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PAPER

Opening a band gap in graphene by C–C bond alternation: a tight binding approach

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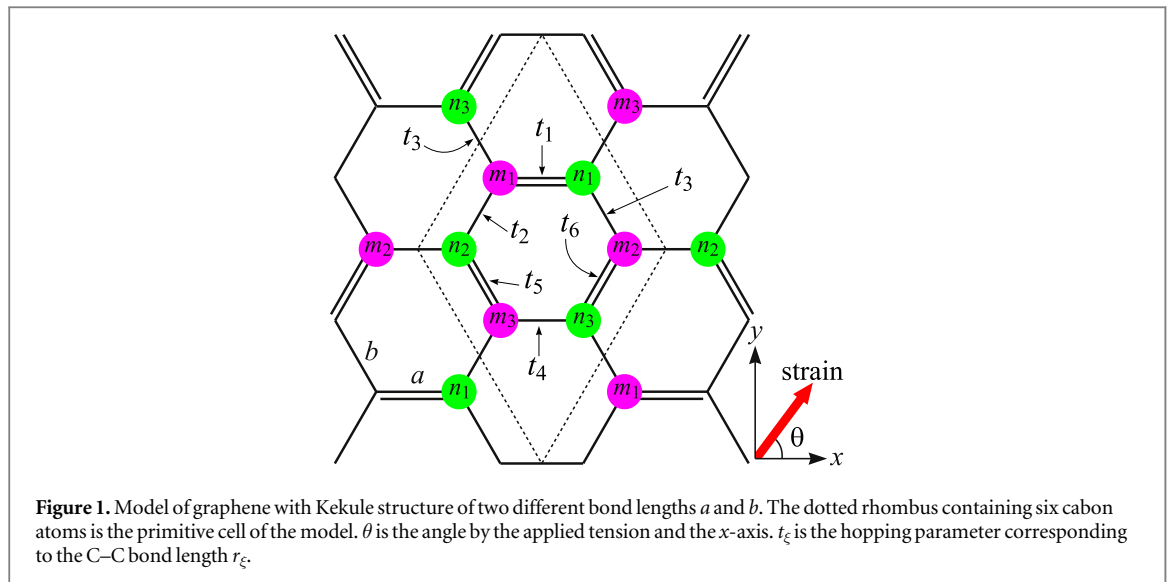
Abstract

In the present work, we consider the electronic properties of graphene with Kekule structure formed from two different C–C bonds in its hexagonal lattice. When the C–C bond alternation was introduced, a small band gap has been opened in the band structure of graphene and it increases linearly by a difference in the bond lengths δ . While the applied strain along the zigzag or armchair direction causes band gap to decrease rapidly to zero, the strain in the other directions can increase the band gap. Interestingly, when the graphene with Kekule structure is strained, its band gap is inversely proportional to the bond length difference δ . Opening a band gap in graphene due to bond alternation and strain can open up new applications in nanoelectronic devices.

1. Introduction

The discovery of graphene in 2004 [1] opened up a great turning point in the studies of layered materials and their applications in nanotechnology. Graphene became a hot topic for both theoretical and experimental research for more than a decade due to its extraordinary and outstanding physical and chemical properties [2]. In the semimetal form with zero energy gap, however, graphene has certain limits in applications in nanoelectronics, such as graphene-based transistors cannot be switched off because the band gap of graphene is zero [3]. Scientists have looked for other materials to overcome this disadvantage [4]. The fact that many graphene-like materials have been found and considered in recently, such as silicene [5], phosphorene [6–8], antimonene [9], or two-dimensional (2D) transition metal dichalcogenides [10]. Along with the search for alternative materials, one also finds ways to open up the band gap in graphene. Fortunately, we can control the band gap of graphene. Recent theoretical studies have indicated that we can alter the electronic energy band structure of graphene by applying strain [11], by placing it on semiconductor substrates [12, 13], or forming graphene-based heterostructures [14–17].

The electronic properties of graphene have been studied by various methods [18–21]. Pereira and his co-workers have shown that an energy gap has occurred in graphene when it is uniaxially deformed. However, these calculations have shown that the deformation threshold for band gap appears to be large (larger than 23.5%). Similarly, first-principles calculations also demonstrated that in the presence of strain larger than 30%, graphene



becomes a semiconductor with a small energy gap [22]. Besides, the electronic properties of graphene also depend strongly on the direction of the applied strain [22–24].

