one of the III – IV semiconductors with a direct energy band gap. The electronic properties of Gallium Arsenide (GaAs) was calculated using the Projector Augmented Wave (PAW) method. The lattice constant was found to be 5.75 Å, the bulk modulus is 62.3 GPa, and the pressure derivative of the bulk modulus is 4.52. The computed values of the electronic properties of GaAs shows that it is a good material for making photovoltaic cells whose importance in renewable energy cannot be over emphasized.

1. Introduction

Currently the world consumes an average of 13 terawatts (TW) of power per year (Goh & McGehee, 2005). It is obvious that with the increase in population and the current level of advancement in technology and development in both developed and developing countries, it can be predicted as has been done by Goh and McGehee (Goh & McGehee, 2005), that by the year 2050, the energy demand is likely to increase to 30 TW (Goh & McGehee, 2005). Presently, the major generation of power is from fossil fuels and if this quantity of power is to be provided by burning fossil fuels; then, the concentrations of carbon dioxide in the atmosphere will become terribly high, leading to substantial global warming, along with many other undesirable consequences. Based on this, one of the most major challenges facing scientists is finding a way to provide the world with this 30 TW of power without releasing carbon into the atmosphere. Although, it is possible for this to be done using carbon sequestration along with fossil fuels or by greatly expanding nuclear power plants and the quantity of energy generated from them; but this also have its own terrible effect on the human health. It is just obvious that what we need is the development of renewable sources of energy. The sun deposits 120,000 TW of radiation on the surface of the earth (Goh & McGehee, 2005), which is more than enough to sustain the world if more efficient means of collecting solar energy can be developed.

Semiconductors are very essential in optimized energy generation and to numerous renewable energy technologies including photovoltaic cells, wind-turbines etc.

Solar cells also known as photo-voltaic (PV) cells work on the principle of photo electric effect, which is most effective on semiconductors in generation of electric power.

There are several semiconductors which are used in several purposes and in several devices and systems. Semiconductors like Silicon (Si), Cadmium Telluride (CdTe) Indium Nitride (InN), Gallium Arsenide (GaAs), etc. are good materials for making photovoltaic cells. While semiconductors like Germanium (Ge), Indium Arsenide (InAs), etc. are good to serve as infrared detectors, making bipolar devices and several other things.

To know which semiconductor that can serve a particular purpose, there is a need to know its electronic properties (total minimum energy, lattice constant, bulk modulus etc.), the structural properties (the density of states, the energy band gap, etc.) and the optical properties (reflectance, transmittance, reflectance, etc.) of the semiconductor.

The optical band gap energy determines what amount of the solar radiation a material can absorb. Optimized band gap for solar cells is close to 1. 5eV. This value corresponds to a wavelength of about 830nm in the infrared region. Only photons with an energy higher than the band gap energy can knock off electrons and generate electricity.

This work will concentrate on finding some of the structural and electronic properties of Gallium arsenide. Gallium arsenide is one of the extrinsic semiconductors. It is a face centered cubic (fcc) crystal with a zinc blende structure.

2. Method of Calculation

Most physical problems that we try to solve like that of solids (e.g. semiconductors) have a large number 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

$$\mathbf{H} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_{r_i}^2 - \sum_l \frac{\hbar^2}{2M_l} \nabla_{R_l}^2 - \sum_{il} \frac{Z_l e^2}{|R_l - r_i|} + \frac{1}{2} \sum_{ij(j \neq i)} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{IJ(I \neq J)} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (1)$$

Where \mathbf{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's 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-Fock method (HF). We will explain a more modern and more powerful method: Density Functional Theory (DFT) (Cottenier, 2013).

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 $n(\mathbf{r})$ of a many-electron system and the external potential V_{ext} which can be used to find other parameters of the semiconductor. The equation is given below.

$$\begin{aligned} E_{V_{\text{ext}}}[\rho] &= \underbrace{\langle \Psi | \hat{T} + \hat{V} | \Psi \rangle}_{F_{HK}[\rho]} + \langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle \\ &= F_{HK}[\rho] + \int \rho(\vec{r}) V_{\text{ext}}(\vec{r}) d\vec{r} \end{aligned} \quad (2)$$

From this theory, we have that the total energy of the system is a functional of the density, and is given by

$$E[n(\mathbf{r})] = \langle \Psi | H | \Psi \rangle = F[n(\mathbf{r})] + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (3)$$

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

$$E[n'(\mathbf{r})] = \langle \Psi' | H | \Psi' \rangle = F[n'(\mathbf{r})] + \int V(\mathbf{r}) n'(\mathbf{r}) d\mathbf{r} > \langle \Psi | H | \Psi \rangle = E[n(\mathbf{r})] \quad (4)$$

