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Charge distribution in graphene from quantum calculation*

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The local charge distributions of different shape graphene sheets are investigated by using the quantum calculations. It is found that the charge distribution on carbon atom is not uniform, strongly depending on its position in the graphene and its local atomic environment condition. The symmetrical characteristic and geometrical structures of graphene also have an important influence on the charge distribution. The charges of atom at the graphene edge are strongly related to their surrounding bonds. It is found that the charges of double-bonded atom at the zigzag edge are closely related to the bond angle, but the charges of double-bonded atom at the armchair edge are mainly influenced by the area of triangle. The charges of triple-bonded atom at the edge are mainly affected by the standard deviation of the length of the associated triple bonds.

Keywords: graphene, charge distribution, geometry

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1. Introduction

Graphene is a two-dimensional (2D) material with a honeycomb sheet consisting of sp^2-bonded carbon atoms.[1–4] Since its birth, graphene has received much attention of researchers due to its excellent properties such as outstanding mechanical properties[5–9] and electrical properties,[10–17] unique optical properties,[18–22] high thermal conductivity,[23] etc. These unique properties make graphene an ideal candidate for a number of applications in semiconductor, charge storages, sensors, and field-emission devices[24–26] based on graphene.

To promote the application of graphene in the field of nanoelectronics in the future, the ability to finely control the electronic and transport properties of this material is required. In recent years, many different methods have been used to improve the electronic properties of graphene, such as edge shape, chemical doping, and geometrical deformation. Ritter and Lyding[27] used the tunneling spectroscopy to find that graphene nanoribbons (GNRs) with a higher fraction of zigzag edges exhibit a smaller energy gap than a predominantly armchair-edge ribbon of similar width. Many studies have shown that doping atoms and defects can improve the electronic structure of graphene and open the energy gap between the valence band and the conduction band, such as B, N, P, via vacancies, and Stone–Wales defects.[28] Pereira and Neto[29] investigated the electronic structures of armchair-edge graphene nanoribbons under a small uniaxial strain by tight-binding calculation and the first-principles calculation. It was found that a small asymmetrical strain introduces a band gap for metallic armchair-edge graphene nanoribbons (AGNRs) and modifies the band gaps for semiconducting AGNRs near the Fermi level. However, the in-depth understanding of the charge distribution, one of the basic issues affecting the graphene's electronic property has not been described up to date.

It was reported that the charges of edge carbon atom accumulate and the charge density significantly increases near the strip edges.[30] The edge effects have been investigated for graphene nanoribbons with minimum lateral dimension in a range of 1.0–4.5 nm by using the first-principles calculations.[11] The distribution of net electric charges and capacitance in finite and multilayer graphene were studied by using both a constitutive atomic charge–dipole interaction model and an approximate analytical solution to Laplace's equation.[31] However, at present, the influence of graphene morphology (e.g., round, rectangle, etc.) on charge distribution, especially the effect on the charge distribution of carbon atoms on different edge shapes has not been detailed. An investigation on charge distribution in graphene is also important for understanding the charge impurities or chemical doping in graphene and promoting its application.

At present, in most of the study of graphene, especially the electronic structure, the first-principles calculation method has been used. In Ref. [32], the first-principles calculation was

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used as a convenient tool to calculate and analyze the electronic structures of some crystalline materials due to the electronic structure that is the most important characteristic of a solid material. Zhou *et al.*[33] have studied hydrogen storage on graphene with Li atoms using the first-principles calculations. They found that hydrogen storage capacity can reach 16 wt.% by adjusting Li coverage on graphene to (3×3) on both sides. Ding *et al.*[34] have studied the structural and electronic properties of monolayer porous graphene (C), BN, and BC2N sheets by using the first-principles calculations. They found that all the porous C, BN, and BC2N sheets with one-hydrogen passivation exhibit direct-band-gap semiconducting behaviors and the porous C, BN, and BC2N sheets have semiconducting behaviors with practical band engineering by different hydrogen passivations. However, the efficiency of the first-principles calculation is too low.

In this paper, we use a semi-empirical molecular orbital program MOPAC devised by Stewart[35] for our calculation. Firstly, we check the validity of the program with a linear-scaling density functional theory software package ONETEP (order-N electronic total energy package).[36] Then we construct some graphene models with different morphologies and calculate their charge distributions by using MOPAC. Finally, we report the local charge distribution in graphenes.

