§5.5 Graphene and Carbon Nanotubes (CNT)

New concept:

Tight-Binding Approximation: the construction of Electron wavefunction is calculated by using the linear combination of atomic orbits (LCAO) method

\( \Phi_n(\vec{r} - \vec{R}_j) \) represents the atomic orbital wavefunction centered at lattice site \( \vec{R}_j \). (\( \vec{r} \) is the location of electron)

Then the wavefunction of the Crystal orbit \( \Psi_k(\vec{r}) \):

\[
\Psi_k(\vec{r}) = \sum_j C_{jk} e^{i \vec{k} \cdot \vec{R}_j} \Phi_n(\vec{r} - \vec{R}_j)
\]

Where \( C_{jk} \) must satisfy the Bloch Condition

\[
C_{jk} = e^{i \vec{k} \cdot \vec{R}_j}
\]
So, \( \Psi_{k}(\vec{r}) = \frac{1}{V} e^{i \vec{k} \cdot \vec{r}} \phi_{n}(\vec{r} - \vec{R}_j) \)
\[= e^{i \vec{k} \cdot \vec{r}} \frac{1}{V} e^{-i \vec{k} \cdot (\vec{R}_j - \vec{R}_i)} \phi_{n}(\vec{R}_j - \vec{R}_i) \]

\( \therefore \Psi_{k}(\vec{r}) = e^{i \vec{k} \cdot \vec{r}} U_{k,n}(\vec{r}) \Rightarrow \text{Block Condition} \)

[This is resulted by the periodicity of the crystal lattice]

or more precisely,
\( \Psi_{k}(\vec{r}) = \frac{1}{\sqrt{NV}} \sum_{j} e^{i \vec{k} \cdot \vec{r}} \phi_{n}(\vec{R}_j - \vec{R}_i) \)

remember: \( \int \phi_{n}^{*}(\vec{r} - \vec{R}_j) \phi_{n}(\vec{r} - \vec{R}_i) \, dr^3 = \delta_{ij} \)

orthogonal
we can always find $E_k = \int \hat{H} \phi_n \phi_n \, d\tau$

$$E_k = \left( \frac{1}{N^2} \right) \left\{ \sum_{i} \frac{\hbar^2}{2m} \left( \vec{r}_j - \vec{R}_i \right) \phi_i^{*}(\vec{r} - \vec{R}_i) \left\{-\frac{\hbar^2}{2m} \vec{r}^2 + V_{n0}(\vec{r} - \vec{R}_i) \right\} \phi_n(\vec{r} - \vec{R}_i) \, d\tau \right\}$$

$$+ \left\{ \sum_{i} \frac{\hbar^2}{2m} \left( \vec{r}_j - \vec{R}_i \right) \phi_i^{*}(\vec{r} - \vec{R}_i) V(\vec{r} - \vec{R}_i) \phi_n(\vec{r} - \vec{R}_i) \, d\tau \right\}$$

Where $-\frac{\hbar^2}{2m} \vec{r}^2$ is the kinetic energy of electron

$V_{n0}(\vec{r} - \vec{R}_i)$ is the potential of the master atom (the atom owning the electron)

$V(\vec{r} - \vec{R}_i)$ is from the neighbor atoms

In Quantum mechanics, we can treat $V(\vec{r} - \vec{R}_i)$ as the perturbation potential

$$H_0 = -\frac{\hbar^2}{2m} \vec{r}^2 + V_{n0}(\vec{r} - \vec{R}_i) \text{ is the unperturbed term.}$$
Therefore \( E_k = E_{n_0} - \alpha_n - \beta_n \frac{z}{R_{ij}} e^{i \vec{r} \cdot \vec{R}_{ij}} \)

\[
E_{n_0} = \frac{1}{NV} \int \phi_n^*(R_i) \left[ -\frac{\hbar^2}{2m} \nabla^2 + U_{n_0} \right] \phi_n(R_i) \, d^3r
\]

\( \alpha_n = -\int \phi_n^*(\vec{r} - \vec{R}_i) \nabla \phi_n(\vec{r} - \vec{R}_i) \, d^3r \)

\( \beta_n = -\int \phi_n^*(\vec{r} - \vec{R}_j) \nabla \phi_n(\vec{r} - \vec{R}_j) \phi_n(\vec{r} - \vec{R}_j) \, d^3r \)

The relationship between \( E_{n_0} \) and \( E_k \) depends on \( R_{ij} = \vec{R}_j - \vec{R}_i \)

Only the nearest atoms will be counted.
5.5.1 Graphene

Two-dimensional crystal lattice
The basis vectors:

\[ \vec{a}_1 = \frac{a}{2}(\sqrt{3}e_x + e_y) \]
\[ \vec{a}_2 = \frac{a}{2}(\sqrt{3}e_x - e_y) \]
\[ a = \sqrt{3}b \]

\[ P = n \vec{a}_1 + m \vec{a}_2 \]  
\[ (4, 1) \]

