

Study Electronic And Mechanical Properties Of Carbon, Silicon, And Hypothetical (Sic) In Diamond Structure Using Generalized Gradient Approximation (Gga) Density Functional Theory (Dft).

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Abstract: *The principles calculations based on Density functional theory (DFT) is adopt of the generalized gradient approximation (GGA). It has studied electronic, mechanical properties lattice constant, cohesive Energy, density of state, bulk modulus, partial density, electronic state density and band structure including diamond structure of C, SI, and Hypothetical (SIC). This study aimed to investigated of the behavior of atoms carbon and silicon in diamond structure using (GGA) density functional theory, study Ground state structure of silicon-carbon (SIC) with diamond structure. The result of GGA calculation is obviously through the electronic properties of carbon, silicon and Hypothetical (SIC) in diamond structure it shows that they correspond with the existing experimental values distribution of crystal band gap and partial density of states. From the results of mechanical properties we can know that they are materials. Though the hardness and stiffness of Silicon-Carbon is lower than diamond, it is superior to the materials of Silicon as a good semiconductor materials.*

Keywords: (GGA) DFT, Ground state structure, carbon, silicon and silicon- carbon (SIC).

I. Introduction

Carbon and silicon both occupy group five on the periodic table and therefore share some chemical characteristics. Both elements have a valency of four and can form covalent bonding with a coordination of four. This reason, they both exist in the diamond structure although while this structure is the stable form for silicon at ambient conditions, it is a met stable form of carbon. Both elements have some significant differences. Whereas silicon prefers bonding under ambient conditions, carbon has the ability to form and (sp) hybridized bonding. Carbon is the smaller atom with closely bound valence electrons whereas silicon is larger with loosely bound electrons. Because of this, tetrahedrally bonded carbon atoms in diamond have a bond length approximately of those in diamond silicon. Carbon is also more electronegative than silicon with the better ability to attract other electrons [1]. Silicon-carbon (SIC) has a diamond structure, despite the different size of C and Si which could prevent it. It is almost as hard as diamond. It is a refractory semiconductor material and has many advantages for use in devices that involve working regime in extreme conditions of temperature, voltage and frequency [2]. Silicon-carbon (SIC) is a compound solid alloy, based on that of the host structure. Diamond(C) shape thereof is changed by atoms of silicon atoms, provided that the hole that is similar to the size of atom will occupy it [3].

Silicon - carbon (SIC) has a largest gap, while diamond has the large gap. Among the considered materials, silicon carbon (SIC) is a bit exceptional because it features a special case of polymorphism: it has several polytypes with different stacking sequences. Since the 3C polytype has the biggest bulk band gap, most experiments considered this particular phase. The primitive cell of silicon-carbon (SiC) is the typical diamond structure: it consists of two interpenetrating (fcc) lattices, all carbon-silicon atom bond in tetrahedral directions. The most stable structure of silicon and diamond at room temperature is exactly the same structure than that of silicon-carbon (SiC), with the sole difference that the lattice constant is smaller than silicon, bigger than carbon with diamond structure [4].

II. Calculation Method And Details

Density functional theory (DFT) is a theory used in chemistry and physics to find a description of ground state properties of solids and molecules using energy functional which depend on the electron density. One of the main goals of DFT is to approximate the exchange-correlation (XC) energy with high accuracy. There are two popular methods in DFT to approximate the XC energy, Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA). LDA is an approximation that only depends on the electronic density at each point in space [5]. GGA is an approximation that depends on the electronic density at each point in space and the gradient of the density [5]. LDA models are generally better for finding the structure of a molecule, where GGA models are better for finding atomization/cohesive energy.

