Atomic Arrangement and Its Effects on Electronic Structures of Graphene from Tight-Binding Description

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Published online on: 25 Apr 2016


Accessed on: 05 Oct 2020

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# 3 Atomic Arrangement and Its Effects on Electronic Structures of Graphene from Tight-Binding Description

_Sirichok Junghawan and Sukit Limpijumnong_

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## ABSTRACT

An exhaustive enumeration method to generate graphene–alloy configurations and the method to calculate or estimate the electronic structures of those configurations will be discussed. The electronic structures of pristine graphene can be qualitatively described by tight-binding method. Tight-binding model is a simple method to understand the contributions of each atomic state. The method is helpful to investigate how chemical bonding, atomic arrangement, and structural symmetry reflect to the electronic structure of a system. Structural stability of monolayer graphene with dopants or impurities is able to be systematically investigated by means of first-principles calculations. However, the method is more expensive than simple tight-binding approximation. Tight-binding method provides an insightful of how the interactions between the constituents influence on the characteristic of electronic structure, which is sensitive to the detailed arrangement of the constituents. Tight-binding calculations of several representative ordering patterns including ribbon, superlattice (SL) or stripe, and scattering arrangements are given to illustrate an idea of how to construct Hamiltonian matrix for such systems. These matrix elements are considered as parameters, which are fitted to reproduce certain properties from experimental data or first-principles calculations. The properties of nanoribbons and superlattices along armchair and zigzag direction have been discussed in the context of the tight-binding approximation, as they provide an informative trend of the electronic properties related to edge modification and inversion symmetry of structure.

## 3.1 TIGHT-BINDING METHOD

During the past decade, graphene (Castro Neto et al. 2009; Geim and Novoselov 2007; Novoselov et al. 2004, 2005), a single layer of graphite with a planar honeycomb structure as illustrated in Figure 3.1, has been extensively studied because of its astonishing properties that are mostly attributed to quantum phenomena from 2D confinement effects (Novoselov et al. 2004, 2005; Zhou et al. 2006). In a perfect graphene, each carbon atom forms $\sigma$-bonds with its three nearest neighbors ($sp^2$ hybridization). The electronic states near the Fermi energy are dominated by the $\pi$ and $\pi^*$ bands, which are derived from the weakly interacting $p_z$ orbitals. The most important characteristic of the electronic structure of graphene is the degenerate states $\pi$ and $\pi^*$ at the $K$ point of graphene (hexagonal) Brillouin zone (BZ) (inset of Figure 3.2), making graphene a zero-bandgap semi-metal (Reich et al. 2002; Wallace 1947).

The tight-binding method is an approximation assuming that the wave functions tightly bound to the atoms, so-called “tight-binding,” such that the atomic wave functions can be used as a basis for expanding the crystal wave functions. The method is helpful to investigate how chemical bonding, atomic arrangement, and structural symmetry reflect to the characteristic of electronic structure. This method is the simplest method for computationally calculating band structures. Since each carbon atom forms bonds with its three nearest neighbors, it is assumed that the wave functions of $s$, $p_x$, and $p_y$ orbitals are tightly bound to the atoms. The method has been widely used and proven to be efficient for studying this class of materials as summarized in Table 3.1. Generally, suppose
that we start with an atomic wave function, for example, \( p_z \) orbital, on a sublattice \( A \) (Figure 3.1), which is centered at coordinate \( \mathbf{R}_A \),

\[
\langle \mathbf{r} | \mathbf{R}_A \rangle = \phi(\mathbf{r} - \mathbf{R}_A). \tag{3.1}
\]

\( \phi(\mathbf{r} - \mathbf{R}_A) \) is an atomic wave function associated with this atom. It is assumed that this state interacts with an atomic wave function on a sublattice \( B \) (Figure 3.1), which is centered at site \( \mathbf{R}_B \),

\[
\langle \mathbf{r} | \mathbf{R}_B \rangle = \phi(\mathbf{r} - \mathbf{R}_B). \tag{3.2}
\]

These two orbitals dominantly attribute to \( \pi \) and \( \pi^* \) bands near the Fermi level. As long as we consider about the electronic structures near the Fermi level, we can form electronic states that can be used as the basis functions for the crystal wave functions assuming that there are no other orbitals, for example, \( s, p_x, \) and \( p_y \) orbitals can mix into the states near the Fermi level since the bands that correspond to the dispersion of bonding and antibonding molecular orbital are \( \pi \) and \( \pi^* \) bands. Given that there are two atoms in the unit cell at sublattices \( A \) and \( B \), we can construct two Bloch states as

\[
| \mathbf{k}_i \rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i \mathbf{k} \cdot \mathbf{R}} | \mathbf{R}_i + \mathbf{R} \rangle, \tag{3.3}
\]

where \( i = A, B \), with the summation running over all the \( N \) unit cells in the crystal (the vectors \( \mathbf{R} \)). It can be verified that these states obey Bloch’s theorem. Let \( \mathbf{R}' \) be another lattice vector,

\[
\langle \mathbf{r} + \mathbf{R} | \mathbf{k}_i \rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}'} e^{i \mathbf{k} \cdot \mathbf{R}'} \phi(\mathbf{r} + \mathbf{R} - \mathbf{R}' - \mathbf{R}). \tag{3.4}
\]

Then, this state at position \( \mathbf{r} + \mathbf{R} \) is given by

\[
\langle \mathbf{r} + \mathbf{R} | \mathbf{k}_i \rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}'} e^{i \mathbf{k} \cdot \mathbf{R}'} \phi((\mathbf{r} + \mathbf{R}) - \mathbf{R}_i - (\mathbf{R}' - \mathbf{R})). \tag{3.5}
\]

where \( \mathbf{R}' - \mathbf{R} \) is another lattice vector. This leads to

\[
\langle \mathbf{r} + \mathbf{R} | \mathbf{k}_i \rangle = e^{i \mathbf{k} \cdot \mathbf{R}} \langle \mathbf{r} | \mathbf{k}_i \rangle \tag{3.6}
\]

that satisfies Bloch’s theorem. The crystal eigenstates can be expanded in these two basis functions, \( | \mathbf{k}_A \rangle \) and \( | \mathbf{k}_B \rangle \). We can construct the approximate crystal eigenstates as

\[
| \mathbf{k} \rangle = \sum_i c_i | \mathbf{k}_i \rangle = c_A | \mathbf{k}_A \rangle + c_B | \mathbf{k}_B \rangle, \tag{3.7}
\]

where the expansion coefficients \( c_A \) and \( c_B \) are to be determined. The eigenstates \( | \mathbf{k} \rangle \) are normalized by \( |c_A|^2 + |c_B|^2 = 1 \). We want to find the eigenvalues \( \varepsilon(\mathbf{k}) \) that are exactly the number of bands that we can expect at each \( \mathbf{k} \)-point of a Hamiltonian operator \( \hat{H} \) such that

\[
\hat{H} | \mathbf{k} \rangle = \varepsilon(\mathbf{k}) | \mathbf{k} \rangle. \tag{3.8}
\]

Inserting the unit operator \( \hat{I} = \sum_j | \mathbf{k}_j \rangle \langle \mathbf{k}_j | = | \mathbf{k}_A \rangle \langle \mathbf{k}_A | + | \mathbf{k}_B \rangle \langle \mathbf{k}_B | \) in front of \( | \mathbf{k} \rangle \) on both sides of the equation and...
### TABLE 3.1
Example of Tight-Binding Method Used to Study Electronic Structures of Graphene and Its Derivatives

<table>
<thead>
<tr>
<th>System</th>
<th>Main Result</th>
<th>Journal</th>
<th>Author</th>
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<td>Graphene and graphite</td>
<td>Electronic structure</td>
<td><em>Phys. Rev.</em> 71, 622 (1947)</td>
<td>P. R. Wallace (Wallace 1947)</td>
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<tr>
<th>System</th>
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Atomic Arrangement and Its Effects on Electronic Structures of Graphene from Tight-Binding Description

multiplying by $\langle k_r |$ where $i = A, B$, we can write this equation in the form

$$\langle k_i | \hat{H} \left( \sum_j | k_j \rangle \langle k_j | \right) | k_r \rangle = \epsilon(k) \langle k_i | \left( \sum_j | k_j \rangle \langle k_j | \right) | k_r \rangle,$$

$$\sum_j \langle k_j | \hat{H} | k_j \rangle = \epsilon(k) \sum_j \langle k_i | \langle k_j | \rangle \langle k_j | \rangle | k_j \rangle = \epsilon(k) \sum_j \langle k_i | \langle k_j | \rangle \langle k_j | \rangle | k_j \rangle = 0,$$

$$\sum_j \left[ H_{ij} - \epsilon(k) \langle k_i | \langle k_j | \rangle \langle k_j | \rangle \right] c_j = 0.$$  \hspace{1cm} (3.9)

In order to solve this system of linear equations, we need to evaluate $\langle k_i | k_j \rangle$

$$\langle k_i | k_j \rangle = \frac{1}{N} \sum_{R-R'} e^{i \langle R-R' \rangle} \langle R_i + R' | | R_j + R' \rangle.$$  \hspace{1cm} (3.10)

It is obvious that $R'' - R' = R$ given that

$$\langle k_i | k_j \rangle = \frac{1}{N} \sum_{R-R'} e^{i \langle R-R' \rangle} \langle R_i + R' | | R_j + R' \rangle.$$  \hspace{1cm} (3.11)

The integral $\langle R_i + R' | R_j + R' \rangle = \langle R_i | R_j \rangle$ is independent to the lattice vectors $R'$ because the relative position between $R_i$ and $R_j + R$ is unchanged under the same translation vector $R'$. The summation over the lattice vectors $R'$ will cancel with the factor $1/N$ because there is no explicit dependence on $R'$ so that

$$\langle k_i | k_j \rangle = \frac{1}{N} \sum_{R-R'} e^{i \langle R-R' \rangle} \langle R_i + R | R_j + R \rangle = \sum_R e^{i \langle R-R' \rangle} \langle R_i | R_j + R \rangle.$$  \hspace{1cm} (3.12)

In the framework of the tight-binding approximation, the overlap integral $\langle R_i | R_j + R \rangle$ is nonzero only for the same orbital on the same atom, that is, only for $i = j$ and $R = 0$, therefore,

$$\langle k_i | k_j \rangle = \langle R_i | R_j \rangle = \delta_{ij}.$$  \hspace{1cm} (3.13)

The two basis functions, $| k_i \rangle$ and $| k_j \rangle$, are orthogonal. With this approximation, Equation 3.9 can be written as

$$\sum_j \left[ H_{ij} - \epsilon(k) \delta_{ij} \right] c_j = 0.$$  \hspace{1cm} (3.14)

This system of equations can have nonzero solutions only if its determinant vanishes,

$$\det \left[ H_{ij} - \epsilon(k) \delta_{ij} \right] = 0.$$  \hspace{1cm} (3.16)

This is known as the secular or characteristic equation. The Hamiltonian matrix $H_{ij} = \langle k_i | \hat{H} | k_j \rangle$ is $N \times N$ matrix, where $N$ is the number of basis functions used for expanding the crystal eigenstates. Alternatively, the eigenvalues can be obtained by directly diagonalizing the Hamiltonian matrix with all the known values of elements $H_{ij}$. The eigenvalues of a symmetric matrix are real. The solutions of this equation yield $N$ eigenvalues $\epsilon_1(k), \epsilon_2(k), ..., \epsilon_N(k)$, which are exactly the number of bands that we can expect for each value of $k$.

