Lecture Note

Introduction to graphene and graphene nanoribbons

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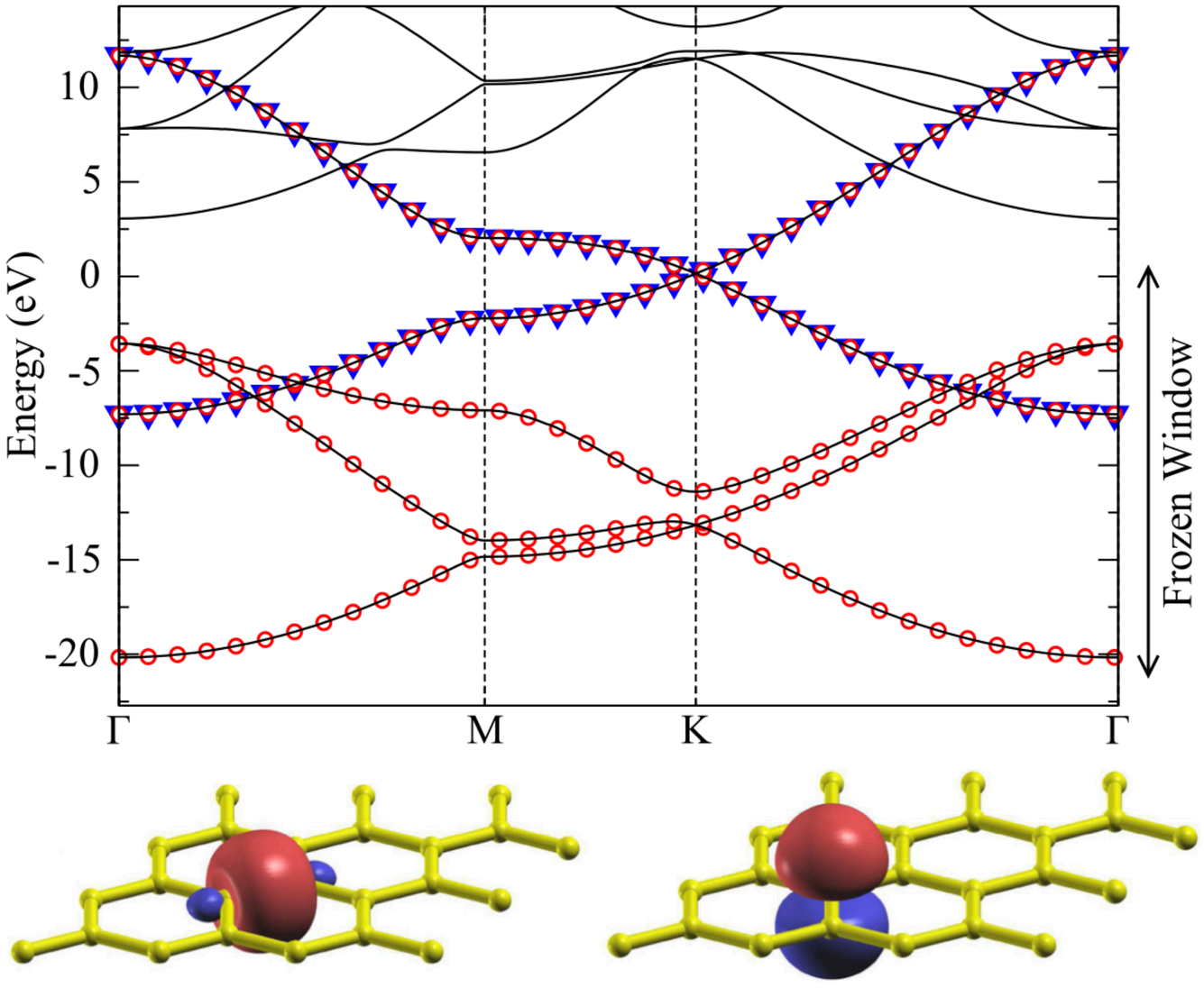
QNS Summer School 2026