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

$$\begin{aligned} E[n(\mathbf{r})] &= \langle \Psi | \mathcal{H} | \Psi \rangle = -\frac{\hbar^2}{2m_e} \int \nabla_{\mathbf{r}}^2 \gamma(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} d\mathbf{r} \\ &+ \int \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \Gamma(\mathbf{r}, \mathbf{r}' | \mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' + \int V(\mathbf{r}) \gamma(\mathbf{r}, \mathbf{r}) d\mathbf{r} \end{aligned} \quad (5)$$

Now we reduce these expressions to a set of single-particle equations. They represent fictitious fermionic particles with the requirement that their density is identical to the density of the real electrons. These particles can be considered to be non-interacting: this is a very important aspect of the nature of the fictitious particles, which will allow us to simplify things considerably, since their behavior will not be complicated by interactions. The assumption that we are dealing with non-interacting particles can be exploited to express the many-body wave function $\Psi(\{\mathbf{r}_i\})$ in the form of a Slater determinant. We can then express the various physical quantities in terms of the single-particle orbitals $\phi_i(\mathbf{r})$ that appear in the Slater determinant (Cottenier, 2013). We obtain

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 \quad (6a)$$

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}') \quad (6b)$$

$$\Gamma(\mathbf{r}, \mathbf{r}' | \mathbf{r}, \mathbf{r}') = \frac{1}{2} [n(\mathbf{r})n(\mathbf{r}') - |\gamma(\mathbf{r}, \mathbf{r}')|^2] \quad (6c)$$

With the help of these equations, we can express the various terms in the energy functional, which take the form

$$F[n(\mathbf{r})] = T^S[n(\mathbf{r})] + \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E^{XC}[n(\mathbf{r})] \quad (7)$$

In this expression, the first term represents the kinetic energy of the states in the Slater determinant (hence the superscript S). Since the fictitious particles are non-interacting, we can take the kinetic energy to be given by

$$T^S[n(\mathbf{r})] = \sum_i \langle \phi_i | -\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}}^2 | \phi_i \rangle \quad (8)$$

Notice that it would have been very difficult to write this expression in a simple form if there were interactions, which we separate out from the electron-electron interaction term in the functional $F[n(\mathbf{r})]$. What remains is the "exchange-correlation" term, $E^{XC}[n(\mathbf{r})]$. This term includes all the effects of the many-body character of the true electron system; we will deal with it separately below. We can now consider a variation in the density, which we choose to be

$$\delta n(\mathbf{r}) = \delta \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) \quad (9)$$

with the restriction that

$$\int \delta n(\mathbf{r}) d\mathbf{r} = \int \delta \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) d\mathbf{r} = 0 \quad (10)$$

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

$$\left[-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}}^2 + V^{eff}(\mathbf{r}, n(\mathbf{r})) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (11)$$

where the effective potential is given by

$$V^{eff}(\mathbf{r}, n(\mathbf{r})) = V(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E^{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (12)$$

where $V(\mathbf{r})$ is the external potential due to the ions; the last term is the variational functional derivative of the yet unspecified functional $E^{XC}[n(\mathbf{r})]$. The single particle equations Eq. (11) are referred to as Kohn–Sham equations and the single particle orbitals $\phi_i(\mathbf{r})$ that are their solutions are called Kohn–Sham orbitals. Since the effective potential is a function of the density, which is obtained from Eq. (6) and hence depends on all the single-particle states, we will need to solve these equations by iteration until we reach self-consistency. As mentioned earlier, this is not a significant problem. A more pressing issue is the exact form of $E^{XC}[n(\mathbf{r})]$ which is unknown. We can consider the simplest situation, in which the true electronic system is endowed with only one aspect of electron interactions (beyond Coulomb repulsion), that is, the exchange property. As we saw in the case of the Hartree–Fock approximation, which takes into account exchange explicitly, in a uniform system the contribution of exchange to the total energy is

$$E^X = -\frac{3}{4} \frac{e^2}{\pi} k_F N \quad (13)$$

Since the total number of electrons in the system can be written as $N = \int n d\mathbf{r}$, we can write

$$E^X[n] = -\frac{3}{4} \frac{e^2}{\pi} \int k_F n d\mathbf{r} = -\frac{3}{4} e^2 \left(\frac{3}{\pi} \right)^{1/3} \int [n]^{1/3} n d\mathbf{r} \quad (14)$$

We can now generalize this to situations where the density is not uniform, and assume that the same expression holds, obtaining (Efthimios, 2003):

$$E^X[n(\mathbf{r})] = \int \epsilon^X[n(\mathbf{r})] n(\mathbf{r}) d\mathbf{r} \quad (15)$$

$$\epsilon^X[n(\mathbf{r})] = -\frac{3}{4} e^2 \left(\frac{3}{\pi} \right)^{1/3} [n(\mathbf{r})]^{1/3} \quad (16)$$

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:

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int \epsilon_{xc}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} + \int F_{xc}[n(\mathbf{r}), |\nabla n(\mathbf{r})|] d\mathbf{r} \quad (17)$$

where F_{xc} is a correction chosen to satisfy one or several known limits for E^{XC} .

