

# Graphene and Carbon Nanotubes

An introduction to electronic properties

G.Bellomia, A.Khosravi, G.Lami

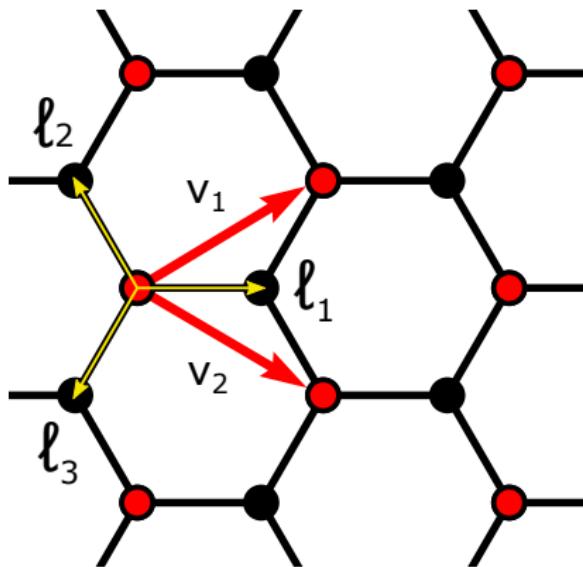
30 October 2019



# Section 1

## Graphene

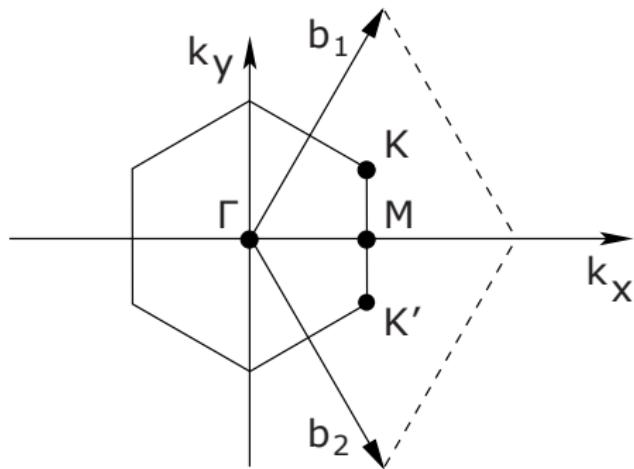
## Graphene lattice



$v_1$ ,  $v_2$  are the primitive vectors of the Bravais lattice

$\ell_1$ ,  $\ell_2$ ,  $\ell_3$  are useful “bond” vectors

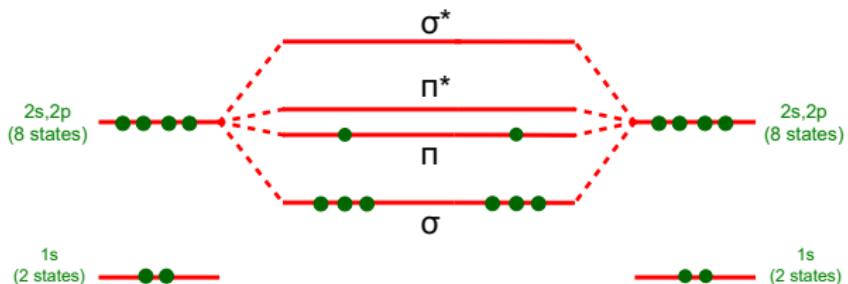
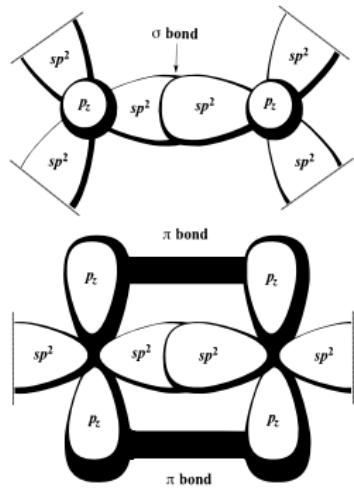
# Reciprocal lattice



Reciprocal primitive vectors  $\mathbf{b}_i$  and Brillouin Zone of the honeycomb lattice

$$\mathbf{b}_i \cdot \mathbf{v}_j = 2\pi\delta_{ij} \quad \forall i, j \quad \Rightarrow \quad \mathbf{b}_{(1)} = \frac{2\pi}{3\ell}(1, \pm\sqrt{3})$$

# Choice of Hilbert space: $\pi$ - $\sigma$ separability



Hybrid  $sp^2$  and pure  $p_z$  orbitals (in a unit-cell) and energy scheme of  $\sigma$  and  $\pi$  bonds. Separability is guaranteed by orthogonality in physical space.

## Nearest-neighbors TB approximation

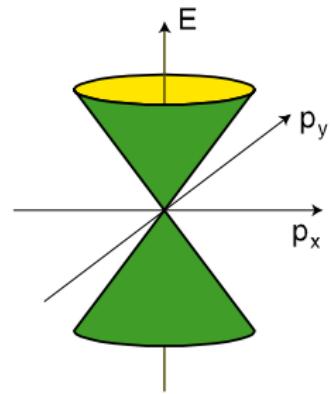
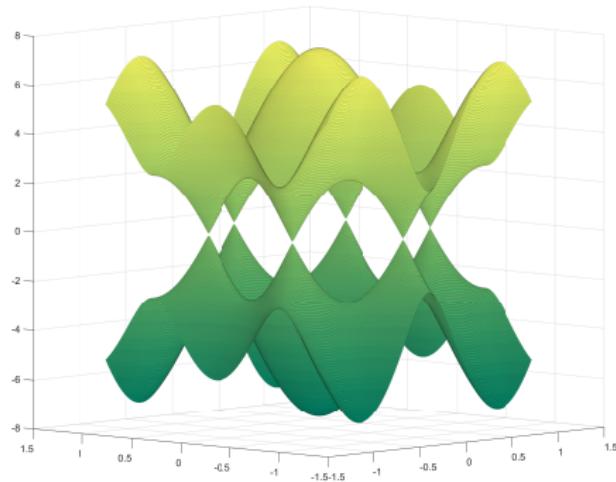
In the basis of Bloch states the Hamiltonian is in  $2 \times 2$  blocks:

$$\mathbb{H}_{\mathbf{k}} = \begin{pmatrix} \varepsilon & -\tau(\mathbf{k}) \\ -\tau^*(\mathbf{k}) & \varepsilon \end{pmatrix} \quad \tau(\mathbf{k}) = t \sum_{n=1}^3 e^{i\mathbf{k}\cdot\boldsymbol{\ell}_n} \quad t \simeq 2.5 \text{ eV}$$

Eigenvalues are:

$$\lambda_{\mathbf{k}}^{\pm} = \varepsilon \pm t \sqrt{\left( \sum_{n=1}^3 \cos(\mathbf{k} \cdot \boldsymbol{\ell}_n) \right)^2 + \left( \sum_{n=1}^3 \sin(\mathbf{k} \cdot \boldsymbol{\ell}_n) \right)^2} = \varepsilon \pm |\tau|$$

