

ENERGETICS OF THE BASIC ALLOTROPES OF CARBON

ABSTRACT

An effort was made in this work to calculate the total ground state energy and electronic band structure of Fullerenes (C_{60}), Graphite and Diamond using FHI-aims Density Functional Theory (DFT) code. The density functionals used are the local-density approximation (LDA) in the parameterization by Perdew and Wang 1992, Perdew and Zunger 1981, 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, fullerenes and graphite were -2072.569 eV, -1027.178 eV and -2070.938 eV respectively. These results agree well when compared to the various exchange and correlation functionals used in this study. Similarly, the results obtained from the computations of the Kohn Sham electronic band gaps of graphite and diamond were 0.00072eV and 5.57611eV, respectively. These are also in agreement when compared to the experimental values of 0eV and 5.5eV. These band gaps are within reasonable overestimation errors of 0.0007eV and 0.08eV respectively. However, the fullerenes band gap of 8.21131eV is not in agreement with the theoretical and experimental values of 1.83eV and 2.3eV, respectively. This is probably due to the Bucky-ball nature of Fullerenes as well as the lattice constants and physical settings used.

Keywords: DFT, LDA, GGA, Band Gap, HOMO, LUMO and Total Ground state Energy.

1. INTRODUCTION

Carbon is found naturally in the earth crust and in the atmosphere. It is abundant and forms a major part of our life. Carbon is a unique and versatile element. It exists in many forms with different structures and properties. It can also be synthesized to form new forms of materials [1]. Carbon is the basic building block of the following Carbon materials: graphite, diamond, fullerene, graphene, Carbon-fiber, Carbon nanotube, lonsdaleite, carbyne and bucky diamonds. Recently, new Carbon form called penta-graphene was discovered using the Vienna Ab initio Simulation Package (VASP) [2]. Similarly, novamene [3] was also discovered and the stable equilibrium structure was computed using Quantum Espresso code. The ability of Carbon to exist in many forms with different structures and properties led researchers into a rigorous research on Carbon nano-material.

The principal allotropes of Carbon are graphite, diamond and Fullerenes. Diamond is associated with the sp^3 hybrid orbital, all four electrons are used to form a tetravalent sigma σ bond in a 3D structure. In each unit cell, diamond has eight Carbon atoms. The bond length is equidistant

41 between the four Carbon atoms, thereby forming a strong covalent bond with a bond angle of
42 109.5° . Diamond is the hardest known material, it is used in cutting, drilling and grinding. It is
43 transparent in the visible range of the electromagnetic spectrum, making it a good candidate for
44 jewellery. It has a high thermal conductivity (more than copper) and low thermal expansion [1
45 and 4]

46 Graphite has a flat layered (planar) structure. Each Carbon atom forms trivalent (sigma σ) bond
47 with three (sp^2 hybrid orbital) other Carbon atoms in a hexagonal shape. The layers are bonded
48 to one another by weak Van-der-Waal forces. This allows the layers to slip over each other. The
49 p_z – orbitals electrons, do also interact: they form a π -mobile electron. Graphite is the most
50 stable and most strongly covalently bonded Carbon allotrope (within the layer). It is soft, opaque,
51 black, used in pencil, lubrication and in nuclear reactor moderator [1 and 4].

52 In recent time, a new Carbon allotrope was discovered by Curl, Kroto and Smalley at Rice
53 University. It is spherical (soccer ball) in shape. It resembles a geodesic dome constructed by an
54 architect in the person of Richard Buckminster Fuller. Hence, it was named in his honour as
55 buckminsterfullerene, shortened as fullerenes (also called buckyballs). It has sixty (60) Carbon
56 atoms arranged in both pentagonal and hexagonal shape. For it to have a spherical shape, it
57 must satisfy the pentagon rule i.e. it must have 12 pentagons and 20 hexagons. Basic Fullerene
58 molecular formula is C_{60} [1 and 4]. Unlike graphite and diamond, fullerene molecule has both sp^3
59 and sp^2 hybrid orbitals, i.e., It has both sigma and pi bond. Fullerene is used as a high-
60 temperature superconductor when doped with K or Rb, it is a possible lubricating aid and is also
61 used in medicine [1 and 5].

