Six-fold symmetry origin of Dirac cone formation in two-dimensional materials

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Abstract
Dirac materials possess many excellent electrical properties, resulting that the search and design of Dirac materials have become a hot research area. Revealing the formation conditions of Dirac cone (DC) can provide theoretical guidance for the search and design of Dirac materials. To obtain the necessary conditions for the formation of DC of two-dimensional (2D) materials with six-fold symmetry (SFS), the DC formation mechanism was analyzed by the ‘divide-and-couple’ approach in the framework of tight-binding theory, confirmed by the subsequent density functional theory calculations. The simple ‘$6n + 2$’ rule was proposed to determine whether the 2D materials with SFS have DCs, i.e. when the number of atoms in a unit cell is $6n + 2$, the systems would possess DCs at the vertex of Brillouin zone for the 2D materials composed of the elements of the IV main group. Moreover, the ‘$3n + 1$’ rule was derived as the condition for the DC formation in graphene-like silagraphene with SFS and used to design a siligraphene $\text{Si}_6\text{C}_8$ with DCs. Understanding the DC formation mechanism of 2D materials with SFS not only provides theoretical guidance for designing novel Dirac materials but also sheds light on the symmetry origin of the formation mechanism of DC.

1. Introduction
Graphene was predicted to own Dirac cone (DC) band structure dated well back to 1947 [1, 2]. However, the DC materials did not become a hot research area until graphene was experimentally synthesized in 2004 [3]. DC can impose materials many excellent properties [4] including very high carrier mobility [5]. Graphene opened the door to study two-dimensional (2D) materials, some of which possess DC band structure including silicene [6, 7], various graphynes [8–14], siligraphenes [15–17], materials containing non-fourth major group elements [18–20], organic materials containing metal atoms [21, 22], and some modified 2D systems [23, 24].

However, the 2D materials with DCs are still rare and become the searching targets for potential applications. The mechanism discussions on the DC formation claim the following requirements: (a) specific symmetry; (b) appropriate tight-binding (TB) parameters; (c) there are few bands other than DC at Fermi level [25].

Understanding the formation mechanisms of DC band structures is of great significance to design Dirac materials. Some researchers [9, 10, 26, 27] use the real space renormalization group (RSRG) [28] scheme to explain the formation mechanisms of the DC band structures of 2D materials. In the RSRG scheme, the atomic cluster between two vertex atoms is reduced into an effective hopping term between the two atoms, thus the complex system can be approximated by a simpler system whose origin of the DC is readily explained. For a detailed introduction to the RSRG scheme, see a recent review article [29].

We have previously explored the formation origin of the DC band structures of some 2D systems using ‘divide-and-couple’ scheme in the framework of TB, in which, according to the characteristics of the system,
atomic wave functions are divided into predefined groups, and then the couplings between atomic wave functions are carried out step by step conceptually. The formation origin of DCs can be revealed by the formation process of the band structure [16, 17, 30, 31]. And through the analysis of the process, we can derive the conditions that the TB parameters (hopping parameters and onsite energy parameters) should be satisfied. For example, in the study about t1-SiC, by using ‘divide-and-couple’ scheme, the conditions that the TB parameters should be satisfied to make the materials have DC are easily derived [16]. The clear physical pictures of the ‘divide-and-couple’ scheme can provide insights for the design of DC materials.

Because the 2D materials with DCs always possess certain symmetry [25], one can use the ‘divide-and-couple’ scheme to explain the formation origin of the DCs of 2D materials by classification according to the symmetry of materials. Graphene holds six-fold symmetry (SFS) as the first experimental Dirac material, however, not all 2D materials with SFS have DCs. To find the conditions of DC formation of 2D materials with SFS, in this work, we used the ‘divide-and-couple’ scheme combining with TB to explain how SFS led to the formation of DC. A simple general ‘$6n + 2$’ rule was proposed to judge whether the 2D material with SFS has DCs. Moreover, according to the ‘$6n + 2$’ rule, a ‘$3n + 1$’ rule was derived as the condition for the DC formation in graphene-like silagraphene with SFS and used to design a siligraphene $\text{Si}_6\text{C}_8$ with DCs that has only SFS but no mirror symmetry.

2. Results and discussion

2.1. ‘$6n + 2$’ rule

2.1.1. Restricted conditions

To reduce the complexity, this work only considered the 2D materials containing the elements of the IV main group. All atoms of the system are located in the same plane, and the bands near the Fermi level are formed by the $p_z$ orbitals of the atoms without the participation of other orbitals. So, if there is no special explanation, the wave functions mentioned in this work refers to the $p_z$ orbital wave functions.

Because there are four electrons in the outermost shell of the IV main group elements, they can occupy half of the s orbital and the p orbitals (four orbitals in total). The onsite energies corresponding to these four orbitals are very close, so the Fermi level is usually near the onsite energies after couplings. The $p_z$ orbitals are not coupled with the other three orbitals, so half of the bands formed by $p_z$ orbitals are usually above Fermi level and half below Fermi level. So, if the $p_z$ orbitals are to form DC, there should be even numbers of $p_z$ bands. Therefore, this work only discussed the case with even numbers of $p_z$ orbitals (in the case of odd numbers of $p_z$ orbitals, DC would not form at Fermi level usually), and it is assumed that the number of $p_z$ bands above is equal to that below Fermi level.