2. Calculation methods

MOPAC is a general-purpose, semi-empirical molecular orbital program for the study of chemical reactions involving molecules, ions, and linear polymers. This model uses self-consistent field (SCF) method to optimize the molecule structure and electron density based on the minimum energy optimization. The electrostatic repulsion and exchange stabilization are key factors in calculation process. This SCF method uses a restricted basis set of one s orbital and three p orbitals (p_x, p_y, and p_z) per atom and ignores their overlap integrals in the secular equation. The main quantities calculated by MOPAC are atomic charge (Q), molecular orbital (P), molecular geometry (G), and heat of formation (H). The results of MOPAC SCF calculations can be compared with experimental results or used in subsequent calculations. In the SCF calculations of MOPAC, molecular orbitals, charges, bond orders, and valences[37,38] were calculated from quantum mechanics. Before the calculation, the geometry must be modified from the input geometry in order to be able to compare with experimental measurements and calculations.

We verify the validity of MOPAC by ONETEP. In Fig. 1, in order to test the validity of MOPAC, we use ONETEP,[36] a linear-scaling density functional theory software package, along with MOPAC to calculate the charge distribution in spiro-OMeTAD ($C_{81}N_4O_8H_{68}$). The spiro-OMeTAD is a hole transportation material for the perovskite solar cells. The charges in this 161-atom molecule from MOPAC and those from ONETEP are shown in Fig. 1. It is found that eight O atoms have the same negative charges (shown in Fig. 1), while four N atoms have also identical negative charges (shown in Fig. 1). Figure 1 also indicates that sixty eight H atoms have slightly different positive charges, which can be linearly fitted (shown in Fig. 1, in blue line, $R^2 = 0.99$); figure 1 also indicates that twenty four C atoms have positive charges, on the contrary, fifty seven C atoms have negative charges. The charges for C atom (red line in Fig. 1) and H atom (blue line) are linearly fitted. This calculation suggests that the MOPAC is feasible to calculate the charge distribution of graphene sheet. Compared with the precise first-principles calculation, the semi-classical quantum MOPAC can be greatly time effective.

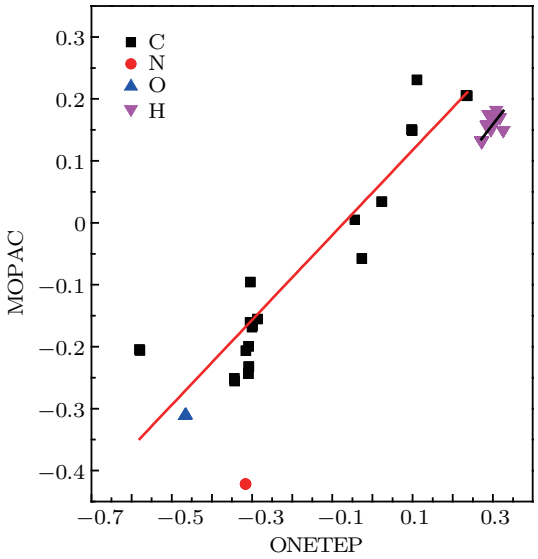


Fig. 1. (color online) Comparison between charges from MOPAC and ONETEP for spiro-OMeTAD ($C_{81}N_4O_8H_{68}$).

3. Results and discussion

3.1. Charge distribution with geometries

As a bird's view of this work, we provide the local charge distributions for some typical graphene models with different shapes and different sizes (Fig. 2), including round, rectangle, hexagon, and asymmetric geometry graphenes. It can be seen that the charge distribution in graphene sheet is not uniform from molecular electrostatic potential field in Figs. 2(a)–2(e). The charges of per atom are closely related to the position (interior or edge) of the atom in the graphene sheet. Firstly, the geometry and size is a key factor to affect the charge distribution. As a result, the symmetrical geometry corresponds to the symmetrical charge distribution. However, the symmetry varies with the geometrical shape of the graphene sheet. For example, the charge distribution exhibits a good symmetry with respect to the X-axis in Fig. 2(b). The charge distributions of top and bottom graphene are symmetric with respect

to the X-axis, and the charges of left and right graphene are symmetric with respect to the Y-axis in Fig. 2(c). The symmetrical relationship can be described by marked charge number in these figures. However, if the geometry of graphene sheet is asymmetric as shown in Fig. 2(e), the charge density is found to be no longer distributed symmetrically. Secondly, the charge distribution at the internal part of the graphene is relatively uniform, and close to zero. This feature is particularly prominent in hexagonal graphene sheets (Fig. 2(d)). The absolute value of the charge of the intermediate atom varies between $0.005|e|$ and $0.01|e|$.

