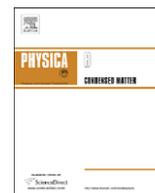




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Electronic properties of zero-dimensional finite-sized nanographene

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ABSTRACT

In this work, we use the tight-binding model to study the low-energy electronic properties of zero-dimensional finite-sized nanographene subject to the influence of an electric field. State energies and energy spacings are found to oscillate significantly with the field strength. The state energies and band gaps also rely upon the type of the nanographene. The electric field will modify state energies, alter energy gaps, and induce the complete energy gap modulations. The band gap of the type-IV nanographene is always zero regardless of the value of the field strength. The variations of the state energies will be directly reflected in the density of states. The numbers and frequencies of the density of states' divergent peaks are strongly dependent on the field strength and the type of the nanographene. Finally, the electron wave functions are found to be localized at certain zigzag lines at zero electric field.

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1. Introduction

The graphite-based systems, such as three-dimensional (3D) graphite, one-dimensional (1D) carbon nanotubes (CNs) [1–4] and graphene nanoribbons [5,6], and zero-dimensional (0D) fullerenes [7] have been studied extensively because of fundamental physics interests and promising applications. Recently, Novoselov et al. [8] succeeded in isolating single sheets of graphite known as graphene. Despite being only one atom thick, their graphene devices are stable under ambient conditions. Subsequent experiments [9–15] have demonstrated that it is feasible to modulate electrical properties of graphene devices by applying an external voltage, which opens up the possibility of graphene microelectronics. Graphene, an infinite single atomic layer of graphite, is a two-dimensional (2D) system and can be regarded as unrolled single-walled CN. Pioneer theoretical studies on graphene were proposed 50 years ago [16–18] and are widely used to explain properties of various graphene-based materials. Studies on the 2D crystals consisting of a single or few graphite layers are numerous. There are observations of unconventional electric field effects in the Hall coefficient [8], and novel quantum Hall effect in monolayer [14] and bilayer graphite [15]. These unusual electronic properties are due to the linear dispersion relation near the Dirac

point. The carriers in graphene are massless Dirac fermions leading to the shifted Hall plateaus [10,14]. Theoretical calculations on the band structures of stacked graphite layers with tight-binding methods found interesting band deformation in these systems [19–22]. This unique band structure of graphene also accounts for the exceptional electronic properties of CNs. Only through changing their diameters and chiral angles, can nanotubes vary from being metallic to semiconducting [2–4]. When graphene is patterned into finite size, 0D nanographene will then be obtained. An essential difference between CNs and planar nanographene is the presence of boundaries. In this sense, the electronic properties of nanographene are characterized more by the boundaries that confine the finite-sized graphene sheet. Previous works [6,23,24] on graphene nanoribbons showed that there are edgestates originating from the nonbonding π electron states at the ribbon edges, and they will influence the electronic properties substantially. According to the model by Nakada et al. [6], the edge states at a zigzag boundary can be delocalized towards the interior of the ribbon and introduce flat bands near the Fermi level in addition to the π and π^* bands of graphene. Ultra-high vacuum STM observations demonstrate the presence of the edge states [25,26]. For 1D graphene nanoribbons, there have been lots of researches on the electronic properties [5,6,23,24,27–30], magnetic properties [31,32], optical properties [33], transport properties [34], and synthesis [35,36]. However, there are only a few works [37–39] on the 0D finite-sized nanographene. In this study, the electronic properties of nanographene in the presence of an electric field are studied by the

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tight-binding method. Their dependence on the length, width, and field strength are investigated.

2. Theory

As displayed in Fig. 1(a), the width and length of a finite-sized nanographene is defined by the number of zigzag lines N_z and the number of armchair lines N_a , respectively. Therefore, a nanographene can be characterized by (N_z, N_a) . The total number of carbon atoms is denoted by N_{tot} . An (N_z, N_a) nanographene can be classified into four categories according to the boundary structures: (I) N_z is even and N_a is odd. All zigzag lines have the same number of carbon atoms, $N_{tot} = N_z \times N_a$. (II) N_z and N_a are even, the first and last zigzag lines have one less carbon atom than the other zigzag lines, and both happen at the last armchair line, $N_{tot} = N_z \times N_a - 2$. (III) N_z is odd and N_a is even. The first zigzag line has one less carbon atom at the last armchair line, and the last zigzag line has one less carbon atom at the first armchair line, $N_{tot} = N_z \times N_a - 2$. (IV) N_z and N_a are odd. The last zigzag line has two less carbon atoms than the others, $N_{tot} = N_z \times N_a - 2$. Electronic properties of finite-sized nanographene are investigated by using the tight-binding model with one electron per π

