Quantum mechanical study of electronic properties of zigzag nanotubes (9,0) (SWCNTs)

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Abstract

Quantum calculations on the most stable structure were carried out for calculating the electronic properties, energies and the charge density at the Carbon and Hydrogen atoms by Semi-empirical method (PM3) of zigzag carbon nano tube CNT (9,0) (SWCNTs), at the equilibrium geometry depending on the pictures of Zigzag CNT(9,0) which was found to has D_3d symmetry point group by applying for (Gaussian 2003) program. In this work the results include calculation the relation for axial bonds length, which are the vertical C-C bonds (annular bonds) in the rings and bonds length which are in the outer ring that called the circumferential bonds. Also include a different kind of vibration modes like breathing, puckering, and deformation bending. They allow a comparative view of the charge density at the carbon atom too. The aromaticity is graded according to the space distribution of the atoms in zigzag nano tube (9,0), the nature of their molecular orbitals depend on, their symmetry, and chirality. Many studies were done measurements to characterize nanotube mechanical properties for successful applications in nanotechnology.

Key words

Single wall carbon nano tube SWCNT, Gaussian 03 program for calculation.

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دراسة في ميكانيك الكم للصفات الالكترونية للانابيب النانوية نوع زكزاك (9,0) (انبوب النانوكاربون احادية الطبقة)

هدى نجم الدين العاني

قسم الكيمياء، كلية العلوم، جامعة بغداد، الجادرية، بغداد، العراق

الخلاصة

تم اجراء حسابات الكم على التركيب الكيميائي الاكثر استقرارية حيث تم حساب الخواص الالكترونية، والطاقات وكثافة الشحنات على ذرات الكاربون والهيدروجين بواسطة الطرائق شبه التجريبية بطريقة (PM3) لانبوب النانوكاربون نوع زكزاك (9,0) للشكل الهندسي المتوازن لانابيب النانوكاربون نوع زكزاك وجد انه يمتلك تماثل من نوع D_3d حسب مجموعة النقطة، بتطبيق برنامج كاوسن 2003 في الحساب تضمنت النتائج حساب العلاقة لاطوال الاواصر C-C المحورية والتي تكون وضعها عمودي في الحلقة، واطوال الاواصر في الحلقه الخارجيه التي تسمى بالمحيطيه، وكذلك دراسة الانماط الاهتزازية مختلفة الانواع وتصنيفها مثل الانماط التنفسيه والانبعاجية والانحناءات التي تسبب تشوة للجزيئة. وتمت مقارنة الكثافة الالكترونية على ذرات الكاربون ايضا .وجد ان الصفات الاورماتية متدرجة حسب ترتيب الذرات في الانبوب النانوكاربون نوع زكزاك. وان طبيعة الاوربيتالات الجزيئية تعتمد على التماثل والترتيب الفراغي. اجريت عدد من الدراسات والحسابات لوصف انابيب النانوية وخواصها الميكانيكية وذلك لتطبيقاتها الناجحة في حقل النانوتكنولوجي.

Introduction

The engineering of nano structures are convergence the chemistry, biology, and information science, the nanosizes are measured in billionths of a meter [1]. Single wall carbon nanotubes are such systems that constructed from rolled sheets of connected carbon hexagons [1]. The orientation of the hexagons with respect to the tube axis determines the type of the nanotube, specified by the diameter, the chirality, and the handedness Fig.1 [2]. Single-wall carbon nanotubes (SWCNTs) formed from graphite sheets of annulated six-membered aromatic rings [2]. Each carbon atom in the sheet has the hybridization of sp^2 [3] see Fig. 1. The character of aromatics in nanotube like graphite, due to the conjugated C-C bonds [4]. According to the distribution spaces of the atoms they have an aromatic propreties, due to the nature of molecular orbitals in nanotube, symmetry and chirality are graded [5]. Many studies for the physical properties of the nanotubes were done [6-11]. Many synthesis efforts by theoretical investigation on nanotubes have grown because of its novel electronic properties and their tremendous potential applications. The simplest kind of single-walled carbon nanotubes (SWNTs) were discovered in 1993 by Iijima group [12, 13]. Some specific defect-free forms of these SWNTs show remarkable mechanical properties and metallic behavior [14]. Especially, the close interconnection between electronic structure and their chirality make CNTs with an ideal applications in electronics devices[15]. These materials have hight potential to use in nano-electronic and nano-mechanical applications or in various devices. New and exciting phenomena have been observed [16], including field emission [17], quantum conductance [18], superconductivity [19], and higher thermal conductivity than diamond [6]. The nanotubes behavior as insulating or metallic depending upon a structure, which is used in prototype devices [16].

