A simple tight-binding model for typical graphyne structures

Zhe Liu¹, Guodong Yu¹, Haibo Yao¹, Lei Liu², Liwei Jiang¹ and Yisong Zheng¹,3

¹ National Laboratory of Superhard Materials, Department of Physics, Jilin University, Changchun 130012, People’s Republic of China
² Chinese Academy of Sciences, State Key Laboratory Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Changchun 130033, People’s Republic of China
E-mail: zys@jlu.edu.cn

New Journal of Physics 14 (2012) 113007 (10pp)
Received 29 July 2012
Published 7 November 2012
Online at http://www.njp.org/
doi:10.1088/1367-2630/14/11/113007

Abstract. A π-electronic tight-binding (TB) model with, at most, three independent parameters is found to well fit the density functional theory results about the dispersions of the conduction and valence bands of α-, β-, γ- and (6,6,12)-graphyne. By means of such a toy model, the electron–hole symmetry in these graphynes is demonstrated. An explicit expression of the dispersion relation of α-graphyne is obtained. The position of the Dirac point on a particular Γ–M line in the Brillouin zone of β-graphyne is analytically determined. The absence of Dirac cones in γ-graphyne is intuitively explained. Based on these interesting results, it is believed that this TB model provides a simple but effective theoretical approach for further study of the electronic and transport properties of these typical graphynes.

³ Author to whom any correspondence should be addressed.
1. Introduction

In addition to graphene, other truly two-dimensional carbon allotropes probably exist, such as the so-called graphyne [1, 2]. The lattice structures of graphynes can be understood to be built by periodically substituting some selected C(sp$^2$)–C(sp$^2$) bonds in the graphene honeycomb lattice with C(sp$^2$)–C(sp)–C(sp)–C(sp$^2$) linkages, each of which is realized by inserting two extra sp carbon atoms. Because such a substitution can be designated at different C(sp$^2$)–C(sp$^2$) bonds, graphynes possess multiple lattice types, some of which are schematized in figure 1. An important feature of graphynes is that they contain acetylene bonds, i.e. carbon triple bonds which connect sp atoms. An acetylene bond is made up of one $\sigma$-bond and two $\pi$-bonds. Thus, the structure of a C(sp$^2$)–C(sp)–C(sp)–C(sp$^2$) linkage is chemically denoted as C–C≡C–C [1, 2].

In recent years, although there have been some theoretical investigations devoted to the electronic and transport properties of graphynes, such carbon structures were always of secondary importance compared with other members of the carbon family, such as carbon nanotube and graphene. This is largely due to the fact that a bulk graphyne has not been experimentally synthesized yet. However, a recent theoretical study of the band structures of graphynes, as shown in figure 1, seems to have intrigued the carbon material research community [3, 4]. By means of an ab-initio calculation, it was found that, similar to the case of graphene, $\alpha$-, $\beta$- and (6,6,12)-graphynes also present Dirac-cone-like band structures around the Fermi level. Unlike $\alpha$, the Dirac points of $\beta$ and (6,6,12) do not appear at the K or K$'$ points in the Brillouin zone (BZ). According to these results, it is reasonably expected that these graphynes can be regarded as competitors of graphene. Meanwhile, this theoretical result will certainly stimulate technical development to fabricate bulk graphyne samples, though so far only nanoscaled graphyne structures are experimentally available [5–9].

It is well-known that a simple $\pi$-electronic TB model clearly shows the linear dispersive nature of low-energy graphene electrons and has been used extensively to analyze their transport behaviors. Unlike graphene, it is not easy to develop a TB model for graphynes, because the coexistence of the sp$^2$ and sp carbon atoms in graphynes makes atomic orbital hybridization more complicated. To date, the band structures and other electronic properties of graphyne systems have been studied mostly by means of the ab-initio calculation [1–4, 10–14]. Just as in the case of graphene, in order to treat the various electronic properties of graphynes, such as the transport and optical processes, a similar TB model is highly desirable.