The generalized gradient approximation is another form of exchange correlation which is non local. GGA takes into account the density of the electron and its gradient at each point in the space. GGA is constructed by starting from the second order density gradient expansion for the exchange correlation hole

surrounding the electron in a system by slowly varying the densities [6, 7]. It is exceptionally successful for small molecules but fails for delocalized electrons in simple metals. It takes a form which includes the gradient density.

$$E_{xc} = \int \epsilon_{xc} f[\rho, \nabla \rho] \rho(r) d^3r \quad (1)$$

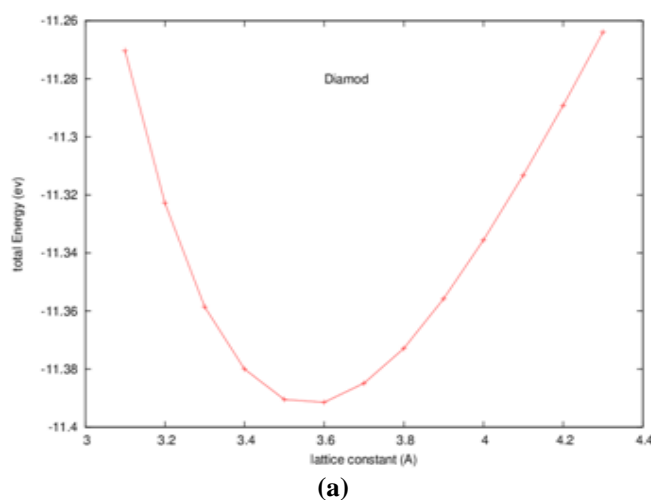
This equation depends only on the general feature of the real space construction where (f) is a parameterized analytic function, and (∇) is the gradient density of the electrons. The equation above is only based on the systems of non-spin electrons. If we consider the system containing electrons with different spins, the system exhibits magnetism and is a straightforward spin polarized material. Now the equation above will take the form of spin densities,

$$E_{xc}[\rho \uparrow, \rho \downarrow] = \int \epsilon_{xc} f[\rho \uparrow, \rho \downarrow, \nabla \rho \uparrow, \nabla \rho \downarrow] \rho(r) d^3r \quad (2)$$

GGA in most cases improves upon the LDA in the description of atoms and solids [8] and it also tends to improve the total energies and atomization energies [9,10]. The local density approximation (LDA) underestimates the lattice constants by 1% while the GGA overestimates the lattice parameters by 1%. It also reduces the chronic over binding of the local density approximations [11]. It tends to improve the energy band gap between valence and conduction bands in the cases of semiconductor and insulator materials [12]. The generalized gradient approximation is efficient in computational cost and is numerically accurate and reliable. We can conclude that GGA tends to satisfy the demands of quantum mechanics and solid state physics. The GGA models. To test a functional, we had to implement this functional into a DFT code, ABINIT [13]. Then properties such as cohesive energy, lattice constant and bulk modulus are calculated. The measuring of the bulk modulus using the GGA functional has not previously been done, and tested if using a pseudo potential model was as accurate as using an all electron model. A pseudo potential model keeps the effective potential of the valence electrons but treats the core electrons as if they were frozen. Most publicly available open source DFT codes use pseudo potentials [14].

III. Calculation Results And Discussion

In this work Energies as a function of volume for carbon, silicon in diamond structure and Hypothetical (SIC) in Diamond structure are shown in figures (1a, 1b and 1c) the structural optimizations were performed with GGA approximation. Combined with the results from other calculated works and experimental data. The minimum point on the curve corresponds to the equilibrium volume of the unit cell which gives us the equilibrium lattice constant.