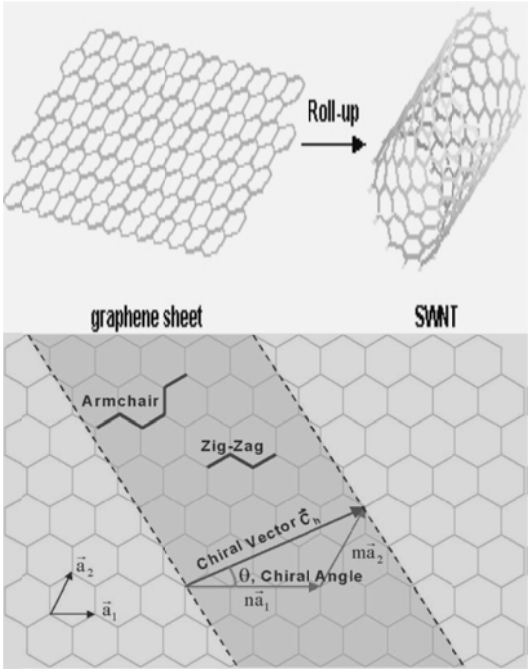


Fig. 1: Diagram showing a hexagonal sheet of graphite is 'rolled' to form a carbon nanotube (SWCNTs).

Similar to graphite they have aromatic character, and posses conjugated C-C bonds [20, 21]. The determination of a romaticity by the atoms distribution, the nature of molecular orbitals, their chirality, and symmetry [22]. CNT could be either single walled (SWNT) with diameters as small as 0.4 nm [23], or multi-walled (MWNT) consisting of malty tubes (e.g. 2-30 each tube one inside the other) the rang of diameters from 5 to 100 nm see Fig. 2 [24].

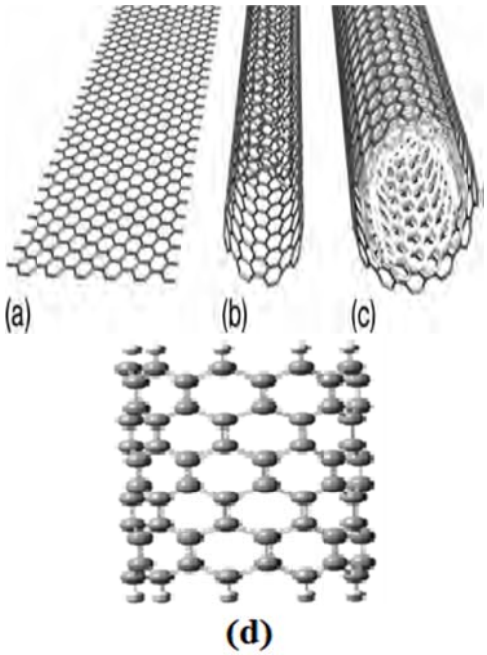
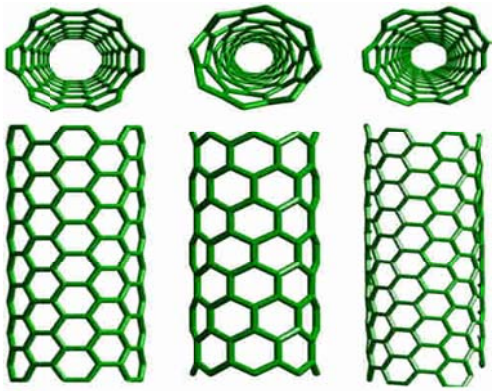


Fig. 2: The structure of a single graphite layer in (a), Single-walled carbon nanotube in (b) and carbon nanotube with three shells multi-walled in (c). zigzag CNT (9,0) in (d).