2.1.2. Wigner–Seitz cell and the possible positions of atoms

The angle between the two lattice vectors of a 2D system with SFS is $120^\circ$ and its Wigner–Seitz cell is a regular hexagon (figure 1(a)). The Brillouin zone of the reciprocal space is also a regular hexagon.
The atoms of the system can be located at different positions in the Wigner–Seitz cell, such as the center, the vertexes, the interior (except for the center), and the edge of the regular hexagon (figure 1(a)). We will discuss these various situations.

2.1.3. Origin of DC by 'divide-and-couple' approach

Next, we adopt the 'divide-and-couple' approach to analyze the origin of DC. This approach includes the following steps generally: (1) for each type of position, the atom wave functions are combined into the eigenfunctions of the symmetry operator which change the K point into either the K point itself or an integer period of difference when the DC at K point in Brillouin zone is discussed. The symmetry operator is the operation of counter-clockwise rotation of $2\pi/3$, i.e. $C_3^1$. (2) The corresponding Bloch function is constructed for each combined function. (3) These Bloch functions are grouped according to the eigenvalues of $C_3^1$ at the K point. (4) The intragroup couplings are considered first, and then the intergroup couplings are considered. The formation origin of DCs can be revealed by the formation process of the band structure.

For the case that there is an atom in the center of the Wigner–Seitz cell, the coordination number of the atom is six due to the SFS of the system. However, this work only discussed the systems composed of the elements of the IV main group, whose coordination numbers generally cannot be six, so this situation is not in the scope of this work.

Now, it is considered that the atoms are located inside the Wigner–Seitz cell (except for the center). If there is an atom at B1, the SFS will produce another five atoms B2 – B6, as shown in figure 1(a). These six atoms are divided into two groups: B1, B3, B5 and B2, B4, B6, each of which possesses three-fold symmetry.

Within each group, the wave functions can be combined to form the eigenfunctions of $C_3^1$:

\[
\begin{align*}
|B_{\text{odd}} - \vec{l}_n\rangle &= \frac{1}{\sqrt{3}} \sum_{m=1,3,5} e^{-i m \frac{2\pi}{3}} |B_m\rangle_n, \quad (1) \\
|B_{\text{even}} - \vec{l}_n\rangle &= \frac{1}{\sqrt{3}} \sum_{m=2,4,6} e^{-i m \frac{2\pi}{3}} |B_m\rangle_n, \quad (2)
\end{align*}
\]

where $|B_m\rangle_n$ is the atomic wave function at the $m$th site of the $n$th Wigner–Seitz cell. The possible values of $l$ are 1, 2, or 3. $|B_{\text{odd}} - \vec{l}_n\rangle$ and $|B_{\text{even}} - \vec{l}_n\rangle$ are all the eigenfunctions of $C_3^1$:

\[
C_3^1 |B_{\text{odd}} - \vec{l}_n\rangle = e^{i l \frac{2\pi}{3}} |B_{\text{odd}} - \vec{l}_n\rangle, \quad (3)
\]

\[
C_3^1 |B_{\text{even}} - \vec{l}_n\rangle = e^{i l \frac{2\pi}{3}} |B_{\text{even}} - \vec{l}_n\rangle. \quad (4)
\]

Then, the Bloch functions corresponding to $|B_{\text{odd}} - \vec{l}_n\rangle$ and $|B_{\text{even}} - \vec{l}_n\rangle$ are written as

\[
|B_{\text{odd}} - \vec{l}_k\rangle = \frac{1}{\sqrt{N}} \sum_n |B_{\text{odd}} - \vec{l}_n\rangle e^{i k \cdot R_n} \quad (5)
\]

\[
|B_{\text{even}} - \vec{l}_k\rangle = \frac{1}{\sqrt{N}} \sum_n |B_{\text{even}} - \vec{l}_n\rangle e^{i k \cdot R_n}, \quad (6)
\]

where $R_n$ is the vector of the center point of the corresponding Wigner–Seitz cell, and $N$ is the total number of cells in the system.

When the system is implemented with the operation of $C_3^1$, the Bloch function $|B_{\text{odd}} - \vec{l}_k\rangle$ becomes:

\[
C_3^1 |B_{\text{odd}} - \vec{l}_k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i (C_3^1)(k) \cdot R_n} C_3^1 |B_{\text{odd}} - \vec{l}_n\rangle \\
= \frac{1}{\sqrt{N}} \sum_n e^{i l \frac{2\pi}{3} (k \cdot R_n)} e^{i (C_3^1)(k) \cdot R_n}. \quad (7)
\]

So $|B_{\text{odd}} - \vec{l}_k\rangle$ is not the eigenfunction of $C_3^1$ at a general point of Brillouin zone, but at K point ($2\pi/3a$, $2\pi/\sqrt{3}a$), it is still the eigenfunctions of $C_3^1$:

\[
C_3^1 |B_{\text{odd}} - \vec{l}_k\rangle = e^{i l \frac{2\pi}{3}} |B_{\text{odd}} - \vec{l}_k\rangle. \quad (8)
\]

Similarly, at the K point,

\[
C_3^1 |B_{\text{even}} - \vec{l}_k\rangle = e^{i l \frac{2\pi}{3}} |B_{\text{even}} - \vec{l}_k\rangle. \quad (9)
\]
Because the possible values of \( l \) are 1, 2, or 3, the corresponding eigenvalues are \( e^{i2\pi l/3} \), \( e^{-i2\pi l/3} \), and 1. There would be no coupling between two Bloch functions at the \( K \) point if they possess different eigenvalues.