# Band Structure

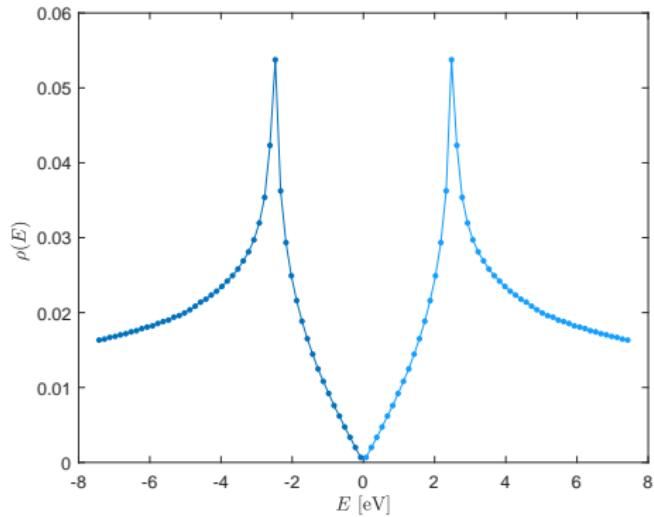


The two bands  $\lambda_k^\pm$  touch each other in the points:

$$\mathbf{K} = \frac{2\pi}{3\ell} \left( 1, \frac{1}{\sqrt{3}} \right)$$

$$\mathbf{K}' = \frac{2\pi}{3\ell} \left( 1, -\frac{1}{\sqrt{3}} \right)$$

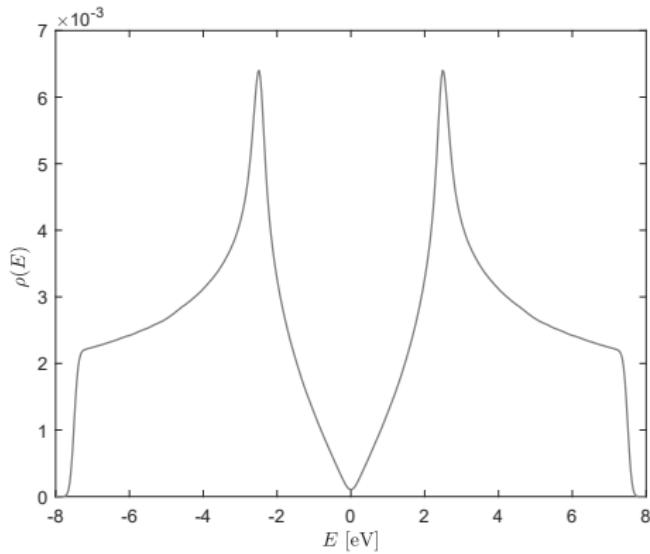
# Density of states



State counting:

$$\rho(\epsilon)d\epsilon = \#\{\text{States in } [\epsilon, \epsilon + d\epsilon]\} \Rightarrow n_i = \frac{\#\{\text{States in } [\epsilon_i - \delta, \epsilon_i + \delta]\}}{\#\{\text{States in } [0, \epsilon_{\max}]\}}$$
$$\sum_i n_i = 2 \quad (\text{Two bands!})$$

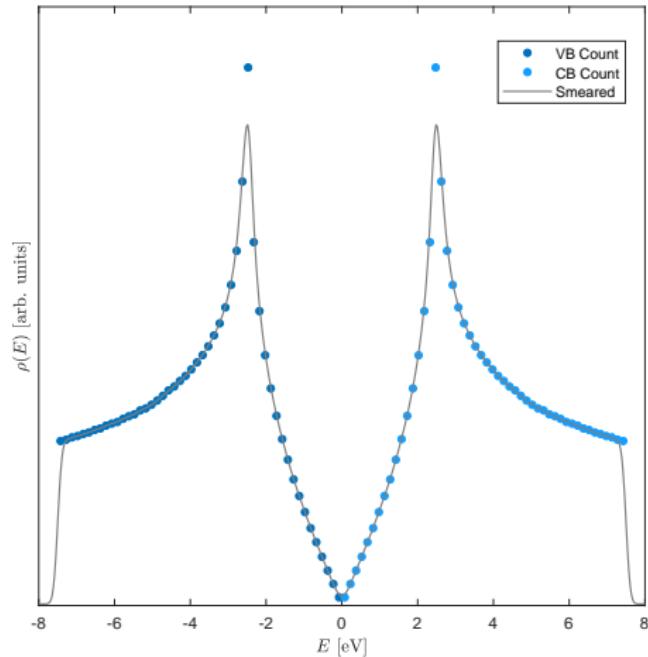
# Gaussian smearing



Gaussian smearing:

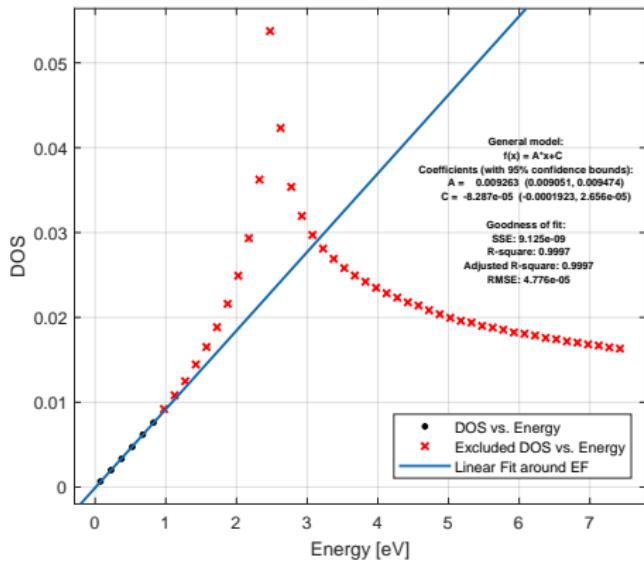
$$\sum_i n_i \delta(\epsilon - \epsilon_i) \mapsto \sum_i n_i g(\epsilon - \epsilon_i), \quad \int_{\mathbb{R}} g(\epsilon) d\epsilon = 1$$

# Gaussian smearing $\Rightarrow$ Experimental-like DOS



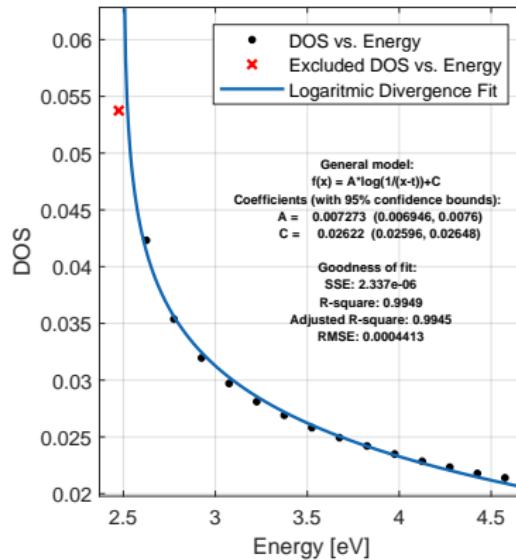
Broadening effect: always present in experiments!

# Graphene is a semimetal!



We have zero gap but DOS goes to zero (linearly)  $\Rightarrow$  **SEMIMETAL**

# Divergence at saddle-points



We have logarithmic divergences at:  $\epsilon = \pm t$ .