Bond alternation in the carbon nanomaterials has been studied for a long time [25, 26]. Actually, Peierls instability suggested in [27] always appears in 1D systems [28, 29] and ring atoms [30] and does not often appear in 2D materials. One has shown that Peierls distortions [31, 32] can lead to the formation of the Kekule structure [33, 34] in carbon nanotubes. Effect of the bond alternation on electronic properties of carbon nanotubes [35] and graphene nanoribbons [36] was also investigated using different methods. Interestingly, Frank and Lieb have demonstrated the possibility of the Peierls distortions in 2D graphene [37]. As new quantum phases of graphene, the Kekule distortion phase has been recently studied [38–40]. However, experimental evidence of the Kekule distortion in graphene just recently published [41, 42]. Recent experimental work has shown that an adatom on the graphene lattice can break the sublattice symmetry of the graphene. The adatom–graphene interaction leads to displacement of the C atoms and forming the Kekule distortion phase [41]. Gutiérrez’s group has observed the formation of Kekule bonds in a graphene monolayer that is epitaxially grown on the copper substrate [41]. Also, Ma and co-workers showed that ordered S monatomic superlattice on a graphene lattice can lead the forming the Kekule structure in graphene with a small band gap of 245 meV [42]. Recently, the formation C–C bond alternation of the Kekule type in graphene due to strain and the change of the hopping parameters in this structure has also been investigated [43].

In this work, we consider the structure of graphene with unequal C–C bonds arranged alternately in the honeycomb lattice to form the Kekule structure. We focus on the effect of bond alternation on electronic properties of graphene in the presence of the strain. The dependence of the energy gap on the difference in bond lengths and applied strain direction has also been studied and discussed in this work.

2. Model and theoretical framework

We design the model of graphene of Kekule structure which is formed by two C–C bonds of different lengths a and b alternating arranged in a hexagonal lattice as shown in figure 1. From figure 1 we can see that the Kekule structure in graphene is formed by two C–C bonds a and b ($a \neq b$) alternated in its hexagonal lattice. When the Kekule structure was introduced, the primitive cell of graphene contains six carbon atom (three m and three n). In this case, the periodic lattice constant along the y -axis $L_y = 4a_y + 2b_y$, is about three times as large as pristine graphene. The translational period along the x -axis is $L_x = 2a_x + 2b$. Compared with the pristine graphene, the area of the Brillouin zone for graphene with Kekule structure as shown in figure 1 is one-third of that of the pristine graphene (see also in [31]).

In presence of in-plane strain, the position vector of carbon atoms can be defined via the strain tensor Λ in the elasticity theory as the following [11]

$$\vec{r}_i = (1 + \Lambda)\vec{r}_{0i}, \quad (1)$$

where \vec{r}_{0i} and \vec{r}_i are the position vectors of the C atoms respectively before and after deformation. The strain tensor Λ can be expressed as [11]

$$\Lambda = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{21} \\ \varepsilon_{12} & \varepsilon_{22} \end{pmatrix} = \varepsilon \begin{pmatrix} \sin^2 \theta - \sigma \cos^2 \theta & (1 + \sigma) \cos \theta \sin \theta \\ (1 + \sigma) \cos \theta \sin \theta & \cos^2 \theta - \sigma \sin^2 \theta \end{pmatrix}, \quad (2)$$

where σ is the Poisson's ratio and θ is the angle between the x axis and the tension direction as shown in figure 1.

We can define the difference in bond length δ using the suggestion of Fujita and co-workers [44] that the difference in the C–C bond length bond can be expressed via the undeformed C–C bond a_0 as $a = a_0 + \delta$ and $b = a_0 - \delta$ with δ can be positive or negative.