orbital. Based on the Huckel approximation, the wave function is the linear combination of the $2p_z$ orbitals,

$$\Psi = \sum_{i=1}^{N_{tot}} A_i \phi(\vec{r} - \vec{R}_i), \quad (1)$$

where $\phi(\vec{r} - \vec{R}_i)$ is the atomic orbital of the carbon atom at \vec{R}_i , and the coefficient A_i is determined by normalization condition. The tight-binding Hamiltonian built from the N_{tot} atomic wave functions is given as

$$H = \sum_i \varepsilon_i(\mathbf{F}) c_i^\dagger c_i + \sum_{i,j,i \neq j} t_{ij} c_i^\dagger c_j, \quad (2)$$

where i, j denotes the atom site, $\varepsilon_i(\mathbf{F})$ is the field-modulated site energy, and c_i^\dagger and c_j are the creation and annihilation operators at sites i and j , respectively. The electric field direction is along the zigzag line, and F is the field strength. $t_{ij} = \gamma_0$ ($= 2.66$ eV) is the transfer integral. Only hoppings between the nearest neighbors are considered. The Hermitian Hamiltonian built from the N_{tot} $2p_z$ orbitals is an $N_{tot} \times N_{tot}$ matrix. After diagonalizing the Hamiltonian, the state energy $E^{c,v}(F)$ can be obtained. The superscripts c and v represent the antibonding π^* state and the bonding π state, respectively.

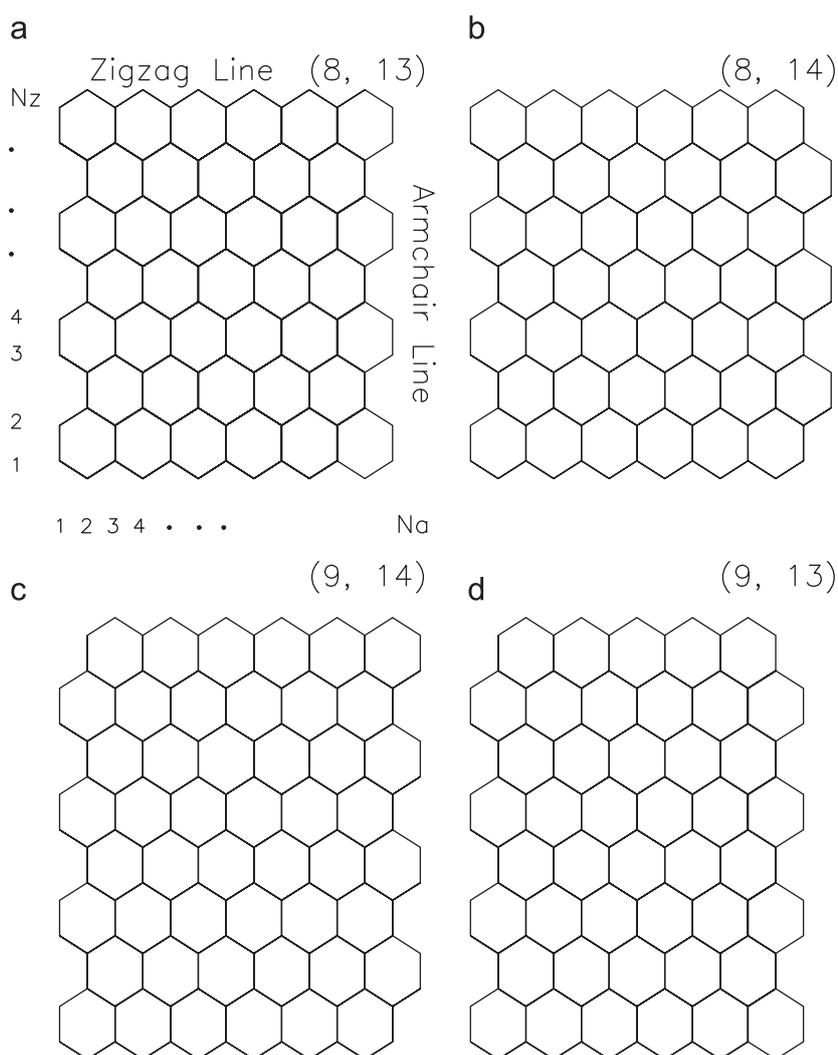


Fig. 1. The geometric structure of the (a) type-I (8, 13), (b) type-II (8, 14), (c) type-III (9, 14), and (d) type-IV (9, 13) nanographene.