Next, the vertex atoms are considered. When an atom is located at a vertex of the regular hexagon, there will be an atom of the same type at each vertex due to the SFS of the system (figure 1(a), \( A_1-A_6 \)). Since a vertex is shared by three hexagons, each Wigner–Seitz cell contains two atoms. Here, let \( A_1 \) and \( A_2 \) belong to the system is formed by the couplings among the Bloch functions \( \phi_k \) at the vertex.

At the \( K \) point, these Bloch functions are all the eigenfunctions of \( \mathbf{H} \) with the same eigenvalue 1. The reason is that if the functions in \( G_1 \) are implemented with the united operations of \( \mathbf{H} \), the Bloch functions are all the eigenfunctions of \( \mathbf{H} \). The eigenfunctions with the eigenvalue 1 are of group 3 (\( G_3 \)), and they are \( |A_1\rangle_k, |A_2\rangle_k \), \( |B_{\text{odd}} - 1\rangle_k \), and \( |B_{\text{even}} - 1\rangle_k \).

At the \( K \) point, there is no coupling between \( |A_1\rangle_k \) and \( |A_2\rangle_k \) due to the different eigenvalues corresponding to the eigenfunctions of \( C_3^1 \).

Now, we only consider the case that there are two atoms at the vertex of the hexagon of the Wigner–Seitz cell and six atoms in the interior of the hexagon (eight atoms in total). The band structure of the system is formed by the couplings among the Bloch functions \( |A_1\rangle_k, |A_2\rangle_k, |B_{\text{odd}} - 1\rangle_k, \) and \( |B_{\text{even}} - 1\rangle_k \). At \( K \) point, these Bloch functions are all the eigenfunctions of \( C_3^1 \), and they can be divided into three groups according to the eigenvalues. The eigenfunctions with the eigenvalue \( e^{i2\pi l/3} \) are of group 1 (\( G_1 \)), and they are

\[
|A_1\rangle_k, |B_{\text{odd}} - 1\rangle_k, |B_{\text{even}} - 1\rangle_k.
\]

The eigenfunctions with the eigenvalue \( e^{-i2\pi l/3} \) are of group 2 (\( G_2 \)), and they are

\[
|A_2\rangle_k, |B_{\text{odd}} - 2\rangle_k, |B_{\text{even}} - 2\rangle_k.
\]

The eigenfunctions with the eigenvalue 1 are of group 3 (\( G_3 \)), and they are

\[
|B_{\text{odd}} - 3\rangle_k, |B_{\text{even}} - 3\rangle_k.
\]

Through the above grouping, we can get the following conclusions: (1) At \( K \) point, there are no intergroup couplings due to the different eigenvalues of \( C_3^1 \). (2) The intragroup couplings of \( G_1 \) and \( G_2 \) are exactly same. The reason is that if the functions in \( G_1 \) are implemented with the united operations of counter-clockwise rotation of \( \pi \), i.e. \( C_3^1 \), and time reversal \( T \), they can be transformed into the corresponding functions in \( G_2 \), i.e.

\[
TC_3^1|A_1\rangle_k = |A_2\rangle_k \quad (18)
\]

\[
TC_3^1|B_{\text{odd}} - 1\rangle_k = -|B_{\text{even}} - 2\rangle_k \quad (19)
\]
Figure 2. Schematic diagram of band structure by TB. (a) None of the couplings are considered, and the onsite energy of A atoms forms two degenerate bands (green line), the onsite energy of B atoms forms six degenerate bands (orange line). Among these bands, G1 and G2 each contain two orange bands and one green band, and G3 contains two orange bands. (b) Only intragroup couplings but not intergroup couplings are considered. Because the intragroup couplings of G1 and G2 are exactly same, the bands of G1 and G2 are completely coincident shown by three blue lines which represent six bands. G3 contains two red bands. (c) Both intragroup and intergroup couplings are considered, and DC is formed at $K$ point.

| G1 | G2 | G3 |
|----|----|----|
| $\langle A_1|\hat{H}|B_{\text{even}} - 1\rangle_k = 0$ | $\langle A_2|\hat{H}|B_{\text{even}} - 2\rangle_k = 0$ | $\langle B_{\text{odd}} - 3|\hat{H}|B_{\text{even}} - 3\rangle_k = -2t_B$ |
| $\langle A_1|\hat{H}|B_{\text{even}} - 1\rangle_k = \frac{1}{\sqrt{3}} e^{-ikA_1}$ | $\langle A_2|\hat{H}|B_{\text{odd}} - 2\rangle_k = \frac{1}{\sqrt{3}} e^{ikA_1}$ | |
| $(e^{-ikA_1} e^{-i\frac{3}{2}\pi} + e^{ikA_1} e^{i\frac{3}{2}\pi} + 1)$ | $(e^{ikA_1} e^{-i\frac{3}{2}\pi} + e^{-ikA_1} e^{i\frac{3}{2}\pi} + 1)$ | |
| $\langle B_{\text{odd}} - 1|\hat{H}|B_{\text{even}} - 1\rangle_k = t_B$ | $\langle B_{\text{odd}} - 2|\hat{H}|B_{\text{even}} - 2\rangle_k = t_B$ | |

$T C^3_{\pi} |B_{\text{even}} - 1\rangle_k = |B_{\text{odd}} - 2\rangle_{k'}$. (20)

So, SFS and time-reversal symmetry guarantee that the intragroup couplings of G1 and G2 are exactly same. Please refer to appendix A for a detailed demonstration.

