Geometrical Deformation and Electronic Structures of One Hexagonal Graphene under External Electric Field

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Abstract

By using QMD (Quantum-molecular Dynamics) method, as well as DFT (Density Function Theory) at B3LYP/6-31G* level, geometrical deformation, failure and electronic structures of one hexagonal graphene under external electric field were investigated. Effects of electric field direction on the electrically-induced deformation, polarization-charge distribution, dipole moment and FMOs (Frontier Molecular Orbitals) of the graphene were discussed. It is found that electrically-induced deformation and failure are easier to occur to graphene under armchair-direction field than under zigzag-direction field; under external electric field, the chemical stability of graphene becomes worse, but at the same electric field intensity graphene under zigzag-field has better chemical stability than under armchair-field; under electric field, the chemically active sites transfer into two ends of graphene, where external electric potential is highest and lowest, respectively.

Keywords: QMD; Graphene; Geometrical deformation; Electronic structures; External electric field

Introduction

Graphene is the first two-dimensional material observed so far. As one novel form of carbon, single-layer graphene sheets were first discovered in 2004 and prepared by mechanical exfoliation of bulk graphite [1]. Later, the method of epitaxial CVD (Chemical Vapor Deposition) on transition metals and SiC surface at high temperature [2-5] was also applied to produce graphene. Although developed very recently, graphene has already found many applications in solar cells [6], liquid crystal devices [7], molecular sensors [8], and nano-sized transistors prototypes [9].

Graphene has exceptional mechanical and electrical properties. Its Young’s modulus reaches 1 TPa and intrinsic strength 130 GPa [10]. In graphene, electron mobility is extraordinarily high and ballistic electron transport is comparable to that of single-walled carbon nanotubes [11,12]. Considering that the electronic properties of graphene sheets can be tuned by dimension and shape [12,13], some “tailoring” techniques combining e-beam lithography, and plasma etching have been developed to cut graphene sheets into desired geometries [14,15], such as triangular, hexagonal, round and ribbon-like graphenes [13,14,16], which provides convenience for scientists designing various graphene devices in future nanoelectromechanical systems. It is well-known that the external electric field can alter the structure, the frequencies of absorption peaks and electronic characters of the carbon nanomaterials e.g. carbon nanotubes [17], therefore understanding of the electric field dependent properties and their manipulation is important for using graphene in electric circuits as a device. Now studies of mechanical properties and electronic structures of graphene have been widely carried out [10,13,16]. However, the report about the effects of electric field direction on electrically-induced failure and electronic structures of graphene has not been found yet.

In this work, QMD (Quantum-molecular Dynamics) technique based on PM3 (Parameter Model 3) method and Newton’s motion law is used to calculate geometrical deformation, polarization-charge distribution and molecular dipole moment of one hexagonal graphene under different external electric fields, and then DFT (Density Function Theory) is utilized to more accurately calculate the FMOs (Frontier Molecular Orbitals). According to the calculations, the effects of electric field direction on the electrically-induced deformation and electronic structures of graphene are discussed. At last, some interesting conclusions are obtained, which is very helpful for us to further recognize the physical properties of graphene.

Model

The studied object

Figure 1 shows the hexagonal graphene to investigate. The graphene sheet has 96 carbon atoms, 132 C-C bonds and 37 regular hexagonal atomic-rings. The graphene, after geometrical optimization (energy minimization), has a height ($H_e$) about 1.54 nm and a width ($L_e$) about 1.70 nm. The external electric field, parallel to the graphene sheet, is applied along armchair- or zigzag-direction, i.e. the x- or y-axis direction (Figure 1), and the electric field intensity $E_e$ takes...
between 0 and 0.07 a.u.. Here the armchair- and zigzag-direction electric fields are respectively called “armchair-field” and “zigzag-field”, for short.

The QMD Technique

The QMD technique [17] is used to simulate the electrically-induced deformation of the graphene under electric field. In the simulations, the positions and velocities of the carbon atoms in the graphene molecule are described with Newton’s motion law:

\[ \ddot{r}_i = \frac{F_i(r_i)}{m_i} \]  
\[ F_i = -\frac{\partial E}{\partial r_i} \]

Where \( \ddot{r}_i \) is the acceleration of the \( i \)th carbon atom, \( r_i \) the coordinates, \( F_i \) the resultant force, and \( m_i \) the atom mass; \( E \) is the system energy, determined by the Schrödinger equation:

\[ \text{Hy} = \text{Ey} \]

Where \( \text{H} = \text{H} + V(r) \), \( \text{H} \) is the Hamiltonian of the isolated molecular system, \( V(r) \) the electric potential of the external electric field, and \( \Psi \), the wave function.