In this paper, we study the possibility of establishing a TB model for graphyne structures as shown in figure 1. For the main result, a simple $\pi$-electronic TB model composed completely of the $p_z$ atomic orbit is developed, which works well to describe the conduction and valence
Figure 1. Lattice structures of four kinds of graphyne. (a) α-graphyne, (b) β-graphyne, (c) γ-graphyne and (d) (6,6,12)-graphyne. The dashed lines specify the unit cell of each structure. (e) The first BZ of α-, β- and γ-graphynes. (f) The first BZ of (6,6,12)-graphyne. The dispersions of the conduction and valence bands of these graphynes along the lines of Γ–M–K–Γ (or Γ–X′–M–X–Γ for (6,6,12)-graphyne) and Γ–Q′–Q–Γ are shown in figure 2.

band characteristics of these graphynes. In such a toy model, no more than three TB parameters are needed to calculate the band structures of these graphynes. However, the obtained results of the dispersion relations of the conduction and valence bands of the graphynes agree well with

New Journal of Physics 14 (2012) 113007 (http://www.njp.org/)
the results from the *ab-initio* calculation, in particular, the Dirac cones (if they occur) in the low-energy region. Therefore, this TB model may contribute a simple, clear and effective way of describing the electronic transport and optical properties of these graphyne structures.

2. The tight-binding (TB) model

We consider four types of graphynes whose lattice structures are shown in figure 1. As mentioned above, it was previously reported that three of them (except γ-graphyne) exhibit Dirac-cone-like band structures around the Fermi level. Now we attempt to develop a TB model to describe such electronic characteristics of these graphynes. In doing so, we perform the *ab-initio* density functional theory (DFT) calculation of the band structures of these graphynes by means of the VASP code. But our main concern is the atomic orbital components of the energy bands around the Fermi level. Our calculation indicates that the conduction and valence bands of typical graphynes, as shown in figure 1, are almost completely composed of the p_z orbit. Based on such a result, we can establish a π-electronic TB model for these graphynes, composed completely of the p_z atomic orbit, and regardless of other orbits.

At first, we suppose the atomic on-site energy in the TB model to be equal to zero, i.e. the Fermi energy of charge-neutral graphynes. Then, according to the different bond lengths in each structure, we need to evaluate the corresponding hopping energies. They are labeled in figure 1 where we find that, for α-graphyne, there are only two distinct hopping energies, but for β- and γ-graphyne, three hopping energies are needed. For (6,6,12)-graphyne, in principle, we need at least five hopping energies to depict the different π bonds distinguished by their surroundings, see figure 1(d). But if we adopt the relation \( t' = t'' = \sqrt{2}t_2 \), only three hopping parameters are independent. Below, we will see that these three parameters are sufficient to describe the band structure of (6,6,12)-graphyne, quantitatively. The reason that we adopt the relation \( t' = t'' = \sqrt{2}t_2 \) is that it can make the Hamiltonian of the reduced lattice Hermitian, as shown in section 3. If such a simple TB model holds true, we can find appropriate values for these TB parameters. Then the TB model can reproduce the DFT results about the band structures of these graphynes. A numerical comparison of the band structures calculated by the TB model with the DFT results is shown in figure 2. From this figure, we can see that, for all the four graphyne structures, the TB model, with appropriate hopping parameters, can fit the DFT results quantitatively. In other words, the simple TB model works well in giving the correct dispersion relations in the low-energy region (in the vicinity of the Fermi level) of the conduction and valence bands of these graphynes, no matter whether the electronic wavevector runs through the high symmetric lines or not. Moreover, the following band characteristics of these graphynes are noteworthy: the band structure of α-graphyne is similar to that of graphene. There are Dirac points at each K point, i.e. the corner of BZ. Dirac points also occur in the band structures of β and (6,6,12)-graphyne. But they occur on high symmetric lines instead of K points. The band of γ-graphyne has no Dirac points, leaving a band gap. Our TB model can quantitatively reproduce these band characteristics.