# Relativistic electrons and Klein paradox

Effective hamiltonian near the K-points:

$$H_D = v_F \mathbf{p} \cdot \boldsymbol{\sigma} \quad \mathbf{p} = \frac{\hbar}{i} \left( \frac{d}{dx}, \frac{d}{dy} \right) \quad v_F = \frac{3t\ell}{2\hbar} \simeq 8 \cdot 10^5 \frac{\text{m}}{\text{s}}$$

Scattering on a barrier:

$$(H_D + V(x)) \Psi(x, y) = E \Psi(x, y) \quad \Psi(x) = \psi(x) e^{ik_y y} |\uparrow\rangle$$

If  $k_y = 0$ , then  $|T|^2 = 1$  (Transparency!) In fact:

$$v_x = v_F \sigma_x$$

and:

$$\frac{d}{dt} v_x = \frac{i v_F}{\hbar} [H, \sigma_x] \propto \sigma_z p_y = 0 \implies \text{No backscattering!}$$

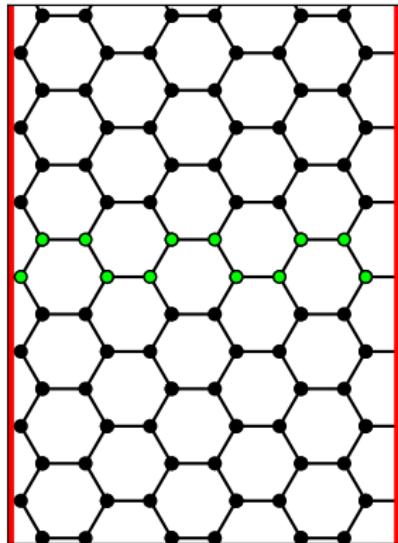
## Section 2

Carbon nanotubes (CNTs)

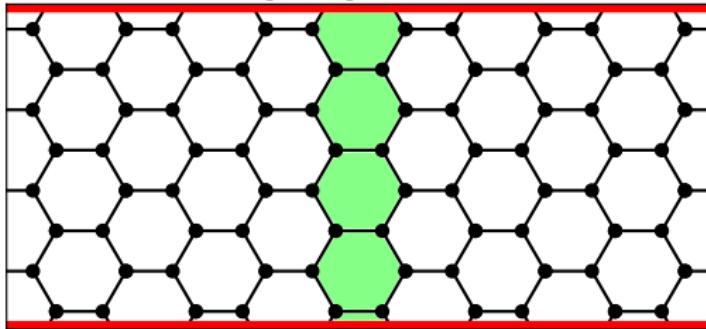
# Two graphene foldings

Addressed nanotubes:

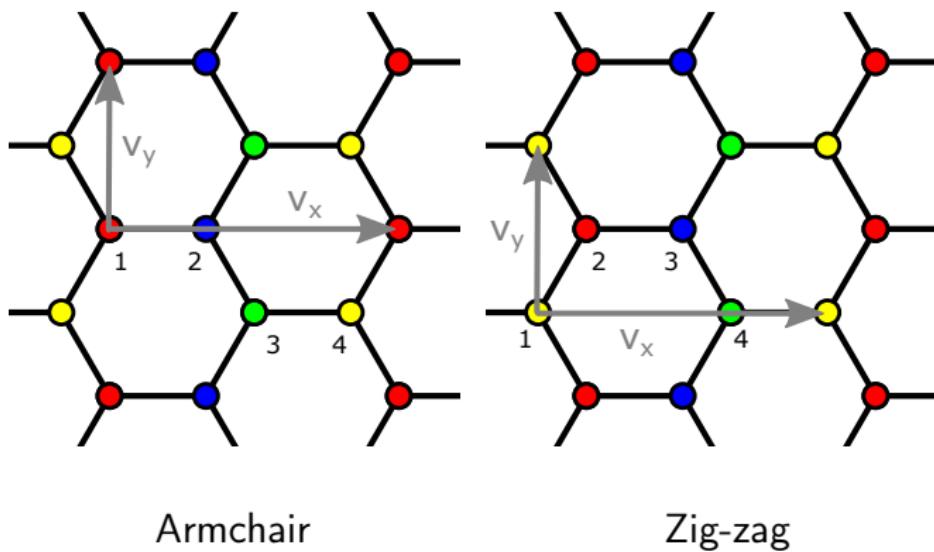
Armchair CNT



Zig-zag CNT



## Unit cells



Armchair

Zig-zag

The 4 basis atoms are indicated with different colors. Primitive vectors  $v_x$ ,  $v_y$  are indicated in grey color.

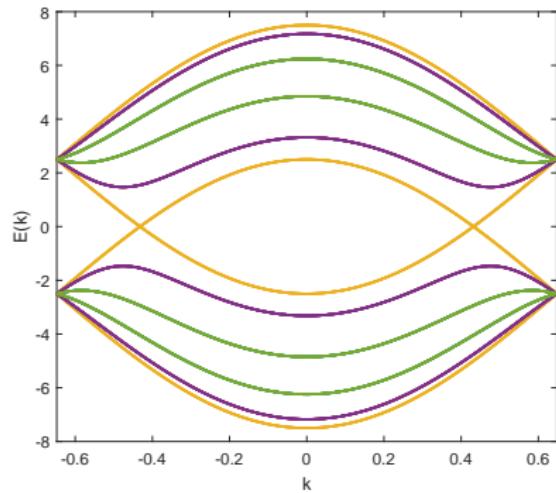
# Tight-binding matrices

$$\mathbb{H}_{\text{ACNT}}(\mathbf{k}) = \begin{pmatrix} \varepsilon & -te^{+i\mathbf{k}\cdot\boldsymbol{\ell}_1} & 0 & -t(e^{+i\mathbf{k}\cdot\boldsymbol{\ell}_2} + e^{+i\mathbf{k}\cdot\boldsymbol{\ell}_3}) \\ -te^{-i\mathbf{k}\cdot\boldsymbol{\ell}_1} & \varepsilon & -t(e^{-i\mathbf{k}\cdot\boldsymbol{\ell}_2} + e^{-i\mathbf{k}\cdot\boldsymbol{\ell}_3}) & 0 \\ 0 & -t(e^{+i\mathbf{k}\cdot\boldsymbol{\ell}_2} + e^{+i\mathbf{k}\cdot\boldsymbol{\ell}_3}) & \varepsilon & -te^{+i\mathbf{k}\cdot\boldsymbol{\ell}_1} \\ -t(e^{-i\mathbf{k}\cdot\boldsymbol{\ell}_2} + e^{-i\mathbf{k}\cdot\boldsymbol{\ell}_3}) & 0 & -te^{-i\mathbf{k}\cdot\boldsymbol{\ell}_1} & \varepsilon \end{pmatrix}$$

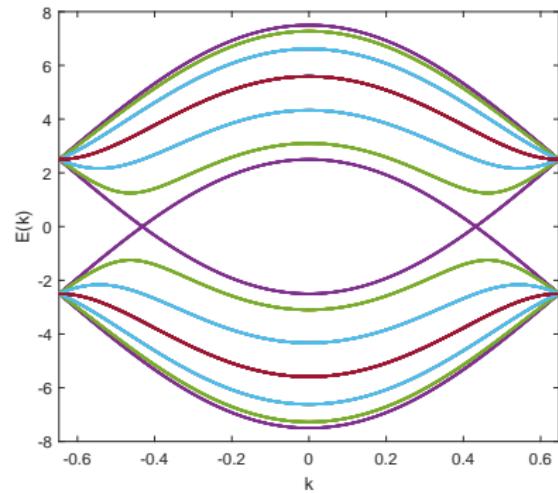
$$\mathbb{H}_{\text{ZCNT}}(\mathbf{k}) = \begin{pmatrix} \varepsilon & -t(e^{-i\mathbf{k}\cdot\boldsymbol{\ell}_3} + e^{-i\mathbf{k}\cdot\boldsymbol{\ell}_2}) & 0 & -te^{-i\mathbf{k}\cdot\boldsymbol{\ell}_1} \\ -t(e^{+i\mathbf{k}\cdot\boldsymbol{\ell}_3} + e^{+i\mathbf{k}\cdot\boldsymbol{\ell}_2}) & \varepsilon & -te^{+i\mathbf{k}\cdot\boldsymbol{\ell}_1} & 0 \\ 0 & -te^{-i\mathbf{k}\cdot\boldsymbol{\ell}_1} & \varepsilon & -t(e^{-i\mathbf{k}\cdot\boldsymbol{\ell}_2} + e^{-i\mathbf{k}\cdot\boldsymbol{\ell}_3}) \\ -te^{+i\mathbf{k}\cdot\boldsymbol{\ell}_1} & 0 & -t(e^{+i\mathbf{k}\cdot\boldsymbol{\ell}_2} + e^{+i\mathbf{k}\cdot\boldsymbol{\ell}_3}) & \varepsilon \end{pmatrix}$$