Up to now, it is still difficult for any multi-atomic system to strictly solve the above Schrödinger equation. So the Born-Oppenheimer assumption is often used to decouple the motion of electrons and nuclei, and the Hartree-Fock assumption to simplify the multi-atomic problem of Equation (3) into a single-electronic problem. According to the Born-Oppenheimer assumption and Hartree-Fock assumption, Equation (3) can be approximately replaced by the Hartree-Fock equation below:

\[ \text{H} \Psi = \varepsilon \Psi \]

where \( \text{H} \) is the single-electronic Hamilton operator, \( \Psi \), the \( n \)th Molecular Orbital (MO), and \( \varepsilon \) the energy of \( \Psi \).

When the LCAO (Linear Combination of Atomic Orbitals) assumption is used, \( \Psi \) can be expressed as

\[ \Psi_n = \sum_{\mu} C_{\mu n} \Phi_{\mu} \]

Where \( \Phi_{\mu} \) is the \( \mu \)th Atomic Orbital (AO) and \( C_{\mu n} \), the coefficient of the AO \( \Phi_{\mu} \).

By using the close-shell model and the RHF (Restricted Hartree-Fock) method [18], Equation (4) can be translated into the following matrix form, i.e. the Roothaan-Hall equation:

\[ \text{FC}–\text{SCE} \]

where \( \text{F} \) is the Fock matrix, \( \text{S} \) the overlapping integrals matrix, \( \text{C} \) the coefficient matrix, and \( \text{E} \) the orbital diagonal energy matrix. By using the SCF (Self-consistent Field) method, we can solve Equation (6) and obtain the molecular energy \( E \).

Considering the calculation efficiency, the semi-empirical PM3 method [19] is first adopted to obtain the geometrical configurations, polarization-charge distribution and molecular dipole moment of the graphene under external electric field, and then single-point calculations of DFT at B3LYP/6-31G* level are performed to obtain the FMOs of the graphene. The pre-, post-processes and computations, as well as the geometrical optimization of graphene are all performed in the famous QM (Quantum Chemistry) software of HyperChem 7®. In the QMD simulations, the time-step takes 0.001 ps and the convergence limit 0.01 Kcal/mol.

Geometrical Deformation Under Electric Field

Figure 2a shows the Mulliken charge distribution of the graphene under no electric field. Figure 2b and 2c present the charge distribution under armchair- and zigzag-fields, respectively, where \( E_e \) takes 0.04 a.u. The charge distributions for other \( E_e \) values are similar to the case of figure 2b and 2c, so they are not given here. Figure 3 presents the change of dipole moment \( D \) with electric field intensity \( E_e \).

From figure 2 and 3, it can be found that:

a) The carbon atoms of graphene under no electric field have very small net-charge, the charge absolute values are less than or equal to 0.068 a.u., and the charge distribution is approximately symmetrical about the \( x \) - and \( y \) -axes. The central carbon-atoms have only 0.001 or 0.006 a.u. net-charge, whereas the atoms at corners of the graphene hexagon have 0.068 a.u. net-charge due to their dangling bonds.

b) Under electric field, the atoms at high electric potential own more positive charge, and those at low electric potential own more positive charge (See figure 2b and 2c), i.e., the graphene is electrically polarized.

c) With increasing \( E_e \), the dipole moment \( D \) increases. When \( E_e \) is still small (\( E_e < 0.04 \) a.u.), the graphene molecule has only small deformation, and the \( D/vs. E_e \) curves are approximately linear; when \( E_e > 0.04 \) au, the dipole moment \( D \) increases rapidly with the increase of \( E_e \).

d) Because of the electrically-induced deformation and the out-plane thermal-fluctuation, the Mulliken charge distribution on the graphene becomes asymmetrical about the \( x \) - and \( y \) -axes.

Figures 4 and 5 shows molecular configurations of the graphene under the armchair- and zigzag-fields, respectively. Figure 6 shows the deformation under the electric fields. In figure 6, the vertical ordinate \( l \) denotes the electrically-induced strain of the graphene along the electric field direction, and \( \varepsilon \) the strain perpendicular to the electric field direction. They are defined as followings:

\[ l = \begin{cases} \frac{(L-L_0)}{L_0} \text{ for the armchair-field applied graphene} \\ \frac{(H-H_0)}{H_0} \text{ for the zigzag-field applied graphene} \end{cases} \]

\[ \varepsilon = \begin{cases} \frac{(H-H_0)}{H_0} \text{ for the armchair-field applied graphene} \\ \frac{(L-L_0)}{L_0} \text{ for the zigzag-field applied graphene} \end{cases} \]

where \( L \) is the length along the armchair-direction (i.e. the \( x \) -axis), and \( H \) the length along the zigzag-direction (i.e. the \( y \) -axis). The arrows in Figure 6 mark the moment of the graphene failing.