In the framework of tight binding model, the Bloch wave functions in the graphene with the primitive cell containing six C atoms can be written as [31]

$$\psi_{i\vec{k}}(\vec{r}) = \sqrt{\frac{6}{N}} \sum_{\vec{R}_\eta} \exp(i\vec{k}\vec{R}_\eta) \phi(\vec{r} - \vec{R}_\eta), \quad (3)$$

where $\vec{k} = (k_x, k_y)$ is wave vector, $\eta = m_i$, n_i ($i = 1, 2, 3$), N is number of C atoms in the unit-cell, \vec{R}_ν is position of the ν -th kind of the carbon atoms, and $\phi(\vec{r})$ is the wavefunction built from the p_z orbital for an isolated C atoms located at the origin. We can obtain the band structure of graphene by diagonalization of Hamiltonian \mathcal{H} which is built based on number of atoms in the primitive cell. As shown in figure 1, the primitive cell of the graphene with the Kekule structure contains six C atoms, the Hamiltonian matrix \mathcal{H} is (6×6) matrix

$$\mathcal{H} = \begin{bmatrix} 0 & \mathcal{H}_{mn} \\ \mathcal{H}_{mn}^* & 0 \end{bmatrix}, \quad (4)$$

where \mathcal{H}_{mn} is the (3×3) matrix which can write as the following

$$\mathcal{H}_{mn} = \begin{matrix} & \begin{matrix} m_1 & m_2 & m_3 \end{matrix} \\ \begin{matrix} n_1 \\ n_2 \\ n_3 \end{matrix} & \begin{bmatrix} t_1 e^{i\vec{k}\vec{r}_1} & t_3 e^{i\vec{k}\vec{r}_3} & t_2 e^{i\vec{k}\vec{r}_2} \\ t_2 e^{i\vec{k}\vec{r}_2} & t_4 e^{i\vec{k}\vec{r}_4} & t_6 e^{i\vec{k}\vec{r}_6} \\ t_3 e^{i\vec{k}\vec{r}_3} & t_5 e^{i\vec{k}\vec{r}_5} & t_4 e^{i\vec{k}\vec{r}_4} \end{bmatrix} \end{matrix} \quad (5)$$

where t_ξ ($\xi = 1, 2, \dots, 6$) is the hopping parameters corresponding to the C–C bond \vec{r}_ξ . Here, the vectors of bonds between carbon atoms are $\vec{r}_1 = m_1 n_1$, $\vec{r}_2 = m_1 n_2$, $\vec{r}_3 = m_1 n_3 = m_2 n_1$, $\vec{r}_4 = m_2 n_2 = m_3 n_3$, $\vec{r}_5 = m_2 n_3$, and $\vec{r}_6 = m_3 n_2$. In the presence of the C–C bond alternation and strain, hopping parameter t_ξ is changed due to the change in the length of the C–C bond. The dependence of the hopping parameter t_ξ on the C–C bond length r_ξ can be expressed via the Harrison formula [45]

$$t_\xi = t_0 \left(\frac{a_0}{r_\xi} \right)^2, \quad (6)$$

where $a_0 = 0.142$ nm and $t_0 = 2.7$ eV are the C–C bond length and hopping parameter of pristine graphene, respectively [46].

3. Results and discussion

In the presence of bond alternation with the bond lengths a and b as show in figure 1, there are only two different hopping parameters $t_1 = t_5 = t_6 = t_0(a_0/a)^2$ and $t_2 = t_3 = t_4 = t_0(a_0/b)^2$. This assumption is agreement with the previous quantum Monte Carlo calculations that there are two different hopping magnitudes when the Kekule structure is introduced [43]. However, when the strain is applied, depending on the applied tension direction θ , there will be four to six different values of hopping parameters that appear in the strained graphene with the Kekule structure. This is different from the case of undimerized (pristine) graphene with two hopping values when strain is applied along the armchair or zigzag axis [47]. As an example, we show dependence of the hopping parameters t_ξ on tension angle θ of graphene with Kekule structure of $\delta = 0.02\text{\AA}$ at $\varepsilon = 5\%$ in figure 2. We can see that, when the is applied along armchair ($\theta = 0$) or zigzag ($\theta = \pi/2$) direction, only four hopping parameters are occurred due to the symmetry of graphene with Kekule structure as shown in figure 1. In these cases, the $t_2 = t_3$ and $t_5 = t_6$. Also, the symmetry of this structure leads the $t_2 = t_4$ and $t_1 = t_5$ at the applied tension angle of $\pi/6$.