The GGA functional recommended for modern calculations is the PBE-GGA functional (Perdew et al, 1996) and that we used.

The calculation of the electronic properties of Gallium Arsenide (GaAs) was done using the Projector Augmented Wave (PAW) method. The projector augmented wave (PAW) method is described 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, $\phi_{i,\text{core}}^a$, 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 $\phi_{i,\text{core}}^a$ orbitals, can be obtained through a linear transformation

$$\psi_n(\mathbf{r}) = \hat{T} \tilde{\psi}_n(\mathbf{r}). \quad (18)$$

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

$$\hat{T} = 1 + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle \tilde{p}_i^a|, \quad (19)$$

where atom a is at the position \mathbf{R}^a . The defining properties of the atom-centered functions are that AE partial waves and smooth PS partial waves are equal outside atom-centered augmentation spheres of radii r_c^a

$$\phi_i^a(\mathbf{r}) = \tilde{\phi}_i^a(\mathbf{r}), \quad |\mathbf{r} - \mathbf{R}^a| > r_c^a \quad (20)$$

and that the projector functions are localized inside the augmentation spheres and are orthogonal to the PS partial waves

$$\langle \tilde{p}_{i_1}^a | \tilde{\phi}_{i_2}^a \rangle = \delta_{i_1 i_2}.$$

Inside the augmentation sphere of atom, a , we can define one-center expansions of an AE and PS state as

$$\psi_n^a(\mathbf{r}) = \sum_i P_{in}^a \phi_i^a(\mathbf{r}) \quad (21)$$

And

$$\tilde{\psi}_n^a(\mathbf{r}) = \sum_i P_{in}^a \tilde{\phi}_i^a(\mathbf{r}), \quad (22)$$

where the expansion coefficients are

$$P_{in}^a = \langle \tilde{p}_i^a | \tilde{\psi}_n^a \rangle. \quad (23)$$

For a complete set of partial waves, we have

$$\psi_n = \psi_n^a \text{ and } \tilde{\psi}_n = \tilde{\psi}_n^a \text{ for } |\mathbf{r} - \mathbf{R}^a| < r_c^a \quad (24)$$

Which leads to

$$\psi_n = \tilde{\psi}_n + \sum_a (\psi_n^a - \tilde{\psi}_n^a). \quad (25)$$

Here, the term in the parenthesis is a correction inside the augmentation spheres only.

We define a PS electron density

$$\tilde{n}(\mathbf{r}) = \sum_n f_n |\tilde{\psi}_n(\mathbf{r})|^2 + \sum_a \tilde{n}_c^a(\mathbf{r}), \quad (26)$$

Where f_n are occupation numbers between 0 and 2, and \tilde{n}_c^a is a smooth PS core density equal to the AE core density n_c^a outside the augmentation sphere. From the atomic density matrix $D_{i_1 i_2}^a$

$$D_{i_1 i_2}^a = \sum_n \langle \tilde{\psi}_n | \tilde{p}_{i_1}^a \rangle f_n \langle \tilde{p}_{i_2}^a | \tilde{\psi}_n \rangle. \quad (27)$$

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

$$n^a(\mathbf{r}) = \sum_{i_1, i_2} D_{i_1 i_2}^a \phi_{i_1}^a(\mathbf{r}) \phi_{i_2}^a(\mathbf{r}) + n_c^a(\mathbf{r}), \quad (28)$$

and

$$\tilde{n}^a(\mathbf{r}) = \sum_{i_1, i_2} D_{i_1 i_2}^a \tilde{\phi}_{i_1}^a(\mathbf{r}) \tilde{\phi}_{i_2}^a(\mathbf{r}) + \tilde{n}_c^a(\mathbf{r}), \quad (29)$$

respectively.

From \tilde{n} , n^a and \tilde{n}^a , we can construct the AE density in terms of a smooth part and atom-centered corrections

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_a (n^a(\mathbf{r}) - \tilde{n}^a(\mathbf{r})). \quad (30)$$

For the kinetic energy, we get

$$\tilde{E}_{kin} = -\frac{1}{2} \sum_n f_n \int dr \tilde{\psi}_n(r) \nabla^2 \tilde{\psi}_n(r), \tag{31}$$

These calculations were done using the Quantum espresso computation codes, which basically solves the equation (11) 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 lattice constant of 10.67 a.u. 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-a₀), for GaAs was carried out to determine its structural parameter.