CENTER FOR QUANTUM NANOSCIENCE

Outline

1. Tight-binding model
2. Graphene
3. Zigzag graphene nanoribbons

- PythTB: a python library for tight binding

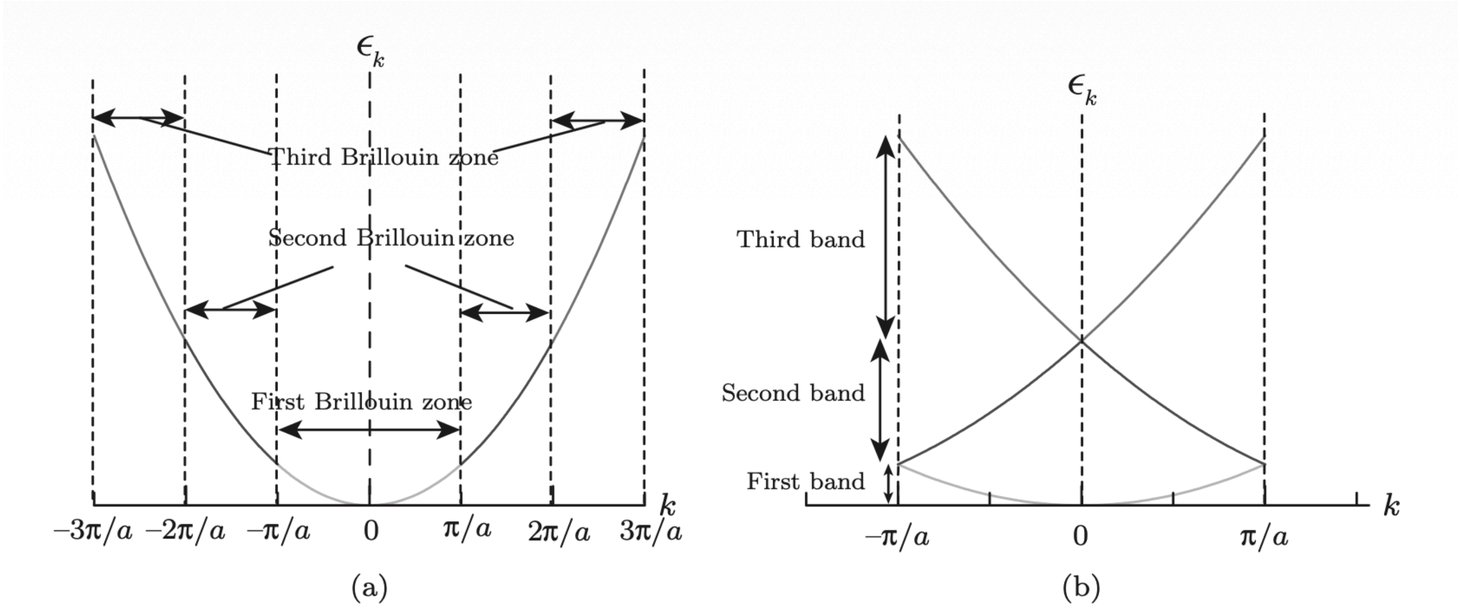

Energy (eV)
10
5
0
-5
-10
-15
-20
Γ
M
K
Γ
Frozen Window

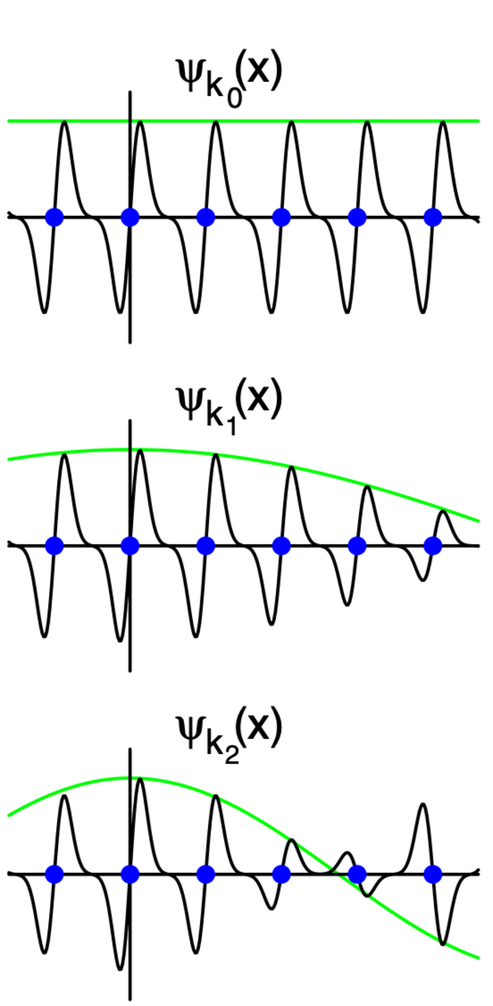
1. Bloch theorem

…plane waves modulated by periodic functions

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

$u_{n\mathbf{k}}(\mathbf{r})$ has the same periodicity as the lattice.