62 Nowadays, Density Functional Theory (DFT) is one of the leading tools used in studying the
63 electronic structure, stability, synthesis, defects, semiconducting and superconducting properties
64 of Carbon materials. DFT is a special computational quantum mechanical first principle method
65 of describing and predicting the electronic structures and properties of atoms, molecules and
66 solids. [19] used DFT GAUSSIAN 3 software to compute the ground state energies and stable
67 structures of diamond, graphite and fullerenes. [20] calculated the stable atomic structure of
68 fullerenes using FHI-aims code. They reported that the most stable structure crystallizes in fcc
69 structure. This crystal structure was used in this study for fullerenes computations.

70 However, the small ($1s^2$) ionic core of Carbon couple with the hybrid orbitals degeneracy
71 presents a challenge to computational modelling. Therefore, It is the purpose of this work to use
72 an all-electron/full potential code (FHI-aims) that uses numeric tabulated atomic basis set to
73 reinvestigate the electronic properties of Carbon basic allotropes. This would also assist towards
74 checking the accuracy and efficiency of FHI-aims in comparison to other programs.

75 2. MATERIALS AND METHODS

76 First principles, or *ab initio* calculations represent the pinnacle of electronic structure calculations.
77 Starting with the fundamental constants and Schrodinger's equation as a postulate, these methods
78 proceed to describe the nature of atomistic systems to a degree that is almost irrefutable. The
79 methods applied in solving Schrodinger's equation break into two main types: Hartree-Fock (HF)
80 based methods and Density Functional Theory (DFT) methods. While both make approximations to
81 make calculations possible, they represent the best available methods for atomistic modelling. The
82 first task is to have a Linux based operating system (OS) (Ubuntu 16.04 version installed for this
83 research work) on a computer. FHI-aims (Fritz Haber Institute-*ab initio* molecular simulations) is not
84 supported on windows. Since FHI-aims is distributed in source code form, the next task is to compile
85 a powerful executable program. For this, the following mandatory prerequisites are needed [6]:

- 86 • A working FORTRAN compiler. A good example is Intel's ifort compiler.
- 87 • A compiled version of the lapack library, and a library providing optimized basic linear algebra
- 88 subroutines (BLAS). Standard commercial libraries such as Intel's mkl provide both lapack and
- 89 BLAS support. Having an optimized BLAS library for a specific computer system is critical for the
- 90 performance of FHI-aims.

91 FHI-aims requires two input files — control.in and geometry.in—located in the same directory
92 from where the FHI-aims binary is invoked. An output file contains the basic information and
93 result of the calculation such as the total energy, atomic forces, etc. The geometry.in file contains
94 all information concerning the atomic structure of the system. This includes the nuclear
95 coordinates, which are specified by the keyword; an atom, followed by Cartesian coordinates (in
96 units of Å) and the descriptor of the species (chemical elements) [7]. The control.in file contains

97 all other physical and technical settings for accurate and efficient convergence of the
98 computations.

99 The full algorithmic framework embodied in the FHI-aims computer program package is
100 described in [6]. The algorithms are based on numerically tabulated atom-centered orbitals
101 (NAOs) to capture a wide range of molecular and materials properties from quantum-mechanical
102 first principles. FHI-aims is a very important code because, an all-electron / full-potential
103 treatment that is both computationally efficient and accurate is achieved for periodic and cluster
104 geometries on equal footing, including relaxation and *ab initio* molecular dynamics. The primary
105 production method for total energies and gradients is density functional theory (LDA and GGA).
106 Additional functionality includes quantum-chemical approaches (Hartree-Fock, hybrid functionals,
107 MP2) and self-energy-based methods (e.g., GW) for electronic spectroscopic properties. FHI-
108 aims allows fully quantum-mechanical simulations for systems up to thousands of atoms and
109 performs efficiently also on massively parallel platforms with possibly thousands of CPUs [6].
110 However, choosing the central computational settings consistently for series of calculations
111 greatly enhances the accuracy of any resulting energy differences (error cancellation). In FHI-
112 aims, the key parameters regarding computational accuracy are actually sub-keywords of the
113 species keyword of control.in, controlling the basis set, all integration grids, and the accuracy of
114 the Hartree potential. These settings, of course, were not retyped from scratch for every single
115 calculation; on the other hand, they remained obvious since these are the central handles to
116 determine the accuracy and efficiency of a given calculation.
117 FHI-aims, therefore, provides preconstructed default definitions for the important sub-keywords
118 associated with different species from Z=1-102 (H-Md). These can be found in the
119 *species_defaults* subdirectory of the distribution, and are built for inclusion into a control.in the
120 file by simple copy-paste.
121 For all elements, FHI-aims offers three different levels of *species_defaults*, however, we used
122 only two of these levels of *species_defaults* in this work:
123 • *light* : Out-of-the-box settings for fast pre-relaxations, structure searches, etc. Actually, no
124 obvious geometry / convergence errors resulted from these settings, and are recommended for

many household tasks. For “final” results (meV-level converged energy differences between large molecular structures etc.), any results from the *light* level should be verified with more accurate post-processing calculations, e.g. *tight*.