The structure of a carbon nanotube due to the angle of rolling of the graphene sheet we'll get three different types of CNTs armchair, zigzag, and chiral (Fig.3).



(a) (b) (c)

Fig.3: Structures of CNTs (a) armchair nanotube; (b) zig-zag nanotube; (c) chiral or helical nanotube.

In this work the vibration modes, the geometrical parameters (bond lengths), the energetic properties and charge density was studied of the zigzag nanotube (9,0) SWCNTs due to its electrical applications. The modes of vibration of SWCNTs [25-28], like bending mode, and radial breathing mode [29, 30], and longitudinal mode [31]. The molecular structures offers good information for the electronic properties of CNTs see Fig.4. Also, CNTs with circular radius could lose their symmetry by the vibration motion, radial and circumferential directions [32, 33]. This result could change suddenly in electrical properties [34], and in turn, significantly affect their performance in nanostructures. Thus, similar to the buckling behavior [35] the vibration of SWCNTs a great interest in nanotube electronic mechanically the efforts [36] have been devoted to capturing the fundamental vibration behaviors of SWCNTs [37, 38] and multi- scale modeling tools [39-42, 43-44]. Recently the interest in the mechanics of SWCNTs has been converted from their basically behaviors to the effect on the properties of internal and external factors [40-41], buckling [43-46] of SWCNTs [Fig.4]. Carbon nanotubes have a remarkable and unique electronic properties due to its small size (0-100) nm, this makes it enter in many applications, like manufacturing, medicine, communication, computation, transportation and many other application areas [47, 48].