To explain the formation process of the band structure clearly, we set the TB parameters, then implemented TB calculations only considering the nearest-neighbor hopping to obtain the various intermediate band diagrams through step-by-step couplings as follows. During TB parameter setting, the hopping energy between a vertex and the nearest B sites and the onsite energy difference are set to be $t = -1.12$ eV as the $V_{ppp}$ value in silicon crystal [32], the hopping energy between a vertex and the nearest B sites and the onsite energy difference are set to be $t = -1.64$ eV and $\Delta E_{AB} = -2.63$ eV as the values in the 2D materials h-SiC [16], respectively.

First, when none of the couplings are considered, the bands were located at the onsite energies of A atoms and B atoms. As shown in figure 2(a), the orange lines are six bands from the onsite energies of B atoms, and green lines are two bands from the onsite energies of A atoms, where, G1 contains two orange lines and one green line, G2 also contains two orange lines and one green line, and G3 contains only two orange lines.

Second, the intragroup couplings of G1 and G2 are shown in figure 2(b). Two orange bands and one green band of G1 in figure 2(a) form three blue bands in figure 2(b), one of which is located near the Fermi level, and the other two are separated on both sides of the Fermi level. Since the intragroup couplings of G1 and G2 are the same exactly, the bands from G2 are also three blue lines completely coincident with the lines of G1. Two orange bands of G2 in figure 2(a) form two red bands in figure 2(b), which are separated on both sides of Fermi level. The coupling parameters of each group are shown in table 1. The coupling parameters in G1 and G2 are same by complex conjugate transformation except for a constant phase factor, so the bands by the intragroup couplings of G1 and G2 are the same exactly.
Third, the intergroup couplings are considered among G₁, G₂, and G₃. There is a band gap between the middle band in G₁ and the middle band in G₂ (these two bands are conduction band (CB) and valence band (VB), respectively). However, at K point, because there are no intergroup couplings among G₁, G₂, and G₃, CB and VB are still in contact, then a DC is formed at Fermi level, as shown in figure 2(c).

The above step-by-step coupling analysis is similar to the analysis in our previous work [17].

From the formation process of band structure above, the addition of six atoms to the interior of the Wigner–Seitz cell results in two more bands in each group of G₁, G₂, and G₃. Thus, there are still odd bands in G₁ and G₂ groups, respectively, and the middle band (CB or VB) in each group of G₁ and G₂ is located near Fermi level after considering intragroup couplings. Further couplings lead to a band gap between CB and VB, but they keep in contact at the K point, thus forming a DC. If there are no atoms at the vertexes of the Wigner–Seitz cell, G₁ and G₂ would contain even bands that are separated on both sides of the Fermi level after considering intragroup couplings. Further couplings cannot lead to the formation of DC at the Fermi level. It can be seen that the key to the formation of DC is to make each of G₁ and G₂ contains odd bands.

Next, we discussed the case that there are atoms on the edge of the Wigner–Seitz cell that can be divided into two cases: (1) at the midpoint of the edge; (2) at the other positions. For the second case [the atoms are located at C₁₋₁₂ (figure 1(a))], the couplings are analogous to that of the atoms inside the Wigner–Seitz cell: the number of atoms is multiple of six, and every six atoms in the edge add two Bloch functions to each group of G₁, G₂, and G₃, so as not to affect the formation of DC. See appendix B for details.

Finally, for the case of atoms at the midpoint of the edge, this will lead to an increase of three atoms in the cell (the cell has six edges, each of which is shared by two cells), which results that the whole cell contains odd atoms due to the atoms in various possible positions discussed before being in the form of even numbers. Thus, a cell includes odd pₓ orbitals, and DC cannot be formed usually, so this case is not within the scope of this work.

2.1.4. Presentation and verification of ‘6n + 2’ rule

From the above analysis, it can be seen that the possible positions of atoms in the Wigner–Seitz cell are vertexes (A), interior except for the center (B), and the edges except for the midpoint (C) of the Wigner–Seitz cell. In a unit cell, A sites contain two atoms, and the numbers of atoms at B and C sites are all a multiple of 6. The condition that the system has a DC at K point is that each of G₁ and G₂ contains an odd number of Bloch functions, which requires that there must be atoms at A sites, but there is no requirement for the existence of atoms at B or C sites. Therefore, when the system has a DC at the K point, the total number N of atoms in a Wigner–Seitz cell is as follows:

\[ N = 6n + 2 \quad (n = 0, 1, 2, \ldots) \]  (21)

Equation (21) can be regarded as the criterion of whether the system with SFS has DC at the K point in the Brillouin zone, dubbed a ‘6n + 2’ rule. When the rule is satisfied, the system has a DC at the K point, and when the rule is not satisfied, the system has no DC at the K point. For example, graphene [2] (N = 2), α-graphyne [8, 30] (N = 8), β-graphyne [11] (N = 20), g-SiC₃ silagraphene [15, 17] (N = 8), and g-SiₓC silagraphene [15, 17] (N = 8) with DC at the K point all satisfy the ‘6n + 2’ rule. However, γ-graphyne [33] (N = 12) and β-graphyne [8] (N = 18) do not have DC at the K point because they do not satisfy the ‘6n + 2’ rule. Although β-graphyne has a DC in the GM path, it does not violate our conclusion on how SFS leads to DC at the K point, because the DC of β-graphyne originates from mirror symmetry [8, 31].