- *tight* : Regarding the integration grids, Hartree potential, and basis cutoff potentials, the settings specified here are rather safe, intended to provide meV-level accurate energy *differences* also for large structures. In the *tight* settings, the basis set level is set to *tier 2* for the light elements 1-10, a modified *tier 1* for the slightly heavier Al, Si, P, S, Cl (the first *spdfgd* radial functions are enabled by default), and *tier 1* for all other elements. This reflects the fact that, for heavy elements, *tier 1* is sufficient for tightly converged ground state properties in DFT-LDA/GGA, but for the light elements (H-Ne), *tier 2* is, e.g., required for meV-level converged energy differences. For convergence purposes, the specification of the basis set itself (*tier 1*, *tier 2*, etc.) may still be decreased/increased as needed [6].

2.1 COMPUTATIONAL DETAILS

Various computations were done for the (Perdew and Wang) pw_lda, (Perdew and Zunger) pz_lda and (Perdew Burke Ernzerhof) pbe_GGA (exchange correlation) XC functionals. A Gaussian occupation broadening width of 0.01eV was selected. The convergence criterion for the SCF of eigenvalues, total energy and density were set to 10^{-2} eV, 10^{-5} eV and 10^{-4} eV, respectively. The structure geometry with a convergence minimum of 10^{-2} eV was optimized, while for the unit cell geometry optimization we selected full unit cell relaxation option. The corresponding convergence criteria for the SCF of the energy derivatives was chosen to be 10^{-4} eV.

Tier 1 basis functions of FHI-aims light species_default basis set was used for the geometry optimization, however, tier 2 tight basis set was used for the post relaxation of the relaxed geometry. BFGS (Broyden, Fletcher, Goldfarb and Shanno) structure optimization algorithm was selected for the geometry relaxation. FHI-aims keyword k_grid was set to 12x12x12 k_grid data point. For the long-range correlation energy interaction effect, we used VdW correction based on Tkatchenko and Scheffler long-range interaction correction.

3. RESULTS AND DISCUSSION

The following tables summarize the output data obtained during FHI-aims computations and are used in discussing the minimum and stable ground state energies for the relaxed/post relaxed computations of the various XC functionals for the three bulk structures.

Table 4.1: Diamond Ground State Energies for Relaxed/Post Relaxed Computations.

Functionals	Computations	Pw_Ida Ground State Energy (eV)	Pz_Ida Ground State Energy (eV)	Pbe (GGA) Ground State Energy (eV)
Relaxed Geometry (Light)		-2056.94097548	-2056.90780088	-2072.47722687
Postrelaxed Geometry (Tight)		-2057.03098622	-2056.99760599	-2072.56851605

From table 4.1, it can be observed that pbe XC functional has the minimum ground state energy for diamond bulk structure. This is in agreement with theory because pbe (GGA) is theoretically a better approximation to XC energy functional than the rest LDA and LSDA [8 and 9]. However, pw_Ida is a bit better approximation when compared to pz_Ida. Similarly, comparing light and tight FHI-aims species_default settings for relaxed and post relaxed computations, tight gives an efficient and accurate converged ground state energies than the light settings. This is a good indication that diamond crystalline structure has been well optimized in the relaxed/postrelaxed FHI-aims computations. The following graphs summarize the output data obtained during FHI-aims computations and are used in obtaining the binding curve pattern for the total energy and the number of iterations.

