

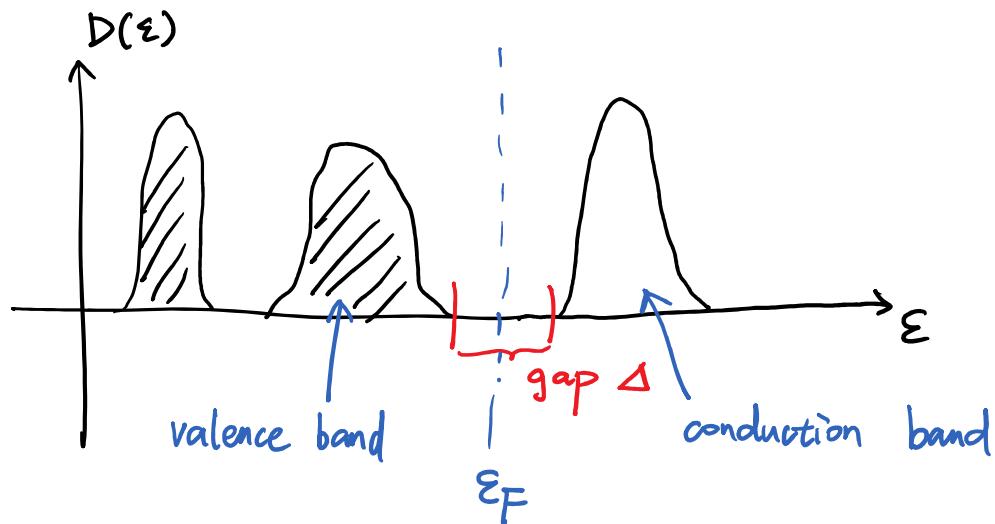
### §3. Band electrons

#### \* Metal, insulator, semiconductor

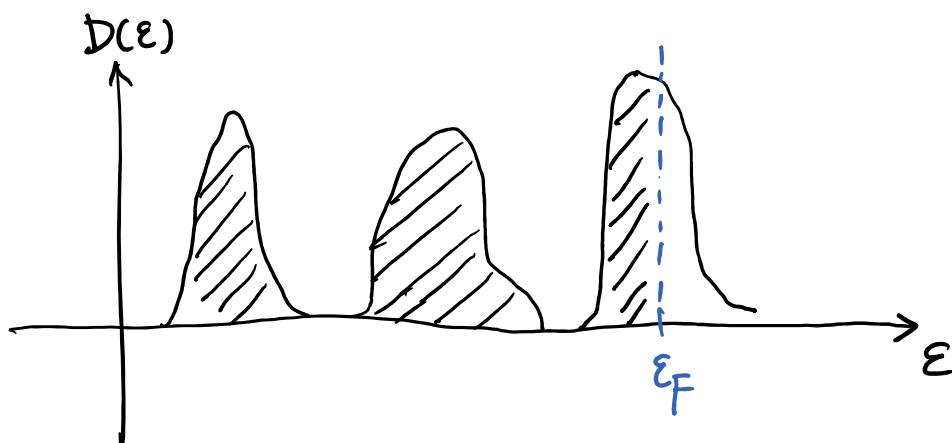
Density of states (DOS) :

$$D(\varepsilon) = 2 \sum_{\vec{k}, n} \delta(\varepsilon - E_n(\vec{k}))$$

Insulator / semiconductor :



Conductor :



Metal: Fermi energy within the band

At least one of the band is partially filled.

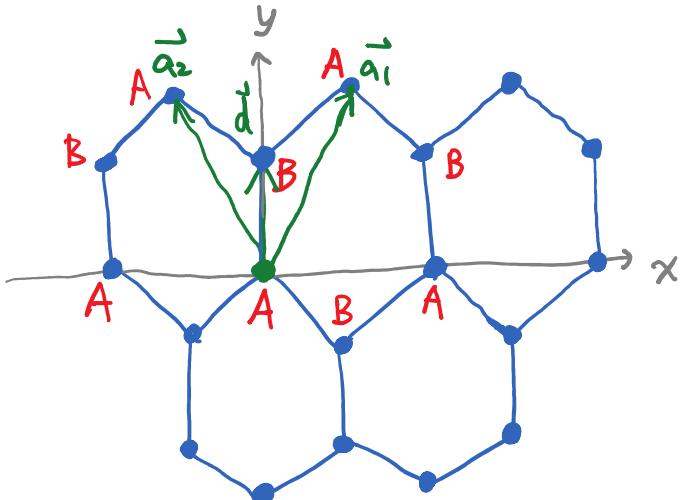
Insulator: Fermi energy within the gap

$T=0$ : Below  $\epsilon_F$  all bands are filled,  
above  $\epsilon_F$  all bands are empty.