\( \vec{a}_1 \) basic cell
Selections:

Figure 5.34 Graphene sheet (single layer of graphite). The small circles denote the location of carbon atoms. Lattice basis vectors are \( \vec{a}_1 \) and \( \vec{a}_2 \), as shown.
5.5.1 Graphene

We can select different basis vectors

\[
a_1 = \sqrt{3} a e_x \quad \text{and} \quad a_2 = \frac{\sqrt{3} a}{2} \left( e_x + \sqrt{3} e_y \right)
\]

\[
\begin{align*}
\mathbf{a}_1^* &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{n}}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{n})} \\
\mathbf{a}_2^* &= 2\pi \frac{\mathbf{n} \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{n} \times \mathbf{a}_1)}
\end{align*}
\]

Reciprocal lattice basis vectors

\[
\begin{align*}
\mathbf{a}_1^* &= \frac{2\pi}{\sqrt{3}a} \left( e_x - \frac{e_y}{\sqrt{3}} \right) \quad \text{and} \quad \mathbf{a}_2^* = \frac{4\pi}{3a} e_y.
\end{align*}
\]
Now consider the nearest neighbor atoms
the coordinates of atom 1, 2, 3:

1. \((-b, 0)\)
2. \((\frac{1}{2}b, \frac{\sqrt{3}}{2}b)\) relative to \((0, 0)\)
3. \((\frac{1}{2}b, -\frac{\sqrt{3}}{2}b)\)

or represented by a

\[
\begin{align*}
1. \left(-\frac{\sqrt{3}}{2}a, 0\right) \\
2. \left(\frac{\sqrt{3}}{2}a, \frac{1}{2}a\right) \\
3. \left(\frac{\sqrt{3}}{2}a, -\frac{1}{2}a\right)
\end{align*}
\]

\[E_{n_0} - \alpha n = 0\]

let \(\lambda_0 = \beta n = 3\text{ eV}\)

\[E_k = \lambda_0 \left| \frac{\mu}{\mu_{ij}} \right| e^{i \mathbf{x} \cdot \mathbf{R}_{ij}}\]

\[= \lambda_0 \left| e^{i \frac{\sqrt{3}}{2}ak_x} + e^{i \frac{\sqrt{3}}{2}ak_x} e^{i \frac{1}{2}ak_y} + e^{i \frac{\sqrt{3}}{8}ak_x} e^{-i \frac{1}{2}ak_y} \right|\]
Therefore

\[ E_k = \sqrt{\delta_0 \left| e^{-i \frac{\sqrt{3}}{2} akx} + e^{i \frac{\sqrt{3}}{2} akx} \left( 2 \cos \frac{1}{2}aky \right) \right|^2} \]

\[ = \delta_0 \left| \cos \frac{\sqrt{3}}{2} akx + 2 \cos \frac{\sqrt{3}}{6} akx \cos \frac{1}{2}aky \right| + \left| -\sin \frac{\sqrt{3}}{2} akx + 2 \sin \frac{\sqrt{3}}{6} akx \cos \frac{1}{2}aky \right| \]

\[ = \delta_0 \sqrt{\cos^2 \frac{\sqrt{3}}{2} akx + 4 \cos^2 \frac{\sqrt{3}}{6} akx \cos^2 \frac{1}{2}aky + 4 \cos^2 \frac{\sqrt{3}}{6} akx \cos \frac{1}{2}aky \sin \frac{1}{2}aky + 4 \sin^2 \frac{\sqrt{3}}{6} akx \cos \frac{1}{2}aky \sin \frac{1}{2}aky - 4 \sin \frac{\sqrt{3}}{6} akx \sin \frac{\sqrt{3}}{6} akx \cos \frac{1}{2}aky} \]

\[ = \delta_0 \sqrt{1 + 4 \cos \frac{\sqrt{3}}{2} akx \cos \frac{1}{2}aky + 4 \cos^2 \frac{1}{2}aky} \]
Due to the bonding and anti-bonding bond.

