Electronic properties of nano-graphene sheets calculated using quantum chemical DFT

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1. Introduction

A sheet of carbon atoms arranged in a two-dimensional hexagonal lattice is known as graphene. These graphene sheets can be transformed into various dimensional carbon materials by self-assembly and is thus the (2D) building block for many carbon materials. For example:- 2D graphene sheets can be periodically stacked to form 3D graphite, it can be rolled to form 1D nanotubes, it can be wrapped into 0D fullerenes (buckyballs), nanocones etc., and all these formations depend on the growth conditions [1–4].

Most of the earlier calculations of graphene were carried out using tight binding approach utilizing translational periodicity of infinite 2D sheet. Due to the recent enhanced interest on graphene and other nano-materials, many quantum chemical analysis of graphene have been done recently, mostly using DFT studies following plane wave pseudo-potential method [10–12] or semi-empirical methods [13]. In order to use the intrinsic translational symmetry of both the method and the molecule, the edges were generally ignored in most of the studies. A few recent studies, how-
ever, have pointed out the need of terminal hydrogens in such calculations [14]. However, those models also have some inherent translational symmetry on some of the directions and hence a true electronic picture of a nano-meter size sheet is still unknown. We have therefore attempted to study properties of real finite size graphene sheet with a number of possible defects and edge effects and compare the results with available experimental findings. In order to calculate electronic properties of small graphene sheet, we have adopted the methodology mostly used to measure properties of small chemical compounds in gas phase, i.e. Hartree–Fock (HF) or density functional theory (DFT) with generalised gradient approximation (GGA). Now we shall try to understand the following phenomena using molecular orbital calculations based on density functional theory i.e., (1) Observation of high electron density along the zig-zag edge and low electron density at the arm-chair edge. (2) Spatial variation of the electron density in nano-graphene as a function of interlayer separation. (3) Variation of HOMO–LUMO gap of graphene sheet as a function of its size. (4) Density of electron orbitals around a mono-vacant site. Phenomena 1 and 2 has been observed experimentally [8,9] while phenomenon 3 and 4 are important for device fabrication using nano-graphene.

2. Methodology

Atomic coordinates of all the carbon atoms arranged in an hexagonal lattice having zig-zag and arm-chair edges with the edges terminated by hydrogen atoms, were generated by the molecular modeling software MOLDEN [15] using standard bond lengths (b(C–C) = 1.421 Å and b(C–H) = 1.009 Å) and all angles equal to 120°. The edges were terminated by hydrogens to form C–H bonds for neutralizing valencies of all the carbon atoms. All the electronic calculations were performed by the free software GAMESS-US [16] using density functional theory (DFT) with B3LYP/6-31G(d,p) method [17]. Three graphene sheets were generated with trans (zig-zag) and cis (arm-chair) edges for different sizes:- (i) smallest graphene sheet (a pyrene molecule) with 16 carbon atoms and 10 hydrogen atoms, (ii) intermediate model with 32 carbons and 14 hydrogens and (iii) largest model with 73 carbons and 21 hydrogens (Fig. 1). Another sheet was generated with all bonds in arm-chair (cis) orientation in one side with 68 carbons and 22 hydrogens (see Fig. 2). We also generated a sheet with a vacancy at the center (Fig. 3), while the valencies of the carbons at the vacant site were fulfilled by adding three hydrogens. This molecule has 72 carbons and 24 hydrogens. We have energy minimized structures of all these molecules after initial model building by Hartree–Fock method with RHF/4-21G basis set by GAMESS-US. All the molecular orbitals were visualized by MOLDEN software.

3. Results and discussion

Graphene is generally infinite two-dimensional sheet, hence quantum chemical calculations using plane wave pseudo-potential and making use of crystalline translational periodicity is quite suitable to understand its electronic properties. However we are interested in...
understanding structure and electronic properties of the edges or its defects due to vacancy creation in finite size graphene sheets of nano-meter dimension. Hence we have adopted the hybrid-DFT formalism, which is suitable for small molecular systems without periodicity. The computational resource requirement in this implementation of DFT is however proportional to $n^4$ where $n$ is the number of electrons, as compared to $n^3$ in other DFT codes utilizing plane wave pseudo-potential [18]. Hence we had to restrict the size of the molecules so as to suite our computational resources.

We have performed geometry optimizations of three perfect graphene models with both cis and trans edges, of different size as shown in Fig. 1 using HF method and compared their orbitals calculated by DFT procedures. The three models of graphene sheets of different sizes have 106 electron in 53 doubly filled orbitals for pyrene (smallest model), 206 electrons in 103 doubly filled orbitals for the intermediate model and we used 460 paired electrons in 230 doubly filled orbitals for the largest model. We used 290, 508 and 1200 basis functions for DFT calculation to describe the electron distribution in the three models consisting of trans and cis edges. This clearly suggests that thorough geometry optimization using DFT is almost impossible. Comparison of energy Eigen values for the highest occupied molecular orbitals (HOMO) or valence

Fig. 2. Total partial charges on the carbon atoms along the edges of (a) largest model and (b) the model containing only cis edge on one side. The number on the edges indicates electron population subtracted from the nuclear charge and the color representation gives indication of the inner carbon atoms also where the positive value/red color represents electron deficiency and the negative value/blue color are representative of excess electron accumulation. Electronic charges were interpolated at finer grid spacing (using matlab) from partial charges of all the atoms of the molecules. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)
band (VB) and lowest unoccupied molecular orbitals (LUMO) or conduction band (CB), which provides direct estimation of band gap, indicates that band gap of pyrene (the smallest model) to be 0.14880H (4.05 eV), the intermediate model has band gap of 0.0944 H (2.57 eV) which reduces to 0.0680 H (1.85 eV) for the largest model. This indicates that finite size graphene will have a band gap which decreases on increasing the dimension of the sheet to near metallic situation (band gap vanishes) [19,20].