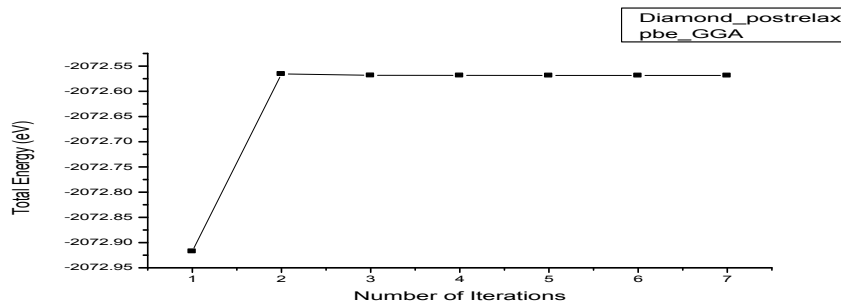
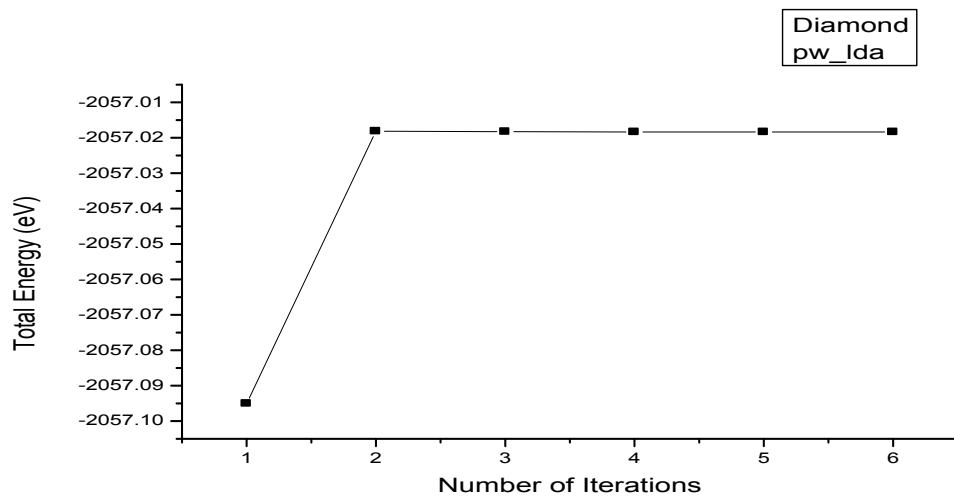


Fig. 4.1: Variations of Total Energy (eV) against Number of Iterations

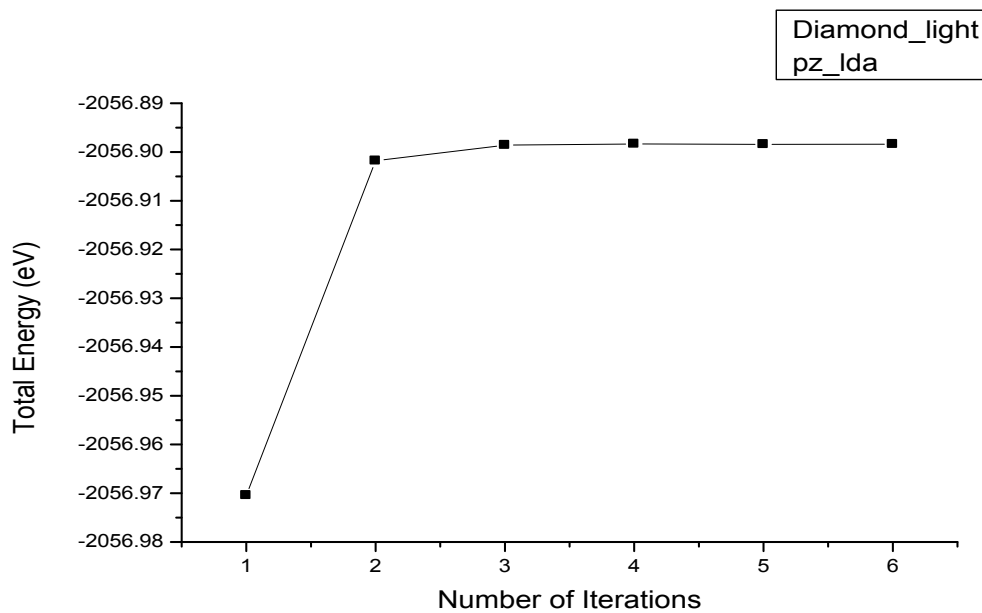
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Fig. 4.2: Variations of Total Energy (eV) against Number of Iterations.



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Fig. 4.3: Variations of Total Energy (eV) against Number of Iterations.

