

COMPUTATIONS OF THE GROUND STATE ENERGIES PER ATOM FOR DIAMOND, FULLERENES AND GRAPHITE USING FHI-aims CODE

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ABSTRACT

In this work the total ground state energy per atom for Fullerenes (C_{60}), Graphite and Diamond were computed using Density Functional Theory (DFT) code FHI-aims (Fritz Haber Institute- *ab initio* molecular simulations). 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 -1028.51549311 eV, -1027.194 eV and -1035.469 eV, respectively. These results agree with both experimental and theoretical results regardless of the exchange and correlation functionals used.

Keywords: Total Ground state Energy per Atom, DFT, FHI-aims, LDA, and GGA.

INTRODUCTION

Carbon is an element that belongs to group IV in the periodic table. It has six (6) electrons and protons each at the ground state level. Carbon has the electron configuration ($1s^2 2s^2 2p^2$). Its four valence electrons and a small ionic core are responsible for Carbon unique structure and properties. These valence electrons are used in the formation of a covalent bond (Pierson, 1993; Rand, Appleyard and Yardim, 2001; Adams and Williams, 2007). However, orbital hybridization occurs during the covalent bond formation. This is the promotion/lifting of an electron from an s orbital to a p orbital to form either sp^3 , sp^2 or sp^1 hybrid orbital. Other group IV elements like silicon, tin and germanium also have this property of orbital hybridization and therefore also crystallize in the diamond structure (Kittel, 1996). However, the numbers of various allotropes formed by Carbon alone due to hybridization outnumber that of all other chemical elements put together.

The principal allotropes of Carbon are graphite, diamond and Fullerenes. These materials have different structures and properties. However, Carbon is the basic building block. Diamond is associated with the sp^3 hybrid orbital (figure 1), all four electrons are used to form a tetravalent sigma (σ) bond. Consequently, diamond is an insulator since there are no free mobile electrons.

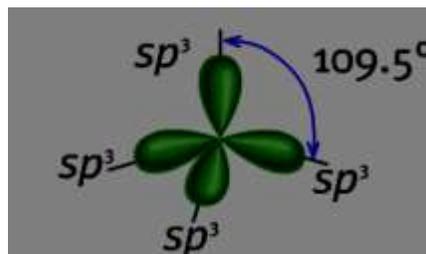


Fig. 1: Sp^3 -Hybrid orbital (Peschel, 2011)

The sp^2 hybrid orbital has three valence electrons that are used to form a trivalent sigma (σ) bond in graphite (Figure 2). The remaining electrons, contained in the p_z - orbitals, do also interact: they form a π - cloud that is delocalized over the entire graphene layer. The π - electrons thus behave like a two - dimensional electron gas, and by their mobility, they cause material properties like an anisotropic electrical conductivity. Hence, graphite is a good conductor as a result of the mobile electron.

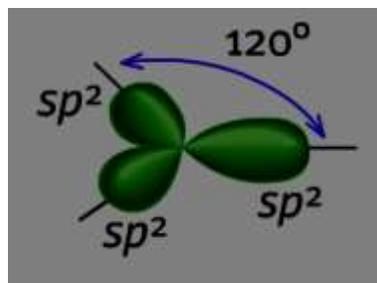


Fig 2: Sp^2 -hybrid orbital (Peschel, 2011)

Unlike graphite and diamond, fullerene molecule has both sp^3 and sp^2 hybrid orbitals (Pierson, 1993). Potential applications of Carbon basic allotropes in many areas of science and technology have led to an extensive research on their structural stability (González *et al*, 2014, Fleming *et al* 1992), electronic structure/energy (Yu *et al*, 2009), as well as thermal (Grochala, 2014), semiconducting (Heggie *et al*, 1998) and superconducting (Byun, 2012) characteristics.

Nowadays, DFT is one of the leading tools used in studying the electronic properties of Carbon materials. DFT is a special computational quantum mechanical first principle method of describing and predicting the electronic structures and properties of atoms, molecules and solids (Parr and Yang, 1989). In this work, using FHI-aims DFT package (Blum *et al*, 2009) structural units of Carbon basic allotropes were simulated in order to obtain their ground state energies per atom. It is advantageous to write out the total energy per atom, not per unit cell, when comparing the stable minimum energies of different crystal structures (Wieferink, Nemeč and Blum, 2011). This makes a difference especially for the diamond structure.