The Hamiltonian matrix elements $H_{ij}$ between atomic states can be obtained by

$$\langle k_i | \hat{H} | k_j \rangle = \frac{1}{N} \sum_{R-R'} e^{i \langle R-R' \rangle} \langle R_i + R' | \hat{H} | R_j + R' \rangle.$$  \hspace{1cm} (3.17)

At this point, an important approximation in the framework of the tight-binding method is introduced by taking the Hamiltonian matrix elements to be nonzero only if: (i) the orbital is on the same atom, that is, for $i = j$ and $R = 0$,

$$\langle k_i | \hat{H} | k_j \rangle = \langle R_i | \hat{H} | R_j \rangle = \epsilon_i \delta_{ij},$$  \hspace{1cm} (3.18)

where the diagonal elements $\epsilon_i$ are referred to as the onsite energies or the energy offset for an atom at site $i$, or (ii) the orbital is at nearest-neighbor sites located at $c_{NN}$,

$$\langle k_i | \hat{H} | k_j \rangle = \sum_R e^{i \langle R \rangle} \langle R_i | \hat{H} | R_j + c_{NN} \rangle.$$  \hspace{1cm} (3.19)

that is, $R_i = R_j + c_{NN}$. The summation running over all $R$ will be nonzero when the nearest neighbors are in the same unit cell ($R = 0$) or when they are across unit cells ($R$ is a
combination of the primitive lattice vectors). The $t_{ij}$ is referred to as the hopping integral between atoms at sites $i$ and $j$. A range of nearest-neighbor sites can be included into hopping elements (Equation 3.19) for better description of Hamiltonian matrix but more hopping integrals $t_{ij}$ have to be included to evaluate the matrix elements. In practice, we can consider $\varepsilon_i$ and $t_{ij}$ as parameters or we can even consider all the matrix elements as parameters as well. In both cases, these parameters are fitted to reproduce certain properties from experimental data or first-principles calculations. Then these parameters can be used to calculate other properties. Alternatively, these parameters can be used as variables to investigate a change in that parameter, that is, $\varepsilon_i$, $t_{ij}$.

The Hamiltonian matrix elements $H_{ij}$ in Equation 3.15 can be obtained by another form of Hamiltonian that is defined as

$$
\hat{H} = \sum_i \varepsilon_i a_i^\dagger a_i - \sum_{i,j} t_{ij}(a_i^\dagger a_j + \text{h.c.}),
$$

(3.20)

where $\varepsilon_i$ is the site energy for an atom at site $i$, $t_{ij}$ is the hopping integral between atoms at sites $i$ and $j$, and $a_i^\dagger$ and $a_i$ are the creation and annihilation operators, respectively, of $\pi$-electron at site $i$. By this definition, $a_i^\dagger$ is equivalent to an atomic state $|\mathbf{R}_i\rangle$, and $a_i$ is equivalent to an atomic state $|\mathbf{R}_i\rangle\rangle$. $\varepsilon_i$ represents the index of summation that is taken over only the nearest neighbors of interest, typically first neighbors, with truncation of farther neighbors. The interactions with farther neighbors, higher-order correction, are ignored for simplicity in most qualitative interpretations. The abbreviation “h.c.” stands for Hermitian conjugate of the term $a_i^\dagger a_j$. Tight-binding method provides an insightful of how the interactions between the constituents influence on the electronic structures.

3.2 ELECTRONIC STRUCTURES OF PRISTINE GRAPHENE AND HONEYCOMB LATTICE

The lattice structure of graphene contains two sublattices per primitive unit cell as shown in Figure 3.1. The primitive unit cell is defined by the primitive lattice vectors,

$$
a_1 = \frac{1}{2} a \hat{x} + \frac{\sqrt{3}}{2} a \hat{y} \quad \text{and} \quad a_2 = \frac{1}{2} a \hat{x} - \frac{\sqrt{3}}{2} a \hat{y},
$$

(3.21)

where $a$ is a lattice constant of graphene. With this choice of lattice vectors, the reciprocal primitive lattice vectors are given by

$$
b_1 = \frac{2\pi}{a} \left( \hat{x} + \frac{1}{\sqrt{3}} \hat{y} \right) \quad \text{and} \quad b_2 = \frac{2\pi}{a} \left( \hat{x} - \frac{1}{\sqrt{3}} \hat{y} \right).
$$

(3.22)

The lattice vectors $\mathbf{R}$ are formed by all possible combinations of lattice vectors

$$
\mathbf{R} = n_1 a_1 + n_2 a_2,
$$

(3.23)

where $n_1$ and $n_2$ are integers. The lattice vectors connect all equivalent points in space. The two sublattices are usually referred to as sublattice “A” and “B” which are indicated by different colors in Figure 3.1. Given that there are two atoms that are located at the two sublattices in the primitive unit cell. Suppose that we choose the position of sublattice $A$ to be at lattice point $\mathbf{R}_A$, then sublattice $B$ will be located at $\mathbf{R}_B = \mathbf{R}_A + \mathbf{c}$ with the basis vector

$$
\mathbf{c} = \frac{2}{3} a_1 + \frac{1}{3} a_2.
$$

(3.24)

The electronic structures of pristine graphene can be qualitatively described by tight-binding model. The Hamiltonian is defined as

$$
\hat{H} = \sum_i \varepsilon_i a_i^\dagger a_i - \sum_{i,j} t_{ij}(a_i^\dagger a_j + \text{h.c.}).
$$

(3.25)

For simplicity, let us start by considering only the hopping integral or the interactions from first nearest neighbors. The summation is taken over only the first nearest neighbors. The interactions with farther neighbors are ignored for a moment. In the unit cell as shown in Figure 3.1, sublattice $A$ is surrounded by three neighbors which are located at $\mathbf{R}_A$, $\mathbf{R}_A + \mathbf{a}_1$, and $\mathbf{R}_A + \mathbf{a}_1 + \mathbf{a}_2$. Therefore, the Hamiltonian in Equation 3.25 can be explicitly written as

$$
\hat{H} = \sum_{\mathbf{R}} (\varepsilon_A | \mathbf{R}_A \rangle \langle \mathbf{R}_A | + \varepsilon_B | \mathbf{R}_B \rangle \langle \mathbf{R}_B |)
$$

$$
- t_{AB} \sum_{\mathbf{R}} (| \mathbf{R}_A \rangle \langle \mathbf{R}_B | + | \mathbf{R}_B \rangle \langle \mathbf{R}_A |)
$$

$$
- t_{AB} \sum_{\mathbf{R}} (| \mathbf{R}_A \rangle \langle \mathbf{R}_A | + | \mathbf{R}_B \rangle \langle \mathbf{R}_B |)
$$

$$
- t_{AB} \sum_{\mathbf{R}} (| \mathbf{R}_A \rangle \langle \mathbf{R}_A | + | \mathbf{R}_B \rangle \langle \mathbf{R}_A | + | \mathbf{R}_A \rangle \langle \mathbf{R}_B | + | \mathbf{R}_B \rangle \langle \mathbf{R}_B |)
$$

(3.26)

where $|\mathbf{R}_A\rangle$ and $|\mathbf{R}_B\rangle$ are the $\pi$ atomic states associated with the atoms at sublattices $A$ and $B$, respectively. $\varepsilon_A$ and $\varepsilon_B$ are the site energies for an atom at sites $A$ and $B$, respectively. $t_{AB}$ is the hopping integral between atoms at sites $A$ and $B$. To evaluate the Hamiltonian matrix elements in Equation 3.15, we need to use two bases for expansion of the crystal wave functions which obey Bloch’s theorem. These bases are given by Equation 3.3,

$$
|\mathbf{k}_A\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i \mathbf{k} \cdot \mathbf{R}} | \mathbf{R}_A + \mathbf{R} \rangle
$$

and

$$
|\mathbf{k}_B\rangle
$$

$$
= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i \mathbf{k} \cdot \mathbf{R}} | \mathbf{R}_B + \mathbf{R} \rangle.
$$

(3.27)
with the summation running over all the $N$ unit cells in the crystal (the vectors $\mathbf{R}$), since the Hamiltonian matrix as a function of $\mathbf{k}$ is defined by

$$
\hat{H}(\mathbf{k}) = \begin{bmatrix}
\langle \mathbf{k}_A | \hat{H} | \mathbf{k}_A \rangle & \langle \mathbf{k}_A | \hat{H} | \mathbf{k}_B \rangle \\
\langle \mathbf{k}_B | \hat{H} | \mathbf{k}_A \rangle & \langle \mathbf{k}_B | \hat{H} | \mathbf{k}_B \rangle
\end{bmatrix}.
$$

(3.28)

or

$$
\hat{H}(\mathbf{k}) = \begin{bmatrix}
H_{AA} & H_{AB} \\
H_{BA} & H_{BB}
\end{bmatrix}.
$$

(3.29)

The Hamiltonian matrix elements can be evaluated by using,

$$
\langle \mathbf{k}_A | = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i \mathbf{R} \cdot \mathbf{R}} \langle \mathbf{R}_A + \mathbf{R} | \text{ and}
$$

$$
\langle \mathbf{k}_B | = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i \mathbf{R} \cdot \mathbf{R}} \langle \mathbf{R}_B + \mathbf{R} |.
$$

(3.30)

The first diagonal matrix element $H_{AA} = \langle \mathbf{k}_A | \hat{H} | \mathbf{k}_A \rangle$ is given by

$$
\hat{H} | \mathbf{k}_A \rangle = \sum_{\mathbf{R}} \left( \varepsilon_{\mathbf{R}} | \mathbf{R}_A \rangle - \frac{t_{\mathbf{R}}}{\sqrt{N}} \langle \mathbf{R}_A | \mathbf{R}_A \rangle \right)
$$

$$
- t_{\mathbf{R}} \sum_{\mathbf{R}} \left( \langle \mathbf{R}_B | \frac{1}{\sqrt{N}} \langle \mathbf{R}_A | \mathbf{R}_A \rangle \right)
$$

$$
- t_{\mathbf{R}} \sum_{\mathbf{R}} \left( \langle \mathbf{R}_B | \frac{1}{\sqrt{N}} e^{i \mathbf{R} \cdot \mathbf{a}_1} \langle \mathbf{R}_A + \mathbf{a}_1 | \mathbf{R}_A + \mathbf{a}_1 \rangle \right)
$$

$$
- t_{\mathbf{R}} \sum_{\mathbf{R}} \left( \langle \mathbf{R}_B | \frac{1}{\sqrt{N}} e^{i \mathbf{R} \cdot (\mathbf{a}_1 + \mathbf{a}_2)} \langle \mathbf{R}_A + \mathbf{a}_1 + \mathbf{a}_2 | \mathbf{R}_A + \mathbf{a}_1 + \mathbf{a}_2 \rangle \right).
$$

(3.31)

The overlap integral $\langle \mathbf{R}_A | \mathbf{R}_B \rangle = 0$ is nonzero only for the same orbital on the same atom, that is, only for $i = j$; hence

$$
\hat{H} | \mathbf{k}_A \rangle = \sum_{\mathbf{R}} \left( \varepsilon_{\mathbf{R}} | \mathbf{R}_A \rangle - t_{\mathbf{R}} \sum_{\mathbf{R}} \langle \mathbf{R}_B | \frac{1}{\sqrt{N}} \right)
$$

$$
- t_{\mathbf{R}} \sum_{\mathbf{R}} \left( \langle \mathbf{R}_B | \frac{1}{\sqrt{N}} e^{i \mathbf{R} \cdot \mathbf{a}_1} \right)
$$

$$
- t_{\mathbf{R}} \sum_{\mathbf{R}} \left( \langle \mathbf{R}_B | \frac{1}{\sqrt{N}} e^{i \mathbf{R} \cdot (\mathbf{a}_1 + \mathbf{a}_2)} \right).
$$