3. Results and discussion

Four nanographenes: type-I (8, 13), type-II (8, 14), type-III (9, 14), and type-IV (9, 13) are chosen as a model study. In general, the states' energies oscillate significantly with F (Fig. 2), and the complete energy-gap modulation (CEGM energy gap opening and closing) occurs frequently except for the type-IV (9, 13) nanographene. Some high-energy states will come to the low-energy regime when the field strength is relatively large. The state energies are symmetric about the Fermi level $E_F = 0$ except for the type-II (8, 14) nanographene. The type-I (8, 13) nanographene has a very small energy gap of $0.0025\gamma_0$ at $F = 0$ (Fig. 2(a)). The electron state energies rely sensitively on F , and the lowest state touches the Fermi level at several F 's (Fig. 2). The type-II (8, 14) nanographene is a small-gap semiconductor with $E_g = 0.017\gamma_0$ at $F = 0$. The state energies are symmetric about the Fermi level only at $F = 0$, and become asymmetric for nonzero F (Fig. 2(b)). This can be explained by the boundary structure. There are two less carbon atoms at the last armchair line. CEGM will also happen in

this case. The type-III (9, 14) nanographene has an energy gap of $0.01\gamma_0$ at $F = 0$. N_{tot} of the type-IV (9, 13) nanographene is an odd number. There is always a state located at the Fermi level for all F (Fig. 2(d)). Therefore, the band gap constantly stays at zero and does not exhibit the CEGM.

The energy gap is also oscillatory with F except for the type-IV (9, 13) nanographene (Fig. 3(a)). For the type-I (8, 13) nanographene, there is a small band gap $0.0025\gamma_0$ at $F = 0$. The energy gap decreases initially with F , touches the zero value at $F = 0.004\gamma_0/\text{eÅ}$, exhibits the CEGM, then rebounds, and attains the peak value $0.27\gamma_0$ at $F = 0.0607\gamma_0/\text{eÅ}$. The band gap fluctuates significantly with F when F is large. The energy gap's behavior of the type-II (8, 14) nanographene is similar to the type-I case. The band gap peak value $0.17\gamma_0$ occurs at $F = 0.0608\gamma_0/\text{eÅ}$. For the type-III (9, 14) nanographene, the band gap grows gradually with F initially, reaches the peak value and then declines. CEGM will also occur. It is of interest to compare our computed results with previous similar work. Li et al. [40] studied the band gap variation of a metallic CN. They reported that for a (18, 0)