# Armchair bands

$N = 5$



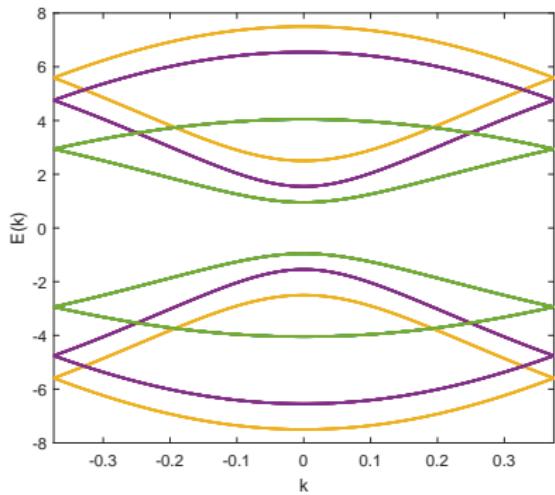
$N = 6$



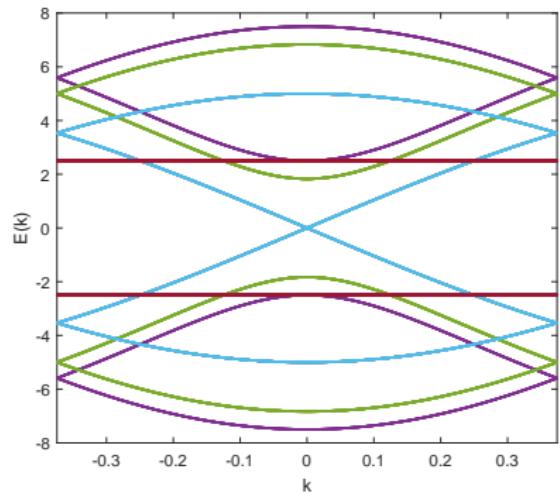
Colors represent different discrete  $k_x$  values

# Zig-zag bands

$N = 5$

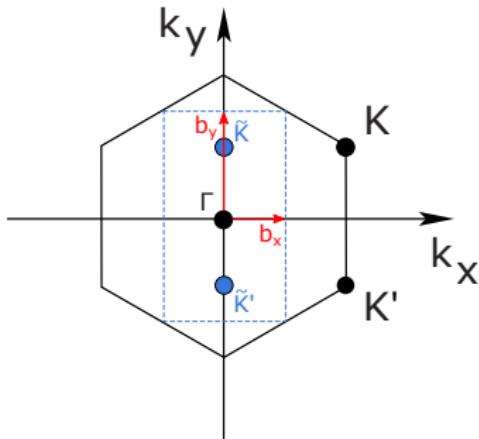


$N = 6$



Colors represent different discrete  $k_y$  values

## Reciprocal lattice for CNT



Our choice for the nanotube Brillouin Zone and the mapping of K-points

$$\mathbf{b}_x \cdot \mathbf{v}_x = 2\pi \quad \mathbf{b}_x \cdot \mathbf{v}_y = 0$$

$$\mathbf{b}_y \cdot \mathbf{v}_x = 0 \quad \mathbf{b}_y \cdot \mathbf{v}_y = 2\pi$$

$$\tilde{\mathbf{K}} = \mathbf{K} - \mathbf{b}_x = \left(0, \frac{2\pi}{3\sqrt{3}\ell}\right) \in \text{BZ}_1$$

## K-space interpretation of the band structure behaviour

Armchair:

$$k_x = \frac{2\pi}{3\ell N} m, \quad m = \begin{cases} 0, \pm 1, \dots, \pm \frac{N}{2} - 1, +\frac{N}{2} & N \text{ even} \\ 0, \pm 1, \dots, \pm \frac{N-1}{2} & N \text{ odd} \end{cases}$$

$k_y$  can assume all values within the  $BZ_1$ .  $\tilde{\mathbf{K}}$ ,  $\tilde{\mathbf{K}}'$  are always allowed wave-vectors (corresponding to  $m = 0$ )!

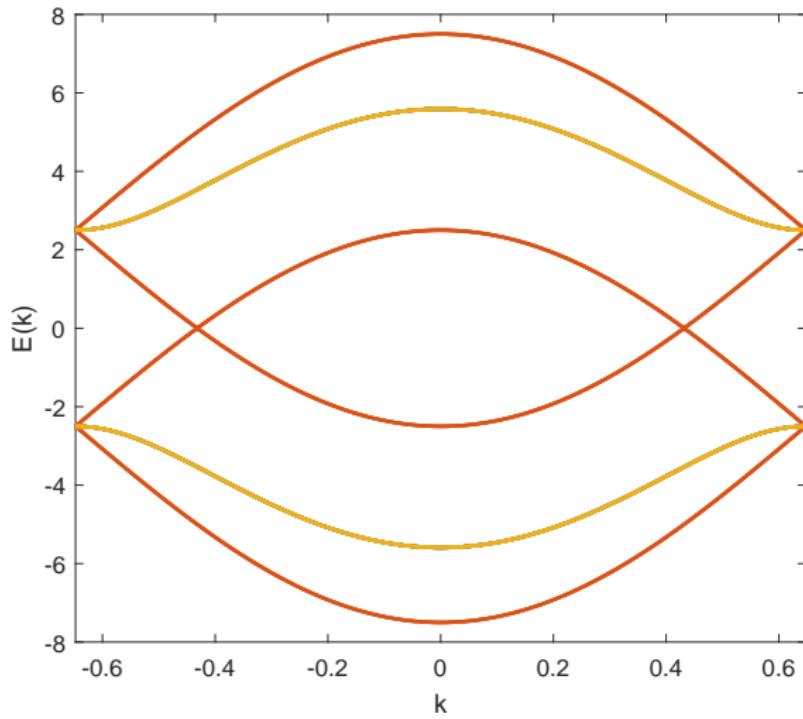
Zig-zag:

$$k_y = \frac{2\pi}{\sqrt{3}\ell N} m, \quad m = \begin{cases} 0, \pm 1, \dots, \pm \frac{N}{2} - 1, +\frac{N}{2} & N \text{ even} \\ 0, \pm 1, \dots, \pm \frac{N-1}{2} & N \text{ odd} \end{cases}$$