(3.32)

The element $H_{AA} = \langle \mathbf{k}_A | \hat{H} | \mathbf{k}_A \rangle$ is

$$
\langle \mathbf{k}_A | \hat{H} | \mathbf{k}_A \rangle = \sum_{\mathbf{R}} \left( \varepsilon_{\mathbf{R}} \frac{1}{\sqrt{N}} \langle \mathbf{R}_A | \mathbf{R}_A \rangle \right) = \varepsilon_{\mathbf{R}} \sum_{\mathbf{R}} \left( \frac{1}{\sqrt{N}} \right) = \varepsilon_{\mathbf{R}}.
$$

(3.33)

By using Equations 3.30 and 3.32, the off-diagonal element $H_{BA} = \langle \mathbf{k}_B | \hat{H} | \mathbf{k}_A \rangle$ is given by

$$
\langle \mathbf{k}_B | \hat{H} | \mathbf{k}_A \rangle = - t_{BA} \sum_{\mathbf{R}} \left( \frac{1}{\sqrt{N}} \langle \mathbf{R}_B | \mathbf{R}_B \rangle + \frac{1}{\sqrt{N}} \varepsilon_{\mathbf{R}} \frac{1}{\sqrt{N}} \langle \mathbf{R}_B | \mathbf{R}_B \rangle \right)
$$

$$
+ \frac{1}{\sqrt{N}} e^{i \mathbf{R} \cdot (\mathbf{a}_1 + \mathbf{a}_2)} \langle \mathbf{R}_B | \mathbf{R}_B \rangle.
$$

(3.34)

Similarly, the second diagonal matrix element $H_{BB} = \langle \mathbf{k}_B | \hat{H} | \mathbf{k}_B \rangle$ can be evaluated, by first considering

$$
\hat{H} | \mathbf{k}_B \rangle = \sum_{\mathbf{R}} \left( \varepsilon_{\mathbf{R}} | \mathbf{R}_B \rangle - t_{AB} \sum_{\mathbf{R}} \langle \mathbf{R}_A | \frac{1}{\sqrt{N}} \right)
$$

$$
- t_{AB} \sum_{\mathbf{R}} \left( \langle \mathbf{R}_B | \frac{1}{\sqrt{N}} e^{-i \mathbf{R} \cdot \mathbf{a}_1} \langle \mathbf{R}_B - \mathbf{a}_1 | \mathbf{R}_B - \mathbf{a}_1 \rangle \right)
$$

$$
- t_{AB} \sum_{\mathbf{R}} \left( \langle \mathbf{R}_B | \frac{1}{\sqrt{N}} e^{-i \mathbf{R} \cdot (\mathbf{a}_1 + \mathbf{a}_2)} \langle \mathbf{R}_B - \mathbf{a}_1 - \mathbf{a}_2 | \mathbf{R}_B - \mathbf{a}_1 - \mathbf{a}_2 \rangle \right).
$$

(3.35)

The element $H_{BB} = \langle \mathbf{k}_B | \hat{H} | \mathbf{k}_B \rangle$ is

$$
\langle \mathbf{k}_B | \hat{H} | \mathbf{k}_B \rangle = \sum_{\mathbf{R}} \left( \varepsilon_{\mathbf{R}} \frac{1}{\sqrt{N}} \langle \mathbf{R}_B | \mathbf{R}_B \rangle \right) = \varepsilon_{\mathbf{R}} \sum_{\mathbf{R}} \left( \frac{1}{\sqrt{N}} \right) = \varepsilon_{\mathbf{R}}.
$$

(3.36)
By using Equations 3.30 and 3.35, the off-diagonal element $H_{AB} = \langle k_A | \hat{H} | k_B \rangle$ is given by

$$
\langle k_A | \hat{H} | k_B \rangle = -t_{AB} \sum_R \left( \frac{1}{N} \langle R_A | R_A \rangle + \frac{1}{N} e^{-i k_A a_R} \langle R_A | R_A \rangle \right)
+ \frac{1}{N} e^{-i (k_A + k_B) a_R} \langle R_A | R_A \rangle),
$$

$$
\langle k_A | H | k_B \rangle = -t_{AB} \sum_R \left( 1 + e^{-i k_A a_R} + e^{-i (k_A + k_B) a_R} \right)
= -t_{AB} \left( 1 + e^{-i k_A a_R} + e^{-i (k_A + k_B) a_R} \right).
$$

Therefore, the Hamiltonian matrix is

$$
\hat{H}(k) = \begin{bmatrix}
\varepsilon_A & -t_{AB} \left( 1 + e^{-i k_A a_R} + e^{-i (k_A + k_B) a_R} \right) \\
-t_{AB} \left( 1 + e^{-i k_A a_R} + e^{-i (k_A + k_B) a_R} \right) & \varepsilon_B
\end{bmatrix}.
$$

(3.38)

In this matrix, one can readily understand that the diagonal elements $H_{AA}$ and $H_{BB}$ are the energies at the atomic site called “onsite energy” or the energy offset for an atom at sites $A$ and $B$. The $H_{AB}$ is the interaction from atom at $B$ sublattices to the atom at sublattice $A$, or vice versa for $H_{BA}$. Notice that, the Hamiltonian matrix is a Hermitian matrix that has two real eigenvalues for each value of $k$. The solutions to this Hamiltonian can be obtained by diagonalizing the Hamiltonian or from the secular equation

$$
\det \left[ \hat{H}(k) - \varepsilon(k) I \right] = 0,
$$

$$
\begin{bmatrix}
H_{AA} - \varepsilon(k) & H_{AB} \\
H_{BA} & H_{BB} - \varepsilon(k)
\end{bmatrix} = 0,
$$

(3.39)

which is

$$
[H_{AA} - \varepsilon(k)][H_{BB} - \varepsilon(k)] - H_{AB}H_{BA} = 0
$$

(3.40)

having solutions

$$
\varepsilon(k) = \frac{1}{2} \left( (H_{AA} + H_{BB}) \pm \sqrt{(H_{AA} - H_{BB})^2 + 4H_{AB}H_{BA}} \right)
$$

(3.41)

or

$$
\varepsilon(k) = \frac{1}{2} \left[ \varepsilon_A + \varepsilon_B \pm \sqrt{\left( \varepsilon_A - \varepsilon_B \right)^2 + 4t_{AB}^2 \left( 1 + e^{-i k_A a_R} + e^{-i (k_A + k_B) a_R} \right)} \right],
$$

(3.42)

where the multiplication

$$
\left( 1 + e^{-i k_A a_R} + e^{-i (k_A + k_B) a_R} \right) \left( 1 + e^{+i k_A a_R} + e^{+i (k_A + k_B) a_R} \right) = 3 + 2 \cos(k \cdot a_R)
$$

$$
+ 2 \cos(k \cdot a_R)
$$

$$
+ 2 \cos(k \cdot (a_R + a_S)).
$$

(3.43)

With $k = k_x \hat{x} + k_y \hat{y}$ and the lattice vectors defined by Equation 3.21, we can evaluate product of

$$
k \cdot a_1 = \frac{1}{2} k_x a + \frac{\sqrt{3}}{2} k_y a,
$$

(3.44)

$$
k \cdot (a_1 + a_2) = k_y a.
$$

For simplicity, we can define

$$
f(k) = 2 \cos(k \cdot a_1) + 2 \cos(k \cdot a_2) + 2 \cos(k \cdot (a_1 + a_2)).
$$

(3.45)

For a simple nearest-neighbor tight-binding model, one obtains the dispersion relation (Reich et al. 2002; Wallace 1947):

$$
\varepsilon(k) = \frac{1}{2} \left[ \varepsilon_A + \varepsilon_B \pm \sqrt{\left( \varepsilon_A - \varepsilon_B \right)^2 + 4t_{AB}^2 \left[ 3 + f(k) \right]} \right].
$$

(3.46)

If the atom at sublattice $A$ is identical to the atom at sublattice $B$ ($\varepsilon_A = \varepsilon_B = \varepsilon$ and $t_{AB} = t$), then the above equation will get reduced to

$$
\varepsilon(k) = \varepsilon \pm t \sqrt{3 + f(k)}.
$$

(3.47)

Here, the atoms at sites $A$ and $B$ are carbon atoms; we can choose the energy offset $\varepsilon = 0$. The values of $\varepsilon$ and $t$ are found by fitting experimental data or first-principles calculations. In practice, $\varepsilon$ and $t$ are adjusted to reproduce a good description of $\pi$ bands at the $K$ point. Based on the first-principles calculations, a typical value of $\varepsilon = 0$ eV and $t = 2.7$ eV are used (Reich et al. 2002). With this choice of reciprocal lattice vectors in Equation 3.22, we can plot the electronic structures of graphene, Equation 3.47, as illustrated in Figure 3.2 within the first BZ as shown in the inset. The band structure of graphene is plotted along $\Gamma - K - M - \Gamma$ directions. The lines connecting the high symmetry points, $\Gamma - K - M - \Gamma$, are defined by

$$
\Sigma = \left[ \frac{2k}{3}, 0 \right],
$$

$$
T = \left[ \frac{2}{3} (1 - k), \frac{k}{2}, \frac{k}{2 \sqrt{3}} \right],
$$

(3.48)

$$
\Lambda = \left[ \frac{1}{2} (1 - k), \frac{1}{2 \sqrt{3}} (1 - k) \right].
$$

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where \(0 \leq k \leq 1\) and the unit along these paths is in the unit of \(2\pi/a\). In the case that the atom at sublattice \(A\) is equivalent to the atom at sublattice \(B\), there will be doubly degenerate energy levels at the \(K\) point or at the six corners of the hexagonal BZ, so-called Dirac point (Zhou et al. 2006). Among the six Dirac points, only two are independent denoted by \(K\) and \(K'\) in the inset of Figure 3.2, where the others are related to \(K\) and \(K'\) by a combination of the reciprocal lattice vectors in Equation 3.22. This characteristic is strongly related to the inversion symmetry of crystal structure, where the inversion center is located between the two sublattices, such that the doubly degenerate levels at the \(K\) point will always be presented in other atomic species as well, for example, silicene (Sahin et al. 2009). If the atom at sublattice \(A\) is different from the atom at sublattice \(B\), the degeneracy is lifted as in the case of hexagonal form of boron nitride (\(h\)-BN) (Pease 1952).

The band structures of \(h\)-BN can be calculated from Equation 3.46 with the onsite energies of boron \(\varepsilon_b = 3.6\) eV and nitrogen \(\varepsilon_n = -1.0\) eV, and the hopping integral \(t_{\text{BN}} = 2.5\) eV, where the values of all parameters are found by fitting first-principles calculations (Junghwan et al. 2011). The difference between the two sublattices creates a direct bandgap instead of doubly degenerate levels at \(K\) point in \(h\)-BN. The bandgap of graphene can be created by several approaches (Peng and Ahuja 2008), one of which is to break the equivalence of \(A\) and \(B\) sublattices. This simple model clearly shows that the equivalence of \(A\) and \(B\) sublattices is crucial to electronic structures of honeycomb structure.