175 The binding curve in Fig. 4.1 shows that the total energy of the bulk crystal of diamond increases
 176 as the number of iteration increases and converges steadily. The resulting binding curve
 177 indicates a stable total energy and also the best-converged energy of -2072.56851605eV for

diamond. This variation pattern for diamond total energy against the number of iterations was found to be the same for the remaining XC functionals used in this study.

Fig. 4.2 and Fig. 4.3 also illustrate the variations of diamond's ground state energies against the number of iterations. It is clear that the graphs variations are almost the same, except that the total energies values are different. In Fig. 4.2 graph, the total energy value increases steadily from the 1st iteration to the 2nd iteration, from where this value decreases a bit and is later maintained until convergence is reached. However, fig. 4.3 shows a slightly different trend. The total energy value rather increases in the third iteration, this value was maintained until convergence was obtained. The resulting binding curve in Fig. 4.3 indicates a stable total energy and also the best-converged energy of -2056.89840811eV for diamond.

Table 4.2: Graphite Ground State Energies for Relaxed/Post Relaxed Computations

Functionals	Pw_Ida Ground State Energy (eV)	Pz_Ida Ground State Energy (eV)	Pbe (GGA) Ground State Energy (eV)
Computations			
Relaxed Geometry	-2044.81236553	-2044.81251118	-2061.63381564
Postrelaxed Geometry (Tight)	-2054.61937938	-2054.63065901	-2070.93836837

From table 4.2, it can be observe that pbe XC functional also has the minimum ground state energy for graphite bulk structure. This is in agreement with theory, because pbe (GGA) is theoretically a better approximation to XC energy than the rest pw_Ida and pz_Ida [9]. However, pw_Ida is slightly a better approximation when compared to pz_Ida. Similarly, comparing light and tight species_default settings for relaxed and post relaxed computations tight gives an efficient and accurate converged ground state energies than the light settings. This is also a good indication that graphite crystalline structure has been well optimized in the relaxed/post relaxed FHI-aims computations.

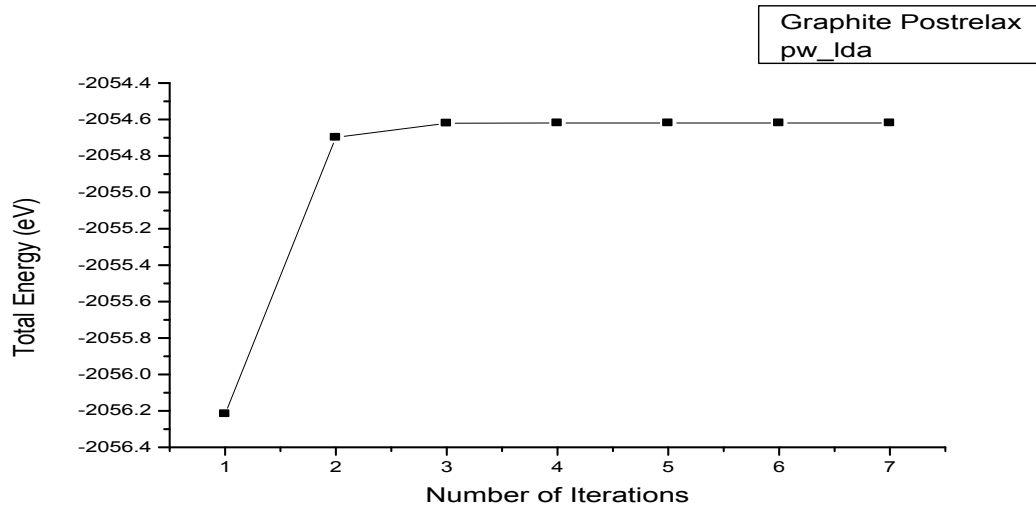


Fig. 4.4: Variations of Total Energy (eV) against Number of Iterations.