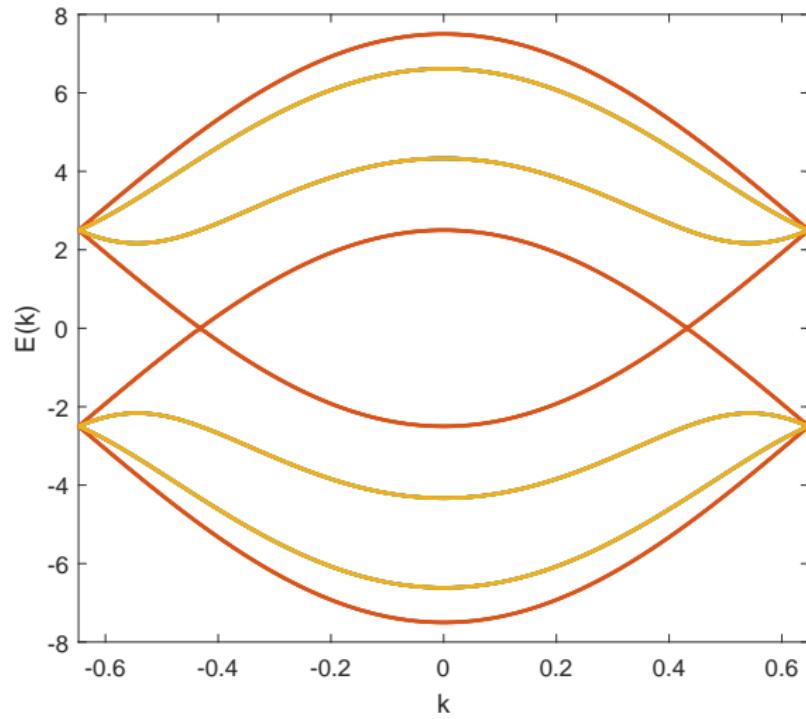
$k_x$  can assume all values within the  $BZ_1$ .  $\tilde{\mathbf{K}}$ ,  $\tilde{\mathbf{K}}'$  points are allowed wave-vectors only if  $N$  is a multiple of 3 (corresponding to  $m = \pm N/3$ )!