A higher-order correction can be made by including the interactions from second nearest neighbors. The Hamiltonian in Equation 3.25 can be written as the Hamiltonian with the interactions from first nearest neighbors \(\hat{H}_{\text{1NN}}\), given by Equation 3.26, plus the Hamiltonian with the interactions from second nearest neighbors \(\hat{H}_{\text{2NN}}\). From the unit cell in Figure 3.1, sublattice \(A\) is surrounded by six neighbors which are located at \(\mathbf{R}_A + \mathbf{a}_1, \mathbf{R}_A + \mathbf{a}_2, \mathbf{R}_A - \mathbf{a}_1, \mathbf{R}_A - \mathbf{a}_2, \mathbf{R}_B - \mathbf{a}_1, \mathbf{R}_B - \mathbf{a}_2\), and \(\mathbf{R}_A - \mathbf{a}_2\). Likewise, the second neighbors of sublattice \(B\) are located at \(\mathbf{R}_B + \mathbf{a}_1, \mathbf{R}_B + \mathbf{a}_2, \mathbf{R}_B - \mathbf{a}_1, \mathbf{R}_B - \mathbf{a}_2\), and \(\mathbf{R}_B - \mathbf{a}_2\) and \(\mathbf{R}_B - \mathbf{a}_1\). Therefore, the Hamiltonian on the upper to the second neighbor interactions \(\hat{H}_{\text{2NN}}\) can be explicitly written as

\[
\hat{H}_{\text{2NN}} = -t'_A \sum_{\mathbf{R}} \left( |\mathbf{R}_A\rangle \langle \mathbf{R}_A + \mathbf{a}_1| + |\mathbf{R}_A\rangle \langle \mathbf{R}_A + \mathbf{a}_2| + |\mathbf{R}_A - \mathbf{a}_1\rangle \langle \mathbf{R}_A - \mathbf{a}_1| + |\mathbf{R}_A - \mathbf{a}_2\rangle \langle \mathbf{R}_A - \mathbf{a}_2| \right)
- t'_B \sum_{\mathbf{R}} \left( |\mathbf{R}_B\rangle \langle \mathbf{R}_B + \mathbf{a}_1| + |\mathbf{R}_B\rangle \langle \mathbf{R}_B + \mathbf{a}_2| + |\mathbf{R}_B - \mathbf{a}_1\rangle \langle \mathbf{R}_B - \mathbf{a}_1| + |\mathbf{R}_B - \mathbf{a}_2\rangle \langle \mathbf{R}_B - \mathbf{a}_2| \right)
\]

(3.49)

\(t'_A\) and \(t'_B\) are the hopping integrals between corresponding second neighbors and atoms at sites \(A\) and \(B\), respectively. The second neighbors Hamiltonian is corresponding to the interactions between the same atomic species with a translation with lattice vector \(\mathbf{R}\). This correction will affect only on the diagonal elements, that is, \(H_{AA}\) and \(H_{BB}\). The off-diagonal elements, that is, \(H_{AB}\) and \(H_{BA}\), will be the same as the matrix in Equation 3.38. In this case, the first diagonal matrix element \(H_{AA} = \langle k_A | \hat{H} | k_A \rangle\) is given by

\[
\langle k_A | \hat{H} | k_A \rangle = \varepsilon_A - t'_A \sum_{\mathbf{R}} \left( e^{ik_a a_1} + e^{ik(a_1 + a_2)} + e^{ik a_2} + e^{-ik a_1} \right) + e^{-ik(a_1 + a_2)} + e^{ik a_2}) \right)
= \varepsilon_A - t'_A \left( e^{ik a_1} + e^{-ik a_1} + e^{ik a_2} + e^{-ik a_2} \right)
+ e^{ik(a_1 + a_2)} + e^{-ik(a_1 + a_2)} \right)
= \varepsilon_A - 2t'_A \left[ \cos(k \cdot a_1) + \cos(k \cdot a_2) \right]
+ \cos k \cdot (a_1 + a_2) \right].
\]

(3.50)

Similarly, the second diagonal matrix element \(H_{BB} = \langle k_B | \hat{H} | k_B \rangle\) is given by

\[
\langle k_B | \hat{H} | k_B \rangle = \varepsilon_B - t'_B \sum_{\mathbf{R}} \left( e^{ik a_1} + e^{-ik a_1} + e^{ik a_2} + e^{-ik a_2} \right)
+ e^{ik(a_1 + a_2)} + e^{-ik(a_1 + a_2)} \right)
= \varepsilon_B - 2t'_B \left[ \cos(k \cdot a_1) + \cos(k \cdot a_2) \right]
+ \cos k \cdot (a_1 + a_2) \right].
\]

(3.51)

With these forms of the diagonal elements, we can construct the Hamiltonian matrix, Equation 3.29, for each value of \(k\).

\[
H_{AA} = \varepsilon_A - 2t'_A \left[ \cos(k \cdot a_1) + \cos(k \cdot a_2) + \cos k \cdot (a_1 + a_2) \right],
\]

\[
H_{AB} = -t_{AB} \left( e^{ik a_1} + e^{-ik(a_1 + a_2)} \right),
\]

\[
H_{BA} = -t_{AB} \left( e^{ik a_1} + e^{ik(a_1 + a_2)} \right),
\]

\[
H_{BB} = \varepsilon_B - 2t'_B \left[ \cos(k \cdot a_1) + \cos(k \cdot a_2) + \cos k \cdot (a_1 + a_2) \right],
\]

(3.52)

and obtain the solutions by Equation 3.41. If the atom at sublattice \(A\) is identical to the atom at sublattice \(B\) (\(t'_A = t'_B \equiv t'\)), then the solution is

\[
\varepsilon(k) = \varepsilon_{\text{1NN}}(k) - 2t' \left[ \cos(k \cdot a_1) + \cos(k \cdot a_2) + \cos k \cdot (a_1 + a_2) \right]
\]

(3.53)
or

\[ \varepsilon(k) = \varepsilon \pm t' \sqrt{3 + f(k)} - t' f(k), \quad (3.54) \]

where \( \varepsilon_{NN}(k) \) is the dispersion relation from first neighbors interactions in Equation 3.47. \( f(k) \) is a function of \( k \) defined by Equation 3.45. According to Reich et al. (2002), the value of \( t' \) for graphene is in the range of \(-0.2t \leq t' \leq -0.02t\) depending on the parameterization of \( \varepsilon \) and \( t \). This second neighbor interaction \( t' \neq 0 \) is responsible for asymmetric feature of the \( \pi \) and \( \pi^* \) bands as shown in Figure 3.3.

The Hamiltonian with third nearest-neighbor interactions \( \hat{H}_{3NN} \) can be made by considering the unit cell in Figure 3.1. Sublattice \( A \) is surrounded by three neighbors which are located at \( \mathbf{R}_B - 2\mathbf{a}_2, \mathbf{R}_A + \mathbf{a}_2, \) and \( \mathbf{R}_B - 2\mathbf{a}_1 - \mathbf{a}_2. \) Likewise, the third neighbors of sublattice \( B \) are located at \( \mathbf{R}_A - 2\mathbf{a}_2, \mathbf{R}_A + \mathbf{a}_2, \) and \( \mathbf{R}_A + 2\mathbf{a}_1 + \mathbf{a}_2. \) Therefore, the Hamiltonian up to the third neighbors \( \hat{H}_{3NN} \) is given by

\[
\begin{align*}
H_{3NN} &= -t_A' \sum_\mathbf{R} \left( | \mathbf{R}_A - \mathbf{a}_2 + | \mathbf{R}_A + \mathbf{a}_2 + | \mathbf{R}_B \right) \\
&\quad - t_B'' \sum_\mathbf{R} \left( | \mathbf{R}_B - 2\mathbf{a}_1 + \mathbf{a}_2 | \mathbf{R}_B + \mathbf{a}_2 + | \mathbf{R}_B \right) \\
&\quad - t_B'' \sum_\mathbf{R} \left( | \mathbf{R}_B - 2\mathbf{a}_1 + \mathbf{a}_2 | \mathbf{R}_A - \mathbf{a}_2 + | \mathbf{R}_B \right)
\end{align*}
\]

\[ (3.55) \]

\( t_A' \) and \( t_B'' \) are the hopping integrals between corresponding third neighbors and atoms at sites \( A \) and \( B \), respectively. The third neighbors Hamiltonian is corresponding to the interactions between different atomic species. This correction will affect the off-diagonal elements, that is, \( H_{AB} \) and \( H_{BA} \), in Equation 3.52. The correction to the third nearest-neighbor interactions is given by the product of \( \langle k_A | \hat{H}_{3NN} | k_B \rangle \) and \( \langle k_B | \hat{H}_{3NN} | k_A \rangle \), which are

\[
\begin{align*}
\langle k_A | \hat{H}_{3NN} | k_B \rangle &= - t_A' \left( e^{-ik(a_2 + a_2)} + e^{ik(a_2 + 2a_1 + a_2)} \right) \\
\langle k_B | \hat{H}_{3NN} | k_A \rangle &= - t_B'' \left( e^{-ik(a_2 + a_2)} + e^{ik(a_2 + 2a_1 + a_2)} \right).
\end{align*}
\]

If the atom at sublattice \( A \) is identical to the atom at sublattice \( B \), we can let \( t_A' = t''_B = t'' \). The eigenvalues of this matrix can be obtained by Equation 3.41 for each value of \( k \). Usually, the second and third neighbor interactions are not significant and generally ignored. However, the change in these interactions can substantially affect the band structure. The value of \( t' \) and \( t'' \) can change the number of Dirac points, their position, and their properties in graphene and graphene-related materials (Bena and Simon 2011). It is interesting to note that the simple first nearest-neighbors tight-binding results give a reasonable feature at the band edge near \( K \) point. Hence, for the larger system, first nearest-neighbor interactions will be our main focus.

### 3.3 Electronic Structures of Graphene via Brick-Type Lattice

The honeycomb lattice structure can be simplified by performing a lattice transformation to the brick-type lattice structure (Wakabayashi et al. 1999) as shown in Figure 3.4. In this model, the direction of each bond is aligned into two perpendicular axes. This transformation can be considered as a distorted honeycomb lattice under the influence of compression in \( y \) direction together with extension in \( x \) direction. The topology of brick-type lattice is still similar to honeycomb lattice but with different lattice vectors. This transformation...