Semiconductor: gap small ( $\Delta: 1 \sim 3 \text{ eV}$ )

Thermally activated electrons can occupy  
conduction bands.  $(n \sim e^{-\Delta/k_B T})$

## \* Energy bands in graphene



$$\left\{ \begin{array}{l} \vec{a}_1 = a \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right) \\ \vec{a}_2 = a \left( -\frac{1}{2}, \frac{\sqrt{3}}{2} \right) \end{array} \right.$$

$$a = 2.46 \text{ \AA} = 4.65 a_B$$

$$\vec{d} = a \left( 0, \frac{\sqrt{3}}{3} \right)$$

$$|d| = 1.42 \text{ \AA} = 2.68 a_B$$

Carbon :  $1s^2 \underset{\text{red bracket}}{2s^2} 2p^2$

Orbital energy  $E_{1s} \approx -288.2 \text{ eV}$

$$\left\{ \begin{array}{l} E_{2s} \approx -16.6 \text{ eV} \\ E_{2p} \approx -11.1 \text{ eV} \end{array} \right.$$

The  $1s$  orbital has much lower energy.

The two electrons in  $1s$  orbital are "core" electrons. The band from this orbital is narrow and well below other bands.

So one may think that this band is completely occupied and just ignore it.

Now we use the tight-bind analysis to build a "minimal" model for graphene.

We will use second-quantized formulation:

$$H = \int d\vec{r} \psi_\sigma^+(\vec{r}) \left[ -\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V(\vec{r}) \right] \psi_\sigma(\vec{r})$$

$$\psi_\sigma^+(\vec{r}) = \sum_{j,n} \underbrace{a_n^*(\vec{r} - \vec{R}_j)}_{a_n(\vec{r} - \vec{R}_j)} c_{j,n,\sigma}^+$$

$a_n(\vec{r} - \vec{R}_j)$ : Wannier function

$c_{j,n,\sigma}^+$  creates an electron "near" position  $\vec{R}_j$  with spin  $\sigma$  and "orbital" index  $n$ .

We are essentially expanding  $\psi_\sigma^+(\vec{r})$  by using the Wannier functions, which form complete basis.

$$c_{j,n,\sigma}^+ = \int d\vec{r} a_n(\vec{r} - \vec{R}_j) \psi_\sigma^+(\vec{r})$$

$$\Rightarrow \{c_{j,n,\sigma}, c_{l,n',\sigma'}^+\} = \delta_{jl} \delta_{nn'} \delta_{\sigma\sigma'}$$

Proof: use  $\int d\vec{r} a_n^*(\vec{r} - \vec{R}_j) a_{n'}(\vec{r} - \vec{R}_l) = \delta_{nn'} \delta_{jl}$

$$\{\psi_\sigma(\vec{r}), \psi_\sigma^+(\vec{r}')\} = \delta(\vec{r} - \vec{r}') \delta_{\sigma\sigma'}$$

An alternative way to make sense of the above Wannier expansion is to start from the more familiar expansion with Bloch functions:

(just another set of complete basis)

$$\psi_{\sigma}^{+}(\vec{r}) = \sum_{\vec{k}, n} \underbrace{\phi_n^{*}(\vec{k}, \vec{r})}_{\text{Bloch function}} C_{\vec{k}, n, \sigma}^{+}$$

$$\phi_n(\vec{k}, \vec{r}) = u_{\vec{k}, n}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$$

$$C_{\vec{k}, n, \sigma}^{+} = \int d\vec{r} \phi_n(\vec{k}, \vec{r}) \psi_{\sigma}^{+}(\vec{r})$$