Computer graphics representation of the highest occupied molecular orbitals (HOMO) for the smallest, intermediate and largest models with trans and cis edges are shown in Fig. 1. We can clearly see that the molecular orbitals located at pure trans edges are more prominent than the orbitals at the cis edges. A very similar property was noted by AFM [8,9] and STM [21] studies. In order to characterize total electronic population on all the atoms we have calculated the Mulliken charges [22] on each of the atoms and their values for carbons at the edges are shown in Fig. 2a and b. In Fig. 2b we show a nano-graphene with arm-chair carbons at a stretch on one side unlike the three models considered earlier. In Fig. 2b we also show the partial electronic (Mulliken) charges on the carbon atoms at the edges to compare it with the orbitals of the largest model shown in Fig. 1. Negative values indicates electron density and positive values are the hole density indicating they are electron deficient. These absolute negative values are clearly much smaller on the carbon atoms at the arm-chair edges than at the zig-zag edges.

The graphene sheet with a vacancy at its center, undergoes significant structural alteration from planarity to accommodate three extra hydrogens at the place of one carbon atom. Electronic population analysis of the HOMO (Fig. 3) clearly shows that significantly more electronic crowd is located near the vacant site. Many groups [7,23–25] have recently studied magnetisation of graphene introduced by edge defect or cavity creation. It was noted that irradiation of graphene sheet by proton (hydrogen ion) gives rise to magnetic moment while those irradiated by alpha particle does not show magnetism [23]. Hence it gives an indication that reduction of carbon by hydrogen around the vacancy giving rise to extra electron occupation around the vacancy may be responsible for observed magnetism in graphite. We can argue with a conjecture that when two hydrogen atoms come close together to form a H₂ molecule the total spin goes to singlet state, whereas when three H atoms come close to form a complex, then the orbital state is antisymmetric and the spin state is symmetric to make the total wave function antisymmetric. Hence, this complex would presumably give rise to high moment state leading to magnetism. Thus, one can guess why proton (H) irradiated samples only shows magnetism and not the alpha particle irradiated samples.

We have further attempted to understand the role of interlayer separation between two graphene sheets in terms of electron accumulation. We considered two graphene layers, each having 54 carbons and 18 hydrogen atoms in two models: (1) with 3.4 Å separation representative of stacked 3D graphite and (2) with 10.0 Å separation emulating practically unstacked graphene layers. The lower layer is shifted in plane so that the carbons of the lower layer are juxtaposed to the centers of the top carbon hexagons. We required 1800 basis functions to represent wave function of all the electrons, which is close to the limiting number of basis functions in the software adopted. In order to understand the enhancement of electrical conductivity as a function of sheet separation, the above two systems were considered. We compared electronic populations of HOMOs of these two systems. It is found that average population of electrons considering only the inner carbons on the closely separated layers (3.4 Å) is 0.0123 (std = 0.011), while that on the well separated layers (10 Å) is 0.0243 (std = 0.0198). Considering the small values of partial charges, we have also calculated these by a better method namely electrostatic surface potential fit (ESP fit) by MOLDEN. Average value of the ESP fit charges are −0.00083 (std = 0.036) and −0.06993 (std = 0.006) for the 3.4 Å and 10.0 Å layers, respectively. Average value of charge, even smaller than its standard deviation, possibly indicates effectively zero charge density on the interior carbon atoms for the closely spaced layers. These results further indicates that there is a net increase in electron population in the inner region of the sheet as a function of sheet separation. This will lead to increase in the electrical conductivity and this has been observed experimentally [8,9]. This charge distribution on the sheet as a function of sheet separation arises as a result of localization/confinement of electron on transformation from 3D graphite to 2D graphene sheet.

4. Conclusion

To summarize, it appears that quantum chemical calculation by using density functional theory by hybrid B3LYP...
functional to consider exchange correlation energy gives electronic properties of nano-graphene as observed experimentally. This method is also suitable for characterizing nano-meter size graphene sheet as periodic boundary condition or translational periodicity of the molecule is not assumed in this method. In our investigation we observed high electron density along the zig-zag edge and low density at the arm-chair edge. We noted increase in the electron density at the central region of the sheet giving rise to spatial variation of the electron density across the sheet in nano-graphene as the interlayer separation is increased. We also observed decrease in the HOMO–LUMO gap of graphene sheet as the size increases. Large enhancement of density of electron orbitals around a monovacant site was also observed.

References