By diagonalization of Hamiltonian (4) we can obtain energy dispersion relations of graphene with Kekule structure. In figure 3, we show a cut of energy dispersion $E(k_x, 0)$ along $k_y = 0$ of graphene with Kekule structure. In the model of graphene with Kekule structure containing six carbon atoms in the primitive cell, at $\delta = 0$, the area of its first Brillouin zone is one-third of that of the pristine graphene as shown in figure 3(a). In this case, the conduction and valence bands intersect at the first Brillouin zone center at the Fermi level. When the bond alternation was introduced, i.e. $\delta \neq 0$, graphene with Kekule structure becomes a semiconductor with an energy gap opening at the center of the first Brillouin zone as shown in figure 3(b). Dependence of energy gap of

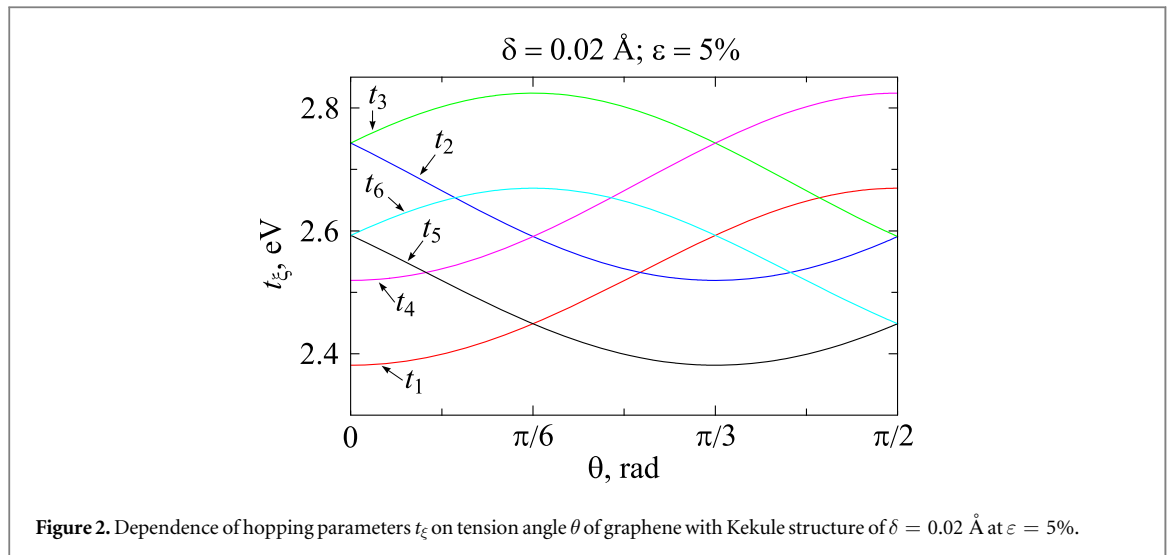


Figure 2. Dependence of hopping parameters t_c on tension angle θ of graphene with Kekule structure of $\delta = 0.02 \text{ \AA}$ at $\epsilon = 5\%$.