The relation with the Wannier expansion is just a basis transformation:

$$\begin{aligned} \psi_{\sigma}^{+}(\vec{r}) &= \sum_{\vec{k}, n} \underbrace{\phi_n^{*}(\vec{k}, \vec{r})}_{\text{Wannier function}} C_{\vec{k}, n, \sigma}^{+} \\ &\quad \parallel \sum_j \frac{1}{\sqrt{N}} C_{j, n, \sigma}^{+} e^{i\vec{k} \cdot \vec{R}_j} \end{aligned}$$

$$\begin{aligned} &= \sum_{j, n} \underbrace{\frac{1}{\sqrt{N}} \sum_{\vec{k}} \phi_n^{*}(\vec{k}, \vec{r}) e^{i\vec{k} \cdot \vec{R}_j}}_{\text{Wannier function}} C_{j, n, \sigma}^{+} \\ &\quad \parallel a_n^{*}(\vec{r} - \vec{R}_j) \end{aligned}$$

$$= \sum_{j, n} a_n^{*}(\vec{r} - \vec{R}_j) C_{j, n, \sigma}^{+} \quad \checkmark$$

As usual we approximate the Wannier functions by using atomic orbital wave functions:

$$\psi_{\sigma}^{+}(\vec{r}) \simeq \sum_{j,n} \left[ a_n^{\text{at}}(\vec{r} - \vec{R}_j) \right]^* c_{j,n,\sigma}^{+}$$

↑  
n: atomic energy levels

$$\begin{aligned} H &= \int d\vec{r} \psi_{\sigma}^{+}(\vec{r}) \left[ -\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V(\vec{r}) \right] \psi_{\sigma}(\vec{r}) \\ &\simeq \int d\vec{r} \frac{1}{N} \sum_{j,l} \sum_{n,n'} \left[ a_n^{\text{at}}(\vec{r} - \vec{R}_j) \right]^* \left[ -\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V(\vec{r}) \right] \\ &\quad \times a_{n'}^{\text{at}}(\vec{r} - \vec{R}_l) \end{aligned}$$

$$\simeq \sum_{j,n} \varepsilon_n c_{j,n,\sigma}^{+} c_{j,n,\sigma} \quad (j=l \text{ term})$$

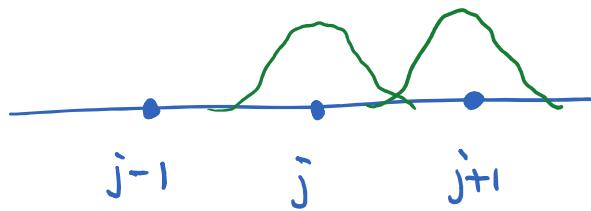
$$+ \sum_{<j,l>} \sum_{n,n'} t_{(j,n);(l,n')} c_{j,n,\sigma}^{+} c_{l,n',\sigma}$$

↗  
(j and l are nearest neighbors.)

Exchange integral:

$$t_{(j,n);(l,n')} = \int d\vec{r} \left[ a_n^{\text{at}}(\vec{r} - \vec{R}_j) \right]^* \left[ -\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V(\vec{r}) \right] a_{n'}^{\text{at}}(\vec{r} - \vec{R}_l)$$

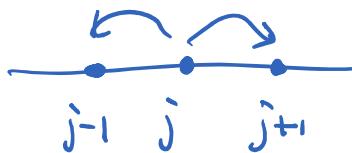
Example : 1D , s-orbital ( $n=1$ )



$$H = \sum_j \varepsilon c_{j,\sigma}^+ c_{j,\sigma} + \sum_j t (c_{j,\sigma}^+ c_{j+1,\sigma} + c_{j+1,\sigma}^+ c_{j,\sigma})$$

also called "hopping integral"

$$H c_{j,\sigma}^+ |0\rangle = \varepsilon c_{j,\sigma}^+ |0\rangle + t (c_{j+1,\sigma}^+ + c_{j-1,\sigma}^+) |0\rangle$$



$$\text{Diagonalization : } c_{j,\sigma} = \frac{1}{N} \sum_k c_{k,\sigma} e^{ikja} \quad k \in FBZ$$

$$H = \sum_{k,k'} \varepsilon \underbrace{\frac{1}{N} \sum_j e^{i(k'-k)ja}}_{\delta_{k,k'}} c_{k,\sigma}^+ c_{k',\sigma}$$

$$+ \sum_{k,k'} t \underbrace{\frac{1}{N} \sum_j e^{i(k'-k)ja}}_{\delta_{k,k'}} (e^{ik'a} + e^{-ik'a}) c_{k,\sigma}^+ c_{k',\sigma}$$