It should be noted that the premise of the ‘6n + 2’ rule as a criterion for the existence or absence of DC is that the bands near the Fermi level are completely formed by the pₓ orbitals without the participation of other orbitals. For example, we insert a carbon atom into each carbon chain of silagraphene [33] and the obtained system satisfies the ‘6n + 2’ rule. However, because there are some bands participated by non-pₓ orbitals near the Fermi level, the system has no clean DCs at the Fermi level. See appendix C for details.

2.1.5. Influence of TB parameters on DC band structure

When the ‘divide-and-couple’ approach is used to analyze the band structure of the system, it is based on the symmetry of the system, which limits the choices of TB parameters. The ‘divide-and-couple’ approach reflects the phenomenon that the different sets of TB parameters can give rise to different band structures. Of course, under the limitation of symmetry, the choice of different TB parameters can also have a slight impact on the band structure. For example, in the ‘divide-and-couple’ approach analysis above, increasing the difference of the onsite energies between B and A a large extent (larger than 5.37 eV) can make the value of the CB at Γ less than that at K so that the DC point deviates from the Fermi-level (see appendix D for details), but this does not affect the existence of DC. Since there are various materials satisfying the ‘6n + 2’ rule, we cannot give the specific range of TB parameters when DC does not deviate from the Fermi level.
However, for the fourth main group materials, when the ‘6n + 2’ rule is satisfied, there will be DC at the Fermi level under the normal case.

2.1.6. Influence of buckled geometry on DC band structure
When the system shows buckled geometry, the bands near the Fermi-level would be coupled with non-\( p_z \) orbitals. However, if the system maintains six-fold rotation symmetry, the wave functions in \( G_1 \) can still be translated to the wave functions in \( G_2 \) by the united operations of counter-clockwise rotation of \( \pi \), i.e. \( C_6^\pi \), and time reversal \( T \), so the intragroup couplings of \( G_1 \) and \( G_2 \) are exactly same, and the VB and CB still degenerate after the intragroup couplings; then the intragroup couplings would open a gap between VB and CB, but VB and CB are still in contact at the \( K \) point because there are no intergroup couplings among \( G_1 \), \( G_2 \), and \( G_3 \) due to the different eigenvalues of \( C_3^1 \), and the DC is formed. Furthermore, the buckled geometry may break six-fold rotation symmetry, however, if the system possesses three-fold rotation symmetry and inversion symmetry (e.g. silicene and germanene), the wave functions in \( G_1 \) can still be translated to the wave functions in \( G_2 \) by the united operations of inversion and time reversal \( T \), so the DC still can be formed.

2.1.7. Possibility of the bands at \( \Gamma \) point being degenerated at the Fermi level
So far we discussed the formation of DC at the \( K \) point in the Brillouin zone. As for the \( \Gamma \) point, we can conclude that there are usually no degenerated bands at the Fermi level by using a similar analysis. See appendix F for detailed analysis.

2.2. ‘3n + 1’ rule
As an example of the application of the ‘6n + 2’ rule, this work designed a silagraphene DC material with SFS and honeycomb structure. The materials can be obtained by replacing some C atoms with Si atoms in graphene. First, the lattice vectors of graphene are redefined, one of which is \( \mathbf{SFS} \) and honeycomb structure. The materials can be obtained by replacing some C atoms with Si atoms in graphene. Then according to the ‘6’ rule, the condition that the silicene with SFS and honeycomb structure possesses DCs is

\[
|l_1 \mathbf{a} + l_2 \mathbf{b}|^2 : N = |\mathbf{a}|^2 : 2
\]

i.e.

\[
N = 2(l_1^2 + l_2^2 - l_1 l_2).
\]

Then according to the ‘6n + 2’ rule, the condition that the silicene with SFS and honeycomb structure possesses DCs is

\[
l_1^2 + l_2^2 - l_1 l_2 = 3n + 1.
\]

According to equation (24), dubbed ‘3n + 1’ rule, the possible values of integer \( l_1 \) and \( l_2 \) are not arbitrary, so not all graphene-like silicene have DC at the \( K \) point. On the other hand, the possible values of integer \( n \) are not also arbitrary, which shows that the possible numbers of atoms of graphene-like silicene have DC at the \( K \) point cannot cover all the numbers of atoms satisfying the ‘6n + 2’ rule.