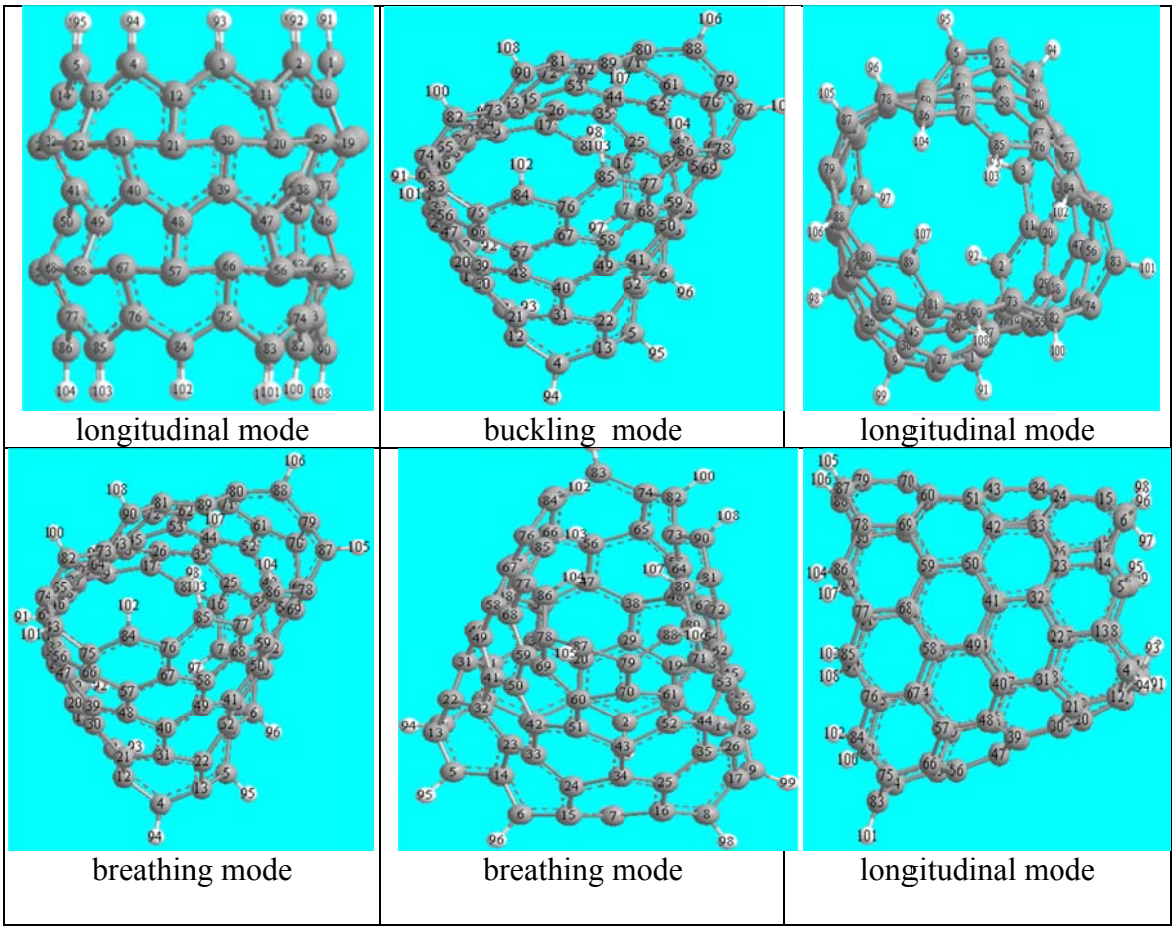


Fig. 4: Structure deformation of a zigzag nanotube (9,0) molecule as caused by its vibration motion modes like longitudinal mode, breathing mode, buckling mode.

Both Gaussian 03 by PM3 method [49], and MOPAC program by PM3 computational packages [50], have been employed to compute the equilibrium geometrical structure, and the energetic properties were applied throughout the present work. Zigzag carbon nanotubes (9,0) have been studied due to its novel properties. The equilibrium geometrical structure and an electronic properties of CNT offer important applications, like its use in nanoelectronic devices, gas sensing, chemical probe, electron transport, energy storage, and biosensors, field emission display, etc. To study the electronic properties of zigzag (9,0), CNT one has to define its geometric parameters; Various quantum mechanical studies were done for the physical properties of zigzag nanotubes [51, 52]. Their thermal and electronic properties are expected to change the structure deformation. The carbon zigzag nanotubes can be described as single-walled (SWNT), its form by rolling mathematically a graphene sheet into a cylinder by the coordinates of the folding vector (n,0), a molecule is composed of anumber of aromatic rings.

Results and discussion

The equilibrium geometry first calculated by PM3 method. Table 1 shows calculated physical properties for zigzag CNT at their equilibrium geometry. Table 2 shows the distribution of charge density of the atoms of zigzag (9,0) CNT as calculated by applying for Gaussian 03 program [49].

Table 1: Some physical properties calculated for ($C_{90}H_{18}$) zigzag CNT(9,0) at their equilibrium geometry calculated by applying Gaussian 03 program.

ΔH_f =Heat of formantion	**769.431 kcal/ mol**
Ionization potential	**6.112 eV**
Electronic energy	**-195288.047 (kcal/ mol)**
Dipole	**1.144 (Debye)**
HOMO energy	**-6.112 eV**
LUMO energy	**-3.575 eV**
ΔE=| LUMO - HOMO |	**2.537 eV**
Total energy	**416.69 kcal/ mol**

Table 2: Distribution of the charge density at zigzag CNT (9,0) atoms calculated by applying Gaussian 03 program.