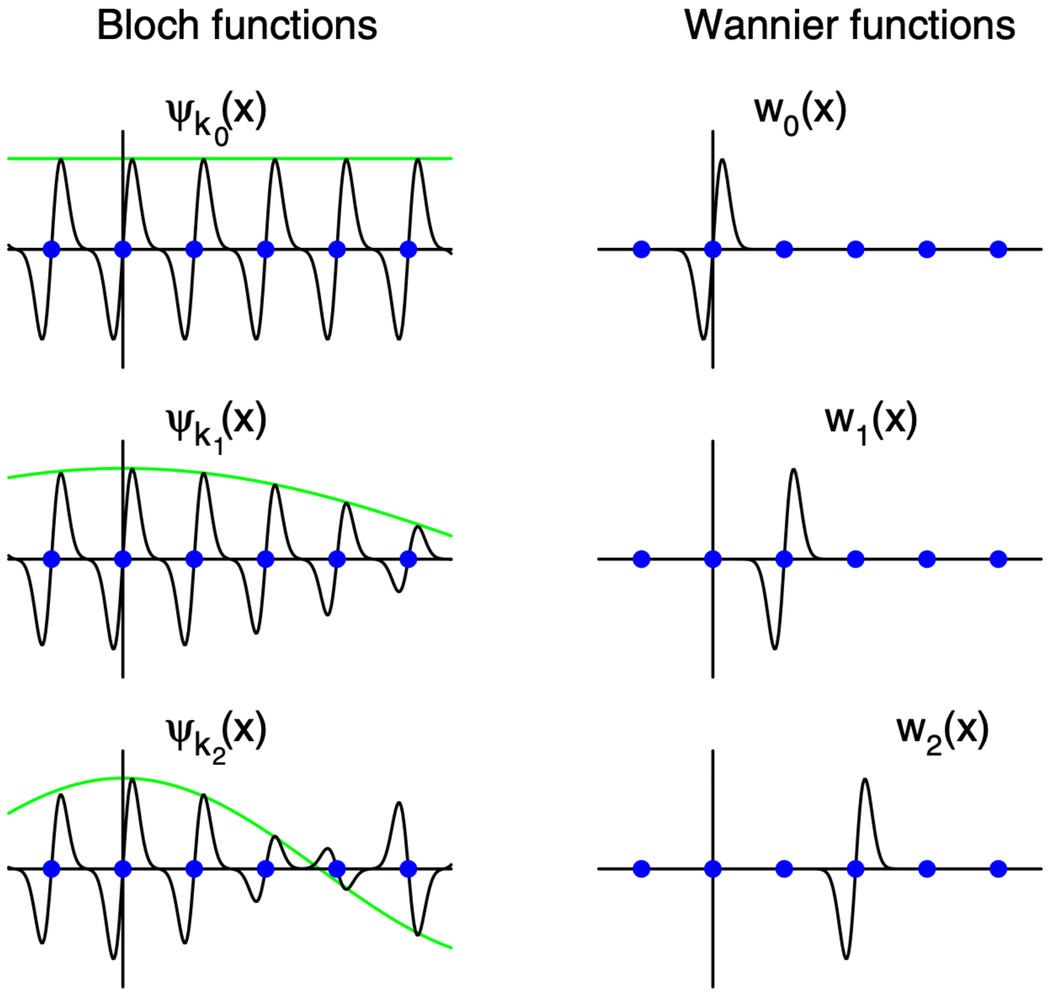
1. Wannier functions

The Wannier function is centered at lattice site $\mathbf{R}$

$$w_{n\mathbf{R}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \int_{\mathrm{BZ}} d\mathbf{k}\; e^{-i\mathbf{k}\cdot\mathbf{R} + i\phi(\mathbf{k})} \psi_{n\mathbf{k}}(\mathbf{r})$$