---

**FIGURE 3.3** Band structures of graphene in comparison with the first and second nearest-neighbor interactions. The values of the parameters used in tight-binding calculations are shown. The horizontal line at 0 eV is considered as the Fermi level.
reduces complexity in the investigation of electronic states near the Fermi energy when considering the overlap between each orbital, that is, $s$, $p_x$, $p_y$, and $p_z$. The unit cell of brick-type lattice contains two sublattices per primitive unit cell as shown in Figure 3.4. The primitive unit cell is defined by the primitive lattice vectors $a_1$ and $a_2$.

$$a_1 = \frac{1}{\sqrt{2}} a \hat{x} + \frac{1}{\sqrt{2}} a \hat{y} \quad \text{and} \quad b_2 = \frac{2\pi}{a} \left( \frac{1}{\sqrt{2}} \hat{x} - \frac{1}{\sqrt{2}} \hat{y} \right).$$  (3.59)

where $a$ is a lattice constant. With this choice of lattice vectors, the reciprocal primitive lattice vectors are given by

$$b_1 = \frac{2\pi}{a} \left( \frac{1}{\sqrt{2}} \hat{x} + \frac{1}{\sqrt{2}} \hat{y} \right) \quad \text{and} \quad b_2 = \frac{2\pi}{a} \left( \frac{1}{\sqrt{2}} \hat{x} - \frac{1}{\sqrt{2}} \hat{y} \right).$$  (3.60)

The Hamiltonian based on the tight-binding model (with second nearest-neighbor interactions) is defined as

$$\hat{H} = \sum_{\mathbf{R}} \left( \varepsilon_A | \mathbf{R}_A \rangle \langle \mathbf{R}_A | + \varepsilon_B | \mathbf{R}_B \rangle \langle \mathbf{R}_B | \right)$$

$$-t_{AB} \sum_{\mathbf{R}} \left( | \mathbf{R}_A \rangle \langle \mathbf{R}_B | + | \mathbf{R}_B \rangle \langle \mathbf{R}_A | ight)$$

$$\langle \mathbf{R}_A - a_1 - a_2 | + | \mathbf{R}_A | + | \mathbf{R}_B | \rangle$$

$$\langle \mathbf{R}_A + a_1 + a_2 | + | \mathbf{R}_A | + | \mathbf{R}_B | \rangle$$

$$-t'_A \sum_{\mathbf{R}} \left( | \mathbf{R}_A \rangle \langle \mathbf{R}_A + a_1 + a_2 | + | \mathbf{R}_A | + | \mathbf{R}_A | \rangle$$

$$\langle \mathbf{R}_A - a_1 - a_2 | + | \mathbf{R}_A | + | \mathbf{R}_A | \rangle$$

$$\langle \mathbf{R}_B | + | \mathbf{R}_B | + | \mathbf{R}_B | \rangle$$

$$\langle \mathbf{R}_B + a_1 + a_2 | + | \mathbf{R}_B | + | \mathbf{R}_B | \rangle$$

$$-t'_B \sum_{\mathbf{R}} \left( | \mathbf{R}_B \rangle \langle \mathbf{R}_B + a_1 + a_2 | + | \mathbf{R}_B | + | \mathbf{R}_B | \rangle$$

$$\langle \mathbf{R}_B + a_1 + a_2 | + | \mathbf{R}_B | + | \mathbf{R}_B | \rangle$$

$$\langle \mathbf{R}_B - a_1 - a_2 | + | \mathbf{R}_B | + | \mathbf{R}_B | \rangle$$

(3.61)

where $| \mathbf{R}_A \rangle$ and $| \mathbf{R}_B \rangle$ are the $\pi$ atomic states associated with the atoms at $A$ and $B$ sublattices, respectively. We can use the two bases in Equation 3.27 for expansion of the crystal wave functions yielding the similar result to Equation 3.54 if the atom at sublattice $A$ identical to the atom at sublattice $B$ ($t'_A = t'_B$). With the reciprocal lattice vectors in Equation 3.60, we can plot the band structures of this system along high-symmetry lines connecting the $\Gamma - M - X - \Gamma$ points as shown in Figure 3.5 within the first BZ as illustrated in the inset of Figure 3.5. These paths are defined by

$$\Sigma = \left[ \frac{k}{\sqrt{2}}, 0 \right],$$

$$Z = \left[ \frac{1}{\sqrt{2}}(1-k) + \frac{k}{2\sqrt{2}}, \frac{k}{2\sqrt{2}} \right],$$

$$\Delta = \left[ \frac{1}{2\sqrt{2}}(1-k), \frac{1}{2\sqrt{2}}(1-k) \right].$$  (3.62)

with the unit of $2\pi/a$ and $0 \leq k \leq 1$. The same set of parameters used in Figure 3.3 is applied to calculate the dispersion relation $\varepsilon(k)$ obtained from Equation 3.54 giving the band structures of graphene in brick-type lattice as shown in Figure 3.5. The first BZ of the reciprocal lattices in Equation 3.60 is a square shape as shown in the inset of Figure 3.5. This square BZ transforms the dispersion relation $\varepsilon(k)$ of hexagonal BZ to a distorted hexagonal BZ (inset of Figure 3.5). The original $K$ point of hexagonal BZ is located at $(\sqrt{2}/3, 0)$ on the $\Sigma$ path. The idea of brick-type lattice transformation can be used to study a distorted honeycomb structure under the influence of external loading that lifts threefold symmetry.
of the bonding between the atoms at sublattices \( A \) and \( B \). In Figure 3.4, the bonding along \( \hat{y} \) axis is the difference from the other two which can be formulated by introducing another hopping integral for this bond. We can define different hopping integral \( t_y \) for the bonding along \( \hat{y} \) axis and obtain the Hamiltonian as

\[
\hat{H} = \sum_{R} \left( \epsilon_A |R_A\rangle \langle R_A| + \epsilon_B |R_B\rangle \langle R_B| \right)
- t_{AB} \sum_{R} \left( (|R_A\rangle \langle R_B| + |R_B\rangle \langle R_A| - a_1 - a_2 \right)
- t_y \sum_{R} \left( (|R_A\rangle \langle R_B| - a_1 + a_2 \right)
\]

The Hamiltonian matrix elements for each value of \( k \) are given by

\[
H_{AA} = \epsilon_A,
H_{AB} = -t_{AB} \left( 1 + e^{-i(k \cdot a_1 + a_2)} \right) - t_y e^{-i(\epsilon_A a_1)},
H_{BA} = -t_{AB} \left( 1 + e^{i(k \cdot a_1 + a_2)} \right) - t_y e^{i(\epsilon_A a_1)},
H_{BB} = \epsilon_B.
\]

The dispersion relation is given by

\[
\epsilon(k) = \frac{1}{2} \left[ \left( H_{AA} + H_{BB} \right) \pm \sqrt{\left( H_{AA} - H_{BB} \right)^2 + 4 H_{AB} H_{BA}} \right].
\]

where

\[
H_{AB} H_{BA} = 2t_{AB}^2 + t_y^2 + 2t_{AB} t_y \left[ \cos(k \cdot a_1) + \cos(k \cdot a_2) \right]
+ 2t_{AB}^2 \cos(k \cdot (a_1 + a_2)).
\]

and

\[
\begin{align*}
  k \cdot a_1 &= \frac{1}{\sqrt{2}} k_x a + \frac{1}{\sqrt{2}} k_y a, \\
  k \cdot a_2 &= \frac{1}{\sqrt{2}} k_x a - \frac{1}{\sqrt{2}} k_y a, \\
  k \cdot (a_1 + a_2) &= \sqrt{2} k_x a.
\end{align*}
\]

With additional parameter \( t_y \), the band structure of distorted honeycomb structure can be investigated. The difference between \( t_y \) and \( t_{AB} \) depends on the amount of distortion. For distorted graphene, the atoms at sites \( A \) and \( B \) are carbon atoms (\( \epsilon_A = \epsilon_B \equiv \epsilon \) and \( t_{AB} \equiv t \)). For qualitative analysis, the value of \( \epsilon \) and \( t \) can be taken from the case of pristine graphene. \( t_y \) can be varied to see how this parameter affects a particular region or electronic level in the band structures. Alternatively, these parameters can be parameterized by fitting to empirical or first-principles data according to interaction type and distance for quantitative analysis. The brick-type lattice is also useful for evaluating the bandgap of graphene nanostructures such as nanoribbons or superlattices.

### 3.4 ELECTRONIC STRUCTURES OF GRAPHENE NANORIBBONS

To utilize graphene as a semiconductor, several approaches to lift the degeneracy and open up the bandgap have been introduced. One approach is to confine or reduce the dimension of graphene. Graphene can be cut to graphene nanoribbons (GNRs). The hexagonal lattice structure can be cut with three different kinds of shape edges, that is, armchair, zigzag, and chiral shape edges. Previous studies show that GNRs can exhibit both metallic and semiconducting properties depending on the geometric and the width of GNRs (Fujita et al. 1996; Nakada et al. 1996; Son et al. 2006; Wakabayashi et al. 1999). Here, we consider two types of GNRs with armchair and zigzag edges, as shown in Figure 3.6, which are the two most relevant ribbon orientations with different ribbon widths. The width of ribbon \( N \) is defined by the number of dimer lines for armchair graphene nanoribbons (AGNR) and by the number of zigzag molecular chains for zigzag graphene nanoribbons (ZGNR). The smallest width of AGNR and ZGNR is \( N = 3 \) containing 6 atoms per unit cell and \( N = 2 \) containing 4 atoms per unit cell, respectively. AGNR and ZGNR give different ribbon widths with the same number of \( N \). The lattice structure of each ribbon can be defined by rectangle with the relevant lattice vector, as shown in Figure 3.6,

\[
a_1 = a \hat{x} \quad \text{and} \quad a_2 = a \sqrt{3} \hat{y} \quad (3.68)
\]

for ZGNR and AGNR, respectively, where \( a \) is a lattice constant. With this choice of lattice vector, the reciprocal primitive lattice vector for ZGNR and AGNR is given, respectively, by

\[
b_1 = \frac{2\pi}{a} \hat{x} \quad \text{and} \quad b_2 = \frac{2\pi}{a \sqrt{3}} \hat{y}. \quad (3.69)
\]

The electronic structures of GNRs can be calculated from the Hamiltonian matrix which can be obtained in the same manner as the previous section. The number of bands is corresponding to the number of states included in the model. If we consider only \( \pi \) orbital from each atom, the number of bands is equal to the number of atom \( n \) which is the dimension of the Hamiltonian matrix,
The matrix elements $H_{ij}$ of Hamiltonian matrix are basically derived by investigating the interactions on each atom in the unit cell and its neighbors which are located in the same unit cell as well as the neighbor cells. Suppose that the interaction between atoms at sites $i$ and $j$ is within the same unit cell, the product $\langle \mathbf{k}_i | \hat{H} | \mathbf{k}_j \rangle$ or matrix element $H_{ij}$ is equal to $t_{ij}$ where $\mathbf{k}_i$ and $\mathbf{k}_j$ are bases for expansion of the crystal wave functions given by Equation 3.3 which obey Bloch’s theorem and have orthogonality given by Equation 3.13. If atom at site $i$ interacts with interacting atom at site $j$ that is within the different unit cell, the matrix element $H_{ij}$ is equal to $t_{ij}$ multiplied by the factor $\exp(-\mathbf{k} \cdot \mathbf{R})$ where the exponent $\mathbf{R}$ is the lattice vector that translates the position of interacting atom at site $j$ to the corresponding site within the same unit cell of atom at site $i$. For instance, the Hamiltonian matrix of AGNR with $N = 3$ is given by

$$
\hat{H}(\mathbf{k}) = \begin{bmatrix}
H_{11} & H_{12} & \cdots & H_{1n} \\
H_{21} & H_{22} & \cdots & H_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
H_{n1} & H_{n2} & \cdots & H_{nn}
\end{bmatrix}
$$

(3.70)

The Hamiltonian matrix of ZGNR with $N = 2$ is given by

$$
\hat{H}(\mathbf{k}) = \begin{bmatrix}
\varepsilon & t(1+e^{-i\mathbf{k} \cdot \mathbf{a}_1}) & 0 & 0 \\
0 & \varepsilon & t & 0 \\
0 & t & \varepsilon & t(1+e^{i\mathbf{k} \cdot \mathbf{a}_1}) \\
0 & 0 & 0 & \varepsilon
\end{bmatrix}
$$

(3.72)

Here we apply typical value of tight-binding parameters ($\varepsilon = 0$ eV and $t = -2.7$ eV) of pristine graphene to GNR system. Nevertheless, the form of analytical solutions to the Hamiltonian matrix is quite complicated. An appropriate approach is to use the numerical method to solve for the eigenvalues corresponding with the Hamiltonian matrix for each value of $\mathbf{k}$. The plots of electronic structures of AGNR with the number of dimer lines $N = 3, 4, 5$ along relevant directions shown in Figure 3.7. Figure 3.8 shows the electronic structures of ZGNR with the number of zigzag molecular chains $N = 2, 3, 4$ along $\mathbf{k} = k\mathbf{a}_x$ where $-\pi/\alpha < k < \pi/\alpha$.

