Original Research Article

FIRST-PRINCIPLES THEORETICAL STUDY ON ELECTRONIC BAND STRUCTURE OF DIAMOND AND GRAPHITE

ABSTRACT

The total ground state energy and electronic band structure of Graphite and Diamond were calculated in this work using FHI-aims Density Functional Theory (DFT) code. The density functionals used are the generalized gradient functional PBE, and PBE+vdW approach as defined by Tkatchenko and Scheffler. The results obtained from the computations of the ground state energies of diamond and graphite were -2056.898408114 eV and -2061.703700984 eV respectively. Similarly, the results obtained from the computations of the electronic band gaps of graphite and diamond were 0.00451936eV and 5.56369215 eV, respectively. These are in good agreement when compared to the experimental values of 0eV and 5.48eV. These band gaps are within reasonable percentage errors of 0.0% and 1.46% respectively.

Keywords: DFT, Diamond, Electronic Band Structure, DOS, and Graphite.

1. INTRODUCTION

For many years the band structure emerging from density functional theory really was the only electronic structure free of empirical parameters that could be calculated to interpret carrier levels, doping, chemical bonding, etc. As such, it still has enormous reach in the community as a baseline against which better (formally more rigorous) approximations are compared [1]. The electronic band structures of graphite and diamond are particularly very important because of their unique semiconducting applications and fascinating properties. Researchers have studied the band structure of simple hexagonal graphite using nonlocal ionic pseudopotential [2], compared the band structure and DOS of the three graphite structures using an *ab* initio norm-conserving pseudopotential [3].

On the other hand, an empirical pseudopotential method was used [4] to calculate the band structure of diamond. Louis *et al,* 1970, also computed the band structure of diamond using nonlocal pseudopotential method. Similarly, band gap of diamond was calculated by [6] using both LDA and

GGA functionals. The methods mentioned above involved an empirical and/or pseudopotential computations, an all-electron/full Potential with numeric atom-centered basis function computational method is therefore necessary to study the band structure of these interesting Carbon allotropes. In this work, electronic band structure of diamond and graphite were simulated using FHI-aims DFT package [7]. The aim of this paper is to re-investigate the ground state electronic properties as well as predict the suitable potential electronic applications of diamond and graphite.

2. MATERIAL AND METHODS

First principles calculations represent the pinnacle of electronic structure calculations. Starting with the fundamental constants and Schrödinger's equation as a postulate, these methods proceed to describe the nature of atomistic systems to a degree that is almost irrefutable. The methods applied in solving Schrodinger's equation break into two main types: Hartree-Fock (HF) based methods and Density Functional Theory (DFT) methods. While both make approximations to make calculations possible, they represent the best available methods for atomistic modeling.

The original idea of DFT (i.e. using the electron density) is dated back to the individual work of [8 and 9]. In Thomas-Fermi model, they showed that the distribution of electrons in an atom is uniform and can be approximated using statistical considerations. In 1964, [10] proved two simple but important theorems, which later become the basis of DFT. In 1965, in a trade of simplicity for accuracy, [11] invented an ingenious indirect approach to the theory in such a way that the kinetic energy can be computed simply to a good accuracy, leaving a small residual correction that is handled separately. They showed that one can build a theory using simpler formulas also referred to as Kohn-Sham (KS) kinetic energy functional and ground state electron density, namely;

$$T_S[n] = \langle \psi_i | -\frac{1}{2}\nabla_i^2 | \psi_i \rangle$$

(1.1)

and

$$n(\vec{r}) = \sum_i^N \sum_S |\psi_i(\vec{r}\vec{S})|^2$$

(1.2)

where ψ_i are the natural spin orbitals. To give a unique value to the KS kinetic energy functional $T_S[n]$ through Eq. (1.1), KS invoked a corresponding non-interacting reference system, with the Hamiltonian:

$$\hat{H}_S = \sum_i^N \left(-\frac{1}{2}\nabla_i^2\right) + \sum_i^N V_S(\vec{r})$$