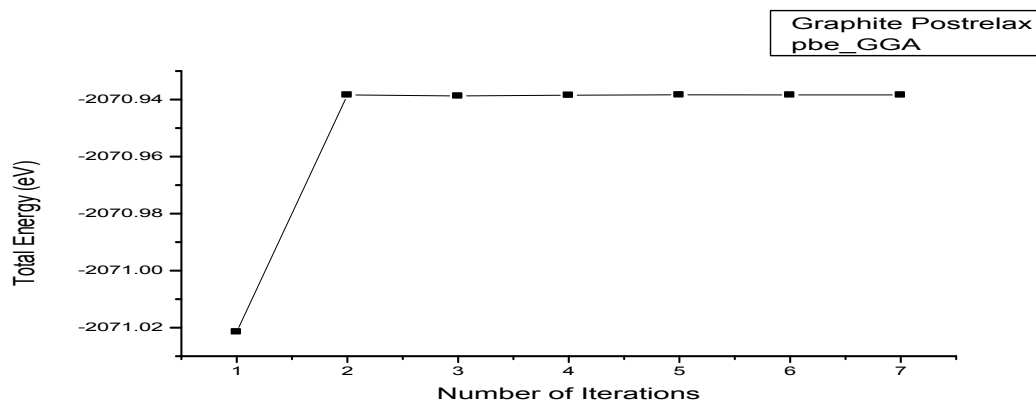


Fig. 4.5: Variations of Total Energy (eV) against Number of Iterations.

Fig. 4.4 and Fig. 4.5 illustrate the variations of ground state energies against a number of iterations for graphite bulk structure. The trend in both Figures increases upwardly to create a curve pattern until it reaches stability at the 3rd, 4th, 5th, 6th and 7th iterations, this can be attributed to the covalent bonding and simple planar hexagonal stacking that exist in the bulk atom of graphite [10]. The resulting binding curve in Fig. 4.5 indicates a stable total energy and also the best-converged energy of -2070.93836837 eV for graphite.

Table 4.3: Fullerenes Ground State Energies for Light and Tight Settings.

Functionals	Pw_Ida Ground State Energy (eV)	Pz_Ida Ground State Energy (eV)	Pbe (GGA) Ground State Energy (eV)
Computations			
L i g h t	-1018.35981067	-1018.35683745	-1027.17026568
T i g h t	-1018.36680612	-1018.36379535	-1027.17849607

210

211 For Fullerenes, ground state energies for relaxed/post relaxed computations were not successful,
212 because FHI-aims could not write out the geometry.in_next_step file let alone post relax
213 processing. We suggest this could be due to the dimension of fullerenes lattice constant of
214 14.17 \AA , physical settings used and/or its spherical shape However, we computed the ground
215 state energies for light/tight settings without structure optimization. Table 4.3 shows fullerenes
216 ground state energies for the three XC functionals using light/tight default settings. The table also
217 shows that, tight default settings gives a more accurate converged minimum ground state energy
218 when compared to the light default settings. This is in good agreement with the theory behind
219 FHI-aims code [6]. Also looking at the XC functional total energy values, it is obvious that pbe
220 gives the minimum ground state energy follow by pw_lda and then pz_lda. Hence, in accordance
221 with theory pbe is much better in approximating the XC energy functional than pw_lda and
222 pz_lda [8 and 9].

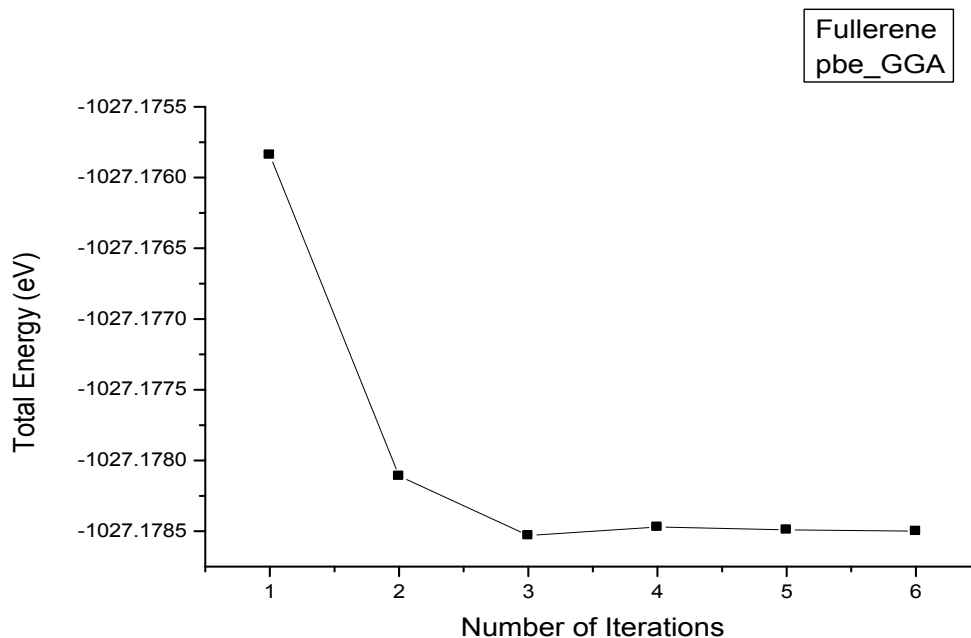


Fig. 4.6: Variations of Total Energy (eV) against Number of Iterations.