3. Result and Discussion

The structural properties of Gallium Arsenide were calculated using the total energy as a function of volume within the PAW with the PBE-GGA as the exchange and correlation function. The convergence criterion employed in this work (i.e. ΔE/atom ≤ 5 meV ≈ 0.0004 Ry) the converged energy cut-offs were found to be approximately 210Ry. For the K-point grid, the results convergence was achieved with 14x14x14 k-point grid at particular lattice constants and energy cut-off.

Next, a set of total energy calculation versus unit cell volume (E-V), which for cubic cells implies energy versus lattice parameter (E-a₀), for GaAs was carried out to determine its structural parameter. Figure 1.0 and table 1.0 shows the lattice parameter dependence of the total energies for GaAs.

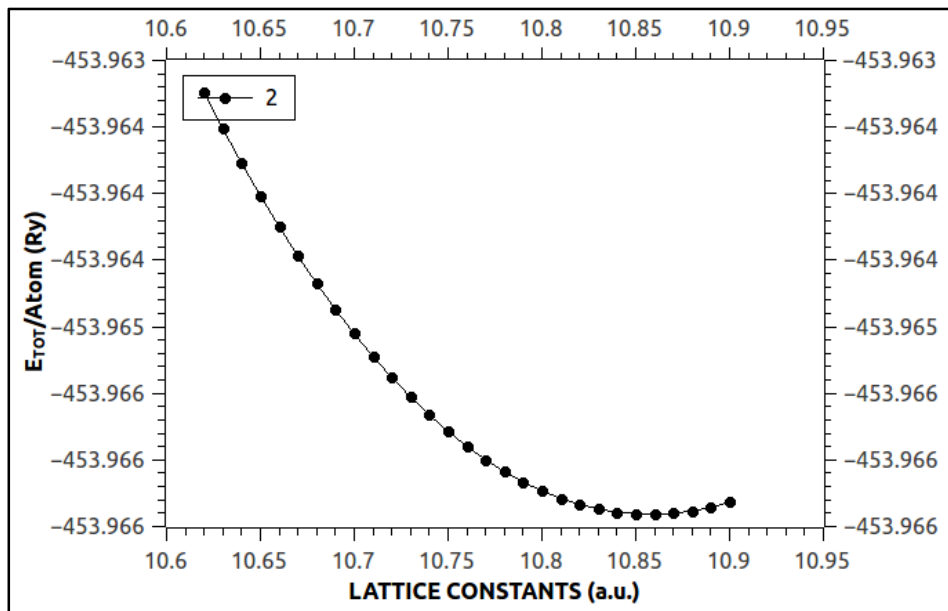


Figure 1: A graph of total energies against Lattice constants

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 5.746Å and a bulk modulus of 62.3 GPa also, pressure derivative of the bulk modulus of 4.52.

The table below gives a comparison of the values gotten from this calculation and that derived from other works and experiment.

GaAs	Present Work	Experiment	Other Works			
			FP-GGA	FP-LDA	LAPW	DFT-LDA
a (Å)	5.746	5.640 (a)	5.6654 (b)	5.7079 (b)	5.74 (c)	5.6527 (d)
B (Gpa)	62.3	77.00 (a)	69.6748 (b)	74.0432 (b)	65.00 (c)	75.195 (d)
B'	4.52		4.3434 (b)	4.8795 (b)		

Table 1: Structural parameters for GaAs

^aRef. (Hellwege et al, 1982)

^bRef (Ziane et al, 2014)

^cRef. (Juan et al, 1995)

^dRef (Hammerschmidt et al, 2008)

From the result, above, the value of the lattice constant obtained from this work only varied by 1.88% from the experimental value as seen in the table above while the bulk modulus varied by 19.09%. the results also gotten are in close agreement with other works as seen in the table above.

4. Conclusion

It is crystal clear that renewable energy is the only remedy to the generation of power without destroying the environment and burning up all available fossils. Rather the energy generated from the sun (solar energy) is constant and can never be used up.

Semiconductors are the key components for optimized energy generation to numerous renewable energy technologies including photovoltaic cells. Technological advancement and development in high power semiconductors further boosts the global demand for semiconductors for alternative energy technologies. The semiconductors are used for transmission of the power of the grid and conversion of the power in the plant.

Semiconductors are inevitable in the development of renewable energy especially that from the sun (solar energy). To use a semiconductor for these purposes, several properties of the semiconductor must be known. From this work some of the properties of Gallium Arsenide has been computed using the Projector Augmented Wave method, and from the computation carried out for Gallium Arsenide it is obvious that it is a very good material for making photovoltaic cells which are of great benefit to the world of Renewable energy.

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