(1.3)

in which there are no electron-electron repulsion terms, and for which the ground state electron density is exactly $n(\vec{r})$. KS thus established that for any real (interacting) system with ground state density $n(\vec{r})$, there always exist a non-interacting system with the same ground state density $n(\vec{r})$ For this system there will be an exact determinantal ground state wave function;

$$\Psi_S = \frac{1}{\sqrt{N!}} \det[\psi_1, \psi_2 \ldots \psi_N] .$$

(1.4)

where ψ_i are the N lowest eigenstates of the one electron Hamiltonian $\hat{H}_S$

$$\hat{H}_S \psi_i = \left[\left(-\frac{1}{2}\nabla_i^2\right) + V_S(\vec{r})\right]\psi_i = \varepsilon_i \psi_i \qquad (1.5)$$

Now, to produce $T_S[n]$ exactly as the kinetic energy component [12] of $T[n]$ in HK theorem, KS reformulate the universal functional as;

$$F[n] = T_S[n] + J[n] + E_{xc}[n] \qquad (1.6)$$

where;

$$E_{xc}[n] = T[n] - T_S[n] + V_{ee}[n] - J[n] \qquad (1.7)$$

The defined quantity $E_{xc}[n]$ is called the exchange-correlation energy functional. The corresponding Euler equation for Eq. (1.7) is;

$$\mu = V_{eff}\left(\vec{r}\right) + \frac{\delta T_S[n]}{\delta n\left[\vec{r}\right]}$$

(1.8)

Where $V_{eff}(\vec{r})$ is the KS effective potential and is defined by;

$$V_{eff}(\vec{r}) = V_{ne}(\vec{r}) + \frac{\delta J[n]}{\delta n[\vec{r}]} + \frac{\delta E_{xc}[n]}{\delta n[\vec{r}]} \qquad (1.9)$$

$$V_{eff}(\vec{r}) = V_{ne}(\vec{r}) + \int \frac{n[\vec{r}]}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 + V_{xc}(\vec{r}) \qquad (2.0)$$

The second term of Eq. (2.0) is the Hartree potential while the XC potential $V_{xc}(\vec{r})$ is given as

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[n]}{\delta n[\vec{r}]}$$

(2.1)

Therefore, for a given $V_{eff}(\vec{r})$, one gets the $n(\vec{r})$ simply by solving the *N* one-electron equations;

$$[(-\frac{1}{2}\nabla_i^2) + V_{eff}(\vec{r})]\psi_i = \varepsilon_i \psi_i \qquad (2.2)$$

and setting .

$$n(\vec{r}) = \sum_{i}^{N}\sum_{S} |\psi_{i}(\vec{r}\vec{S})|^{2}$$

(2.3)

The effective potential from Eq. (1.9) depends on the electron density; therefore the Kohn-Sham equations have to be solved self-consistently. The electronic total energy *E* is typically calculated using the sum over the Kohn-Sham eigenvalues;

$$E = \sum_{i}^{N} \varepsilon_{i} - \frac{1}{2}\iint \frac{n(\vec{r}_{1})\, n(\vec{r}_{2})}{|\vec{r}_{1} - \vec{r}_{2}|} d\vec{r}_{1}\, d\vec{r}_{2} + E_{xc}[n] - \int V_{xc}(\vec{r})\, n(\vec{r})\, d\vec{r} \qquad (2.4)$$

The Kohn-Sham scheme is in principle exact. The approximation only enters when we have to decide on an explicit form for the unknown functional for the exchange-correlation energy $E_{xc}[n]$ and its corresponding potential $V_{xc}(\vec{r})$. The main goal of modern DFT is therefore to find better approximations to these two functionals. A great variety of different approximations to $V_{xc}(\vec{r})$ have been developed. For many years the local density approximation (LDA) has been used [13]. In LDA, the exchange correlation energy density at a point in space is taken to be that of the homogeneous electron gas with the local electron density. Thus the total exchange correlation energy functional is approximated as,

$$E_{xc}^{LDA} = \int n(\vec{r})\, \varepsilon_{xc}(n(\vec{r}))\, d\vec{r}$$

(2.5)

From which the potential is obtained using Eq. 2.1. However, LDA can have significant errors in its approximations for some physical and chemical properties computations. Recently, an effective potential that depend both on the local density and the magnitude of its local gradient are widely used. They are known as generalized gradient approximations (GGA) functionals. The GGA's total exchange correlation energy functional is approximated as,

$$E_{xc}^{GGA}[n_{\uparrow,} n_{\downarrow}] = \int \varepsilon_{xc}(n_{\uparrow,} n_{\downarrow,} \vec{\nabla} n\uparrow \vec{\nabla} n\downarrow) n(\vec{r}) d\vec{r} \quad (2.6)$$

There are many GGA versions among which is the Perdew Burke Ernzerhof (pbe) functional (1997) used in this study. On the other hand, there are many DFT computational codes among which is the FHI-aims package. FHI-aims is a computer program package for computational materials science based only on quantum-mechanical first principles mathematical model. It uses solution methods of DFT to compute the total energy and derived quantities of molecular or solid condensed matter in its electronic ground state (Blum *et al,* 2009). In addition, FHI-aims allow describing a wave-function based molecular total energy calculation based on Hartree-Fock and many-body perturbation theory (MP2 and MP4).