- $\phi(\mathbf{k})$ reflect the **gauge freedom**
- Choosing $\phi(\mathbf{k})$ to minimize spread gives **maximally localized Wannier functions**
- Form a complete orthonormal basis

$$\int d\mathbf{r}\; w^*_{n\mathbf{R}}(\mathbf{r}) w_{m\mathbf{R}'}(\mathbf{r}) = \delta_{nm}\delta_{\mathbf{R}\mathbf{R}'}$$



(Marzari & Vanderbilt 1997)

1. Tight-binding Hamiltonian

$$H_{\mathbf{R},\mathbf{R}'} = \langle w_{n\mathbf{R}} | \hat{H} | w_{m\mathbf{R}'} \rangle = \int d\mathbf{r}\; w^*_{n\mathbf{R}}(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right] w_{m\mathbf{R}'}(\mathbf{r})$$

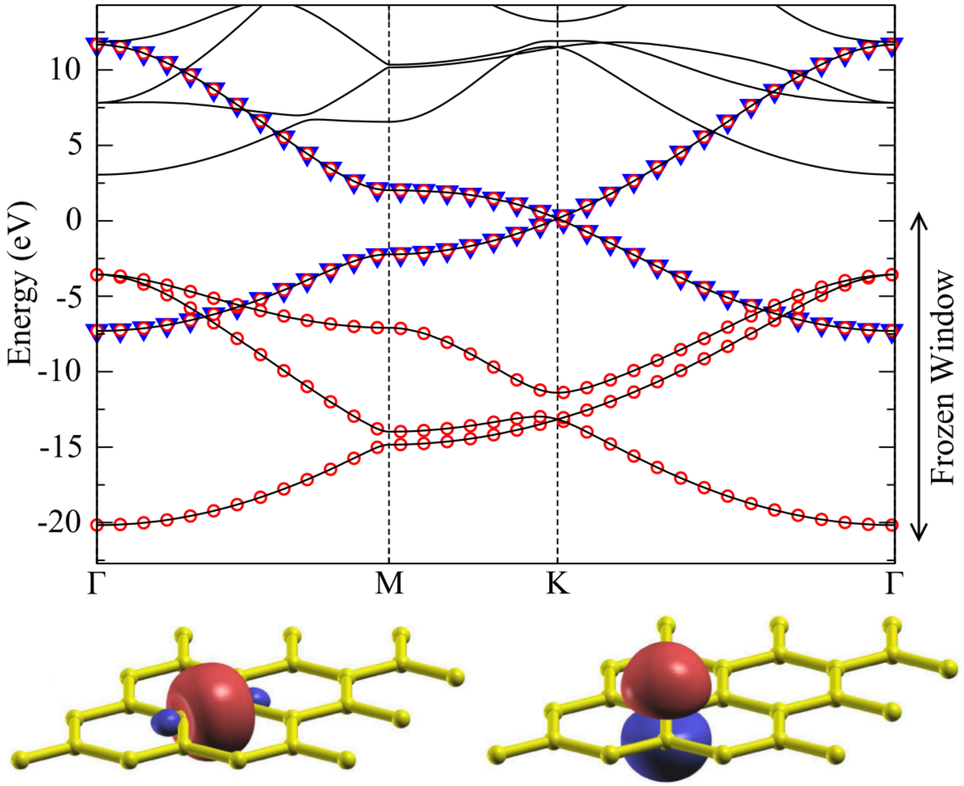
$$H_{\mathbf{R},\mathbf{R}'} = \sum_{\mathbf{R},\mathbf{R}'} t_{\mathbf{R},\mathbf{R}'} | w_{n\mathbf{R}} \rangle \langle w_{n\mathbf{R}'} | + \sum_{\mathbf{R}} \varepsilon_{\mathbf{R}} | w_{n\mathbf{R}} \rangle \langle w_{n\mathbf{R}} |$$

Or in the second quantization form $\hat{H}_{\mathrm{TB}} = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{i \neq j} t_{ij} c_i^\dagger c_j$

with $c_i^\dagger$ creating an electron in the localized orbital at site i ($\{c_i, c_j^\dagger\} = \delta_{ij}$).