3. More results from the TB model

Now, the TB model developed above is applicable to depict the electronic properties of typical graphyne structures near the Fermi level. With such a simple model, we can further work out some important electronic characteristics of these graphynes.
Figure 2. Band structures on the lines of $\Gamma$–M–K–$\Gamma$ (or $\Gamma$–X’–M–X–$\Gamma$ for (6,6,12)-graphyne) and $\Gamma$–Q’–Q–$\Gamma$ of four kinds of graphyne. (a), (b) $\alpha$-graphyne. (c), (d) $\beta$-graphyne. (e), (f) $\gamma$-graphyne. (g), (h) (6,6,12)-graphyne. RTB represents the results calculated by TB model with renormalized hopping energies. The hopping energies are in units of eV.

New Journal of Physics 14 (2012) 113007 (http://www.njp.org/)
Figure 3. A C(sp$^2$)–C(sp)–C(sp)–C(sp$^2$) linkage generally appearing in graphynes. $t_2$, $t_3$, $t_a$, $t_b$, $t_c$ and $t_d$ denote the TB hopping energies at the corresponding bonds.

At first, as in the case of graphene, the carriers in these graphynes possess electron–hole symmetry. Namely, the dispersions of the conduction and valence bands are mirror symmetric with respect to the Fermi energy. Such a feature can be readily seen by noting that all the carbon atoms in these graphynes can be divided into two groups (the solid and hollow circles in figure 1). And in our TB model, the hopping energy, i.e. the atomic interaction, only exists between the carbon atoms belonging to distinct groups. Thus, the TB Hamiltonian has the following matrix form:

$$
H = \begin{bmatrix}
0 & V^\dagger \\
V & 0
\end{bmatrix},
$$

where $V$ describes the inter-group atomic interaction. Such a Hamiltonian implies that for a given electronic wavevector $\mathbf{k}$, $\pm E(\mathbf{k})$ are both the allowed eigen energies corresponding to the eigen states $\psi = [a(\mathbf{k}), \pm b(\mathbf{k})]^T$, with $a(\mathbf{k})$ and $\pm b(\mathbf{k})$ being the electronic probability amplitudes of the atoms belonging to the two distinct groups for the same electronic wavevector. Therefore, the conduction and valence bands are mirror symmetric with respect to the Fermi energy. From the band structures as shown in figure 2, we can see that such a symmetry holds true in the low-energy region. This implies that the next nearest neighbor interaction in the TB model is ignorable weak and that the TB model including only the nearest neighbor interaction is a good approximate approach.

Next we show that based on our TB model, it is possible to simplify the lattice structures of graphynes and obtain some analytical results by the renormalization method, which was introduced conceptually in [15]. We start such a derivation from the TB eigen equations which, taking a C(sp$^2$)–C(sp)–C(sp)–C(sp$^2$) linkage as shown in figure 3 as an example, are given by

$$
EC_1 - t_a C_a - t_b C_b - t_2 C_2 = 0, 
$$

$$
EC_2 - t_2 C_1 - t_3 C_3 = 0, 
$$

$$
EC_3 - t_3 C_2 - t_2 C_4 = 0, 
$$

$$
EC_4 - t_c C_c - t_d C_d - t_2 C_3 = 0.
$$

By eliminating $C_2$ and $C_3$ (the electronic probability amplitudes of these atoms) in the above equations, we get the following two equations:

$$
E \left(1 - \frac{t_2^2}{E^2 - t_3^2}\right) C_1 - t_a C_a - t_b C_b - \frac{t_2^2 t_3}{E^2 - t_3^2} C_4 = 0, 
$$

New Journal of Physics 14 (2012) 113007 (http://www.njp.org/)
Figure 4. The reduced lattices of four types of graphyne with the renormalized TB hopping parameters. (a) $\alpha$-graphyne, (b) $\beta$- and $\gamma$-graphyne, and (c) (6,6,12)-graphyne. The numbered atoms are mentioned in the text around equations (12) and (13).