# The End

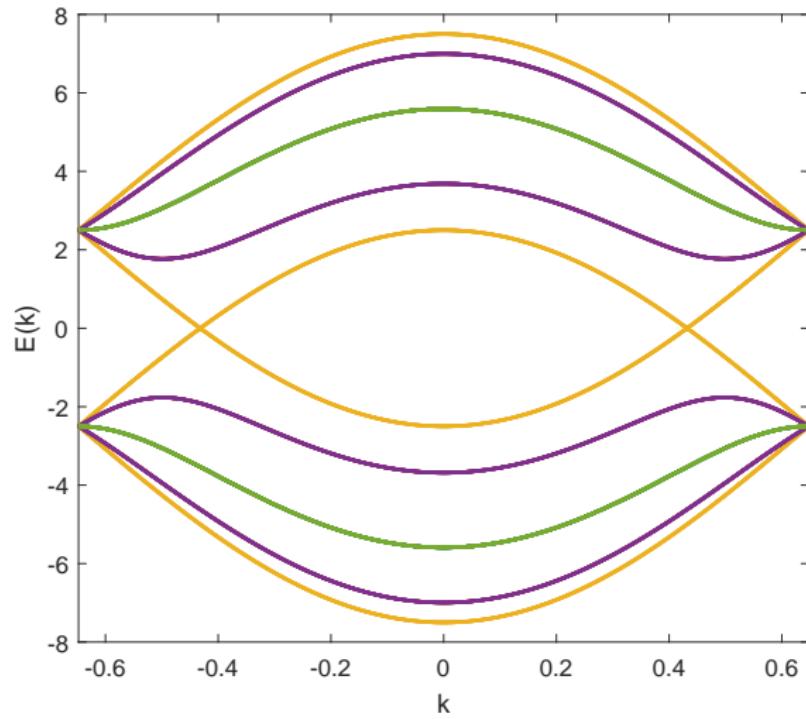
# Armchair for N = 2



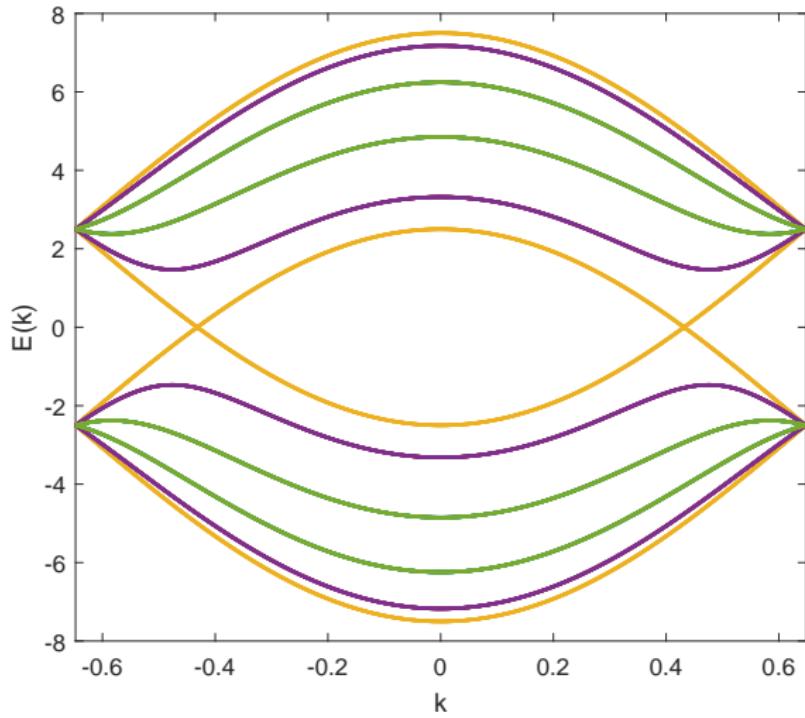
# Armchair for N = 3



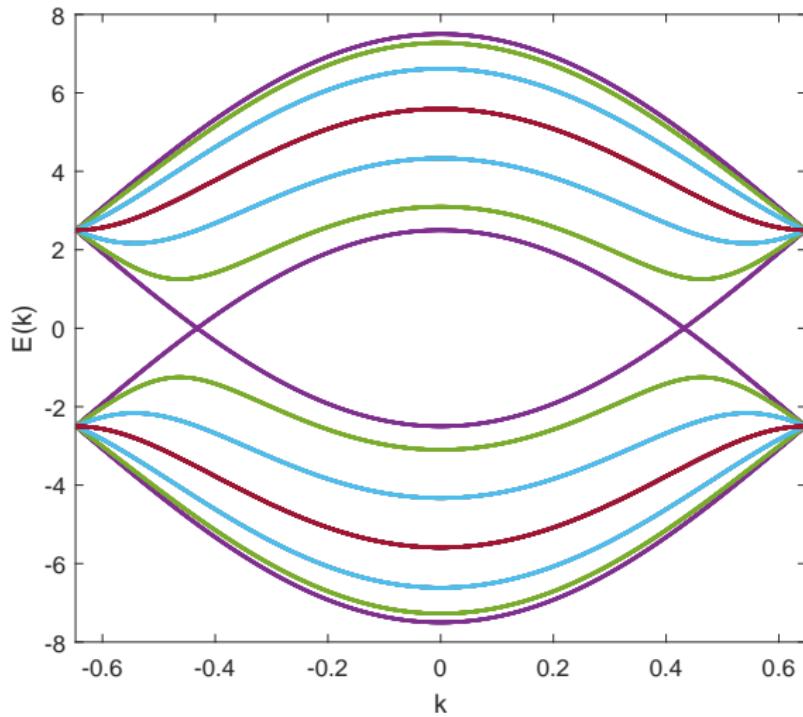
# Armchair for N = 4



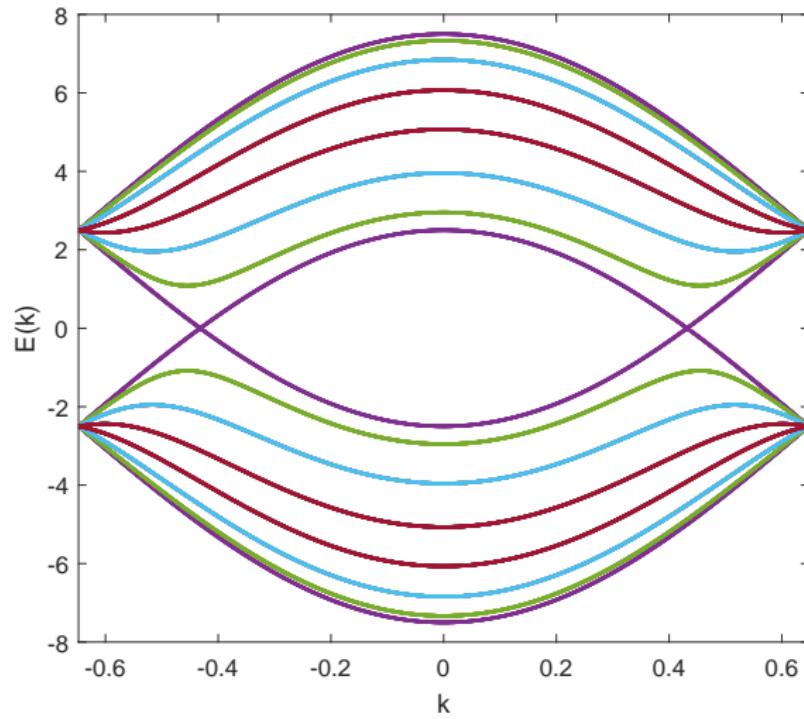
# Armchair for N = 5



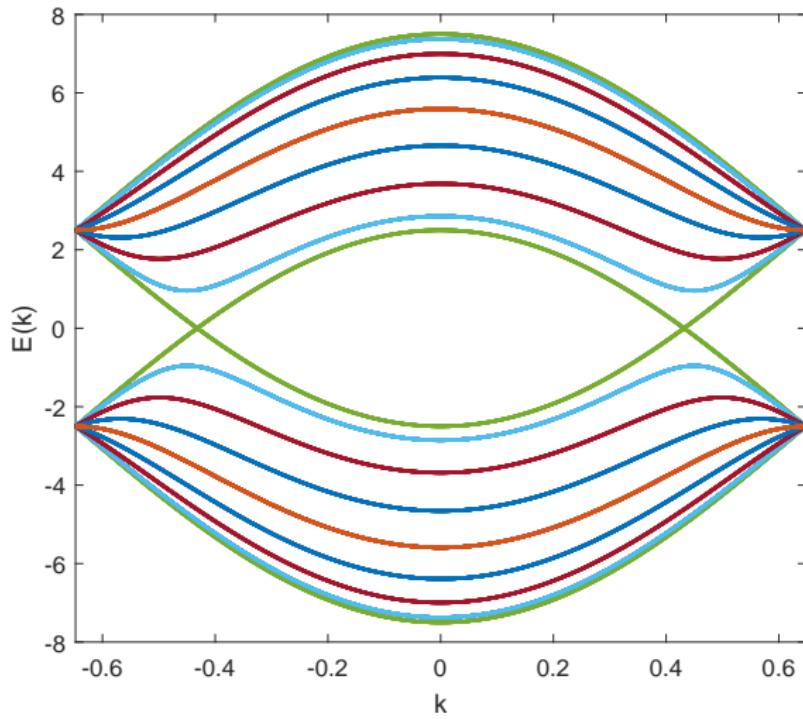