1. Take-home message

Energy band of graphene from DFT



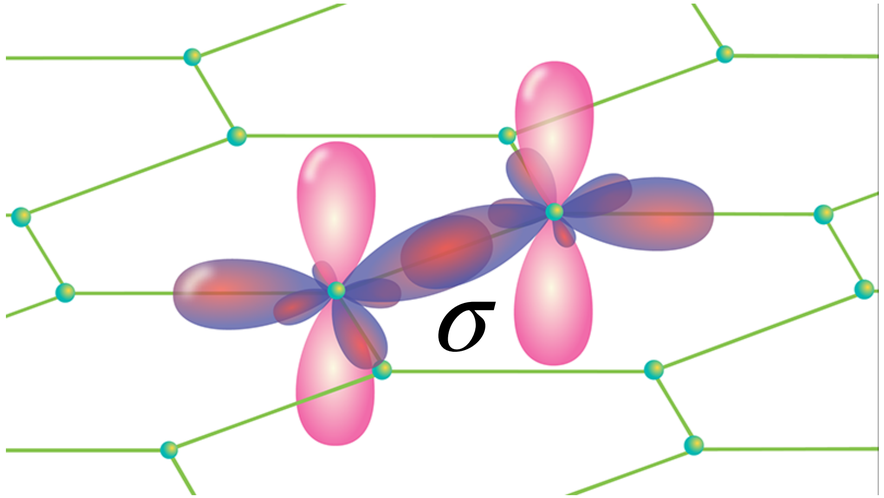
electronic states are well described by a set of

orbitals localized at lattice sites

and ***electrons move by hopping between them***

DFT → Wannierization → ε_{ij}, t_{ij}

2. Graphene

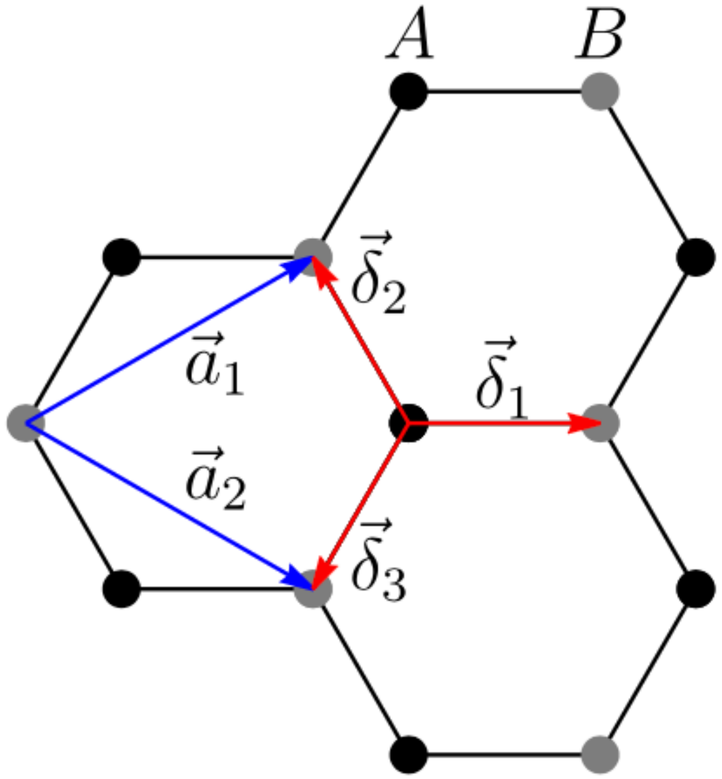


- Carbon: $2s^2 2p^2$
- sp^2 hybridization → 3 in-plane σ bonds (120°)
- **One p_z orbital per atom**, perpendicular to the plane
- Nearest-neighbor hopping $t \approx 2.7$ eV

2. Lattice structure

Non Bravais lattice

(two inequivalent sites A, B)



Primitive lattice vectors

$$\vec{a}_1 = \frac{a}{2}(3,\sqrt{3}), \quad \vec{a}_2 = \frac{a}{2}(3,-\sqrt{3}) \qquad a \approx 1.42\text{Å}$$

Nearest neighbor vectors

$$\vec{\delta}_1 = a(1,0), \quad \vec{\delta}_2 = \frac{a}{2}(-1,\sqrt{3}), \quad \vec{\delta}_3 = \frac{a}{2}(-1,-\sqrt{3})$$

Tight-binding Hamiltonian

$$H = -t \sum_{\mathbf{R}} \sum_{i=1}^{3} a_{\mathbf{R}}^{\dagger} b_{\mathbf{R}+\delta_i} + \text{h.c.}$$

2. Band structure in k-space

Fourier transform the fermionic operators $\begin{pmatrix} a_{\vec{R}_{m,n}} \\ b_{\vec{R}_{m,n}} \end{pmatrix} = \frac{1}{\sqrt{N_{\text{unit}}}} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}_{m,n}} \begin{pmatrix} a_{\vec{k}} \\ b_{\vec{k}} \end{pmatrix}$.