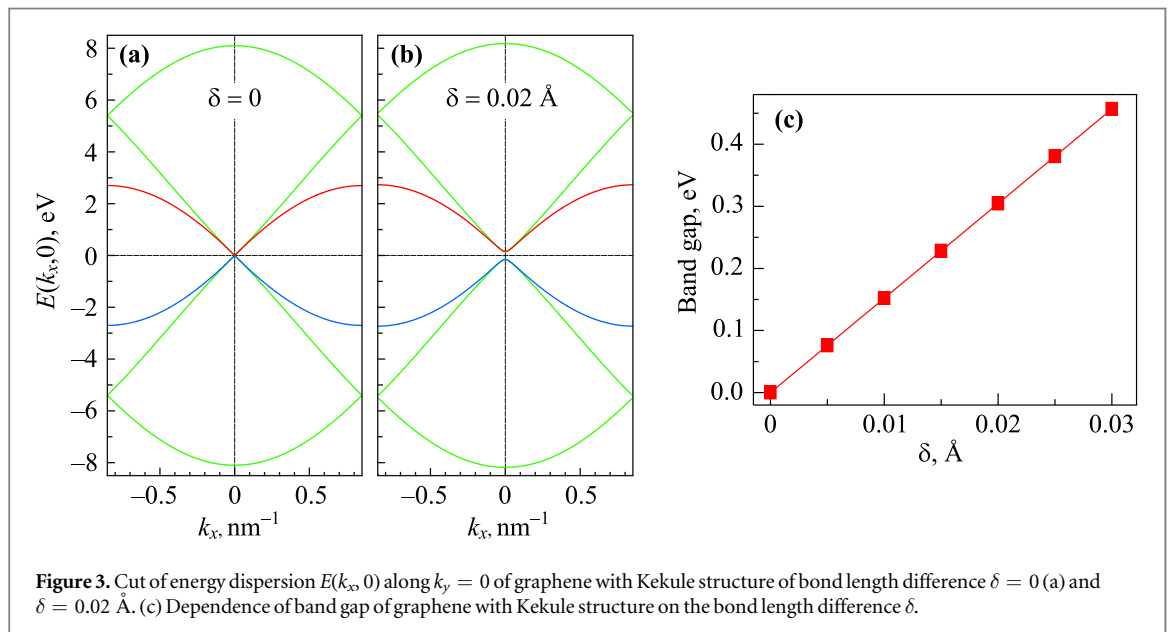
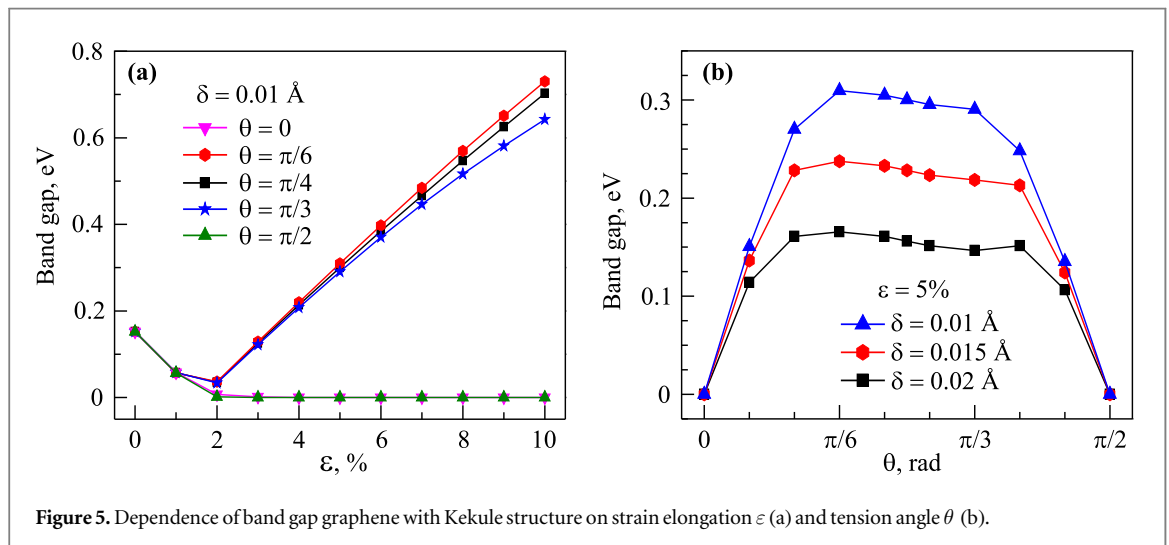
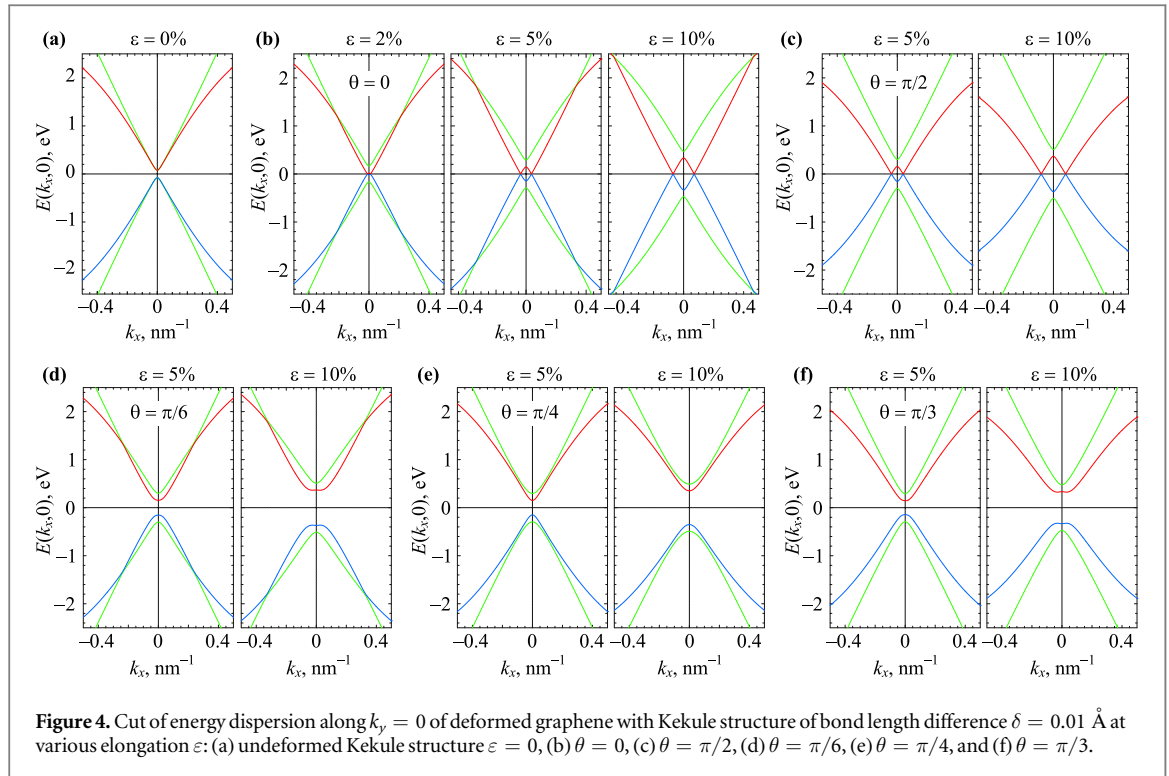