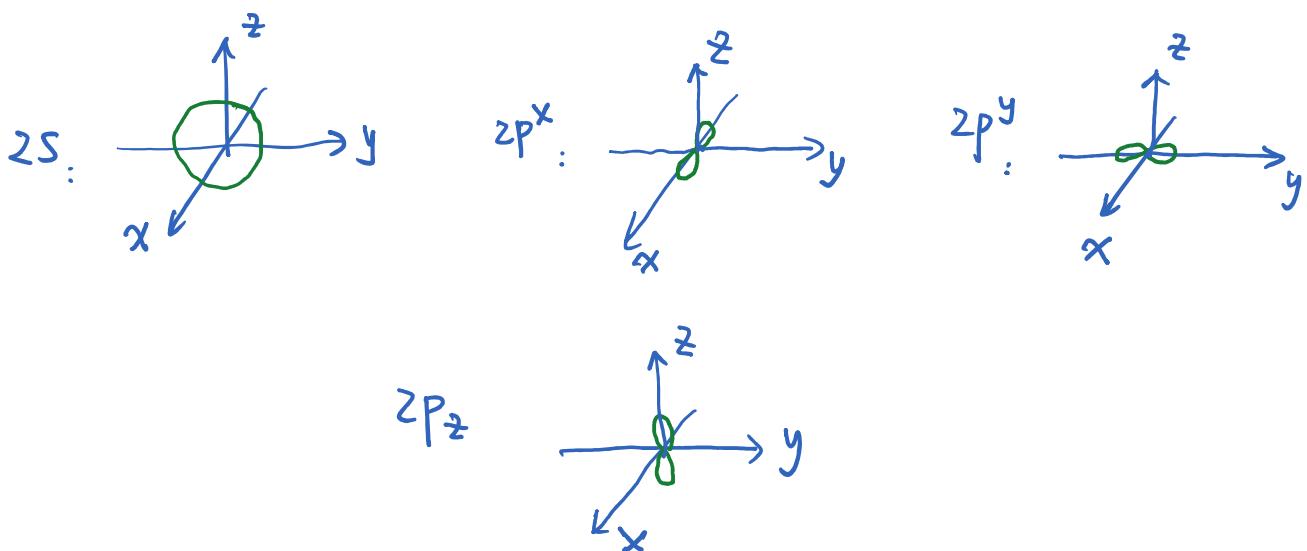
$$= \sum_k \underbrace{[\varepsilon + 2t \cos(ka)]}_{\text{red wavy line}} c_{k,\sigma}^+ c_{k,\sigma} \quad \checkmark$$

Now we are ready for a tight-binding model for graphene, involving 2s and 2p orbitals:

$$H = \sum_{\langle j,l \rangle} \sum_{n,n'} t_{(j,n);(l,n')} c_{j,n}^+ c_{l,n'} + \sum_{j,n} E_n c_{j,n}^+ c_{j,n}$$

- |         |               |                 |   |
|---------|---------------|-----------------|---|
| $n = 1$ | $\rightarrow$ | 2s orbital      | ( spin index $\sigma$<br>suppressed for<br>simplicity ) |
| $n = 2$ | $\rightarrow$ | 2p $_x$ orbital |   |
| $n = 3$ | $\rightarrow$ | 2p $_y$ orbital |   |
| $n = 4$ | $\rightarrow$ | 2p $_z$ orbital |   |

$$t_{(j,n);(l,n')} = \int d\vec{r} \left[ a_n^{at}(\vec{r} - \vec{R}_j) \right]^* \left[ -\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V(\vec{r}) \right] a_{n'}^{at}(\vec{r} - \vec{R}_l)$$



S, P<sub>x</sub>, P<sub>y</sub> even under  $z \rightarrow -z$

P<sub>z</sub> odd under  $z \rightarrow -z$  !

Consequence:  $t_{(j, n=4); (l, n'=1, 2, 3)} = 0$  !