2.1 Computational Details

Total ground state energy of graphite and diamond were calculated in the Generalized Gradient Approximation (GGA) and Local Density Approximation (LDA) using the [14] and [15], exchange-correlation energy functionals respectively. The calculation was performed by using Brillouin-zone of 12×12×12 k-point grids for the SCF convergence. For the interplanar lattice parameter c of graphite, vdW effects correction based on [16] was included into the PBE functional. In order to generate a smooth-looking DOS, we used a denser 8×8×8 k-space grid to integrate the DOS for diamond. The factors by which the original k-space grid from the SCF cycle is increased are now (8, 8, 8). Together with the original k-grid of 12×12×12, this makes for a 96×96×96 integration mesh that is used for the DOS. However, we used a less dense 5×5×5 k-space grid to integrate the DOS for graphite. A Gaussian broadening of 0.05eV was used for both structures DOS computations. We used an experimental lattice constant of a = 3.567 Ǻ and a = 2.461 Ǻ, c = 6.708Ǻ for diamond and graphite respectively.

3. RESULTS

The following table summarize the output data obtained during FHI-aims computations,

Table 1.2: Band gaps for Diamond and Graphite

Bands Structure	Lowest unoccupied state (eV)	Highest occupied state (eV)	Energy difference (eV)
Graphite	-6.22855848	-6.23307784	0.00451936

Diamond	-2.66537760	-8.22906975	5.56369215

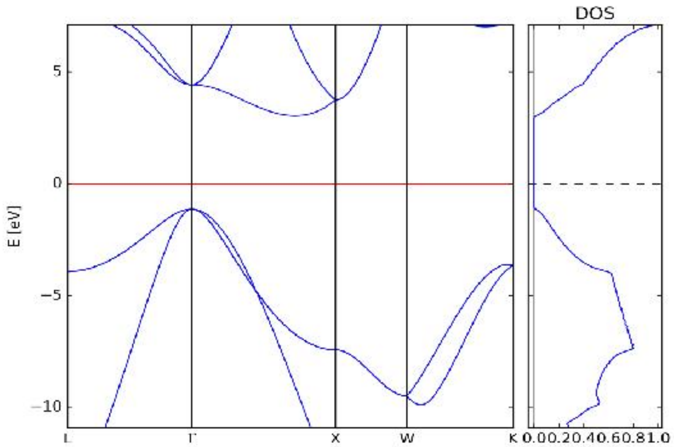

Fig. 1.1 Band Structure and Density of States of the bulk Diamond as generated by the 'aimsplot.py' script.