MATERIALS AND METHODS

First principles or *ab initio* calculations represent the pinnacle of electronic structure calculations. Starting with the fundamental constants and Schrodinger'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 DFT methods. While both make approximations to make calculations possible, they represent the best available methods for atomistic modeling (Carlson, 2006). The first task is to have a Linux based operating system (OS) (Ubuntu 16.04 version installed for this research work) on a computer. FHI-aims is not supported on windows. Since FHI-aims is distributed in source code form, the next task is to compile an executable program. Therefore a working FORTRAN compiler was also installed. The full algorithmic framework embodied in the FHI-aims computer program package is described in Blum *et al* (2009). The algorithms are based on numerically tabulated atom-centered orbitals (NAOs) to capture a wide range of molecular and materials properties from quantum-mechanical first principles. An all-electron / full-potential treatment that is both computationally efficient and accurate is achieved for periodic and cluster geometries on equal footing, including relaxation and *ab initio* molecular dynamics.

Computational Details

Computations were done for the (Perdew and Wang) *pw_lda*, (Perdew and Zunger) *pz_lda* and (Perdew, Burke Ernzerhof) *pbe* (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 full unit cell relaxation option was used for the unit cell geometry optimization. BFGS (Broyden, Fletcher, Goldfarb and Shanno) structure optimization algorithm was selected for the geometry relaxation. *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 for fullerenes and graphite.

Figure 3 shows crystalline structures that were used for computational simulations. In (Figure 3a), diamond crystalline lattice is presented. For graphite (Figure 3b), graphene sheets are shown, however a unit cell of the bulk graphite structure was used for this work. This is because for periodic systems, in order to obtain the bulk electronic structure we only need to compute for the unit cell basis atoms positions and the three lattice vectors. Fullerene structure is observed in (Figure 3c), presented as a sphere composed of 60 carbon atoms (C_{60}).

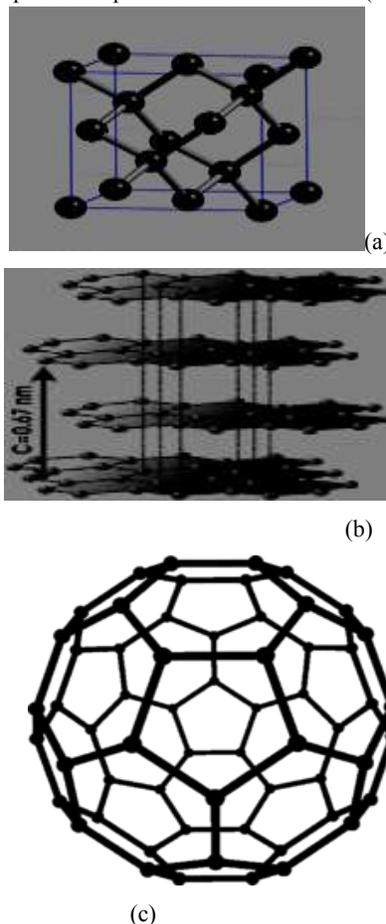


Fig. 3: Structures Simulated (a) Diamond (b) Graphite and (c) Fullerenes (C_{60})

The data used for these periodic systems' geometry computations are shown in table 1

Table 1: Input Data used in Geometry.in File.