Atom no. type	Charge	Atom electronic density
C_1 outer atom	-0.229	4.229
C_2 outer atom	-0.212	4.212
C_3 outer atom	-0.129	4.129
C_4 outer atom	-0.015	4.015
C_5 inner atom	0.073	3.926
C_6 inner atom	0.092	3.907
C_7 inner atom	0.038	3.961
C_8 outer atom	-0.069	4.069
C_9 outer atom	-0.175	4.175
H_{91} low charg	0.118	0.881
H_{92} low charg	0.117	0.882
H_{93} low charg	0.114	0.886
H_{94} low charg	0.109	0.890
H_{95} low charg	0.106	0.893

The heat of formation is The ΔH_f ,The Highest Occupied Molecular orbital is HOMO, The Lowest Unoccupied Molecular orbital is LUMO, ΔE = | LUMO – HOMO| Energy gap.

Fig. 5 shows the structure of molecular levels the HOMO and LUMO of (9,0) zigzag tube and Fig. 6 shows the equilibrium geometry for zigzag (9,0) (CNT).

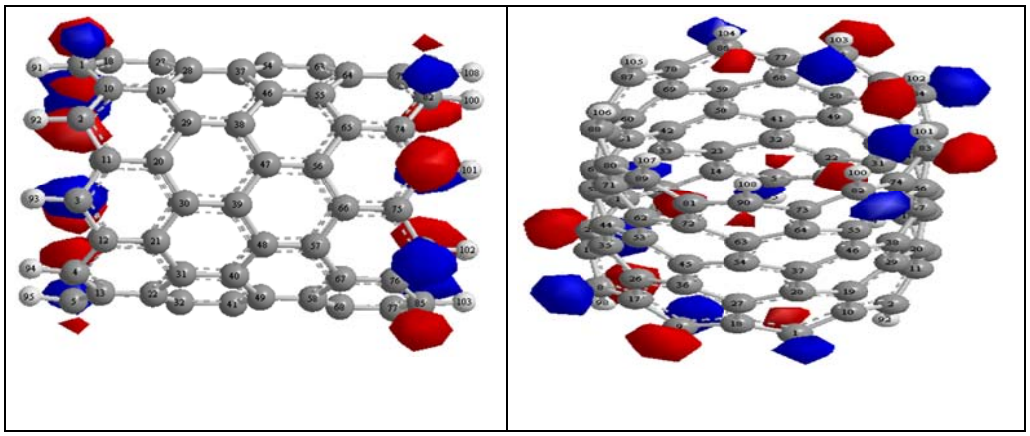


Fig.5: The Structure of molecular energy levels the HOMO and LUMO of (9,0) zigzag tube at their equilibrium geometry by using GOW03 program.

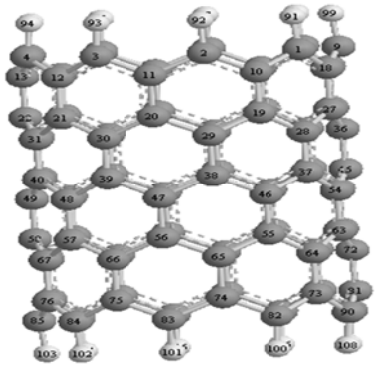


Fig. 6: Equilibrium geometry for zigzag (9,0) (CNT).