Next, we discussed possible DC materials by using the ‘3n + 1’ rule. When \( n = 0 \), then \( l_1 = 1, l_2 = 0 \) (or other equivalent solutions), and the corresponding material is graphene, which can be regarded as a special kind of silicene. When \( n = 1 \), then \( l_1 = 2, l_2 = 0 \) (or other equivalent solutions), and the corresponding material is g-SiC\(_3\) or g-Si\(_2\)C\(_3\), which was theoretically predicted to have DC [15, 17]. When \( n = 2 \), then \( l_1 = 1, l_2 = 3 \) (or other equivalent solutions), the Dirac silicene material Si\(_6\)C\(_8\) was designed in this work. When \( n = 3 \), equation (24) has no integer solutions; and when \( n = 4 \), equation (24) has integer solutions (such as \( l_1 = 4, l_2 = 1 \)). Therefore, the silicene with SFS and honeycomb structure does not have DC at the \( K \) point in the Brillouin zone if its atomic number \( N \) in a unit cell is in the open interval \( 14 < N < 26 \).

2.3. DFT calculations
For confirmation, we optimized the atomic structure of Si\(_6\)C\(_8\) by DFT (figure 3(a)) and calculated the band structures and density of states (figure 3(b)). It was confirmed that Si\(_6\)C\(_8\) does have DC at the \( K \) point. Si\(_6\)C\(_8\) has only SFS, but no mirror symmetry, which indicates that the formation of DC does originate from SFS. The stability of Si\(_6\)C\(_8\) is proved by its phonon spectrum without imaginary frequency. See appendix F for details.
Figure 3. (a) Atomic structure of Si₆C₈, in which the yellow ball represents Si atom, the gray ball represents C atom, and all the atoms are in the same plane. (b) Band structure (left) and density of states (right) of Si₆C₈.

3. Conclusions

In this work, by using the ‘divide-and-couple’ scheme [17], the condition of DC at the K point in Brillouin zone caused by the SFS of 2D materials formed by the IV main group elements is analyzed, that is, the total number of atoms in a unit cell should satisfy ‘6n + 2’ rule, with the conditions of the restriction that there are no atoms at the center and the midpoint of the edge of the Wigner–Seitz cell. This rule holds not only when the system presents a flat geometry, but also even if the system presents a buckle geometry as long as the system possesses six-fold rotation symmetry. Furthermore, when the buckle geometry breaks six-fold rotation symmetry, but as long as the system still has three-fold rotation symmetry and inversion symmetry, the ‘6n + 2’ rule still holds.

The ‘6n + 2’ can be used to explain the origins of DC formation in various graphyne and silagraphe materials, and can also guide the designs for new DC materials. According to this rule, we further derived the condition that the graphene-like silagraphe with SFS has a DC at the K point, ‘3n + 1’ rule, by which, the Dirac material Si₆C₈ is designed. This material has only SFS, but no mirror symmetry, which indicates that the formation of DC does originate from SFS.

Also, the focus of this study was limited to the fourth main group elements. If the electron filling of bands was carefully considered, the analytical method discussed in this work can be extended to analyze whether the 2D materials formed by non-fourth main group elements exhibit DCs.

4. Computation methods

In the DFT calculations, the Vienna ab initio simulation package (VASP) [34, 35] was used at the GGA-PBE [36] level, and the projector augmented-wave method [37] was adopted for the pseudopotentials. The energy cutoff for plane-wave basis expansion was 750 eV. The k-point sampling adopted an (11 × 11 × 1) Monkhorst–Pack mesh for most self-consistent field (SCF) iteration calculations. A 5.0 × 10⁻⁷ eV per atom energy tolerance was adopted in SCF iteration. In the geometry optimization with a conjugated gradient method, the distance between two adjacent atom layers was fixed to be 20 Å to avoid mirror image interaction at periodic boundary conditions, the other cell parameters and atom parameters were all relaxed, and the convergence criteria was that the remaining force on each atom is lower than 0.001 eV Å⁻¹.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Appendix A. Demonstration on why the intragroup couplings of $G_1$ and $G_2$ are exactly same

The system possesses SFS and time-reversal symmetry, resulting that the intragroup couplings of $G_1$ and $G_2$ are exactly same. The reason is that if the functions in $G_1$ are implemented with the united operations of counter-clockwise rotation of $\pi$, i.e. $C_6^n$, and time reversal $T$, they can be transformed into the corresponding functions in $G_2$, i.e.

\[
TC_6^1|A_1\rangle_k = TC_6^3 \left[ \frac{1}{\sqrt{N}} \sum_{n} |A_1\rangle_n e^{ik (R_n + A_1)} \right] \\
= T \left[ \frac{1}{\sqrt{N}} \sum_{n} |A_2\rangle_n e^{ik (-R_n - A_2)} \right] \\
= \frac{1}{\sqrt{N}} \sum_{n} (|A_2\rangle_n e^{ik (R_n + A_2)}) \\
= |A_2\rangle_k
\]

\[
TC_6^3|B_{\text{odd}} - 1\rangle_k = TC_6^3 \left[ \frac{1}{\sqrt{N}} \sum_{n} |B_{\text{odd}} - 1\rangle_n e^{ik R_n} \right] \\
= TC_6^3 \left[ \frac{1}{\sqrt{N}} \sum_{n} \left( \sum_{m=1,3,5} |B_m\rangle_n e^{-i(m-3) \frac{\pi}{3}} \right) e^{ik R_n} \right] \\
= T \left[ \frac{1}{\sqrt{N}} \sum_{n} \left( \sum_{m=2,4,6} |B_m\rangle_n e^{-i(m-3) \frac{\pi}{3}} \right) e^{ik (-R_n)} \right] \\
= -\frac{1}{\sqrt{N}} \sum_{n} \left( \sum_{m=2,4,6} |B_m\rangle_n e^{i(m-3) \frac{\pi}{3}} \right) e^{ik R_n} \\
= -\frac{1}{\sqrt{N}} \sum_{n} \left( \sum_{m=2,4,6} |B_m\rangle_n e^{i(m-2) \frac{\pi}{3}} \right) e^{ik R_n} \\
= -\frac{1}{\sqrt{N}} \sum_{n} |B_{\text{even}} - 2\rangle_n e^{ik R_n} \\
= -|B_{\text{even}} - 2\rangle_k. \quad (A.2)
\]