Crystal Structure	Lattice Constant a_0	Atomic Coordinates	Lattice Vectors	Space Group
Diamond	3.567Å	0.0 0.0 0.0 0.89175 0.89175 0.89175	0.0 1.7835 1.7835 1.7835 0.0 1.7835 1.7835 1.7835 0.0	$Fd\bar{3}m$ Diamond
Graphite	2.461Å $c=0.6708\text{nm}$ $=6.708\text{Å}$	0.0 0.0 0.0 0.0 -1.421 3.354	1.2305 -2.131 0.0 1.2305 2.131 0.0 0.0 0.0 6.708	P6/mmc (hcp)
Fullerenes	$1.417\text{nm}=14.17\text{Å}$	0.0 0.0 0.0	0 7.085 7.085 7.085 0 7.085 7.085 7.085 0	$Fm\bar{3}m$ (FC)

RESULTS

Tables 2-4 summarize the output data obtained during FHI-aims computations, and are used in discussing the minimum and stable ground state energies per atom for the relaxed/post relaxed computations of the various XC functionals for the three bulk structures.

Table 2: Diamond Ground State Energies per Atom.

Functionals Computations	Pw_lda Ground State Energy (eV)	Pz_lda Ground State Energy (eV)	Pbe (GGA) Ground State Energy (eV)
Postrelaxed	-1028.51549311	-1028.49880299	-1036.28425802
Tight	-1028.50917036	-1028.49324090	-1036.28407877

Table 3: Graphite Ground State Energies per Atom.

Functionals Computations	Pw_lda Ground State Energy (eV)	Pz_lda Ground State Energy (eV)	Pbe (GGA) Ground State Energy (eV)
Postrelaxed	-1027.30972390	-1027.31536863	-1035.46922145
Tight	-1022.44427887	-1022.44147573	-1030.85749115

Table 4: Fullerenes Ground State Energies per Atom.

Functionals Computations	Pw_lda Ground State Energy (eV)	Pz_lda Ground State Energy (eV)	Pbe (GGA) Ground State Energy (eV)
Tight	-1018.38223235	-1018.37922158	-1027.19392231

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 per atom against number of iterations.

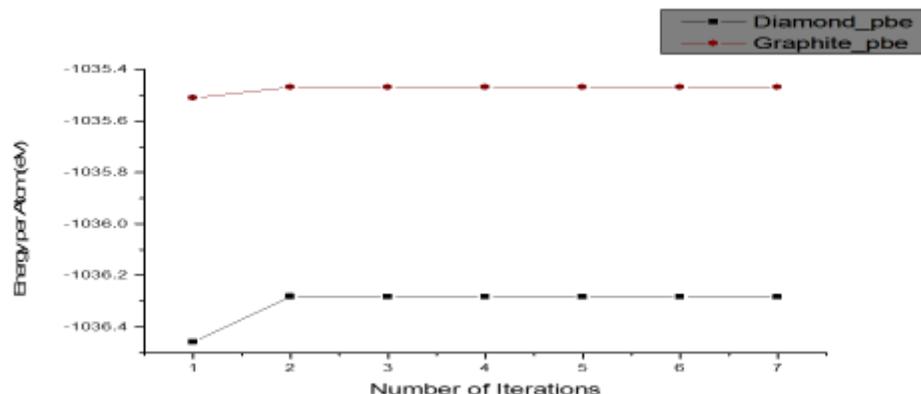


Fig. 4: Variations of Total Energy per Atom (eV) against Number of Iterations.

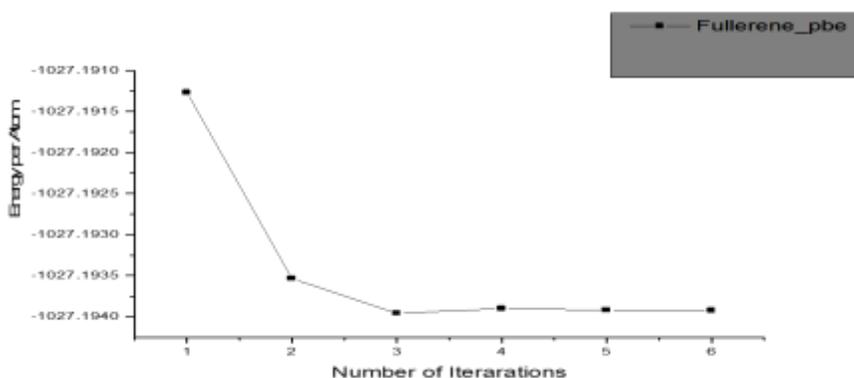


Fig. 5: Variations of Total Energy per Atom (eV) against Number of Iterations.