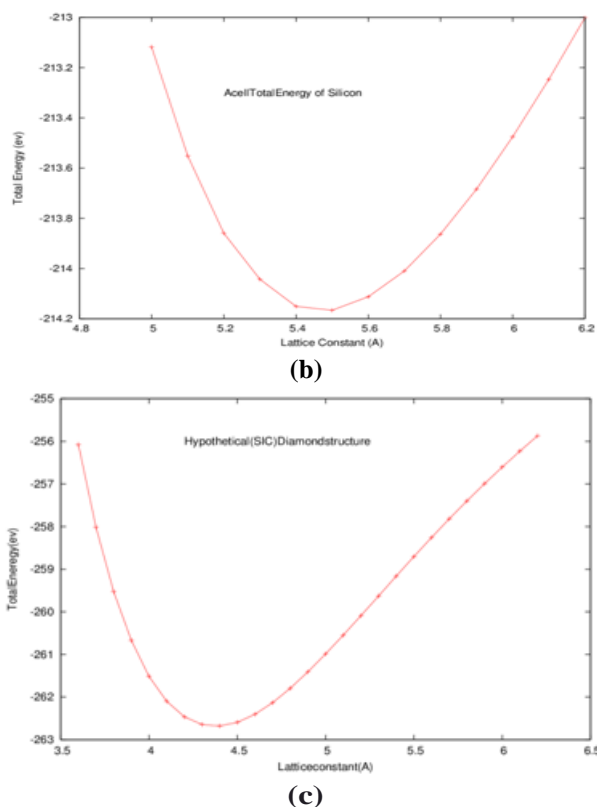


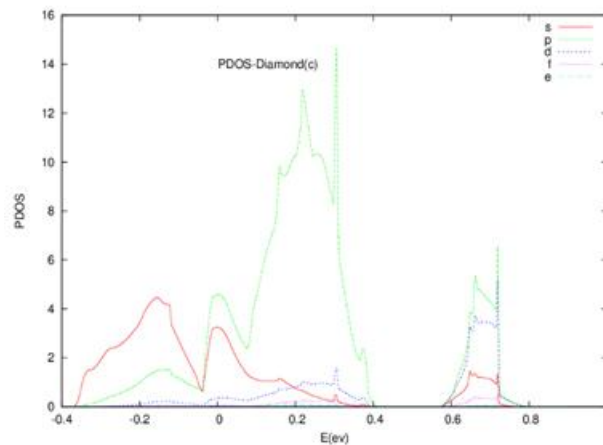
Figure (1) total energy and lattice constant in (a) carbon, (b) silicon and(c) Hypothetical (SiC) in Diamond structure.

This work GGA	Structure	Spacegroup	ao(Å)	Vo(Å ³)	Ecoh(eV)	B ₀ (mbar)	B' ₀
	(C) diamond	Fd-3m	3.600	0.00142	-238.54	50.42	3.63
	(Si) diamond	Fd-3m	5.500	40.79	-214.15	5.72	5.07
	SiC diamond	Fd-3m	4.380	20.03	-262.31	10.76	5.35
Other work LDA	(C) diamond	Fd-3m	3.560	45.160	7.940	43.800	3.500
	(Si) diamond	Fd-3m	5.430	160.37	4.850	92.000	3.600
	SiC diamond	Fd-3m	4.360	82.940	13.320	212.00	3.700
Experimental	(C) diamond	Fd-3m	3.567	45.390	7.370	44.300	4.000
	(Si) diamond	Fd-3m	5.429	160.010	4.630	99.000	4.200
	SiC diamond	Fd-3m	4.360	82.880	12.680	224.000	

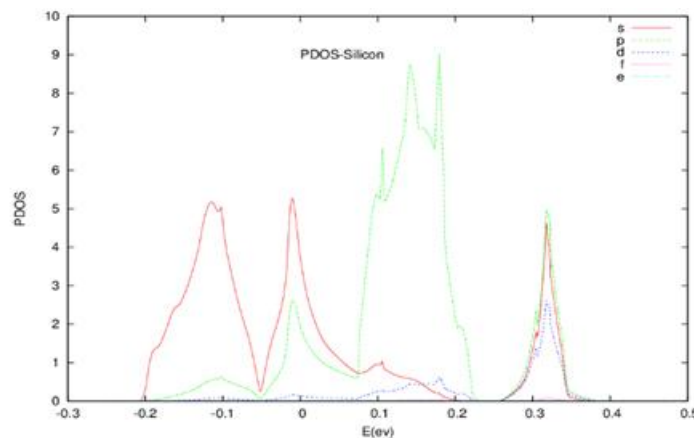
Table1. Comparison cohesive energy, lattice constants (a_0), equilibrium volume (V_0), bulk modulus (B_0) and pressure derivative of the bulk modulus (B'_0) with experimental and other work [15].