Similarly:

\[
TC_6^3|B_{\text{even}} - 1\rangle_k = TC_6^3 \left[ \frac{1}{\sqrt{N}} \sum_{n} (|B_{\text{even}} - 1\rangle_n e^{ik R_n}) \right] = |B_{\text{odd}} - 2\rangle_k. \quad (A.3)
\]

Appendix B. Influence of the edge atoms excluding the midpoint atoms of Wigner–Seitz cell on the formation of Dirac cone

Due to the SFS and translational symmetry, if there is one atom at $C_1$ on the edge (except for the midpoint), an additional 11 atoms will be generated at $C_2$–$C_{12}$, as shown in figure 1(a) in the manuscript. Among the 12 atoms, $C_7$–$C_{12}$ can be obtained by translating $C_1$–$C_6$ into integer lattice vectors, so each Wigner–Seitz cell contains six atoms. Here, let $C_1$–$C_6$ belong to the hexagon with the center point vector being 0. Similar to the treatment of atomic wave functions at the position $B_1$–$B_6$ in the manuscript, these
six atomic wave functions are combined into the eigenfunctions of the operator $C_1^l$ (which counter-clockwise rotates the wave function by $2\pi/3$):

\[ |C_{\text{odd}} - \ell_n^l \rangle = \sum_{m=1,3,5} e^{-il\psi} |C_{m}^l \rangle_n \quad (l = 1, 2, 3) \]  

(B.1)\n
\[ |C_{\text{even}} - \ell_n^l \rangle = \sum_{m=2,4,6} e^{-il\psi} |C_{m}^l \rangle_n \quad (l = 1, 2, 3) \]  

(B.2)\n
\[ C_3^l |C_{\text{odd}} - \ell_n^l \rangle = \sum_{m=1,3,5} e^{-il(m-2)\frac{2\pi}{3}} |C_{m}^l \rangle_n = e^{i\frac{2\pi}{3}} |C_{\text{odd}} - \ell_n^l \rangle \]  

(B.3)\n
\[ C_3^l |C_{\text{even}} - \ell_n^l \rangle = \sum_{m=2,4,6} e^{-il(m-2)\frac{2\pi}{3}} |C_{m}^l \rangle_n = e^{i\frac{2\pi}{3}} |C_{\text{even}} - \ell_n^l \rangle. \]  

(B.4)\n
The corresponding Bloch functions of $|C_{\text{odd}} - \ell_n^l \rangle$ and $|C_{\text{even}} - \ell_n^l \rangle$ are:

\[ |C_{\text{odd}} - \ell_k^l \rangle = \frac{1}{\sqrt{N}} \sum_n e^{ikR_n} |C_{\text{odd}} - \ell_n^l \rangle \]  

(B.5)\n
\[ |C_{\text{even}} - \ell_k^l \rangle = \frac{1}{\sqrt{N}} \sum_n e^{ikR_n} |C_{\text{even}} - \ell_n^l \rangle. \]  

(B.6)\n
At the $K$ point in the Brillouin zone,

\[ C_3^l |C_{\text{odd}} - \ell_k^l \rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik(C_3^l)^{-1}R_n} e^{i\frac{2\pi}{3}} |C_{\text{odd}} - \ell_n^l \rangle \]  

(B.7)\n
\[ = \frac{1}{\sqrt{N}} \sum_n e^{i\frac{2\pi}{3}R_n} e^{i\frac{2\pi}{3}} \sum_n e^{ikR_n} e^{i\frac{2\pi}{3}} |C_{\text{odd}} - \ell_n^l \rangle \]  

(B.8)\n
Similarly:

\[ C_3^l |C_{\text{even}} - \ell_k^l \rangle = e^{i\frac{2\pi}{3}} |C_{\text{even}} - \ell_k^l \rangle. \]
Similar to the case of the atoms at positions B₁–B₆,

\[ TC_{6}^{δ}(|C_{\text{odd}} - 1\rangle_{k}) = TC_{6}^{δ} \left[ \frac{1}{\sqrt{N}} \sum_{n} (C_{\text{odd}} - 1)_{n} e^{ikR_{n}} \right] \]

\[ = TC_{6}^{δ} \left[ \frac{1}{\sqrt{N}} \sum_{n} \left( \sum_{m=1,3,5} |C_{m}\rangle_{n} e^{-im\pi/6} R_{n} \right) \right] \]

\[ = T \left[ \frac{1}{\sqrt{N}} \sum_{n} \left( \sum_{m=2,4,6} |C_{m}\rangle_{n} e^{-i(m-3)\pi/6} \right) \right] \]

\[ = -\frac{1}{\sqrt{N}} \sum_{n} \left( \sum_{m=2,4,6} |C_{m}\rangle_{n} e^{im\pi/6} \right) e^{ikR_{n}} \]

\[ = -\frac{1}{\sqrt{N}} \sum_{n} \left( \sum_{m=2,4,6} |C_{m}\rangle_{n} e^{i(m-2)\pi/2} \right) e^{ikR_{n}} \]

\[ = -\frac{1}{\sqrt{N}} \sum_{n} (C_{\text{even}} - 2)_{n} e^{ikR_{n}} \]

\[ = -|C_{\text{even}} - 2\rangle_{k} \] \hspace{2cm} (B.9)