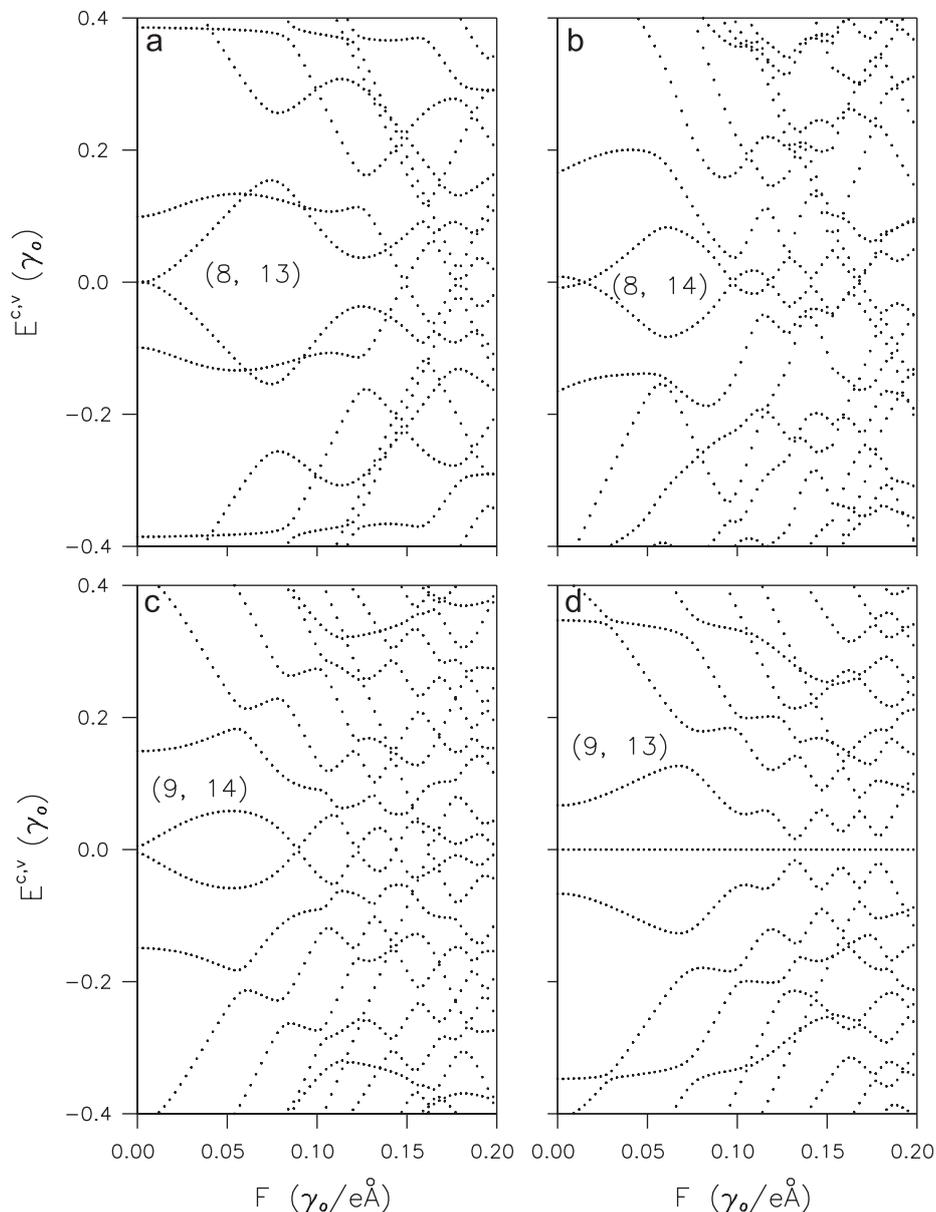


Fig. 2. The state energies versus the electric field strength F for the (a) type-I (8, 13), (b) type-II (8, 14), (c) type-III (9, 14), and (d) type-IV (9, 13) nanographene.