Figure 3. Cut of energy dispersion $E(k_x, 0)$ along $k_y = 0$ of graphene with Kekule structure of bond length difference $\delta = 0$ (a) and $\delta = 0.02 \text{ \AA}$. (c) Dependence of band gap of graphene with Kekule structure on the bond length difference δ .

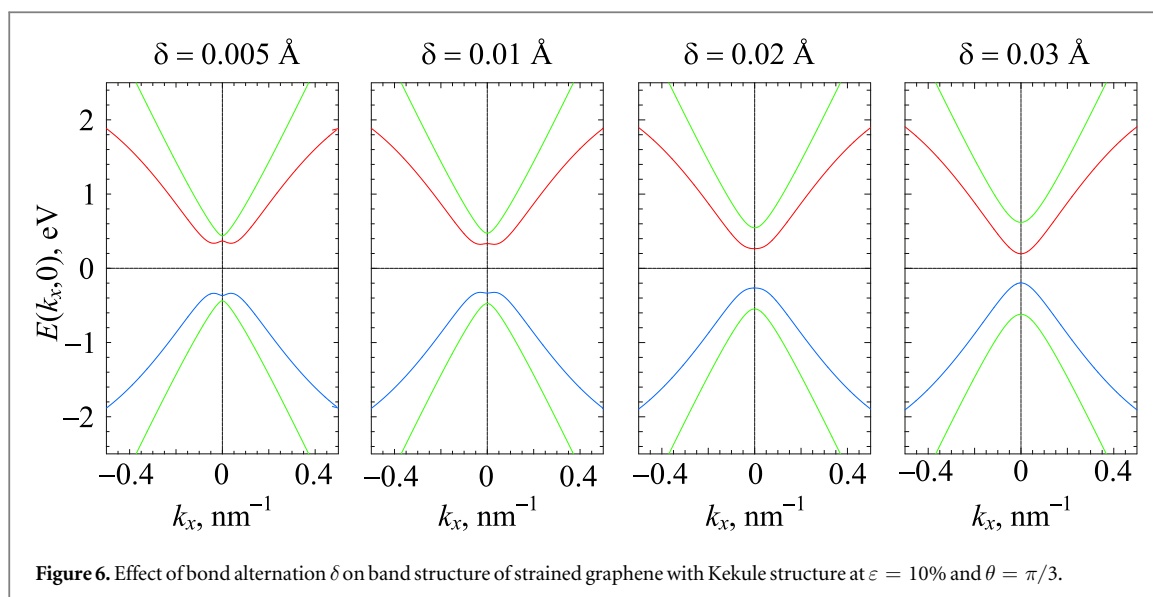
graphene with Kekule structure on the bond length difference δ is also in figure 3(c). Our calculations demonstrate that the band gap of graphene with Kekule structure depends linearly on the C–C bond length difference δ . Also, the lowest conduction band is always located at the center of the first Brillouin zone.