Hamiltonian in the k-space: $H_{\text{graphene}}(\vec{k}) = \begin{pmatrix} 0 & t f(\vec{k}) \\ t f^*(\vec{k}) & 0 \end{pmatrix}$

where $f(\vec{k}) = \sum_{i=1}^{3} e^{i\vec{k}\cdot\vec{\delta}_i} = e^{-ik_x a} + 2e^{ik_x a/2} \cos\left(\frac{\sqrt{3}k_y a}{2}\right)$.

Energy band: $E_{\pm} = \pm t \sqrt{3 + 2\cos\left(\sqrt{3}k_y a\right) + 4\cos\left(\frac{\sqrt{3}}{2}k_y a\right)\cos\left(\frac{3}{2}k_x a\right)}$.

2. Band structure in k-space

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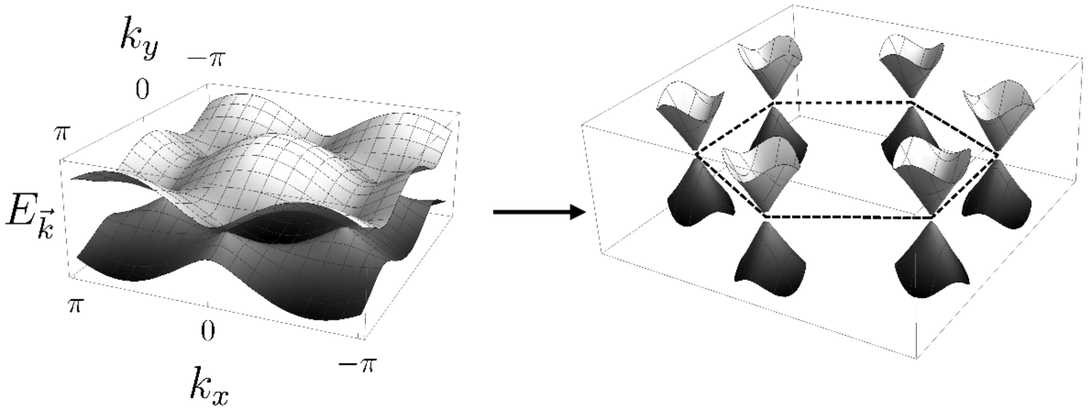
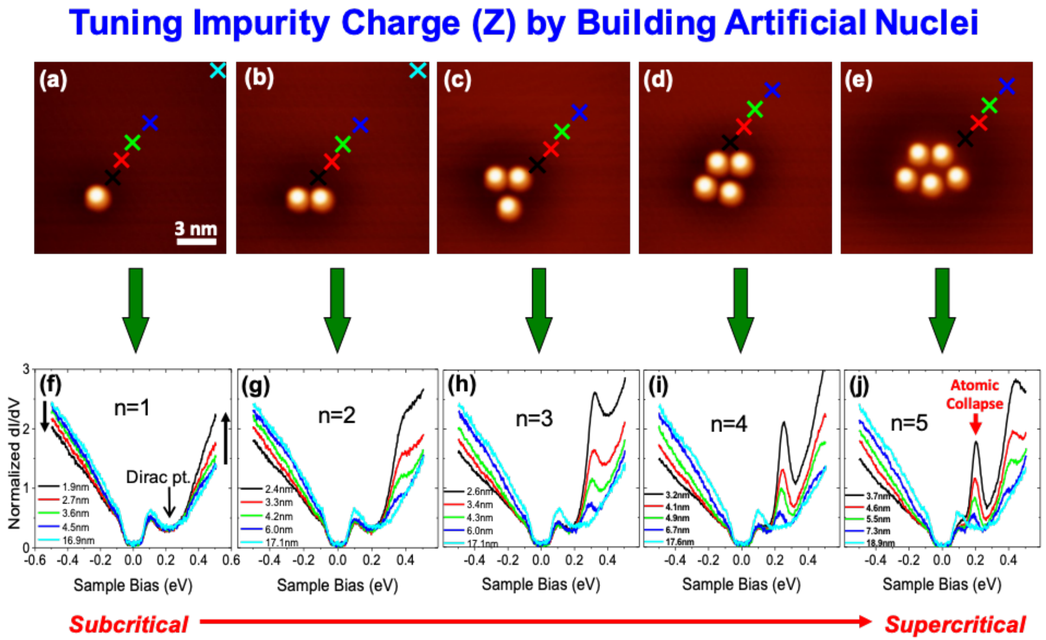