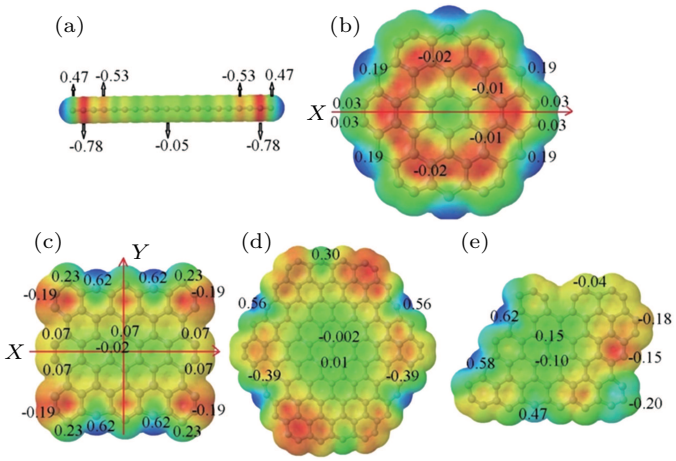


Fig. 2. (color online) Carbon atoms with (a) chain, (b) round, (c) rectangle, (d) hexagonal shape, and (e) asymmetrical geometry graphene sheet. The number indicates the charges on the atoms and color refers to electrostatic potential: blue represents positive charge and red refers to negative charge.

We can compare our results with other research results. Silvestrov and Efetov[30] calculated the charge distribution in the graphene strip by a gate voltage, i.e., electrostatic approach, demonstrating a strong increase of the charge density near the strip edge. Wang and Scharstein[31] calculated the charge density of mono-layered graphene by using the numerical method. They found that the charge density at the edge is higher than that in the center of graphene. From the experimental viewpoint,[39,40] the charge distribution in graphene is also inhomogeneous. The above conclusions are in good agreement with our calculations results.

Thirdly, we analyze the change of atomic charges with distance from the center of a round grapheme sheet. The change of atomic charge with distance from the center in 148 atoms hexagon graphene is shown in Fig. 3(a). As seen in Fig. 3(b), when the distances of atoms from the center are equal (that is, radius R is constant), the charges of atoms are essentially the same. In addition, the atomic charge with distance from the center exhibits an oscillatory distribution. The oscillation becomes more and more obvious with increasing radius R. The greater the radius R, the greater the charge transfer of atoms is. However, the charge distribution at the edge of the graphene is not uniform and it is related to the local structure. In the following sections, we will focus on the influence of the edge structure on its charge distribution.

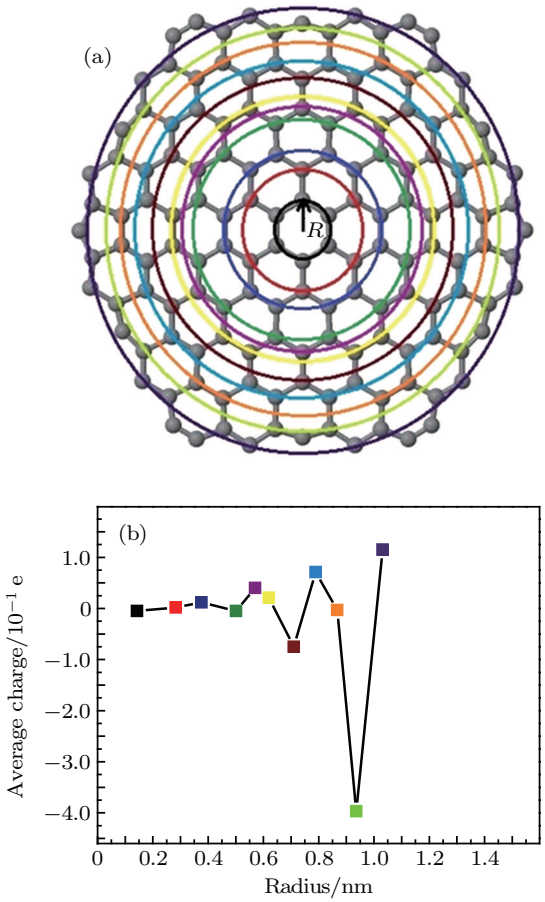


Fig. 3. (color online) (a) 148-atom hexagon graphene and (b) atomic charge varying with distance from the center, where the colors correspond to the different values of radius R.