We next investigate the effect of the in-plane strain on the electronic properties of graphene with Kekule structure. Our calculations demonstrate that the electronic properties of graphene with Kekule structure is greatly altered by the in-plane strain, especially the lowest (highest) subband of the conduction (valence) band. In this study, the overlap matrix is chosen by the unit matrix, therefore the conduction and valence bands are symmetric across the Fermi level $E_F = 0$. In figure 4 we show the energy dispersion of graphene with Kekule of $\delta = 0.01 \text{ \AA}$ under strain. The band gap of graphene with Kekule of $\delta = 0.01 \text{ \AA}$ at $\epsilon = 0$ (unstrained) is 0.152 eV as shown in figure 4(a). When strain is applied along the x -axis ($\theta = 0$) or the y -axis ($\theta = \pi/2$), the band gap rapidly dropped to zero (at around 2% of elongation). The conduction band minimum is no longer located at the first Brillouin zone center, the lowest subband of the conduction band changes its shape and forms two minimums locating near the center of the first Brillouin zone. In these cases, as shown in figures 4(b), (c) the conduction and valence bands intersect at the Fermi level. In other tension directions ($\theta \neq 0$; $\theta \neq \pi/2$), strained graphene with Kekule structure is a semiconductor with small band gap being opened near the Fermi level as shown in figures 4(d), (e), (f). Dependence of the band gap of graphene with Kekule structure on strain ϵ and tension angle θ is shown in figure 5. In figure 5(a), we show the calculations for the dependence of band gap on the ϵ at various θ in the case of the bond length difference $\delta = 0.01 \text{ \AA}$. In this case, we can see that the band gap decreases rapidly as the strain increases from 0 to 2%. Then, except for the applied strain along the x and y



axes as mentioned above, the strain causes the energy gap of graphene to increase linearly by strain. Our calculations also show that energy gap is greatest when graphene is strained along the applied tension direction $\theta = \pi/6$. However, as shown in figure 5(b), the difference in band gap in the cases of the applied strain direction θ from $\pi/6$ to $\pi/3$ is very small. In addition, under the same applied strain, the band gap is inversely proportional to the bond length difference δ .

In the case of undimerized graphene, an energy gap may appear in graphene due to strain engineering. However, previous calculations have shown that, in small strain limits, the shape of the subbands near the Fermi level is almost unchanged by the applied strain and the energy gap can only be opened at the K point [11, 47]. Focusing on the effect of bond alternation on band structure, as an example, in figure 6, we plot the band structure of graphene with Kekule structure under strain of 10% along tension direction $\theta = \pi/3$. We can see that the bond alternation in the hexagonal lattice of graphene not only affects the energy gap but also the shape of the lowest conduction and highest valence subbands. In the presence of the same strain, the two-peak shape that is symmetric across the vertical line passing through the center of the first Brillouin zone tends to occur in small δ cases. Further, the shape of these subbands depends also on the tension direction θ as shown in figure 4.



4. Conclusion

In conclusion, using the tight binding approximation, we considered the effect of the C–C bond alternation on electronic properties of graphene. When the Kekule structure was introduced, a small energy gap appears in graphene and one can manipulate it by strain. Energy gap depends not only on the difference in the C–C bond length δ but also on the applied strain, especially the direction of applied strain on the graphene. The appearance of the energy gap in graphene is important in the application of graphene to nanoelectronic devices.

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