$\downarrow$

$2p_z$

$\downarrow$

$2s, 2p_x, 2p_y$

$$H = H_\pi + H_\sigma$$

$\downarrow$

$2p_z$

$\downarrow$

$2s, 2p_x, 2p_y$  ( $\sigma$  electron)

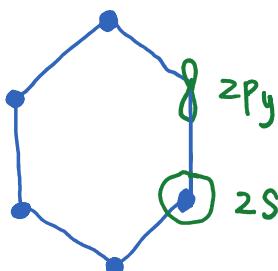
( $\pi$  electron)

$sp^2$  hybridization

$\sigma$ -electron part:

$$H_\sigma = \sum_{<j, l>} \sum_{n, n'=1, 2, 3} t_{(j, n); (l, n')} C_{j, n}^+ C_{l, n'} + \sum_{j, n=1, 2, 3} \epsilon_n C_{j, n}^+ C_{j, n}$$

Example:



$$t_{(j, 1); (l, 3)} = \int d\vec{r} \left[ a_1^{at} (\vec{r} - \vec{R}_j) \right]^* \left[ -\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V(\vec{r}) \right] a_3^{at} (\vec{r} - \vec{R}_l)$$

$\downarrow$

$2s$

$\downarrow$

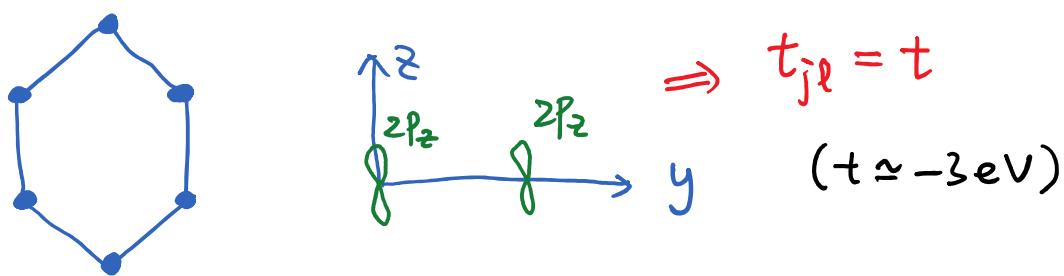
$2p_y$

$\pi$ -electron part:

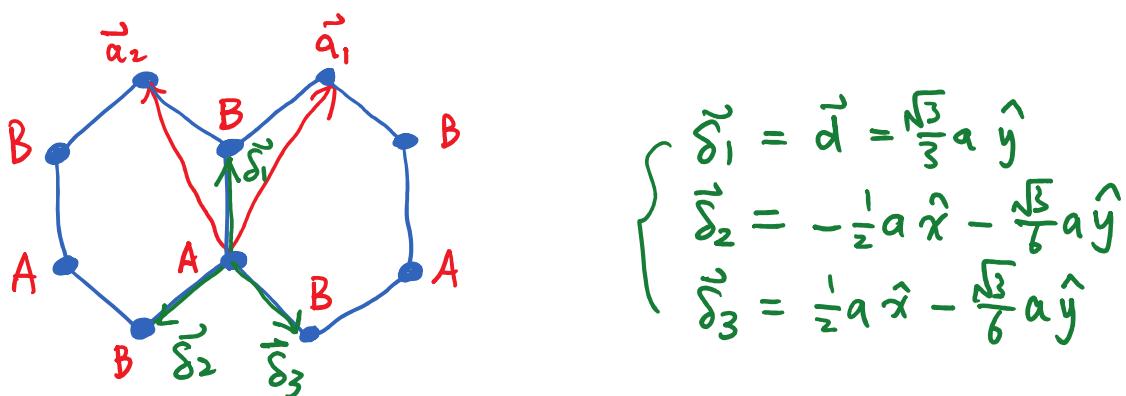
$$H_{\pi} = \sum_{\langle j,l \rangle} t_{jl} c_j^+ c_l + \sum_j \varepsilon c_j^+ c_j$$

$\downarrow$

$2P_z$  ( $n=4$  suppressed)



Below we focus on the  $\pi$ -electron part.



$$H_{\pi} = t \sum_{\vec{r} \in R_n} \sum_{\vec{\delta} = \vec{\delta}_1, \vec{\delta}_2, \vec{\delta}_3} (C_{\vec{r},A}^+ C_{\vec{r}+\vec{\delta},B} + C_{\vec{r}+\vec{\delta},B}^+ C_{\vec{r},A})$$

$\downarrow$

$R_n = n_1 \vec{\alpha}_1 + n_2 \vec{\alpha}_2$

$$+ \varepsilon \sum_{\vec{r} \in R_n} (C_{\vec{r},A}^+ C_{\vec{r},A} + C_{\vec{r}+\vec{\delta}_1,B}^+ C_{\vec{r}+\vec{\delta}_1,B})$$