3.2. Local charge distribution

3.2.1. Charge distribution at the edge of graphenes

3.2.1.1. Double-bonded atoms at the zigzag edge

Graphene can exhibit either quasi-metallic or semiconducting behavior, depending on the atomic structure of its edge.[41] Firstly, we study the charge distribution of double-bonded atom at the zigzag edge. In Fig. 4(a), we set the length of the rectangular graphenes to be a constant (1.93 nm) along the X-axis and the width to be different, i.e., $y = 0.76$ nm, 1.196 nm, 1.629 nm, respectively. The colored atoms represent double-bonded atoms at the zigzag boundary. As seen in Fig. 4(b), the charge distribution and charge values of the double-bond atom are kept constant with the width of graphene increasing (y value). In other words, the length of graphene (x value) determines the charge distribution of double-bonded atom at zigzag edge, and the width alteration has negligible effect on the charges.

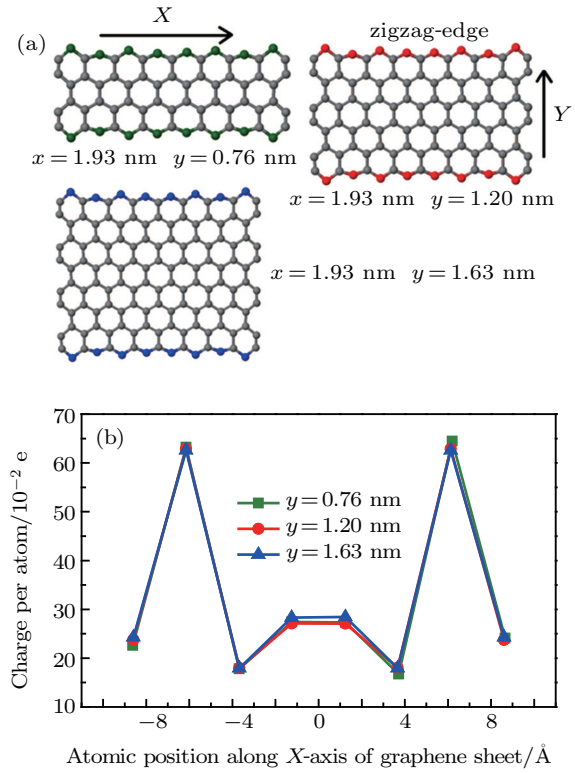


Fig. 4. (color online) (a) Rectangular graphenes and (b) charge distribution of the double-bond atom at zigzag edge.

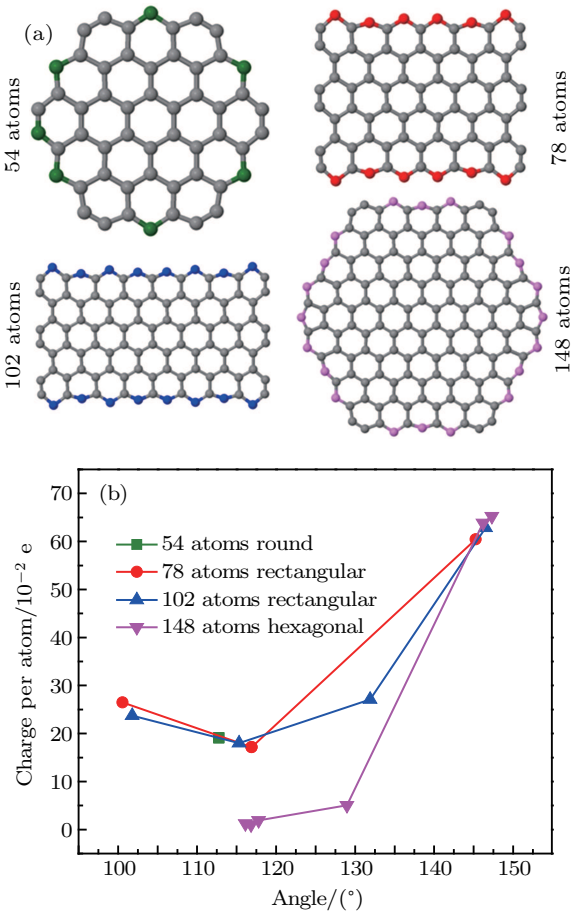


Fig. 5. (color online) (a) Different graphene shapes and (b) angle effect on atomic charge at the zigzag-edge atoms.