Finally, the calculations show that similar to the CNTs [53-56], Mainly in a zigzag CNTs, the charge densities are intensified at circumferential atoms. The axial carbon atoms have diminishing charges, whereas H_2 atoms are charged positively, the C atoms are with negative charge as in Table 2. In this study we calculated the MO, Table 1. The HOMO and LUMO of a negatively charged state are at the cap localized under electric fields. This fact of localization plays in the field emission an important role. Obviously, the vibration of zigzag nanotube causes a deformation in its geometry Fig. 4. The results include the assignment of all puckering, breathing, and clock-anticlockwise bending vibrations; structure deformation is expected to change their thermal and the electronic properties. The equilibrium geometries according to the point group is (D_{3d}) as shows in Fig. 7 and it show of the bond length in a zigzag (9,0) SWCNT, The structure of zigzag CNT(9,0), shown in Fig. 8 indicating the comparison between the C-C axial (C-Ca) and C-C circumferential (C-Cc)as listed, Table 3. which show the calculated bond distances of zigzag CNT (9,0) by Gaussian 03; This demonstrate that the C-C axial (C-Ca) and C-C circumferential (C-Cc) bond length is in minimum energy structure. The charge accruing on the sharpness of the tip of the nano tube called Mulliken charge. The charge is stronger in zigzag tubes than in armchair tubes. This suggests that the charge accumulation is mainly determined by the sharpness of the tip, not by its detailed atomic structure, Fig. 7. Finally, the calculations show that similar to the carbon nanotubes [57-58], mainly the densities of charge are concentrated at the circumferential carbon and hydrogen atoms of zigzag tube. The electronic properties of SWCNT, for conductivity parallel with their physical properties. The carbon axial atoms from outer to center diminishing charges. The H_2 atoms are charged positively, and the C atoms are charged negatively, see Table 2. CNTs, will have numerous applications and take a place in the development and technologies in future.

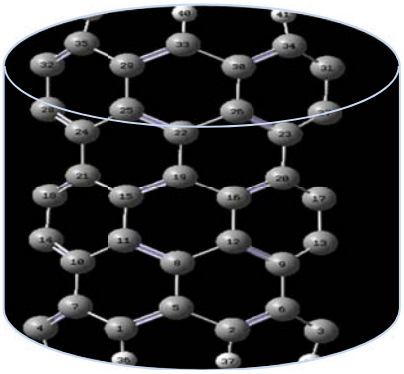


Fig. 7: Repetitive sections of bonds and angles of zigzag CNT (9,0) at the equilibrium geometries according to the point group (D_{3d}).

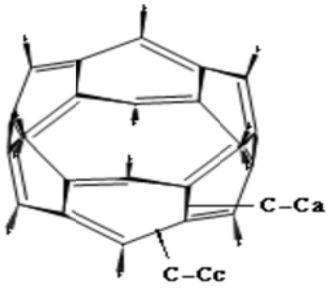


Fig. 8: Structure of zigzag CNT(9,0) indicating the two types of C-C bonds; C-C axial (C-Ca) and C-C circumferential(C-Cc).

Table 3: The calculated bond distances of a zigzag CNT (9,0) by Gaussian 03.

Atom- bond no.	Bond Length(A^0)
C_{29}--C_{35}(C-Cc)	1.415
C_{30}--C_{33}(C-Cc)	1.415
C_{30}=C_{34}(C-Cc)	1.403
C_{30}=C_{34}(C-Cc)	1.403
C_{26}-- C_{30}(C-Ca)	1.420
C_{25}--C_{29}(C-Ca)	1.420
C_2--H_{37}	1.102
C_{33}--H_{40}	1.102

Conclusion

Calculations of quantum mechanics were carried out by Gaussian 03 program, the result investigated the unique electrical properties, The geometry structure for a zigzag Nanotube are sensitive, In this paper we studied some electronic properties for a zigzag carbon Nanotubes (SWCNTs), like the (MO), the LUMO, and the HOMO, The charge localized at the cap, which charged negatively, and the charge density was calculated at the atoms in zigzag CNTs. The comparative view the charge density allowed at the carbon atom. The calculations show that the charge densities are mainly concentrated at the hydrogen atoms (positively charge) and at the circumferential outer carbon atoms (negatively charge). The axial carbon atoms and the circumferential carbon atoms have diminishing charges from outer to the center of the CNTs that increasing electro negativity. Depending on CNTs structure, They (armchair, some zigzag) have metallic properties, the study of vibration modes of zigzag(9,0) nanotube causes a deformation in its geometry fig.3, that expected to change their thermal and electronic properties, CNTs are much better conductors of electricity because there is less scatter off electrons Carbon nanotubes possess extraordinary mechanical properties and are among the strongest materials known.

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