# Armchair for N = 6



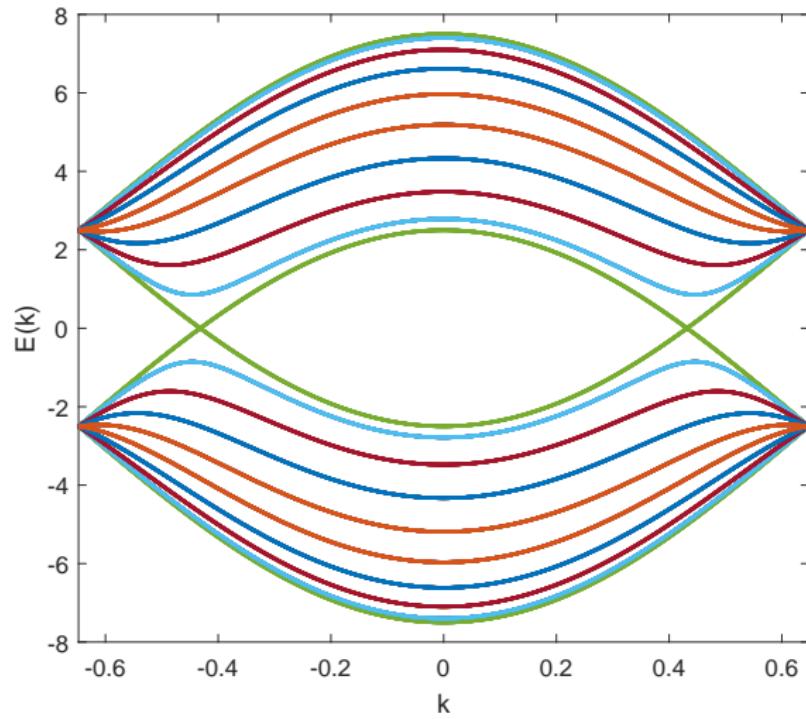
# Armchair for N = 7



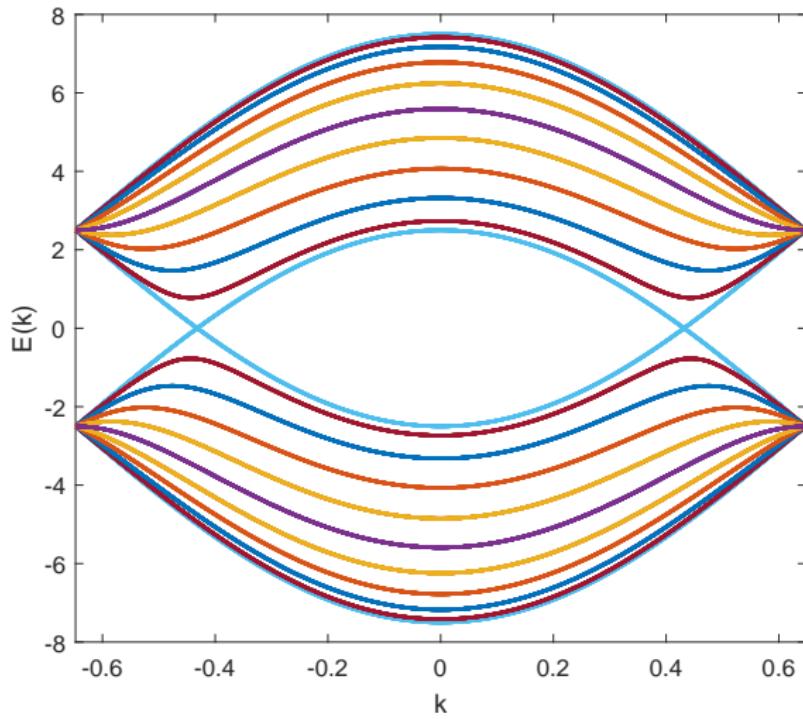
# Armchair for N = 8



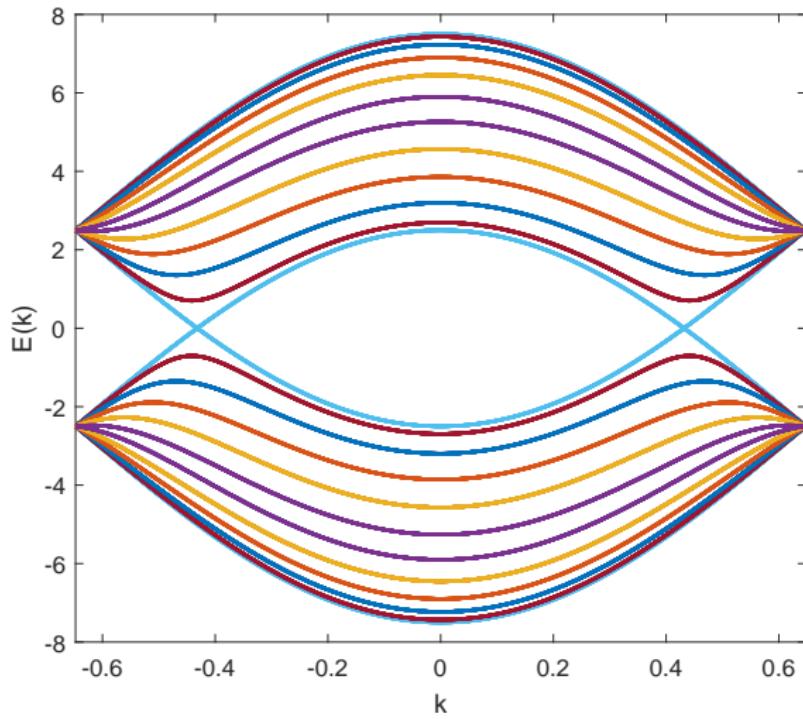
# Armchair for N = 9



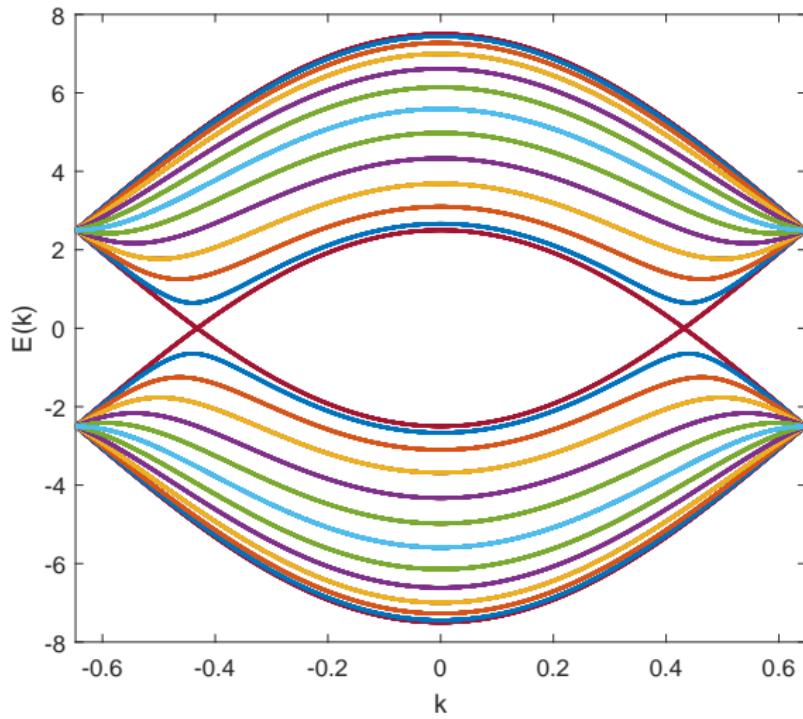
# Armchair for N = 10



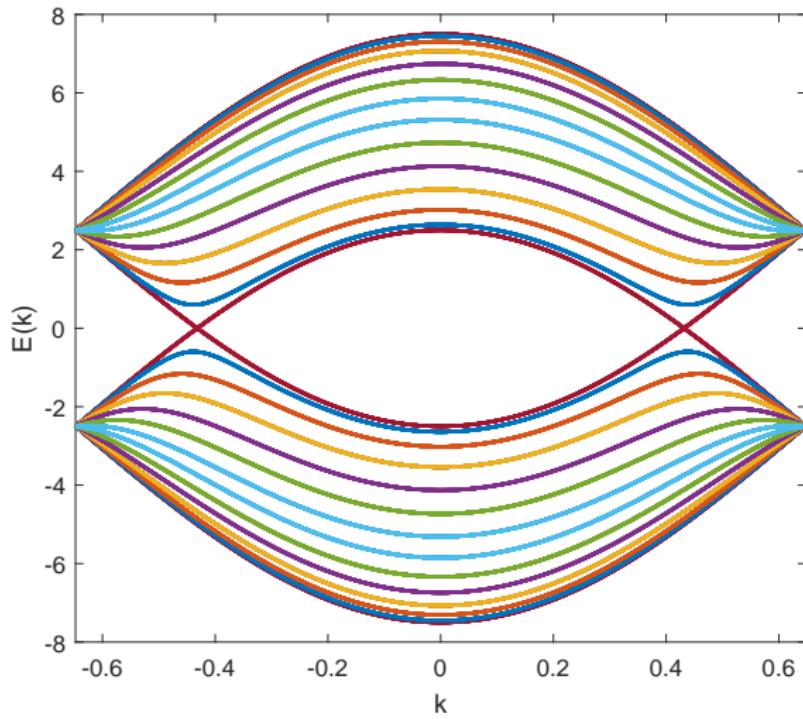