In Figure (1a) Our calculated equilibrium lattice constant for carbon with diamond structure was found to be 3.6Å more than the result reported by Chang et al. [16] employing LDA [17] and more than the experimental result. We observe that our calculated equilibrium lattice constant is closer to the experimental value when compared to the work reported by Chang et al[16]. Our calculated bulk modulus was found to be 50.42(mbar) more than the experimental bulk modulus and more than that done by Chang et al [16]. The overall results show that carbon in the diamond structure is a hard material. In Figure (1b) the case of silicon in the diamond structure, our calculated equilibrium lattice constant was found to be 5.5Å more than the value calculated by Ying et al[18]. When compared to the experimental work, our result was found to be 5.5Å more. We observe that silicon has a greater lattice constant compared to carbon. This is caused by the excess of p core states in the silicon atom having large atomic radius than carbon atom. Our calculation for the bulk modulus is 5.72(mbar) less than the calculated work reported by Ying et al. [18] and less than the experimental value. The over all results show that silicon in the diamond structure is not as hard as carbon. Figure(1c) our calculations for SiC in the Hypothetical (Si-C) in Diamond structure, our lattice constant was found to be 4.38Å, more than in the work of Chang et al [16] and the experimental data. Our calculated lattice constant was found to be more

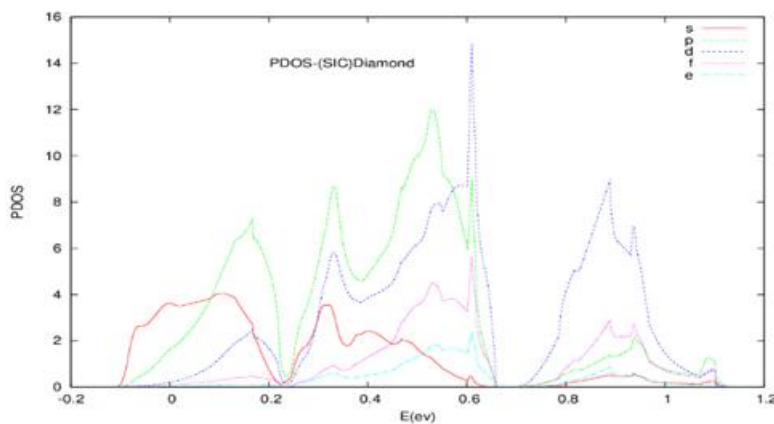
than that of carbon but less than that of silicon. The calculated bulk modulus was found to be 10.75(mbar) less than the experimental data and less than the value reported by Chang et al. [16]. Our results reveal that SiC the Hypothetical (SiC) in Diamond structure falls under Hard material than the experimental data and less than the value reported by Chang et al. [16].Table1. Show Comparison cohesive energy, lattice constants (a_0), equilibrium volume (V_0), bulk modulus (B_0) and pressure derivative of the bulk modulus (B'_0) with experimental and other work [15]. Our results reveal that the Hypothetical (SiC) in Diamond structure falls under Hard material.



(a).PDOS diamond (C) structure



(b).PDOS Diamond (SI) Structure.



(c). Hypothetical(SiC) Diamond(fcc) structure.

Figure 2. partial density of states (PDOS) of (a) Carbon,(b) Silicon, and (c) Hypothetical silicon - carbon (SiC) in Diamond structure.

Figure 2(a) The partial density of state (PDOS) of carbon(c) in Diamond structure. The low-energy area of Valence band is mainly constituted by (C 2s and C 2p) orbital electrons. The high-energy area is mainly

constituted by (C 2p and C 2d) orbital electrons. Figure 2(b) gives the partial density of state (PDOS) of Silicon in diamond structure. The low-energy area of Valence band is mainly constituted by (Si 3s, Si 3p) orbital electrons. The High-energy area is mainly constituted by (Si 3p and Si 3s) orbital electrons.