Figure 4.6 illustrates the variations of Fullerenes ground state energies for the pbe XC functionals against a number of iterations. The trend in Fig. 4.6 decreases downwardly to create a curve pattern until it becomes stable at the 4th, 5th and 6th iterations, this can be attributed to the covalent bonding and spherical shape that exist in the bulk atom of fullerenes [10 and 11].

In this paper, we find out that all the three variants of the total energy from FHI-aims output file are the same for diamond structure but are all different in the case of graphite and fullerenes. This shows that fullerenes and graphite have narrow and zero HOMO-LUMO (highest occupied molecular orbital - lowest unoccupied molecular orbital) gap respectively, while diamond has a wide HOMO-LUMO gap. These results are in good agreement with experimental and theoretical literature [10 and 12]. Tables 4.4-4.6 show estimated values for lowest unoccupied state (CBM), highest occupied state (VBM), overall HOMO-LUMO gap and smallest direct gap for diamond, graphite and fullerenes as obtained from the three XC functionals used in this study.

Table 4.4: Diamond Electronic Band Structure for Postrelaxed Computations

Functionals	Pw_Ida Ground State Energy (eV)	Pz_Ida Ground State Energy (eV)	Pbe (GGA) Ground State Energy (eV)

Bands			
Valence Band Maxima (VBM)	- 8 . 5 4 3 1 0 4 9 7	- 8 . 5 3 3 8 7 2 4 3	- 8 . 1 0 9 8 8 4 0 3
Conduction Band Minima (CBM)	- 4 . 3 4 3 0 0 0 7 8	- 4 . 3 4 3 5 6 0 4 1	- 3 . 9 5 7 7 8 6 1 8
HOMO-LUMO Gap	4 . 2 0 0 1 0 4 1 9	4 . 1 9 0 3 1 2 0 1	4 . 1 5 2 0 9 7 8 5
Smallest Direct Gap	5 . 6 1 4 5 7 4 2 7	5 . 6 0 7 1 1 3 1 9	5 . 5 7 6 1 1 3 2 5

238

239 From table 4.4, using the estimated overall HOMO-LUMO gap, FHI-aims code predicted that
240 diamond appears to be an indirect band gap. This agrees well with the report of Pierson, 1993.
241 The smallest direct gap of 5.57611325eV for pbe_GGA is in good agreement with theoretical and
242 experimental values [10 and 21] with an overestimation percentage error of 1.43%. According to
243 FHI-aims output file, since the gap value is above 0.2eV, the system is most likely an insulator or
244 a semiconductor. This FHI-aims output file comment agrees exactly with theoretical and
245 experimental data. Diamond was characterized in many literatures to be an insulator [4],
246 however, it was also considered as an indirect wide band gap semiconductor [1] that is suitable
247 for high-temperature electronic applications. The rest XC functionals pw_Ida and pz_Ida Smallest
248 Direct Gap are also in good agreement with experimental values of 5.5eV [10] with an
249 overestimation error of 1.96%.

250 Table 4.5: Graphite Electronic Band Structure for Postrelaxed Computations

Functionals	Pw_Ida Ground State Energy (eV)	Pz_Ida Ground State Energy (eV)	Pbe (GGA) Ground State Energy (eV)
Bands			
Valence Band Maxima (VBM)	- 7 . 0 7 4 1 5 4 1 3	-7.33934792	- 6 . 8 1 3 1 3 4 4 5
Conduction Band Minima (CBM)	- 7 . 0 6 5 6 9 0 1 1	- 7 . 3 3 8 6 1 8 3 4	- 6 . 8 0 8 5 2 6 9 2
HOMO-LUMO Gap	0 . 0 0 8 4 6 4 0 2	0 . 0 0 0 7 2 9 5 8	0 . 0 0 4 6 0 7 5 3
Smallest Direct Gap	0 . 2 1 3 0 8 6 4 5	0 . 4 1 5 4 1 8 8 4	0 . 3 0 7 2 4 6 8 3