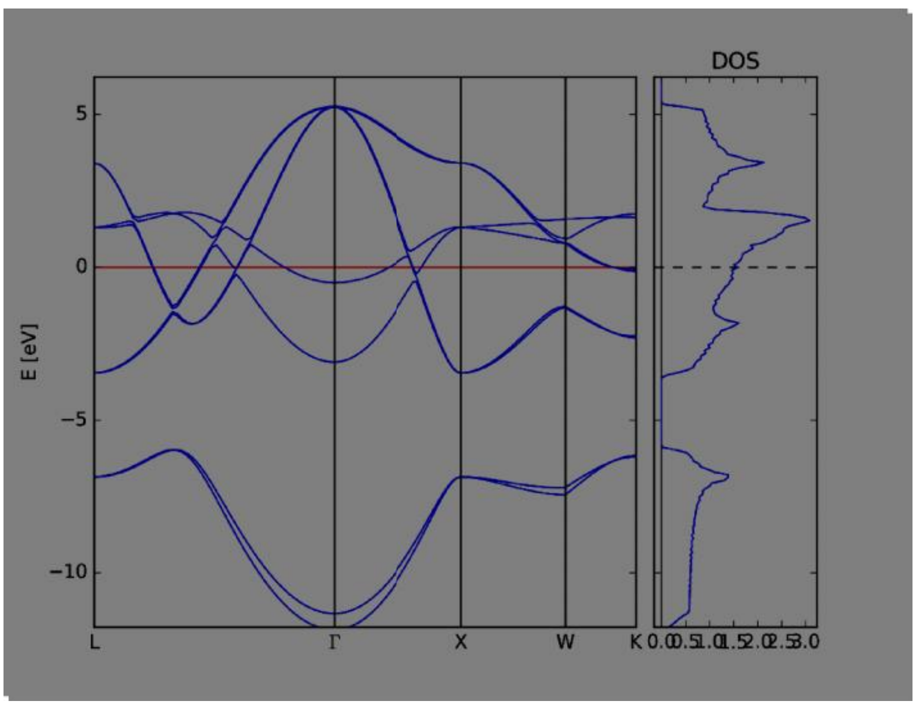

Fig. 1.2 Band Structure and Density of States of the bulk Graphite as generated by the 'aimsplot.py' script.

4. DISCUSSIONS

Fig. 1.1 and 1.2 show the band structures and DOS for diamond and graphite respectively. The position of the Fermi level in the band structure of these crystals is shown by the zero on the energy scale and that of symmetry points are indicated by vertical lines on the band graph in Fig. 1.1 and Fig. 1.2.

In Fig. 1.1, there is an important characteristic of the band structure, namely the range of energies where there are no electronic states across the entire Brillouin zone; this is the band gap. The Fermi level within the band gap shows that all state below it remain occupied and all state above remain unoccupied. From the plot and shown in Table 1.2, the energy difference between the lowest unoccupied state and the highest occupied state along reciprocal space direction number one is 5.56369215 eV. This value differs from other theoretical and experimental values by 0.12 eV and 0.08 eV, respectively [6 and 17]. Since the valence band maximum at Γ-point, and the conduction band minimum partially at X -point are on different symmetry point, it shows that diamond is an indirect band gap semiconductor with a large energy gap value of 5.56 eV. Similar result of an indirect band gap semiconductor for AlAs and diamond were also computed using FHI-aims code [18 and 19]. The DOS for the unit cell in Fig 1.1 also shows that the number of the electronic states in the valence bands is more than that of the conduction bands.

In Fig. 1.2, there is another important characteristic of the band structure, namely a narrow or zero gap range of energies where there are no electronic states; this energy band gap has a value of 0.00451936 eV as shown in Table 1.2. This approximately zero-gap value agrees with other theoretical and experimental values (Krueger, 2010; Charlier *et al,* 1994) [3 and 20]. It is obvious that the Fermi level lies within the conduction band, this shows that the conduction band is partially filled. The bands can be seen to touch at the entire L-K region of the Brillouin zone. The overlapping points on the Fermi level is between π- nonbonding orbitals in different graphite planes. This is simply because, in graphite the strong bonding between the segments connecting nearest-neighbour atoms within the layers (intralayer) is described by sp^2 hybridized 2s, $2p_x$, and $2p_y$ atomic orbitals (σ-states), and the weak interlayer bonding is derived from the overlap between $2p_z$ orbitals (π-states) perpendicular to the graphitic planes. The resulting band structure consists of bonding π and σ-states and anti-bonding π * and σ * states forming the valence and conduction bands, respectively. The weak interactions between graphitic planes is such that these bands split which leads to a zero-gap semiconductor and create a wide overlap semimetal [3 and 17]. The splitting of the bands at the Fermi level is in agreement with experiment [2]. As the electronic nature of a structure depends on the density of states in the region of the Fermi level, the theoretical overlap three regions of peaks are presented in the DOS of Fig. 1.2.

5. CONCLUSION

The total ground state energy and electronic band structure of Graphite for hcp and Diamond crystal were calculated using the LDA in the parameterization by Perdew and Zunger 1981, the generalized gradient functional PBE, and PBE+vdW approach as defined by Tkatchenko and Scheffler. The results of the total energy required for binding/stability of the ground state during the optimized process were found to converge faster with the 12x12x12 k-grid points in the Brillouin zone of the FHI-aims code. We have found that a DFT LDA/GGA calculation of diamond and graphite electronic band structure and DOS gives correct location and shape of the Fermi level, band gap, VBM and CBM. The comparison between theory and experiment is better than could have been expected from band-gap studies with similar formalism.

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