Similarly:

\[ TC_{6}^{δ}(|C_{\text{even}} - 1\rangle_{k}) = \frac{1}{\sqrt{N}} \sum_{n} TC_{6}^{δ}(e^{ikR_{n}}|C_{\text{even}} - 1\rangle_{n}) = |C_{\text{odd}} - 2\rangle_{k} \] \hspace{2cm} (B.10)

The six Bloch functions expressed in equations (B.5) and (B.6) can be divided into the G₁, G₂, and G₃ groups described in the manuscript according to their eigenvalues for C₁, then the number of Bloch functions contained in each group is increased by 2. So, the parity of the number of the Bloch functions contained in each group remains unchanged, thus the formation of the DC is not affected by the existence of the atoms on the edge (except for the midpoint) of the Wigner–Seitz cell.

Appendix C. Atomic structure and band structure of a derivative of δ-graphyne

We insert a C atom into each carbon chain of δ-graphyne [11] to obtain the derivative of δ-graphyne, whose atomic structure after geometric optimization by DFT calculations is shown in figure C1(a). The system contains six-membered carbon rings and carbon chains, and all the atoms of this system are in the same plane. Because each carbon chain contains three atoms, this system is dubbed as δ-graphyne-3 here. The atomic structure of δ-graphyne-3 possesses SFS, and the total number of atoms in a cell is 26 (= 6 × 4 + 2), which satisfies the ‘6n + 2’ rule proposed in the manuscript. However, there is no clean DC near the Fermi energy from the band structure of δ-graphyne-3 by DFT as shown in figure C1(b).

The reason is that there are some bands formed by non-pz orbitals near the Fermi energy (see the partial density of states of δ-graphyne-3 by DFT shown in the right side of figure C1(b)), which does not meet the premise of the ‘6n + 2’ rule. This situation is easy to judge by the atomic structure of the system: δ-graphyne-3 has three atoms in a chain, and because the carbon chain and the vertex atoms should be connected by a single bond, so it is impossible to form the single-triple bond alternating structure that the carbon chain should possess, resulting in the formation of non-bond energy levels, thus the bands from non-pz orbitals are formed near the Fermi energy. The relevant parameters of DFT calculations can be found in the manuscript.

Appendix D. Influence of TB parameters on DC band structure

As in the manuscript, when only the case that there are two atoms at the vertex and six atoms inside was considered, we further discuss the band structure. Here, we discuss the effect on the band structure when the hopping energies (t₁ = -1.12 eV, t₂ = -1.64 eV) remain unchanged and the difference between the onsite energies of B and A (∆E_BA) is increased. As ∆E_BA is increased, the CB at Γ Move down, i.e. when ∆E_BA = 5.37 eV the value of CB at Γ is equal to the value of DC point (as shown in figure D1(a)); when
\[ \Delta E_{BA} = 7.00 \text{ eV}, \] the value of CB at \( \Gamma \) is 0.262 eV lower than the value of DC point, which moves the DC point 0.127 eV upward from the Fermi level (as shown in figure D1(b)). Our previous articles have similar discussions [17].

**Appendix E. Analysis on whether there are degenerated bands at the Fermi level at the \( \Gamma \) point**

We discussed the formation of DC at the \( K \) point in the Brillouin zone in the manuscript. Here, we discuss the possibility that the bands degenerate at the Fermi level at the \( \Gamma \) point (figure 1(b)). According to the discussions in the manuscript, the Bloch functions corresponding to the atoms at positions B (and C) are grouped in a similar way to that in the case of point \( K \); each group of \( G_1, G_2, \) and \( G_3 \) is assigned two Bloch functions; While the Bloch functions corresponding to the two atoms at points A are the eigenfunctions of the operator \( C_3^1 \), and their eigenvalues are all 1 at the \( \Gamma \) point, so they should be assigned to \( G_3 \). Therefore,
no matter whether there are atoms at A points, each of G1 and G2 contains even numbers of Bloch functions, then there are usually no degenerated bands at the Fermi level at Γ point.

Appendix F. Phonon spectrum of Si6C8

To investigate the stability of Si6C8 designed in the manuscript, its phonon spectrum is calculated by PHONOPY using the finite displacement method [38]. A supercell of $2 \times 2 \times 1$ is built first, and the scf-cycle is run with VASP [34, 35] for the fore calculations. The k-point sampling for the supercell calculations adopts a $7 \times 7 \times 1$ Monkhorst–Pack mesh. Other calculation parameters can be found in the chapter ‘Computation methods’. The phonon spectrum of Si6C8 is shown in figure F1, and there is no virtual frequency found, proving its stability.

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