According to Figures 4-6, it can be found that:

a) With increasing \( E_e \), the graphene is elongated along the electric field direction, and shortens in the direction perpendicular to the electric field, the deformation (strain) \( \varepsilon \) perpendicular to the electric field is much smaller than that \( l \) along the electric field direction; when \( E_e < 0.03 \) a.u., the deformation \( l \) is slight, and when \( E_e > 0.03 \) a.u., \( l \) becomes significant. The maximal
A) The charge distribution of graphene (a) under no electric field, (b) under the armchair-field with the intensity of 0.04 a.u., and (c) under the zigzag-field with the intensity of 0.04 a.u.

b) When $E_e$ reaches certain critical value $E_c$, a few carbon atoms at low electric potential for the armchair-field and at high electric potential for the zigzag-field, break away from the graphene as shown in figure 4d and figure 5d, and the graphene fails. The $E_c$ is 0.06 a.u. and 0.07 a.u. for the cases of the armchair- and zigzag-fields, respectively.

c) At the same field intensity $E_e$, the graphene under the armchair-field has larger deformation $l_{max}$ than under the zigzag-field, which implies that the armchair-field can more easily induce deformation than the zigzag-field.

d) The electrically-induced failure is easier to occur at the corners of the hexagonal graphene, where the external electric potential is highest or lowest.

In 2003, the mechanical deformation of one (5,5) carbon nanotube under external electric field was investigated by Guo and Guo [20]. It is found that the nanotube’s end toward the anode got negative charges, the one toward the cathode had got positive charges, and the polarization deformation occurred to the carbon nanotube. The electrically-induced strain for the present graphene should be due to the same reason, i.e. electric polarization.

Electronic Structures Under Electric Field

In terms of Frontier Molecular Orbital (FMO) theory [21,22], it is considered that FMOs, i.e. the MOs (Molecular Orbitals) near the LUMO (Lowest Unoccupied MO) and HOMO (Highest Occupied MO), determine the chemical properties of one molecule. The LUMO and HOMO energy can reflect molecular electrophilicity and nucleophilicity, respectively. The LUMO energy is close to the molecular electrophilic potential in value, and the higher the HOMO energy is, the more easily the molecule loses electron. The energy-gap between the LUMO and HOMO can reflect the capability of electron
transferring from the occupied MO to the unoccupied one. The narrower the energy-gap is, the more chemically active the molecule is. In addition, according to the electron density distribution of the LUMO and HOMO, the chemically active sites of the molecule can also be found.

Figure 7 presents the change of the HOMO, LUMO, LUMO-HOMO energy for the graphene under the applied armchair- and zigzag-fields. Figures 8 and 9 shows the spatial distribution of the HOMO and LUMO under the armchair-field, respectively. Figures 10 and 11 shows the distribution of the HOMO and LUMO under the zigzag-field, respectively.

From Figure 7, it can be seen that:

a) With increasing electric field intensity $E_e$, the HOMO energy of the graphene under the armchair-and zigzag-fields increases, the LUMO energy and LUMO-HOMO energy-gap decrease, which implies that the graphene becomes easier to react with not only other nucleophilic group, but also electrophilic molecule, i.e., the graphene under electric field becomes more chemically active.

b) Under the same field-intensity, the graphene under the armchair-field has higher HOMO energy, but lower LUMO and LUMO-HOMO energy than under the zigzag-field, which implies that the graphene under the zigzag-field has better chemical stability than under the armchair-field.

c) The graphene under no electric field has the HOMO energy of -4.80 eV, LUMO energy of -7.27 eV and LUMO-HOMO energy-gap of 2.47 eV. From Kheirabadi et al. [13], it was found that the LUMO-HOMO energy-gap of graphenes depends on the dimensions, and the LUMO-HOMO energy-gap of the quasi-circular graphene with 96 carbon atoms is about 2.11 eV according to DFT calculations at B3LYP/6-31G level. The energy-gap result agrees with ours very well, which shows the validity of our present calculations.
From figures 8-11, it can be seen that:

a) Without electric field applied, the HOMO covers the entire graphene relatively evenly, and the LUMO is distributed around the circumference of the graphene molecule, especially on those zigzag-edge atoms.

b) Under external electric field, the HOMOs translate to the high electric potential end, and the LUMOs to the low electric potential end, which implies that the high electric potential end of the graphene becomes electrophilic active sites, and the low electric potential end becomes nucleophilic sites.

Note: In figure 10b, the graphene geometrically warps at its right-bottom corner, so the HOMO becomes unsymmetrical about the y-axis.

Conclusions

The QMD and DFT methods are used to investigate geometrical deformation, failure and electronic structures of one hexagonal graphene under different external electric field, and the results can be concluded as followings:

a) Under electric field, the graphene is polarized and elongated along electric field direction. The electrically-induced failure is easier to occur at the corners of the hexagonal graphene, where the external electric potential is highest or lowest.

b) The armchair-field can more easily induce graphene to geometrically deform than the zigzag-field.

c) At the same electric field intensity, the graphene in the zigzag-field has better chemical stability than in the armchair-field.

d) Under electric field, graphene becomes more chemically active, and its two ends of the high and low electric potential become electrophilic and nucleophilic active sites, respectively.

References


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