With these simple models, AGNRs are either metallic or semiconducting depending on their widths, and ZGNRs are always metallic regardless of the width (Nakada et al. 1996). The bandgap of semiconducting AGNRs decreases as a function of increasing widths as shown in Figure 3.9. The plot of calculated bandgap of AGNRs versus $N$ exhibits three distinct family behaviors that can be separated into three different categories as $N = 3p$, $3p + 1$, and $3p + 2$ (where $p$ is positive integer). AGNR could be metallic if $N = 3p + 2$ and be semiconducting for $N = 3p$ or $N = 3p + 1$. From these simple models, the bandgap of ZGNR and AGNR with $N = 3p + 2$
The bandgap of AGNR with \( N = 3p \) and \( N = 3p + 1 \) is comparable for the same \( p \). However, the results from these simple tight-binding models are different from the first-principles calculations or higher-level calculation methods and there are no metallic GNRs. The discrepancies are due mainly to the different behaviors of chemical bonding at the edges of ribbons which cannot be described by a single hopping integral \( t \). To be more realistic, the edge atoms of GNRs are passivated by some atoms or molecules so that the hopping integrals and the onsite energies of atoms at the edges would be different from the atoms in the middle of the GNRs. Such effects would reduce the bonding distances between atoms at the edges and induce approximately 12% increase in the hopping integral between \( \pi \)-orbitals (Son et al. 2006). The correction to tight-binding models could be done by replacing the hopping integral of atoms at the edges with \( (1 + \delta)t \) where \( \delta = 0.12 \). The onsite energy of atoms at

**FIGURE 3.7** Band structures of armchair GNRs (in the range of \(-\pi/a < k < \pi/a\)) for the number of dimer lines \( N = 3, 4, 5 \) without the correction \( \delta = 0 \) and with the correction \( \delta = 0.12 \) to the hopping parameter \( t \) are indicated by black and gray solid curves, respectively. The onsite energy \( \epsilon = 0 \) and the hopping integral \( t = -2.7 \) eV are used in tight-binding calculations. The horizontal line at 0 eV could be considered as the Fermi level.

**FIGURE 3.8** Band structures of zigzag GNRs (in the range of \(-\pi/a < k < \pi/a\)) for the number of zigzag molecular chains \( N = 2, 3, 4 \) without the correction \( \epsilon_{a} = \epsilon_{b} = 0 \) and with the correction \( \epsilon_{a} = -\epsilon_{b} = 0.25 \) eV to the onsite energies of atoms at the edges are indicated by black and gray solid curves, respectively. The onsite energy \( \epsilon = 0 \) and the hopping integral \( t = -2.7 \) eV are used for other terms in tight-binding calculations. The horizontal line at 0 eV could be considered as the Fermi level.

**FIGURE 3.9** Bandgap of armchair GNRs as a function of width calculated from simple tight-binding models with the hopping integral \( t = -2.7 \) eV (square symbol) and with the correction \( \delta = 0.12 \) to the hopping parameter \( t \) (circle symbol).
the edges could be defined by an additional parameter $\varepsilon_\delta$. However, from previous study, there is no contribution from the variation in the onsite energies ($\varepsilon_\delta$) at the edges to the first order (Son et al. 2006), so we can use $\varepsilon_\delta = \varepsilon = 0$. With these corrections, the Hamiltonian matrix of AGNR with $N = 3$ is given by

$$
\hat{H}(k) = \begin{pmatrix}
\varepsilon_\delta & (1 + \delta)t & 0 & 0 & 0 \\
(1 + \delta)t & \varepsilon_\delta & t & 0 & 0 \\
0 & t & \varepsilon & t e^{-tk_a} & 0 \\
t & 0 & \varepsilon & t e^{-tk_a} & 0 \\
0 & 0 & 0 & t & \varepsilon_\delta (1 + \delta)t \\
0 & 0 & t & 0 & (1 + \delta)t \varepsilon_\delta \\
\end{pmatrix}
$$

(3.73)

Similarly, the Hamiltonian matrix of AGNR for larger $N$ ($N = 4$ and so on) could be obtained in the same manner. For example, the Hamiltonian matrix of AGNR with $N = 4$ is given by

$$
\hat{H}(k) = \begin{pmatrix}
\varepsilon_\delta & (1 + \delta)t & 0 & 0 & 0 & 0 & 0 & 0 \\
(1 + \delta)t & \varepsilon_\delta & t & 0 & 0 & 0 & 0 & 0 \\
0 & t & \varepsilon & t e^{-tk_a} & 0 & t & 0 & 0 \\
0 & t & \varepsilon & t e^{-tk_a} & 0 & t & 0 & 0 \\
0 & 0 & 0 & t & \varepsilon & t & 0 & 0 \\
0 & 0 & t & 0 & \varepsilon & t & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & t & \varepsilon_\delta (1 + \delta)t e^{-tk_a} & 0 \\
0 & 0 & 0 & 0 & 0 & t & 0 & \varepsilon_\delta (1 + \delta)t e^{-tk_a} \\
\end{pmatrix}
$$

(3.74)

The band structures of AGNR with $N = 3, 4, 5$ are shown in Figure 3.7. It clearly shows how the electronic structures change with an additional parameter $\delta$. The correction to hopping integral of atoms at the edges is strongly correlated to the lift of the doubly degenerate states at the zone edge ($\pi/a$ or $\pi/a$) for $N = 3, 5$ and at the crossing bands for $N = 4, 5$. This correction creates bandgap for AGNR with $N = 5$ or group of AGNRs with $N = 3p + 2$. The variation of bandgaps of AGNRs with correction to the hopping integral of atoms at the edges is shown in Figure 3.9. All AGNRs are now semiconductors with bandgaps that decrease as a function of ribbon width.

With the correction to atoms at the edges, the Hamiltonian matrix of ZGNR with $N = 2$ is given by

$$
\hat{H}(k) = \begin{pmatrix}
\varepsilon_a & t(1 + e^{-ik a_1}) & 0 & 0 \\
t(1 + e^{-ik a_1}) & \varepsilon & t & 0 \\
0 & t & \varepsilon & t(1 + e^{ik a_1}) \\
0 & 0 & t(1 + e^{ik a_1}) & \varepsilon_\beta \\
\end{pmatrix}
$$

(3.75)

Since the atoms on opposite edge of ZGNRs belong to different sublattices, the onsite energy of atoms at the edges could be defined separately as $\varepsilon_a$ and $\varepsilon_\beta$ for sublattices $A$ and $B$, respectively. Similarly, the Hamiltonian matrix of ZGNR for larger $N$ ($N = 3$ and so on) could be obtained in the same manner. For example, the Hamiltonian matrix of ZGNR with $N = 3$ is given by

$$
\hat{H}(k) = \begin{pmatrix}
\varepsilon_a & t(1 + e^{-ik a_1}) & 0 & 0 \\
t(1 + e^{ik a_1}) & \varepsilon & t & 0 \\
0 & t & \varepsilon & t(1 + e^{-ik a_1}) \\
0 & 0 & t & t(1 + e^{-ik a_1}) \varepsilon_\beta \\
\end{pmatrix}
$$

(3.76)

If the $\varepsilon_a = \varepsilon_\beta = \varepsilon$, ZGNRs are always metallic as shown in Figure 3.8. The first-order correction can be made by using different values for $\varepsilon_a$ and $\varepsilon_\beta$. From first-principles calculations based on density functional theory (DFT) (Fujita et al. 1996), it has been shown that ZGNRs are semiconductors, and they present spin-polarized edges. This opens up bandgap of ZGNR, which can be investigated by setting value of $\varepsilon_a$ and $\varepsilon_\beta$. This correction lifts the doubly degenerate states at the zone edge ($-\pi/a$ or $\pi/a$) resulting in band gaps for ZGNRs. We can clearly see that the electronic structures around the Fermi level and the zone edges are sensitive to the modification of the edges of GNRs. Especially, for ZGNRs, the onsite energies of atoms at the edges affect specific states around the Fermi level as clearly shown in Figure 3.8. These states mainly belong to the orbitals of atoms at the edges, so-called edge states. The edge states around the Fermi level form flat bands that attribute to a very large density of states at the Fermi level and play a crucial role in the magnetic properties of GNRs (Fujita et al. 1996).

It is interesting to see what would happen if an atom at sublattice $A$ is different from an atom at sublattice $B$, which lifts the inversion symmetry of nanoribbons. Suppose that boron and nitrogen atoms are at sublattices $A$ and $B$, respectively. The tight-binding parameters taken from $h$-BN (Junghawan et al. 2011), that is, the onsite energy of boron $\varepsilon_b = \varepsilon = 3.6$ eV, the onsite energy of nitrogen $\varepsilon_n = \varepsilon_\beta = -1$ eV, and the hopping integral $t = -2.5$ eV, could be used for atoms that are not on the edges of ribbon. Similar to AGNRs, the correction to the hopping integral of atoms at the edges could be done by replacing $t$ with $(1 + \delta)t$. The onsite energies of atoms at sublattices $A$ and $B$ at the edges could be defined by an additional...
parameter $\varepsilon_\alpha$ and $\varepsilon_\beta$, respectively. For armchair boron nitride nanoribbon (ABNR) with $N = 3$, the Hamiltonian matrix is given by

$$
\hat{H}(k) = \begin{bmatrix}
\varepsilon_\alpha & (1+\delta)t & 0 & t & 0 & 0 \\
(1+\delta)t & \varepsilon_\beta & t & 0 & 0 & 0 \\
0 & t & \varepsilon_\alpha & e^{-i k a_2} & 0 & t \\
0 & t & 0 & \varepsilon_\alpha & (1+\delta)t & \varepsilon_\beta \\
0 & 0 & t & 0 & (1+\delta)t & e^{-i k a_2} \\
0 & 0 & t & 0 & (1+\delta)t & e^{-i k a_2} \\
\end{bmatrix}
$$

(3.77)

Similarly, the Hamiltonian matrix of ABNR for larger $N$ ($N = 4$ and so on) could be obtained in the same manner. For example, the Hamiltonian matrix of ABNR with $N = 4$ is given by

$$
\hat{H}(k) = \begin{bmatrix}
\varepsilon_\alpha & (1+\delta)t & 0 & t & 0 & 0 \\
(1+\delta)t & \varepsilon_\beta & t & 0 & 0 & 0 \\
0 & t & \varepsilon_\alpha & e^{-i k a_2} & 0 & t \\
0 & t & 0 & \varepsilon_\alpha & (1+\delta)t & \varepsilon_\beta \\
0 & 0 & t & 0 & (1+\delta)t & e^{-i k a_2} \\
0 & 0 & t & 0 & (1+\delta)t & e^{-i k a_2} \\
\end{bmatrix}
$$

(3.78)