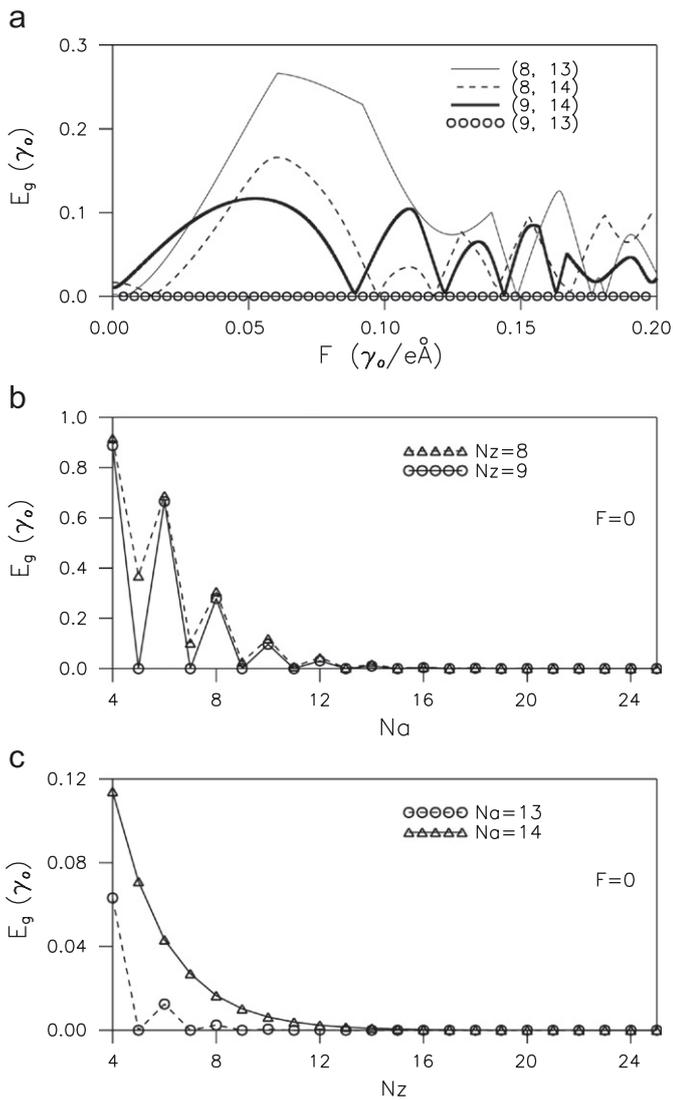


Fig. 3. The energy gap versus (a) the electric field strength F for four types of nanographene, (b) N_a with $N_z = 8, 9$, at $F = 0$, and (c) N_z with $N_a = 13, 14$, at $F = 0$.

nanotube, a field of 0.2 V/\AA (or $0.075\gamma_0/e\text{\AA}$) will open a band gap of the value 0.09 eV (or $0.034\gamma_0$). Based on the experimental work carried out by Chiu et al. [41], the band gap appears at a field of 10^7 V/cm (or $0.038\gamma_0/e\text{\AA}$) for a metallic CN. The gap opening in a nanographene happens at F value which is smaller than that in nanotube. In the presence of a transverse electric field, the onsite energy of the i th carbon atom in a nanographene or nanotube will be perturbed by the amount $\Delta E = -eFx_i$, where x_i is the coordinate of the i th carbon atom along the field direction. Nanographene is a planar structure. Rolling it up into a tube will certainly reduce the corresponding x_i values and subsequently the influences of F on the band gap. The electronic structures also vary sensitively with the size of the nanographene, and are reflected in the N_a and N_z dependence of the energy gap (Figs. 3(a) and (b)). The general trend is that the band gap diminishes with growing N_a or N_z . When N_a or N_z is greater than 16, the energy gap almost decreases to zero. On the other hand, E_g oscillates noticeably with N_a or N_z except for the $N_a = 14$ case. With fixed N_z , adjacent N_a 's correspond to different types of nanographenes. For example, with $N_z = 9$, it is type-III nanographene and has nonzero band gap when N_a is even, and becomes zero gap type-IV system when N_a is odd. When

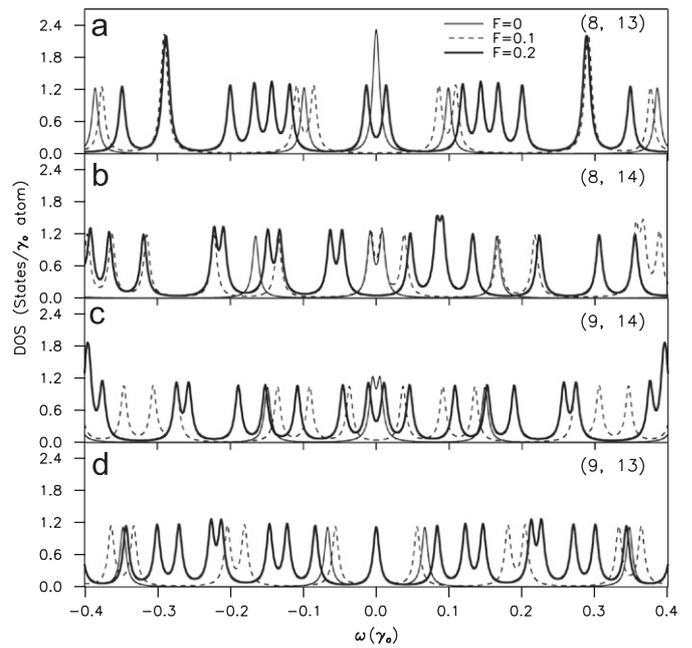


Fig. 4. Density of states for the (a) type-I (8, 13), (b) type-II (8, 14), (c) type-III (9, 14), and (d) type-IV (9, 13) nanographene for different F 's.