See page 158

\[ E_{\text{crs}} = \pm \phi_0 \sqrt{1 + 4 \cos \frac{\pi}{2} a k_x \cos \frac{\pi}{2} a k_y + 4 \cos^2 \frac{\pi}{2} a k_y} \]

\text{any bandgap?}
When $E(k)$ close to $k$ point

$$E = V_f k$$

$V_f$: Fermi Velocity $\approx 9.7 \times 10^5$ m/s

compared with the massless photon $E = ck_0$

the electrons near the $\pi$-band crossing point $k$
act more like photons than particles with mass,

In this case, the electrons are called Dirac fermions
§5.5.2 Carbon Nanotubes

If we cut the CNT, the ending cross-section is zigzag CNT.

\[ \text{armchair CNT} \]

the other type (not zigzag nor armchair) we call them chiral CNT.

the circumference of the CNT - chiral vector, \( \vec{C}_h \)

\[ \vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \]
5.5.2 Carbon Nanotubes

CNT lattice constant

\( a_{zz} = 3b \)

\( a_{ac} = a = \sqrt{3}b \)

CNT radius:

\[
\frac{|C_h|}{2\pi} = \frac{\sqrt{3}b}{2\pi} \sqrt{n^2 + nm + m^2}
\]

\( C_h = na_1 + ma_2 \)
5.5.2 Carbon Nanotubes

Forming armchair, zigzag, and chiral carbon nanotubes, denoted by the index \((n, m)\).

\[ C_h = n\vec{a}_1 + m\vec{a}_2 \]

CNT radius:

\[ r = \frac{|C_h|}{2\pi} = \frac{\sqrt{3}b}{2\pi} \sqrt{n^2 + nm + m^2} \]

\((n, 0)\) for zigzag CNTs

\((n, n)\) for armchair CNTs

\((n \neq m)\) for chiral CNTs
5.5.2 Carbon Nanotubes

Zigzag CNTs (n, 0)  
\[ a_{zz} = 3b \]

Armchair CNTs (n, n)  
\[ a_{ac} = a = \sqrt{3b} \]

\[ k_{\perp} = k_{x,q} = \frac{2\pi q}{n3b}, \quad \text{--- armchair - CNT} \]
\[ k_{\perp} = k_{y,q} = \frac{2\pi q}{n\sqrt{3b}}, \quad \text{--- Zigzag - CNT} \]

In the transverse direction (radial direction)  
The wavenumber, \( k \), becomes quantized by the finite circumference  
radial direction:  
\[ q\lambda_{\perp} = 2\pi r \]
\[ \text{wavenumber: } k_{\perp} = \frac{2\pi}{\lambda_{\perp}} \]
For armchair CNT
\[ E_{ac}(k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos(\frac{\pi a}{\sqrt{3}}) \cos(\frac{k_y a}{\sqrt{3}}) + 4 \cos^2(\frac{k_y a}{2})} \]
\(-\pi < k_y a < \pi, \; \theta = 1, 2, \ldots, 2n, \; \text{CNT axis} = y-\text{axis}\)

For zigzag CNT
\[ E_{zz}(k_x) = \pm \gamma_0 \sqrt{1 + 4 \cos(\frac{\sqrt{3} k_x a}{2}) \cos(\frac{\pi a}{\sqrt{3}}) + 4 \cos^2(\frac{\pi a}{2})} \]
\(-\pi < k_x a < \pi, \; \theta = 1, 2, \ldots, 2n\)

prove: armchair CNTs are metallic \( (E_g = 0) \)

In general, if \( (2n+m)/3 \) is an integer, the CNT is metallic.

Semiconductor CNT have band gap \( E_g = \frac{5\gamma_0 a}{2\sqrt{3} r} \approx 0.383 \text{ eV} \)

\( dt \) is the CNT radius in nm
5.5 Graphene and Carbon Nanotube devices

- 16 -
5.5 Graphene and Carbon Nanotube devices

- Graphene and Carbon Nanotube devices show promise in various applications due to their unique electrical properties.

- The diagram illustrates the structure of a graphene-based device, highlighting the Source, Gate, and Drain regions.

- The graph on the right shows the relationship between the drain-source voltage ($V_{ds}$) and the drain current ($I_D$) for different gate voltages ($V_g$).

- The image on the bottom left depicts the fabrication process with labels for $V_{DD}$, $V_{g1}$, $V_{g2}$, SET1, SET2, MWNT, and $V_{out}$.

- The right image shows a nanotechnological layout with a CMOS-type 5-stage carbon nanotube ring oscillator and CMOS-type inverter.
Chapter 5 Related knowledge

Semiconductor doping

P dopant, $E_d = 0.044$ eV

B dopant, $E_a = 0.045$ eV
Chapter 5 Related knowledge

Bonding and antibonding band

Figure 5.24 Depiction of combining atomic orbitals of lithium to form molecular states of Li₂. (a) Two Li atoms are brought into close proximity. The atomic s shells interact, forming antibonding (top) and bonding (bottom) molecular orbitals. The 2s¹ electron from each atom will go into the lowest energy state, as depicted in (b).
Chapter 5 Related knowledge

Effect of electric field on energy band

Define the electron flowing from high E position to low E position