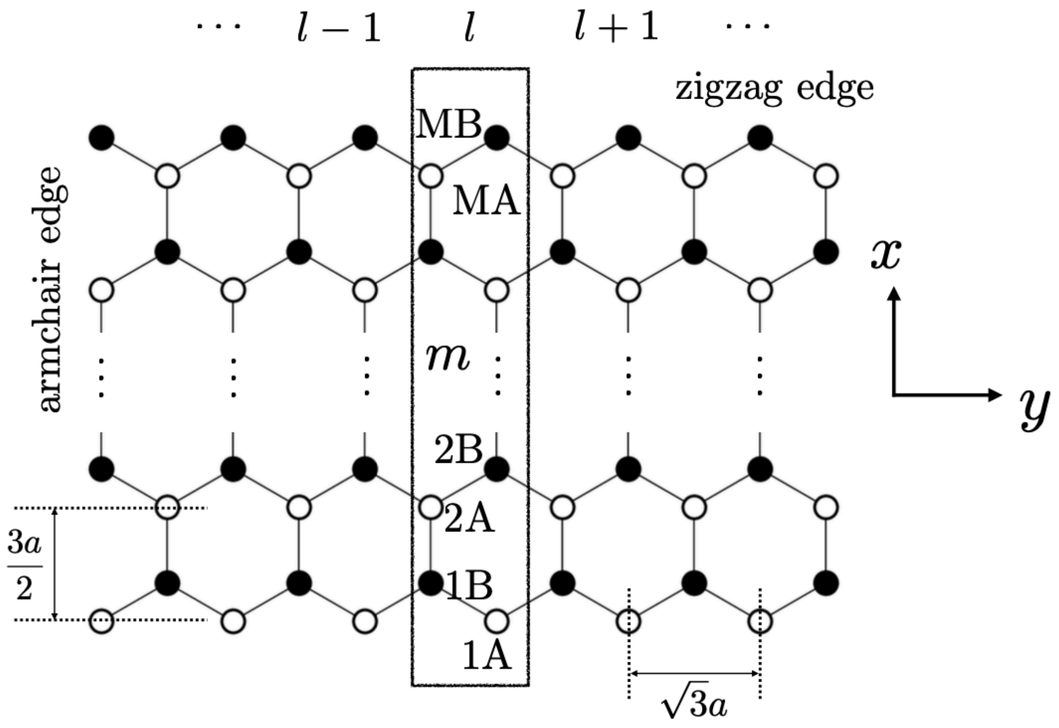
- **Linear dispersion** $E_{\pm} = \pm \hbar v_F |\mathbf{k}|$.
- The Fermi velocity

$$v_F = \frac{\sqrt{3}\,t\,a}{2\hbar} \approx 0.9 \times 10^6 \text{ m/s} \approx \frac{c}{300}\,.$$

Fine structure constant $\alpha_g \approx 2.2$

graphene is a strongly-coupled version of QED

3. Zigzag graphene nanoribbon



2.2.2 Hamiltonian and symmetries

The tight-binding Hamiltonian for electrons in ZGNR takes the following forms

$$H_{\text{non-interaction}} = -t\sum_{l,\sigma}\left(\sum_{m=1}^{M} a^{\dagger}_{l,m,\sigma}b_{l,m,\sigma} + \sum_{m=1}^{M-1} a^{\dagger}_{l,m+1,\sigma}b_{l,m,\sigma}\right) - t\sum_{l,\sigma}\left(\sum_{1\le m\le M, m \text{ odd}} a^{\dagger}_{l,m,\sigma}b_{l+1,m,\sigma} + \sum_{1\le m\le M, m \text{ even}} a^{\dagger}_{l+1,m,\sigma}b_{l,m,\sigma}\right) + \text{h.c.} \tag{2.12}$$

where l and m respectively denote unit cell and site in a unit cell, as shown in Fig. 2.3. σ ($\sigma = \{\uparrow,\downarrow\}$) denotes spin. In Eq. (2.12), the operators in the upper line share the same unit cell index l so they correspond to intracell hopping terms. Similarly, the lower ones correspond to intercell hopping. Note that there are $2M$ carbon atoms in a unit cell, which