Secondly, our calculations and analyses indicate that the value of bond angle has a great effect on the charge transfer of the carbon atom at the zigzag boundary. Several typical models, e.g., round, rectangular, and hexagonal graphene sheets are used to calculate the atomic charges with the changes of these bond angles as shown in Fig. 5(a). In Fig. 5(b), it is found that all atoms display positive charges. When the graphene sheet is round, the bond angle of each double-bonded atom is averaged, i.e., 112.75°, and the atom loses 0.191 electrons (green). When the graphene sheet is in rectangular and hexagonal shapes, the ability of carbon atom to lose electrons gradually decreases and then gradually increases with bond angle increasing. The bond angle varies from 100° to 130° and the ability of atoms to lose electrons weakens accordingly. When the bond angle of atom is about 116°, the charge transfer is found to be least, ranging from +0.11 to 0.12 e. When the bond angle increases from 130° to 148°, the ability of atoms to lose electrons is enhanced. When the bond angle is about 148°, the amount of charge transfer is the largest, reaching +0.64 e. Generally, it can be clearly seen that the bond angle has a great influence on the charge of double-bonded atom at the zigzag edge.

3.2.1.2. Double-bonded atoms at the armchair edge

Figure 6 shows the rectangular graphene models of double-bonded atoms at the armchair edges. The local environmental effects on atomic charges on the armchair boundary are studied. In Fig. 6(a), we construct three types of graphenes with different widths (y = 1.629, 2.063, 3.363 nm) along the Y-axis and with the same length along the X-axis (four benzene rings). Figure 6(b) indicates that the charge distribution characteristics of double-bonded atoms at the armchair edge in graphene with different widths are the same, where charge distribution is oscillatory and gradually weakens from the side to the center. It is also found that each atom has a negative charge. This character is more obvious in graphene with y = 3.363 nm (the blue curve in Fig. 6(b)). In addition, when the width of graphene changes, the charge values of the two atoms at the top are essentially constant, i.e., 0.185 e and 0.044 e, respectively.

In Fig. 6(c), we set the width of the rectangular graphenes to be a constant, and their length is variable (x = 0.7, 1.19, 1.432, and 1.925 nm, respectively). The effect of length on the charge distribution of double-bonded atom in armchair is investigated. As seen in Fig. 6(d), the charge profile of armchair-edge shows no major difference with width changing, when the length of graphene is changed. The charge value of each atom at the same position along the y direction is almost unchanged.

Here, we study the effects of local atomic environment (bond length and bond angle) on atomic charge value. In this

study, two graphene sheets with different sizes are selected for calculation as shown in Fig. 7(a). The atomic charge value of double-bonded atoms at armchair edge is collectively influenced by bond angle and bond length. As seen in Fig. 7(b), the ability of atom to gain electrons becomes weaker with increasing the area of the triangle, which is formed by two bond lengths and bond angles of double-bonded atoms (e.g., in Fig. 7(a)). Especially, when the area varies from about 6.701 to 0.6752 Å^2, the curve rapidly rises, indicating an increase of the ability t of lose electrons. When the area is large enough (about 0.6770 Å^2), the negative charges of double-bonded atoms are transformed into positive charges. The curve is found to change gently. This observation confirms that the size of triangle area is a key parameter to determining the atomic charge value of double-bond atoms at the armchair edge.