DISCUSSION

According to the output files of FHI-aims used in the computations, we obtained the ground state electronic free energy per atom for the three XC functionals. Table 2 shows that pbe_GGA XC functional has the minimum diamond's electronic ground state energy per atom. However, pw_lda gives a better result (-1028.51549311eV) for both post relaxed and tight options when compared to pz_lda. This is comparable to the previously reported DFT energies of -1028.527419 eV/atom (Bross and Bader, 1995). This tells us that the pw_lda of the XC functional used here is accurate in describing the ground state energy per atom of carbon atoms. Comparing postrelaxed and tight computations options, it is obvious that postrelaxed gives the minimum total energy per atom. This is a good indication that diamond crystalline structure has been well optimized in the relaxed/post relaxed FHI-aims computations.

Table 3 also shows that pbe_GGA XC functional has the minimum electronic ground state energy per atom for graphite. However, pz_lda gives a better result for postrelaxed option when compared to pw_lda and vice-versa for tight setting options. Also, comparing postrelaxed and tight computations options, it is clear that postrelaxed gives the minimum total

energy per atom and agrees with FHI-aims theory. That 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. using tight (Blum *et al*, 2009). This is also a good indication that graphite structure has been well optimized in the relaxed/post relaxed FHI-aims computations.

For Fullerenes, ground state energies per atom for relaxed/postrelaxed computations were not successful, because FHI-aims could not write out the geometry.in_next_step file let alone post relax processing. This could be due to the dimension of fullerenes lattice constant of 14.17Å and/or its spherical shape. However, we computed the ground state energies per atom for tight settings without structure relaxation.

Table 4 also shows that pbe_GGA XC functional has the minimum electronic ground state energy per atom for fullerene bulk structure. However, pw_lda gives a better result when compared to pz_lda. This is a good indication that pbe_GGA is a better approximation for the XC functional (Parr and Yang, 1989; Fiolhais *et al*, 2003), followed by pw_lda when using FHI-aims tight default settings. This computed ground state energy

differs by 2.36eV from that of (María and Tröger, 2017) for the energy of the 3P ground state of carbon atom.

The binding curve in Figure 4 shows that the total energy per atom of the bulk crystal of diamond increases as the number of iteration increases and converges steadily. The resulting binding curve indicates a stable total energy and also the best converged energy of -1036.284 eV for diamond.

The graphite's trend in Figure 4 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 hexagonal stacking that exist in the bulk atom of graphite (Carlson, 2006; Krueger, 2010).

Figure 5 illustrates the variations of Fullerenes ground state energies per atom for the pbe XC functional against number of iterations. The trend in the Figure decreases downwardly to create a curve pattern until it becomes stable at the 4th, 5th and 6th iterations; this could be due to the covalent bonding and spherical shape that exist in the bulk atom of fullerenes. These variation patterns for diamond, graphite and fullerenes total energies per atom were found to be similar to those obtained by Abdu et al (2018) for the total ground state energy for each of the bulk structures.

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CONCLUSION

The total ground state energy per atom of Fullerenes (C_{60}) for FCC, Graphite for HCP and Diamond crystal were calculated using 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 of the total energy required for binding/stability of the ground state during the optimized process were found to converge faster with the 12x12x12s k-grid points in the Brillouin zone of the FHI-aims code. Similarly, FHI-aims tight/postrelaxed settings were found to give more accurate converged results. In terms of the XC functionals, pbe_GGA yielded better results than LDA. The trends of results obtained are better and has fast convergence when compared with that of Gonzalez et al, 2014. This is because in our computations, Fullerene needs the lowest amount of energy to sustain the crystallographic structure (-1027.194 eV), followed by graphite (-1035.469 eV). However, for diamond higher energy values are needed to maintaining stability, the obtained data was: -1036.284 eV. While in Gonzalez et al, 2014 the reverse was the case. In general, FHI-aims code has shown better accuracy and calculation of the ground state energies within a reasonable computational time when compared to some other DFT theoretical programs observed in literature.

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