The band structures of ABNR with $N = 3, 4, 5$ are shown in Figure 3.10. The splitting of doubly degenerate states and crossing bands caused by parameter $\delta$ is similar to the case of AGNRs. For zigzag boron nitride nanoribbons (ZBNR), the Hamiltonian matrix for ZBNR with $N = 2$ is given by

$$
\hat{H}(k) = \begin{bmatrix}
\varepsilon_\alpha & t(1+e^{-i k a_1}) & 0 & 0 \\
t(1+e^{i k a_1}) & \varepsilon_\beta & t & 0 \\
0 & t & \varepsilon_\alpha & t(1+e^{i k a_1}) \\
0 & 0 & t & \varepsilon_\beta \\
\end{bmatrix}
$$

(3.79)

Similarly, the Hamiltonian matrix of ZBNR for larger $N$ ($N = 3$ and so on) could be obtained in the same manner. For example, the Hamiltonian matrix of ZBNR with $N = 3$ is given by

$$
\hat{H}(k) = \begin{bmatrix}
\varepsilon_\alpha & t(1+e^{-i k a_1}) & 0 & 0 \\
t(1+e^{i k a_1}) & \varepsilon_\beta & t & 0 \\
0 & t & \varepsilon_\alpha & t(1+e^{i k a_1}) \\
0 & 0 & t & \varepsilon_\beta \\
\end{bmatrix}
$$

(3.80)

The band structures of ZBNR with $N = 2, 3, 4$ are shown in Figure 3.11. This type of nanoribbons shows interesting
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features of the electronic structures that depend on onsite energies at the edges (\(\epsilon_a\) or \(\epsilon_b\)). If the onsite energy is stronger (more positive or more negative) than the onsite energy of middle atom, the extrema of valence band or conduction band (depending on the sign of onsite energy) are slightly shifted away from the zone edge (\(-\pi/a\) or \(\pi/a\)). For example, if the onsite energies of atoms at the edges are increased by 20% that are \(\epsilon_a = 1.2\epsilon_A\) and \(\epsilon_b = 1.2\epsilon_B\), the valence band maximum and the conduction band minimum are shifted about \(\pi/4a\) from the zone edge as shown by black solid line in Figure 3.11. If the onsite energies of atoms at the edges are decreased by 20% that are \(\epsilon_a = 0.8\epsilon_A\) and \(\epsilon_b = 0.8\epsilon_B\), the flat bands of the valence band and the conduction band near the zone edges are changed. The flat bands at the zone edges are significantly changed due to edge modification which implies that these states would be highly localized on atoms at the edges. Therefore, the modification of nanoribbon edges by some foreign atoms or molecules could manipulate the edge states and the properties of nanoribbons. The boundary regions play an important role so the edge effects influence strongly the \(\pi\) electron states near the Fermi level.

3.5 ATOMIC ARRANGEMENT AND ITS EFFECTS ON ELECTRONIC STRUCTURES OF GRAPHENE: A CASE OF GRAPHENE/BORON NITRIDE SHEET SUPERLATTICES

An approach for modification of GNR edges and manipulation of the properties of GNRs is forming an SL structure between graphene and boron nitride (BN). A SL structure is formed by mixing graphene and BN with different stripe widths (number of molecular chains). The simple models of the two most relevant orientations of the SLs, that is, zigzag (Z) or armchair (A) molecular chains, are shown in Figures 3.12 and 3.13, respectively. The zigzag and armchair SLs with one alternating chain are referred as 1Z and 1A, respectively. A corresponding SL structure (for 1Z or 1A) with inversion symmetry could be modeled by doubling the supercell and swap the atomic types in one of the stripes as illustrated in Figures 3.12 (1Z) and 3.13 (1A). Other SL structures of graphene and BN with different number of stripe widths could be modeled in the same manner. Based on nearest-neighbor tight-binding model, there are three possible onsite energy values \(\epsilon_C, \epsilon_B,\) and \(\epsilon_N\). In addition, there are four hopping integrals \(t_{CC}, t_{CB}, t_{CN},\) and \(t_{BN}\). These seven parameters (three onsite energies and four hopping integrals) could be adjusted or fitted to reproduce certain properties from first-principles calculations. One of the advantage of tight-binding model is that the contribution from each parameter could be examined by adjusting its value and

![FIGURE 3.11](image)

**FIGURE 3.11** Band structures of zigzag boron nitride nanoribbons (in the range of \(-\pi/a < k < \pi/a\)) for the number of zigzag molecular chains \(N = 2, 3, 4\) without the correction \(\epsilon_a = \epsilon_b = 0\) (gray solid curves), and with the correction to the onsite energies of atoms at the edges if the onsite energies of atoms at the edges are increased by 20% (black solid curves) or decreased by 20% (dashed curves). Suppose that boron and nitrogen atoms are at sublattices A and B, respectively. The onsite energies \(\epsilon_a = 3.6\) eV, \(\epsilon_b = -1\) eV, and the hopping integral \(t = -2.5\) eV are used in tight-binding calculations. The horizontal line at 0 eV could be considered as the Fermi level.

![FIGURE 3.12](image)

**FIGURE 3.12** Zigzag superlattices with one alternating molecular chain, 1Z and 1Zi. The gray, dark gray, and black spheres represent B, N, and C atoms, with light gray highlighting the graphene stripe. The first BZ of 1Z structure is shown together with the primitive hexagonal BZ. The gray line shows the first BZ of 1Zi structure. The inversion center is marked by asterisks.
inspecting the change of electronic structures. The general form of the Hamiltonian matrix is

$$\hat{H}(\mathbf{k}) = \begin{bmatrix}
H_{11}(\mathbf{k}) & H_{12}(\mathbf{k}) & \cdots & H_{1N}(\mathbf{k}) \\
H_{21}(\mathbf{k}) & H_{22}(\mathbf{k}) & \cdots & H_{2N}(\mathbf{k}) \\
\vdots & \vdots & \ddots & \vdots \\
H_{N1}(\mathbf{k}) & H_{N2}(\mathbf{k}) & \cdots & H_{NN}(\mathbf{k})
\end{bmatrix}$$

(3.81)

The Hamiltonian matrix is Hermitian matrix, so we can explicitly write down only the upper triangular elements. The Hamiltonian matrix with nearest-neighbor interactions for 1Z SL is given by

$$\hat{H}(\mathbf{k}) = \begin{bmatrix}
\varepsilon_C & t_{CC}(1 + e^{-i\mathbf{k}\cdot \mathbf{a}_1}) & 0 & t_{CN}e^{-i\mathbf{k}\cdot \mathbf{a}_2} \\
t_{CC}(1 + e^{i\mathbf{k}\cdot \mathbf{a}_1}) & \varepsilon_C & t_{CB} & 0 \\
0 & t_{CB} & \varepsilon_B & t_{BN}(1 + e^{i\mathbf{k}\cdot \mathbf{a}_1}) \\
0 & 0 & t_{BN}(1 + e^{-i\mathbf{k}\cdot \mathbf{a}_1}) & \varepsilon_N
\end{bmatrix}$$

(3.82)

where the upper triangular elements are

$$H_{11} = \varepsilon_C, H_{12} = t_{CC}(1 + e^{-i\mathbf{k}\cdot \mathbf{a}_1}), H_{13} = t_{CN}e^{-i\mathbf{k}\cdot \mathbf{a}_2},$$
$$H_{22} = \varepsilon_C, H_{23} = t_{CB},$$
$$H_{33} = \varepsilon_B, H_{34} = t_{BN}(1 + e^{i\mathbf{k}\cdot \mathbf{a}_1}),$$
$$H_{44} = \varepsilon_N.$$

(4.83)

The Hamiltonian matrix for 1Zi SL is given by

$$H_{11} = \varepsilon_C, H_{12} = t_{CC}(1 + e^{-i\mathbf{k}\cdot \mathbf{a}_1}), H_{13} = t_{CN}e^{-i\mathbf{k}\cdot \mathbf{a}_2},$$
$$H_{22} = \varepsilon_C, H_{23} = t_{CN},$$
$$H_{33} = \varepsilon_N, H_{34} = t_{BN}(1 + e^{i\mathbf{k}\cdot \mathbf{a}_1}),$$
$$H_{44} = \varepsilon_B, H_{45} = t_{CB},$$
$$H_{55} = \varepsilon_C, H_{56} = t_{CC}(1 + e^{i\mathbf{k}\cdot \mathbf{a}_1}),$$
$$H_{66} = \varepsilon_C, H_{67} = t_{CB},$$
$$H_{77} = \varepsilon_B, H_{78} = t_{BN}(1 + e^{-i\mathbf{k}\cdot \mathbf{a}_1}),$$
$$H_{88} = \varepsilon_N.$$

(3.84)

The Hamiltonian matrix for 1A SL is given by

$$H_{11} = \varepsilon_C, H_{12} = H_{14} = t_{CC}, H_{18} = t_{CN}e^{-i\mathbf{k}\cdot \mathbf{a}_2},$$
$$H_{22} = \varepsilon_C, H_{23} = t_{CC}, H_{27} = t_{CB}e^{-i\mathbf{k}\cdot \mathbf{a}_2},$$
$$H_{33} = \varepsilon_C, H_{34} = t_{CC}e^{-i\mathbf{k}\cdot \mathbf{a}_2}, H_{36} = t_{CN},$$
$$H_{44} = \varepsilon_C, H_{45} = t_{CB},$$
$$H_{55} = \varepsilon_B, H_{56} = H_{58} = t_{BN},$$
$$H_{66} = \varepsilon_N, H_{67} = t_{BN},$$
$$H_{77} = \varepsilon_B, H_{78} = t_{BN}e^{-i\mathbf{k}\cdot \mathbf{a}_2},$$
$$H_{88} = \varepsilon_N.$$

(3.85)

The Hamiltonian matrix for 1Ai SL is given by

$$H_{11} = \varepsilon_C, H_{12} = H_{14} = t_{CC}, H_{16} = t_{CN}e^{-i\mathbf{k}\cdot \mathbf{a}_2},$$
$$H_{22} = \varepsilon_C, H_{23} = t_{CC}, H_{25} = t_{CB}e^{-i\mathbf{k}\cdot \mathbf{a}_2},$$
$$H_{33} = \varepsilon_C, H_{34} = t_{CC}e^{-i\mathbf{k}\cdot \mathbf{a}_2}, H_{36} = t_{CB},$$
$$H_{44} = \varepsilon_C, H_{45} = t_{CN},$$
$$H_{55} = \varepsilon_N, H_{56} = H_{58} = t_{BN},$$
$$H_{66} = \varepsilon_B, H_{67} = t_{BN},$$
$$H_{77} = \varepsilon_N, H_{78} = t_{BN}e^{-i\mathbf{k}\cdot \mathbf{a}_2}, H_{79} = t_{CB},$$
$$H_{88} = \varepsilon_N.$$

(3.86)

To start with the fitting, one would optimize all three onsite energies ($\varepsilon_C, \varepsilon_B, \text{and } \varepsilon_N$) and two of the hopping integrals ($t_{CC}$ and $t_{BN}$) to reproduce the $\pi$ band and bandgap of graphene.
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and BN obtained from experimental data or first-principles calculations. Then these five parameters would be kept fixed while the remaining two hopping integrals \( t_{CB} \) and \( t_{CN} \) are optimized, to reproduce the \( \pi \) band near the Fermi level, or adjusted, to gain qualitative interpretation, for each SL. First, \( \varepsilon_c \) is set to zero and \( t_{CC} \) is optimized (optimized value is \( t_{CC} = -2.7 \text{ eV} \)) to reproduce the \( \pi_{CC} \) band of graphene (Figure 3.2). Second, \( \varepsilon_b \), \( \varepsilon_N \), and \( t_{BS} \) are optimized (optimized values are \( \varepsilon_b = 3.6 \text{ eV}, \varepsilon_N = -1 \text{ eV}, \text{ and } t_{BS} = -2.5 \text{ eV} \)) to reproduce the \( \pi_{BN} \) band and bandgap of BN (Figure 3.2) (Jungthawan et al. 2011). In order to investigate the effects of the bonding at the edges, \( t_{CB} \) and \( t_{CN} \) are set to zero, that is, turning off the interactions between C–B and C–N at the edges. By diagonalizing the Hamiltonian matrix (Equations 3.83 through 3.86), one obtains the dispersion relation for the case of non-interacting edges as shown in Figures 3.14b and 3.15b for zigzag and armchair SLs, respectively.