\[ E \left( 1 - \frac{t_2^2}{E^2 - t_3^2} \right) C_4 - t_c C_c - t_d C_d - \frac{t_2^2 t_3}{E^2 - t_3^2} C_1 = 0. \] (7)

By the same token, we can further eliminate all the sp atoms in the acetylene bonds. After such a processing and considering the low-energy limit condition $E \ll \min\{t_1, t_2, t_3\}$, the four graphyne lattices, under our consideration, evolve into reduced lattices with renormalized TB hopping parameters, see figure 4. In detail, the reduced lattice of $\alpha$-graphyne is equivalent to that of graphene with a renormalized and uniform hopping parameter $\tau = -t_2^2 t_3/(3t_2^2 + t_3^2)$ (figure 4(a)). For $\beta$-graphyne, as shown in figure 4(b), there are two distinct renormalized hopping parameters: $\tau_1 = -\frac{t_2^2 t_3}{2t_2^2 + t_3^2}$ and $\tau_2 = \frac{t_1 t_2^2}{2t_2^2 + t_3^2}$. The reduced lattice of $\gamma$-graphyne is equivalent to that of $\beta$-graphyne, but the two renormalized hopping parameters take different values: $\tau_1 = t_1 t_2^2/(t_2^2 + t_3^2)$ and $\tau_2 = -\frac{t_2^2 t_3}{t_2^2 + t_3^2}$.

As a result, we can immediately write out the explicit dispersion relation of $\alpha$-graphyne by just following the TB result for graphene. That is

\[ E(k) = \pm \tau \sqrt{1 + 4 \cos^2 \frac{1}{2} k_x a + 4 \cos \frac{1}{2} k_x a \cos \frac{\sqrt{3}}{2} k_y a}. \] (8)

We infer from such a result that the low-energy electrons in $\alpha$-graphyne can be described by the massless 2D Dirac equation with a renormalized Fermi velocity. The Fermi velocity of graphene is given by $v_F = \sqrt{3} a_0/2$, where $t \simeq 2.80$ eV is the hopping energy and $a_0 \simeq 2.46$ Å is the lattice constant of graphene [16]. For $\alpha$-graphyne, which has a reduced lattice equivalent to that of graphene, its Fermi velocity is also proportional to the renormalized hopping energy and lattice constant of this graphyne. From the values $\tau \simeq 0.76$ eV and $a \simeq 6.97$ Å, we can estimate that the electronic Fermi velocity in $\alpha$-graphyne ($\simeq 6.97 \times 10^5$ m s$^{-1}$) is slightly smaller than that of graphene ($\simeq 9.06 \times 10^5$ m s$^{-1}$). The situation for $\beta$- and $\gamma$-graphyne is more complicated because their reduced lattices are not equivalent to that of graphene. Instead there are six ‘atoms’ in the unit cell of their reduced lattices, see figure 4(b). However, by a simple derivation, we
find that the squared eigen energy of the two kinds of graphyne is determined by an equation 
\[ \det[E^2 - U^\dagger U] = 0 \]
with the matrix \( U \) given by
\[
U = \begin{bmatrix}
\tau_1 & \tau_2 e^{i\theta_1} & \tau_1 \\
\tau_1 & \tau_2 e^{i\theta_1} & \tau_1 \\
\tau_2 e^{-i\theta_1} & \tau_1 & \tau_1 
\end{bmatrix},
\]
where the phase factors are \( \theta_1 = -k_x a/2 + \sqrt{3}k_y a/2, \theta_2 = k_x a/2 + \sqrt{3}k_y a/2 \) and \( \theta_3 = k_x a \).