251

252 From table 4.5, using the estimated overall HOMO-LUMO gap, FHI-aims predicted that graphite
253 also appears to be an indirect band gap. The smallest direct gap of 0.21308645eV for pw_Ida is

in good agreement with theoretical [13] and experimental values [10]. According to FHI-aims output file, since the HOMP-LUMO gap value (0.00072958eV) is rather small (approximately zero gap) and we use a finite k-point grid, the material is most likely metallic in the sense that there are states at or near the Fermi level. This FHI-aims output comment shows that graphite is a conductor, and it agrees exactly with theoretical [13] and experimental data. Also, the approximately zero gap value of FHI-aims output file is in agreement with the literature [10]. The rest XC functionals pz_Ida and pbe_GGA Smallest Direct Gap are also in good agreement with experimental values within small overestimation errors.

Table 4.6: Fullerenes Electronic Band Structure for Tight Settings Computations

Functionals	Bands	Pw_Ida Ground State Energy (eV)	Pz_Ida Ground State Energy (eV)	Pbe (GGA) Ground State Energy (eV)
Valence Band Maxima (VBM)		- 1 3 . 6 0 2 4 8 6 4 1	- 1 3 . 6 0 7 0 6 5 6 0	- 1 3 . 7 1 2 2 8 4 0 8
Conduction Band Minima (CBM)		- 5 . 3 9 1 1 7 2 1 0	- 5 . 3 9 5 3 9 6 1 3	- 5 . 2 5 9 0 4 2 6 9
HOMO-LUMO Gap		8 . 2 1 1 3 1 4 3 1	8 . 2 1 1 6 6 9 4 7	8 . 4 5 3 2 4 1 3 8
Smallest Direct Gap		8 . 2 1 1 3 1 4 3 2	8 . 2 1 1 6 6 9 4 8	8 . 4 5 3 2 4 1 3 9

From table 4.6, using the estimated overall HOMO-LUMO gap, FHI-aims predicted that fullerenes also appears to be an indirect band gap. The smallest direct gap of 8.21131432eV for pw_Ida and the remaining XC functionals values do not agree with the theoretical value of 1.83eV [12] and experimental value of 2.3eV [Byun 2012, PhD Dissertation, Pennsylvania State University]. According to the FHI-aims output file, since the gap value is above 0.2 eV. The system is most likely an insulator or a semiconductor. This FHI-aims output prediction agrees exactly with theoretical and experimental data, fullerenes was reported to be a band insulator, direct band-gap semiconductor [1]. In addition, fullerenes can be converted from a semiconductor into a conductor or even superconductor when doped with alkali metals [14]. The rest XC functionals pz_Ida and pbe_GGA Smallest Direct Gap are also not in good agreement with theoretical [12] and experimental values.

It can be easily observed that all the electronic band gaps above are overestimated by certain percentage errors. This is because generally, DFT overestimates the band gap energy of solids [8].

5. CONCLUSION

The total ground state energy and electronic band structure of Fullerenes (C_{60}) for FCC, Graphite for hcp and Diamond crystal were calculated using the local-density approximation (LDA) in the parameterization by [15-17], and PBE+vdW approach as defined by [18]. 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. Similarly, FHI-aims tight/post relaxed settings were found to give more accurate converged results. In terms of the XC functionals, pbe_GGA was better in approximating the XC energy functional than LDA. The result presented above have confirmed a faster and more accurate prediction of the electronic band structure and total energies of solids considered when compared to literature report of other studies reporting similar band gaps and/or total energies. Major findings of this research are; Graphite is a zero gap conductor (0.00072958eV), diamond is a wide band gap semiconductor (5.57611325eV). These are in good agreement with experimental values of 0eV and 5.45eV, respectively. However, fullerenes is also a wide band gap semiconductor (8.21131431eV). This band gap does not agree with what was obtainable in the literature (1.83eV and 2.3eV). This discrepancy might probably be due to the present DFT calculations of the solid fullerene's lattice constant, spherical shape and the optimized parameters used in the study.

Conversely, Graphite is a suitable candidate for optoelectronic and other electronic devices. Diamond is suitable for high temperature thermal electronic devices, while fullerenes is a good material for conversion into conductors and superconductors.

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