3. Zigzag graphene nanoribbon

2.2.3 Energy bands

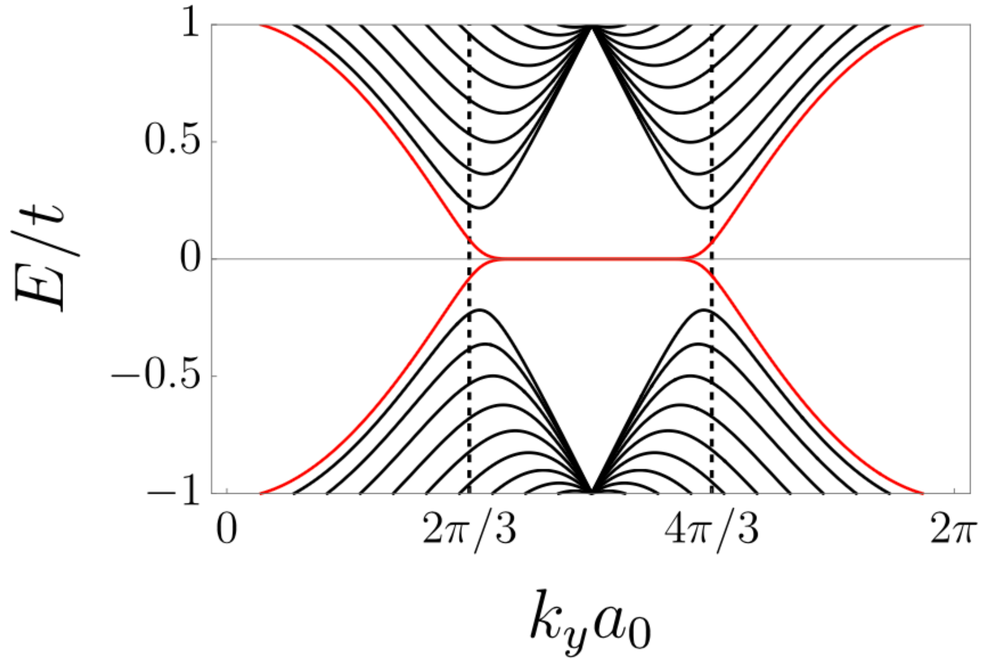
To solve its energy bands, one needs to Fourier transform the annihilation and creation operators along y-direction as follows

$$\begin{pmatrix} a_{l,m,\sigma} \\ \\ b_{l,m,\sigma} \end{pmatrix} = \frac{1}{\sqrt{L}} \sum_{k_y} e^{ik_y y_{lm}} \begin{pmatrix} A_{k_y,m,\sigma} \\ \\ B_{k_y,m,\sigma} \end{pmatrix}, \tag{2.13}$$

$$H_\sigma = \sum_{k_y \in \mathrm{BZ}} \begin{pmatrix} A^\dagger_{k_y,1,\sigma} & B^\dagger_{k_y,1,\sigma} & A^\dagger_{k_y,2,\sigma} & B^\dagger_{k_y,2,\sigma} & \cdots \end{pmatrix} H_\sigma(k_y) \begin{pmatrix} A_{k_y,1,\sigma} \\ B_{k_y,1,\sigma} \\ A_{k_y,2,\sigma} \\ B_{k_y,2,\sigma} \\ \vdots \end{pmatrix}, \tag{2.14}$$

where

$$H_\uparrow(k_y) = \begin{pmatrix} 0 & -g_{k_y} & 0 & \cdots \\ -g_{k_y} & 0 & -t & \cdots \\ 0 & -t & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}_{2M \times 2M}, \tag{2.15}$$



Take-home messages

- Tight-binding model
- Graphene: linear dispersion at Dirac points
- Zigzag (nor armchair) graphene nanoribbon:

  localized edge states