In principle, we are able to obtain an explicit expression of the dispersion relations of \( \beta \)- and \( \gamma \)-graphyne by solving the equation \( \det[E^2 - U^\dagger U] = 0 \). But we do not write out such a result since it looks too complicated and tedious. Instead we turn to treating an interesting issue, i.e. we try to determine, analytically, the position of the Dirac point which occurs on the high symmetric \( \Gamma \)–\( M \) line of \( \beta \)-graphyne. Noting that Dirac points appear at \( E = 0 \), we can readily find that their position in the BZ is determined by the condition \( \det U = 0 \), which is equivalent to
\[
2\tau_3^2 - \tau_2^2 \left( 2 e^{-i\beta} \cos \frac{\sqrt{3}}{2} k_y a + e^{i\beta} a \right) + \tau_2^3 = 0.
\]

By detailed analysis, we find that this equation can only be satisfied for \( \beta \)-graphyne and on the high symmetric \( \Gamma \)–\( M \) line in the BZ (see figure 1(e)). The position of the Dirac point is then explicitly determined by
\[
k_y = \frac{2}{\sqrt{3}a} \left[ \pi - \arccos \left( \frac{2\tau_1^3 - \tau_1^2 \tau_2 + \tau_2^3}{2\tau_1^2 \tau_2} \right) \right].
\]
Substituting the renormalized hopping energies, the argument of the arccos function can be obtained. It equals 0.653 and 1.277 for \( \beta \)- and \( \gamma \)-graphyne, respectively. So, for \( \beta \)-graphyne, the position of the Dirac point is given by \( k_y = 0 \) and \( k_y = 2.636 \) (in units of \( 1/a \)). This result coincides with both the DFT and TB calculations. For \( \gamma \)-graphyne, its renormalized hopping parameters give the result \( |(2\tau_3^2 - \tau_2^2 \tau_2 + \tau_2^2)/\tau_2^2 \tau_2| = 1.277 > 1 \). This indicates that there is no Dirac point for this graphyne. For (6,6,12)-graphyne, it is too complicated to work out the analytical results of the band structure. Moreover, in order to make the Hamiltonian of the reduced lattice Hermitian, we have to add some conditions to the hopping parameters. For example, the TB eigen equations on atoms 1 and 2 (labeled in figure 4(c)) after the renormalization process are
\[
EC_1 + \frac{t_1^2 t_3}{2t_2^2 + t_3^2} C_2 + \frac{t_2^2 t_3}{2t_2^2 + t_3^2} C_3 - \frac{t_1 t_3^2}{2t_2^2 + t_3^2} C_4 = 0,
\]
\[
EC_2 + \frac{t_1^2 t_3}{t_2^2 + t_3^2} C_1 - \frac{t_1 t_3^2}{t_2^2 + t_3^2} C_5 - \frac{t_1 t_3^2}{t_2^2 + t_3^2} C_6 = 0.
\]
We can see that only when \( t''^2 = 2t_3^2 \) (i.e. \( t' = \sqrt{2}t_2 \)) will the Hamiltonian be Hermitian. By the same token, from the TB equations for atoms 2 and 6, we can work out another condition \( t'' = t' \). Thus, there are only three independent hopping parameters for (6,6,12)-graphyne and we have three distinct renormalized hopping energies: \( \tau_1 = t_1 t_3^2/(2t_2^2 + t_3^2), \tau_2 = -\sqrt{2}t_2^2 t_3/(2t_2^2 + t_3^2) \) and \( \tau_3 = -2t_1^2 t_2^2/(2t_2^2 + t_3^2) \) which are labeled in figure 4(c). The dispersion relations for the four kinds of graphynes calculated by the TB model, using reduced lattices and renormalized hopping energies (abbreviated to RTB), are also given in figure 2. These results agree well with both the DFT and TB calculations in the low-energy region.
Table 1. Original and renormalized hopping energies of the TB models for graphynes (in units of eV).