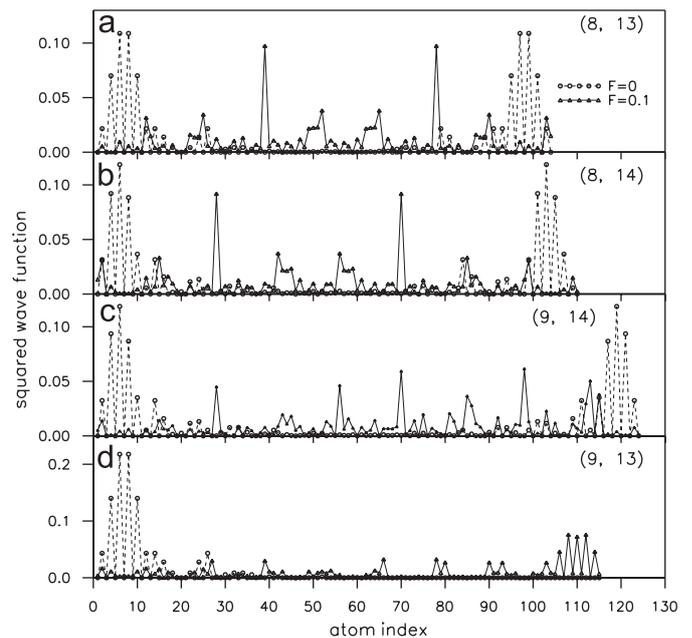


Fig. 5. The squared wave functions of the states nearest to the Fermi level for the (a) type-I (8, 13), (b) type-II (8, 14), (c) type-III (9, 14), and (d) type-IV (9, 13) nanographene at $F = 0$ and $0.1\gamma_0/e\text{\AA}$.

$N_a = 14$, it switches between type-I and type-II nanographene. The N_z -dependence of these two systems is similar.

An important parameter of the electronic properties is the density of states (DOSs), defined as

$$D(\omega, F) = \sum_{i=1}^{N_{\text{tot}}} \frac{1}{\pi} \frac{\Gamma}{[\omega - E_i(F)]^2 + \Gamma^2}, \quad (3)$$

where $\Gamma = 5 \times 10^{-3}\gamma_0$ is the broadening parameter. The low-energy DOSs are shown in Fig. 4. As a result of the discrete features of the electronic states, the DOS exhibits many delta-function-like divergent peaks, whose heights are related to the

state degeneracy. In general, there are more DOS peaks at $F = 0.2\gamma_0/e\text{\AA}$, because some high-energy states will come to the low-energy regime when the field strength is large. Just like the state energy, the DOSs are symmetric about the Fermi level $E_F = 0$ for all F 's except for the type-II (8, 14) nanographene. There appears to be a doubly degenerate peak at the Fermi level for the type-I (8, 13) nanographene at $F = 0$ (Fig. 4(a)). In fact, they are two nearby peaks with energies at $\pm 0.00125\gamma_0$ and mixed under broadening computation. The inclusion of an electric field will alter the peak frequencies, and create new peaks. For the type-II (8, 14) nanographene, the DOS is symmetric about the Fermi level only at $F = 0$, and becomes asymmetric for nonzero F . For the type-IV (9, 13) nanographene, there is always a DOS peak located at the Fermi level for all F . The squared wave functions of the states nearest to the Fermi level are displayed in Fig. 5. At $F = 0$, the wave functions of the type-I, type-II, and type-III nanographene are mainly localized at the first and last zigzag lines, but those of the type-IV nanographene are mostly situated at the first zigzag line. A nonzero F will delocalize the wave functions.

4. Concluding remarks

In conclusion, the tight-binding model has been employed to investigate the low-energy electronic properties of OD finite-sized nanographene subject to the influence of an electric field. State energies and energy spacings are found to oscillate significantly with the field strength. The state energies and band gaps also rely upon the type of the nanographene. The electric field will modify state energies, alter energy gaps, and induce the CEGMs. The band gap of the type-IV nanographene is always zero regardless of the value of the field strength. The variations of the state energies will be directly reflected in the DOSs. The numbers and frequencies of the DOSs divergent peaks are strongly dependent on the field strength and the type of the nanographene. The electron wave functions are found to be localized at certain zigzag lines at zero electric field.

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