In figure 2(c), from top to bottom it listed the partial density of state (PDOS) of silicon and carbon of (Si-C) in diamond structure. The Valence band is composed of two sub bands. The sub band of low-energy area is mainly composed of (Si 3s, Si 3p and C 2s) orbital electrons. The sub band of high-energy area is mainly made up of (Si 2s, Si 2p, Si 3d and C 2s, C 2p) orbital electrons. In the sub band of high-energy area, the low-energy area is mainly composed of (Si 3s and C 2p) orbital electrons and the high-energy area is mainly composed of (Si 2p and C 2s) orbital electrons.

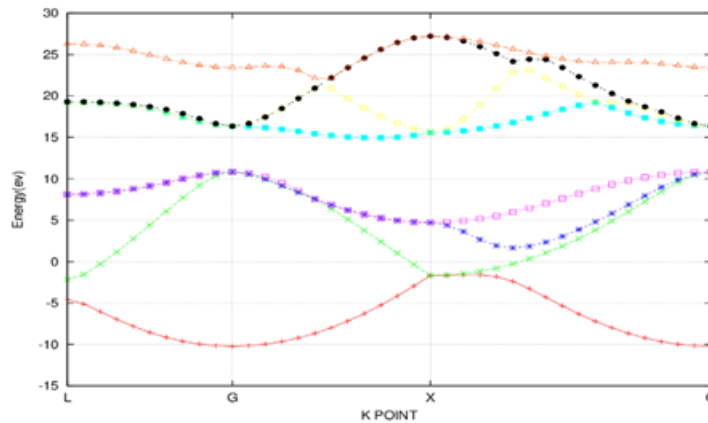


Figure 3a.Band structure of Carbon in Diamond structure

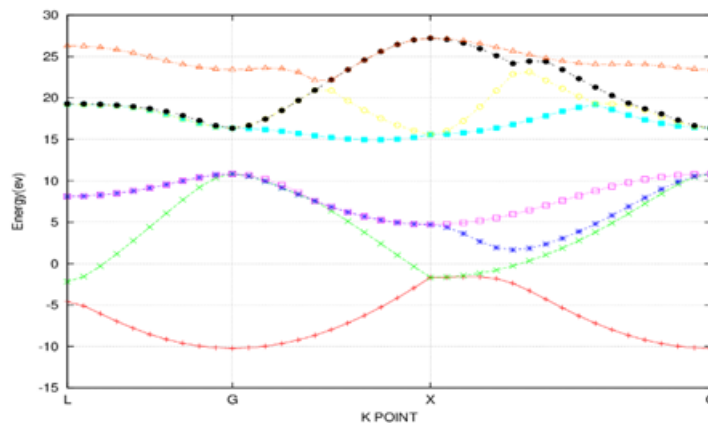


Figure 3b.Band structure of Silicon in Diamond structure.

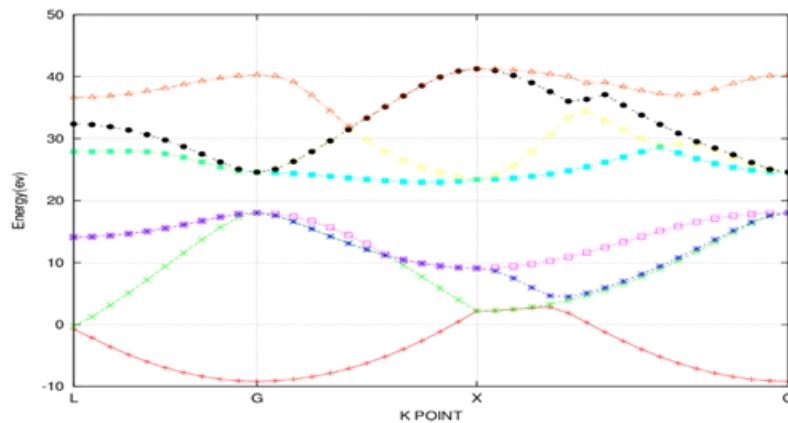


Figure 3c.Band structure of Hypothetical(SiC) in Diamond structure.