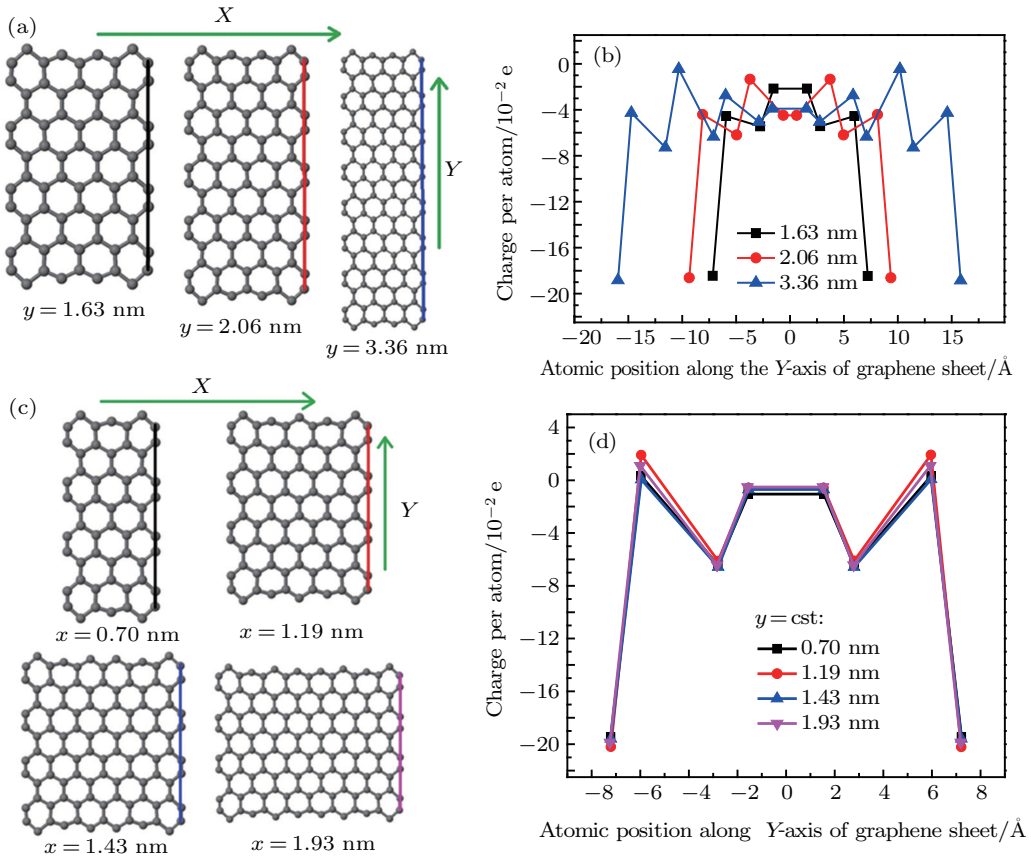


Fig. 6. (color online) (a) Graphenes with different widths and x = constant, (b) double-bond atomic charge at armchair-edge along Y-axis of graphene, (c) graphenes with different widths and y = constant, and (d) double-bond atomic charge at armchair edge along the Y-axis of graphene, where the colors correspond to the different graphene sheets.

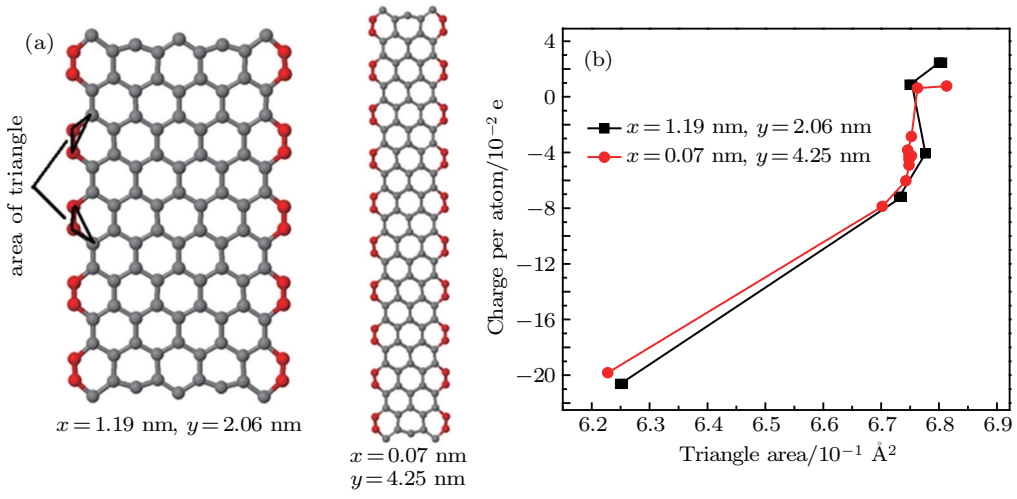


Fig. 7. (color online) (a) Carbon atoms with double-bond atoms at armchair edge and (b) charge per atom versus triangle area.