|        | $t_1$ | $t_2$ | $t_3$ | $\tau_1$ | $\tau_2$ | $\tau_3$ |
|--------|-------|-------|-------|----------|----------|----------|
| $\alpha$-graphyne | – | –2.85 | –7.50 | 0.76 | – | – |
| $\beta$-graphyne | –2.00 | –2.70 | –4.30 | 0.95 | –1.12 | – |
| $\gamma$-graphyne | –2.75 | –3.11 | –4.04 | –1.73 | 1.50 | – |
| (6,6,12)-graphyne | –2.50 | –2.95 | –6.25 | –1.87 | 1.36 | 1.93 |

4. Summary

Although graphynes have both sp and sp$^2$ carbon atoms, which lead to more complicated orbital hybridization than the case of graphene, we find a simple $\pi$-electronic TB model with, at most, three independent hopping parameters which is available for four typical graphynes, i.e. $\alpha$-, $\beta$-, $\gamma$- and (6,6,12)-graphyne. When these TB hopping parameters are evaluated appropriately, such a toy model can describe, quantitatively, the band structures near the Fermi level of these graphynes. To conclude, we summarize these TB parameters in table 1. Incidentally, although our TB model with the hopping parameters listed in table 1 works well in describing the band structures of graphynes, we cannot guarantee that these parameter values are the best ones for the TB model of these graphynes. The possibility of further refining these parameters may exist for obtaining a more satisfactory coincidence between the TB and DFT results. Recently, graphynes have been viewed as competitors of graphene for electronic applications, since some carbon structures display Dirac-cone-like band structures, similar to that of graphene. In contrast to the status of graphene study, the investigation of the electronic properties of graphynes is in its infancy. Many subjects, for example, magneto-transport, optical processes, quantum confinement and nanostructures, have, so far, been hardly involved. Our TB model provides a simple but effective theoretical approach which can perform a detailed study of these aspects of graphynes.

Acknowledgments

This work was supported by the National Nature Science Foundation of China (grant nos. NNSFC11074091 and NNSFC91121011), the Natural Science Foundation of Jilin Province of China (grant no. 20101511), and Graduate Innovation Fund of Jilin University (project 20121037). At last we thank the High Performance Computing Centre (HPCC) of Jilin University for calculation resource.

References

[1] Baughman R H, Eckhardt H and Kertesz M 1987 J. Chem. Phys. 87 6687
[2] Narita N, Nagai S, Suzuki S and Nakao K 1998 Phys. Rev. B 58 11009
[3] Malko D, Neiss C, Vienes F and Gorling A 2012 Phys. Rev. Lett. 108 086804
[4] Srinivasu K and Ghosh S K 2012 J. Phys. Chem. C 116 5951
[5] Bunz U H F, Rubin Y and Tobe Y 1998 Chem. Soc. Rev. 28 107
[6] Diederich F 1994 Nature 369 199

New Journal of Physics 14 (2012) 113007 (http://www.njp.org/)
[7] Marsden J A, Palmer G J and Haley M M 2003 Eur. J. Org. Chem. 2003 2355
[8] Kehoe J M, Kiley J H, English J J, Johnson C A, Petersen R C and Haley M M 2006 Org. Lett. 8 2933
[9] Li G, Li Y, Liu H, Guo Y, Li Y and Zhu D 2010 Chem. Commun. 46 3256
[10] Narita N, Nagai S, Suzuki S and Nakao K 2000 Phys. Rev. B 62 11146
[11] Luo G et al 2011 Phys. Rev. B 84 075439
[12] Coluci V R, Braga S F, Legoas S B, Galvão D S and Baughman R H 2003 Phys. Rev. B 68 035430
[13] Pan L D, Zhang L Z, Song B Q, Du S X and Gao H-J 2011 Appl. Phys. Lett. 98 173102
[14] Zhou J, Lv K, Wang Q, Chen X S, Sun Q and Jena P 2011 J. Chem. Phys. 134 174701
[15] Kim B G and Hyoung J C 2012 Phys. Rev. B 86 115435
[16] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 Rev. Mod. Phys. 81 109