The dispersion curves are shown for wave vectors along a path in the first Brillouin zone. Here, the path is described by the wave vectors, L,G ,X , G which are points in the Brillouin zone . The energy of the valence band (VB) at (G) is the highest energy in the VB and is called valence band maximum (VBM). The energy of the conduction band (CB) from (X) is the lowest energy in the CB and is called conduction band minimum (CBM). (Figure 3a), gives the band structure of(carbon) in Diamond structure, it indicates that the top position of valence band lie on the (G) point , the bottom position of conduction band at(X) point . The indirect bandgap, between (G) and (X) different (K) point $E_g=4.75\text{eV}$ which is bigger than silicon. The small size of C atoms allows them to get close to each other before experiencing net repulsive forces, and relaxed (C–C) bonds are considered to be relatively short. The corresponding large overlap of the orbitals of adjacent C atoms in a (C–C) covalent bond causes a large energy separation between the occupied bonding orbitals and the unoccupied antibonding orbitals. This effect ultimately gives rise to a large forbidden energy gap between the VB and CB states in the electronic structure of bulk diamond.

Figure (3b). The energy of the valence band (VB) at (G) is the highest energy in the VB and is called valence band maximum (VBM). The energy of the conduction band (CB) at (X) point is the lowest energy in the CB and is called conduction band minimum (CBM). Due to the crystal symmetry, the calculated band structure is given where an indirect band gap between (G) and (X) different (K) point $E_g = 0.167\text{eV}$ is clearly seen showing this material to be semiconductor with a completely filled valence bands. It shows that the top position of valence band lie on the point of (G), the bottom position of conduction band locate at (X) point. This size of the band gap gives a clear indication that silicon in the diamond structure is a semiconductor material.

In figure (3c).The indirect bandgap $E_g=5.386\text{ eV}$, in (sic) with diamond structure, has large difference comparing to the carbon with diamond structure, and silicon with diamond structure . It indicates the typical characteristics of bond of the (Si-C) in Diamond structure with indirect band gap. it shows that the top position of valence band lie on the(G) point , The energy of the valence band (VB) is the highest energy , on the (X) point is the lowest energy in the CB and is called conduction band of Brillouin zone. The indirect bandgap, between (G) and (X) different (K) point $E_g=5.387\text{eV}$, more than value of (C) with diamond structure and (SI) with diamond structure. This size wide band gap shows that Hypothetical (SiC) in Diamond structure to be semiconductor, if not an insulator material.

Carbon in diamond structure forms very strong C-C bonds so it has large band gap. Thermal energy available at room temperature isn't enough to excite any electrons from the filled band to the empty band. Silicon in diamond structure have significantly weaker bonding between their atoms. This results in a smaller band gap. At room temperature, some of the electrons have enough energy to move into the conduction bands. This means that there are some orbitals in the valence band and in the conduction band that hold only one electron. Electrons can travel through the material through these orbitals[19]. Silicon and carbon (SiC) in diamond structure, we observe that when calculating the energy gap of silicon - carbon in the structure of the diamond, and found that it is greater than the value of the energy gap of (silicon and carbon) in diamond structure each separately when calculated, which is supposed to be the value of energy gap of (silicon – carbon) in the structure of diamond that between the two values for each of silicon and carbon.

As a result, the diamond is often considered to be a wide-bandgap semiconductor, if not an insulator. The minimal bandgap is indirect, with a value of 4.75eV for carbon , which can be compared to corresponding values of 0.167eV for silicon and 5.386eV for silicon-carbon (SiC), with diamond (fcc) structure, respectively, for the group-IV semiconductors silicon and silicon-carbon (SiC)with diamond structure[20]. Each carbon atom, silicon atom, and silicon-carbon (SiC) atoms in cubic diamond (fcc) contributes four valence electrons to four directional tetrahedral covalent sp^3 bonds linking nearest neighbors. The diamond structure is a good example of strong tetrahedral covalent bonding where the atoms share a valence electron with each neighbor[1].