3.2.1.3. Charge distribution of triple-bonded atom at the edge

There are some atoms forming triple bonds with their neighbor atoms at the zigzag edge or armchair edge as shown in Fig. 8. The triple-bond lengths have effect on the charge distribution of triple-bonded atoms, and the effect is relatively large. Figure 9 shows the relationships between the atomic charge and the standard deviation for the three bonds around the atoms in rectangle and hexagon models. It can be seen that there are two parts of the different characteristics in rectangle graphene sheet. The charge of the atoms is found to increase initially with increasing standard deviation, and then decreases. It is also found that charge increases with increasing standard deviation if the triple-bonded atom is located on the armchair edge. As the standard deviation increases, the values of charges of atom change from negative to positive. For example, in the 3# and 4# atoms in Fig. 8(b), the standard deviation of 3# atom is least (0.011) and gains 0.07 electrons. The standard deviation of 4# atom is larger (0.042) and loses 0.11 electrons. The rectangle graphene contains a higher percentage of armchair edges than hexagonal graphene (as shown in Fig. 9). However, when the triple-bonded atoms are located on the zigzag edge, charge decreases gradually with increasing standard deviation. The atoms are found to have negative charge due to the change of atom position. For hexagonal graphene, the triple-bonded atoms are located on zigzag edge. Hence, the curve decreases monotonically as the standard deviation increases. The ability to gain electrons gradually increases with increasing standard deviation. It can be seen that the charge distribution of triple-bond atoms is influenced by atom position in addition to the standard deviation of the bond length.

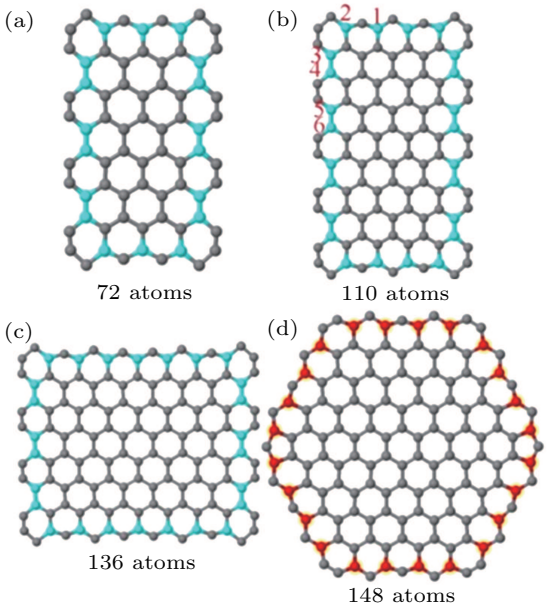


Fig. 8. (color online) Edge atoms with three bonds in graphene.

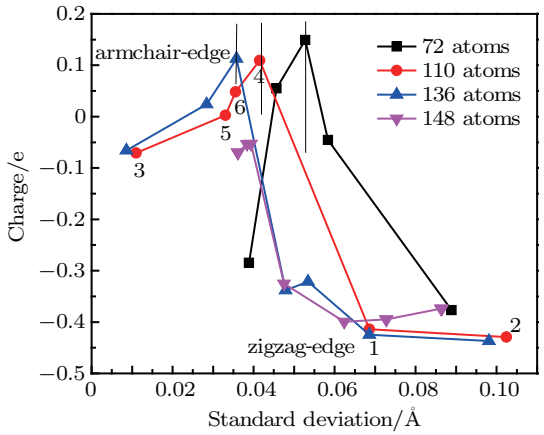


Fig. 9. (color online) Charges of triple-bond atoms versus their standard deviation for three bond lengths.

Our simulation can infer that each piece of graphene has its special characters including the character of charge distribution. However, the atom charge distributions follow almost the same principle, strongly depending on the atom position in the graphene and the local bond environment. Our results can be helpful in understanding the newly experimentally observed electron emission, charge impurity and chemical doping phenomena in 2-dimension nanostructures.

4. Conclusions

The charge distributions in different morphology graphenes and atomic chains are investigated by semi-quantum calculations. Our main findings are as follows. (i) The charge transfer at edge is much larger than in the internal part. The charge distribution has the same symmetry as that of the carbon atom distribution. (ii) The charge of double-bonded atom at zigzag edge has a strong dependence on bond angle, while the charge distribution of double-bonded atoms at the armchair edge has a strong dependence on the area of the triangle. (iii) The charge of triple-bonded atom at the edge is affected by the standard deviation of three bond lengths around it and also affected by the position (armchair edge or zigzag edge) of atom simultaneously.

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