The electronic structure of 1Z and 1Zi SLs can be viewed as a combination of electronic structures of the corresponding width ZGNR and ZBNR. In Figure 3.14b, the bands of graphene domain have closed bandgap and the bands of BN domain have wide bandgaps. Because the ZBNR has a wide bandgap, the electronic structure from the ZGNR plays the dominant roles near the band edges. To gain qualitative interpretation, we can turn on and adjust the interactions between C–B and C–N at the edges. When the hopping integrals \( t_{CB} \) and \( t_{CN} \) are turned on, we can optimize the bands to fit the first-principles calculations or adjust the bands to investigate the effect of each interaction to the electronic structures. The hopping integrals \( t_{CB} \) and \( t_{CN} \) lift the degeneracy of the ZGNR edge states at \( x \) where \( t_{CB} \) (or \( t_{CN} \)) allows a coupling of energy levels between C and B (or N) at the edges. The coupled \( \pi \)-states are split into C–B (or C–N) bonding state (\( \pi_{CB} \) or \( \pi_{CN} \)) and antibonding state (\( \pi_{CB}^{\ast} \) or \( \pi_{CN}^{\ast} \)), as shown in Figure 3.14a for 1Z SL and Figure 3.14c for 1Zi SL. The \( \pi_{CB} \) and \( \pi_{CB}^{\ast} \) states (coupled \( \pi_{CC} \) and \( \pi_{CC}^{\ast} \) states) are located above \( \pi_{CN} \) and \( \pi_{CN}^{\ast} \) (coupled \( \pi_{BN} \) and \( \pi_{BN}^{\ast} \) states), respectively. As a result, the \( \pi_{CB} \) and \( \pi_{CN} \) states become valence band maximum and conduction band minimum states, respectively. For 1Z SL, the difference between the two graphene edges breaks the symmetry, leading to bandgap opening. In contrast, for 1Zi SL, the two edges of any graphene stripe are identical because of the inversion symmetry. As a result, C–B and C–N edge states can cross, leading to a closed bandgap. Note that the optimized values of \( t_{CB} \) and \( t_{CN} \) to fit the first-principles calculations for 1Z and 1Zi are \( t_{CB} = -2.1 \text{ eV} \) and \( t_{CN} = -2.3 \text{ eV} \), and \( t_{CB} = -1.8 \text{ eV} \) and \( t_{CN} = -1.0 \text{ eV} \), respectively. The optimized values are quite different, indicating that they are not very transferable.

In the previous section, we have demonstrated that within nearest-neighbor tight-binding model, AGNRs are either metallic or semiconducting depending on their widths, which are defined by the number of dimer lines \( N \). The bandgap of AGNRs is categorized into three distinct groups as \( N = 3p, 3p + 1, \text{ and } 3p + 2 \) (where \( p \) is integer). AGNR could be metallic if \( N = 3p + 2 \) and be semiconducting for \( N = 3p \) or \( N = 3p + 1 \). From these simple models, the bandgap of ZGNR and AGNR with \( N = 3p + 2 \) are always zero. The bandgap of AGNR with \( N = 3p \) and \( N = 3p + 1 \) is comparable for the same \( p \), so that 1A and 1Ai SLs have a graphene domain width equal to the closed bandgap AGNRs. On the other hand, ABNRs always have wide bandgap. The electronic structures of 1A and 1Ai SLs can be considered as a combination of the electronic structures of the corresponding width AGNR and ABNR as shown in Figure 3.15b. Since the ABNR has a wide bandgap, the electronic structure from the graphene stripe plays a dominant role near the band edges. When the hopping integrals \( t_{CB} \) and \( t_{CN} \) are turned on, the interactions

![Figure 3.14](image-url)

**FIGURE 3.14** Calculated \( \pi \) and \( \pi^{\ast} \) bands of 1Z (a) and 1Zi (c) based on a tight-binding method (gray solid curves) in comparison with the band structures obtained from first-principles calculations (black dashed curves) (Jungthawan et al. 2011). The tight-binding bands calculated without interactions between graphene and BN stripes (\( t_{CB} \) and \( t_{CN} \) are set to zero) for 1Z (b) are shown. The band edge states are shown using gray and dark gray dashed curves. The unit of tight-binding parameters is eV.
at the ribbon edges open up the bandgap, as shown in Figure 3.15a for 1A SL, by allowing couplings between AGNR and ABNR at the edges that lift the degeneracy between $\pi_{CC}$ and $\pi^*_{CC}$ state. In armchair SLs, each edge contains an equal number of C–B and C–N bonds. This leads to a mixed C–B and C–N character at each band edge, with energy levels comparable to those of the graphene states ($\pi_{CC}$ and $\pi^*_{CC}$) causing the splitting of AGNR state. The bandgap opening effect is reduced by the inversion symmetry as can be seen in Figure 3.15c for 1A$i$ SL, where the splitting of AGNR state is less than the reduction by the inversion symmetry. As a result, the crossing by the inversion symmetry is observed. Note that the optimized values of $t_{CB}$ and $t_{CN}$ to fit the first-principles calculations for 1A and 1A$i$ are $t_{CB} = -2.1$ eV and $t_{CN} = -1.6$ eV, and $t_{CB} = -3.1$ eV and $t_{CN} = -1.7$ eV, respectively. The orientation and ordering play crucial roles in the electronic structure of SLs. The electronic structures reveal particular states that are sensitive to the detailed arrangement of constituents.

3.6 ENUMERATION METHOD TO GENERATE GRAPHENE–ALLOY CONFIGURATIONS: A CASE OF GRAPHENE/BORON NITRIDE ALLOYS

A systematic enumeration method to generate graphene–alloy configurations can be performed by the algorithm for generating superstructures based on Hart and Forcade (2008). The tight-binding method can be used to calculate or estimate the electronic structures of those configurations. Under nonequilibrium growth condition, whereas some atomic configuration can be controlled, the properties of graphene can be modified by forming nanostructure or changing atomic arrangement. In order to understand the properties of graphene, the tight-binding method is a simple and an effective approach to understand the underlying mechanism of the change of properties due to atomic arrangement. The configurations of graphene–alloy compounds could be generated by Alloy Theoretic Automated Toolkit (ATAT) (van de Walle 2009; van de Walle et al. 2002). As a representative case, we will discuss about the atomic arrangement of single-sheet graphene/BN alloys with the BC$_2$N stoichiometric ratio ($1-BC_2N$). The number of configurations

![FIGURE 3.15](image_url) The calculated $\pi$ and $\pi^*$ bands of 1A (a) and 1A$i$ (c) based on a tight-binding method (gray solid curves) in comparison with the band structures obtained from first-principles calculations (black dashed curves) (Jungthawan et al. 2011). The tight-binding bands calculated without interactions between graphene and BN stripes ($t_{CB}$ and $t_{CN}$ are set to zero) for 1A (b) are shown. The band edge states are shown using gray and dark gray dashed curves. The unit of tight-binding parameters is eV.

![FIGURE 3.16](image_url) Unique unit cell shapes found by ATAT. The 4/8 atoms cell is indicated by gray solid line/dark gray dashed line, respectively. The smallest supercell (16 atoms) containing all structures is indicated by dark gray solid line. The numerical values in the unit cells indicate atomic position corresponding to the bases listed in Table 3.2.
and cell shapes generated by ATAT for $1 - \text{BC}_2\text{N}$ with up to 8 atoms in a unit cell are $6 + 236$ configurations (6 and 236 configurations for 4 and 8 atoms in a unit cell, respectively) and 2 + 5 cell shapes. There are a number of equivalent configurations (some of the configurations can be represented by more than one unit cell). Previous theoretical works showed that $1 - \text{BC}_2\text{N}$ compounds disfavor B–B and N–N neighboring (Blase 2000; Blase et al. 1999; Liu et al. 1989), and hence the configurations having such disfavored bonds can be discarded.

After exclusion of the redundant configurations that are the configurations with disfavor bonds or repetitive configurations (i.e., some of configurations can be represented by more than one unit cell), the total number of unique configurations is $3 + 43$ configurations from $1 + 3$ unique unit cells.

The four unique unit cells are illustrated in Figure 3.16. For each unit cell, the lattice vectors and bases are tabulated in Table 3.2. The smallest supercell containing all these structures is 16 atoms cell with lattice vectors of $a_1 = 2a\hat{x}$ and $a_2 = 2\sqrt{3}a\hat{y}$ in Cartesian coordinate. This supercell contains roughly $3^{16}$ structures including 900, 900 structures of $1 - \text{BC}_2\text{N}$. A unit cell with 8 atoms contains roughly $3^8$ structures (420 structures are $1 - \text{BC}_2\text{N}$). It is clearly shown that most of the structures are equivalent and only 46 representative structures belong to the four unique unit cells. The direct enumeration approach to generate alloy configurations is vastly efficient. The method provides a practical number of configurations (irreducible representation), which are computationally feasible for comprehensive study by first-principles calculations or for qualitative study by tight-binding method.

In Table 3.2, the atomic position of each configuration can be obtained by converting configuration number from base-10 ($n_{10}$) to base-3 ($n_3$) number. The digits 0, 1, and 2 correspond to C, B, and N. For instance, the configuration $57_{10}$ (20103) is a 4-atoms configuration containing two C at (1/2, $\sqrt{3}/2$) and (1/2, $\sqrt{3}/2$), one B at (1/2, 5/6), and one N at (1, $\sqrt{3}$). The calculation by tight-binding method can be performed similarly to the previous section.

### ACKNOWLEDGMENTS

This work has been supported by the Thailand Research Fund (TRF) under the TRF Senior Research Scholar (Grant No. RTA5680008) and the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its program of Center of Excellence Network. S. Junghawack acknowledges financial support from the TRF and Suranaree University of Technology (Grant No. TRG5680092).

### REFERENCES


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**Table 3.2**

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<tr>
<th>Cell Shape</th>
<th>Lattice Vectors (in Unit of a)</th>
<th>Bases (in Unit of a)</th>
<th>Configuration Number ($n_{10}$)</th>
<th>Number of Configuration</th>
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<td>(1/2, 5/6)</td>
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<td></td>
<td></td>
<td>(1/2, $\sqrt{3}/2$)</td>
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</tr>
<tr>
<td>8-I</td>
<td>(1, $\sqrt{3}$)</td>
<td>(1/2, 1/6)</td>
<td>318, 396, 1746, 1800</td>
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<td>(1/2, $\sqrt{3}/2$)</td>
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<td>(1, 0)</td>
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**Note:** The atomic ordering for each unit cell is indicated by base-10 number. The actual position is obtained by converting configuration number to base-3 number (see text). The lowest four energetic configurations are underlined.