IV. Conclusion

In this work we employed the first principles pseudopotential method within the density functional theory (DFT) and the generalised gradient approximation (GGA) to perform total energy calculations on bulk and adsorbed systems. We studied various electronic and physical properties of the systems involving carbon, silicon and silicon carbon in diamond structure. We utilised the GGA pseudopotential in a methodology based on the plane wave approach. The ABINIT simulation packages developed were used to perform the calculations. In order to obtain accurate and comparable results to previously published work we initially determined the total energy convergence of carbon and silicon with respect to energy cutoff and k-points sampling of the Brillouin zone. The energy cutoff of carbon was found to be high compared to silicon. The 2p states in carbon are localised because of the lack of a p core state: hence a large number of plane waves is required to achieve a high degree of accuracy. Once the convergence was successfully tested, we proceeded to calculate the bulk properties of (carbon) in diamond structure, silicon in the diamond structure and silicon-carbon (SiC) with diamond structures. Our results were compared with previous theoretical and experimental results which were available. Interestingly our results within the GGA are close to the experimental data. When compared to the

other work where LDA was employed. Since the (SiC) with diamond structure is an existing experimental structure, our results shows that this structure is plausible and has an interesting properties.

References

- [1]. Richard. Ch. Andrew. First principles studies of Si-C alloys. Department of Physics, University of Pretoria, FE, 2013.
- [2]. Gervasoni J.L. Furnari J.C. Density of Electron States and Volume of Solution of Hydrogen in SiC Alloys. Journal of Energy and Power Engineering, 8 (2014), 390-393.
- [3]. W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, Physical Review 140 (4A) (1965) A1133-A1138.
- [4]. Marton.A.Voros . Ab initio investigations on the electronic and optical properties of group IV semiconductor nanocrystals. Department of Atomic Physics. Budapest University of Technology and Economics. 2013.
- [5]. Jijun Zhao, Alper buldum, Jie Han, and Jian Ping Lu. "Gas molecule adsorption in carbon nanotubes and nanotube bundles." Nanotechnology 13, 195 (2002).
- [6]. D. C. Langreth and M. J. Mehl. Phys.Rev.A., 1983, 38:3098.
- [7]. A. D. Becke. Phys.Rev.Lett, 1988, 77:18.
- [8]. J. Perdew, K. Burke, and M. Ernzerhof. Phys. Rev. Lett, 1996 77:18.
- [9]. Y. Zhang and W. Yang. Phys.Rev.Lett, 1998, 80:890.
- [10]. B. Hammer, L. B. Hansen, and J. K. Norskov. Phys.Rev.B, 1999, 59:7413.
- [11]. W. Kohn and L. J. Sham. Phys.Rev, 1965 140:A1133.
- [12]. Z. Wu and R. E Cohen. Phys.Rev.B, 2006, 73:235116.
- [13]. Jean-Michel Beuken, Yann Pouillon, and Xavier Gonze. "ABINIT." (May 2010).
- [14]. Seth Ross. Measuring The Performance Of Recent Generalized gradient Approximations To Density Functional Theory In molecules And Solids, BALL STATE UNIVERSITY, Dec, 2010.
- [15]. Refilwe. E.Mapasha . Theoretical studies of graphene and graphene-related materials involving carbon and silicon. Department of Physics. University of Pretoria. 2011.
- [16]. K. J. Chang and M. L. Cohen. Phys.Rev B, 1987, 15:8196-8201.
- [17]. L. Hedin and B. I. Lundqvist. J.Phys.G, 1971 4:2064.
- [18]. M. T. Yin and M. L. Cohen. Phys.Rev.B, 1981, 24:6121-6124.
- [19]. Prof.Pat.Sh.(2012).ElementalCarbon,Silicon,Germanium.(online).<http://butane.chem.uiuc.edu/pshapley/GenChem2/C3/1.html>.Dec2 014.
- [20]. Micha l. Po. 30 Dec 2008. Electronic Properties of Single Crystal CVD Diamond and its Suitability for Particle Detection in Hadron Physics Experiments. Universit'atin Frankfurt am Main.