# Armchair for N = 11



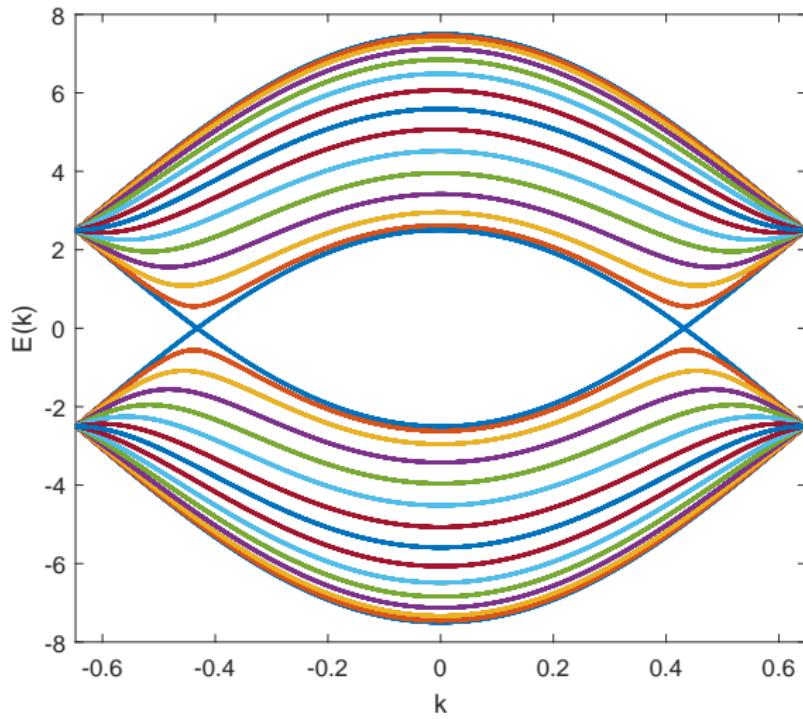
# Armchair for N = 12



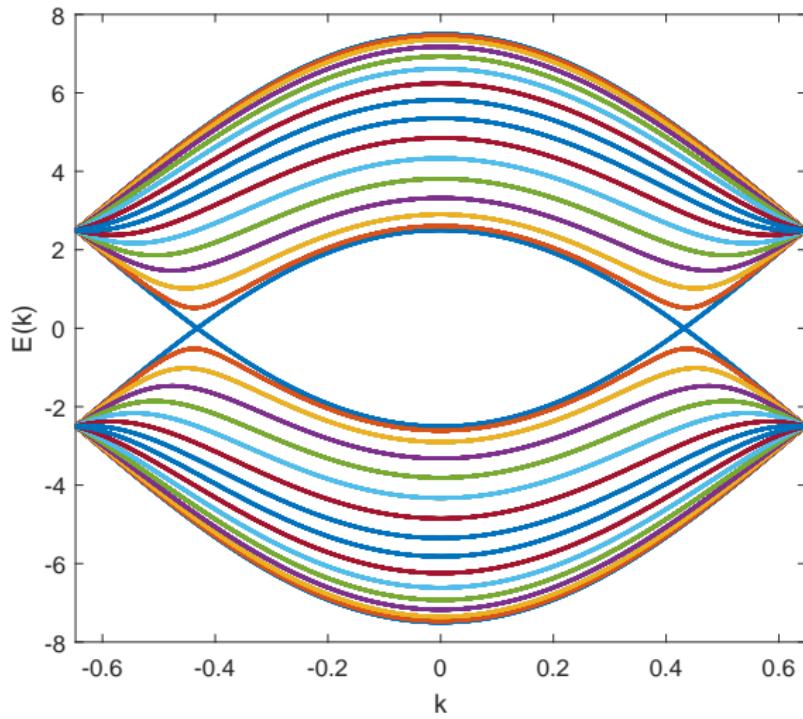
# Armchair for N = 13



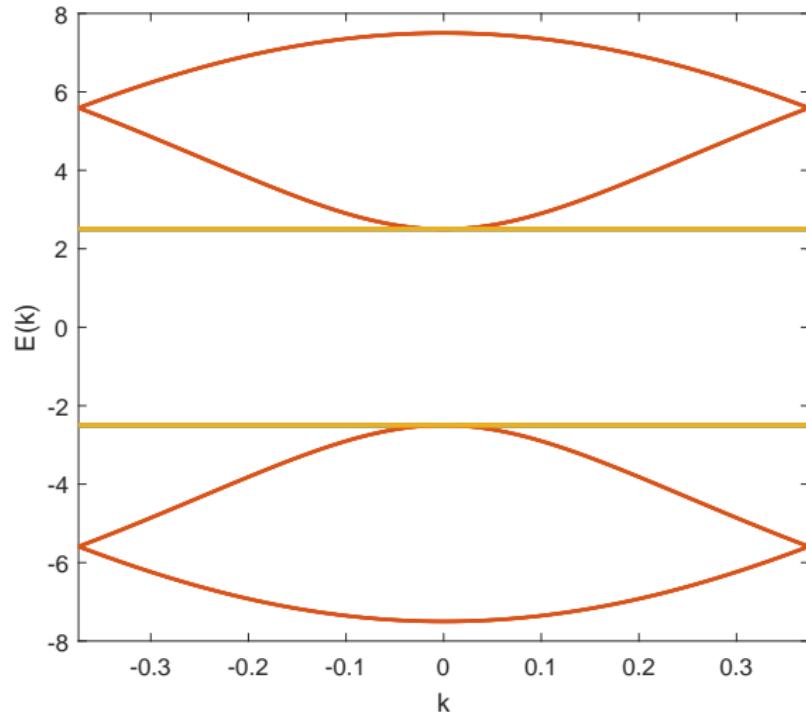
# Armchair for N = 14



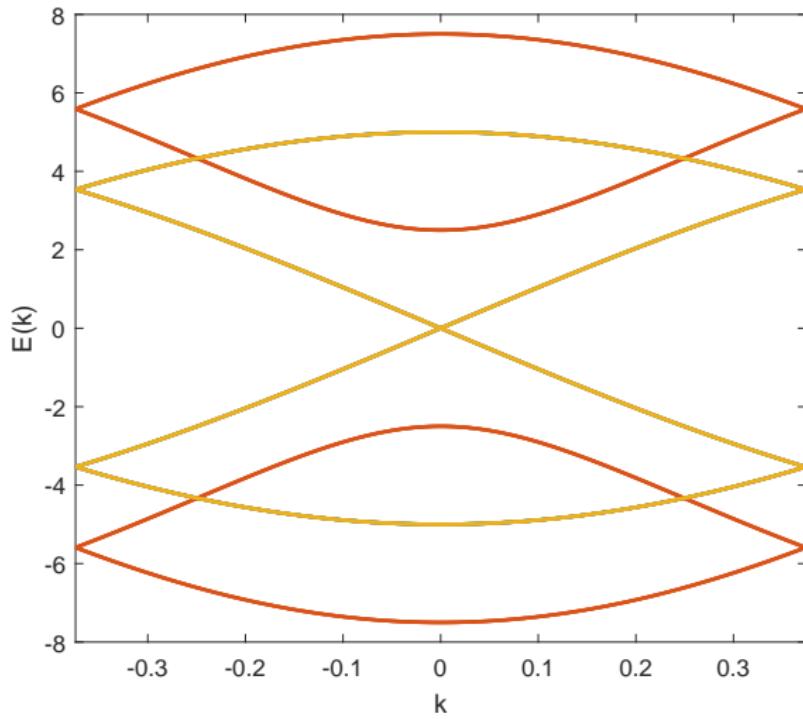
# Armchair for N = 15



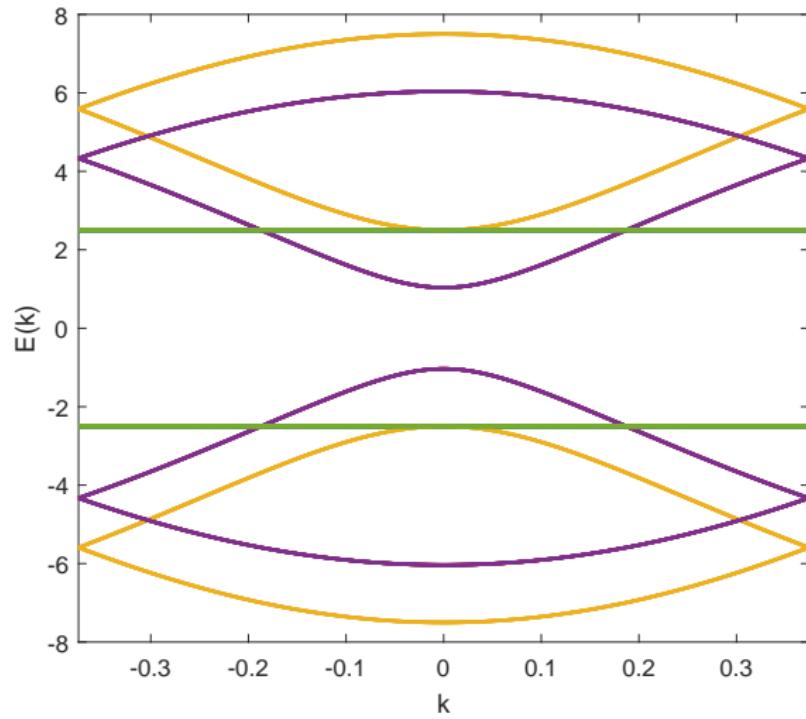
## Zig-zag for N = 2



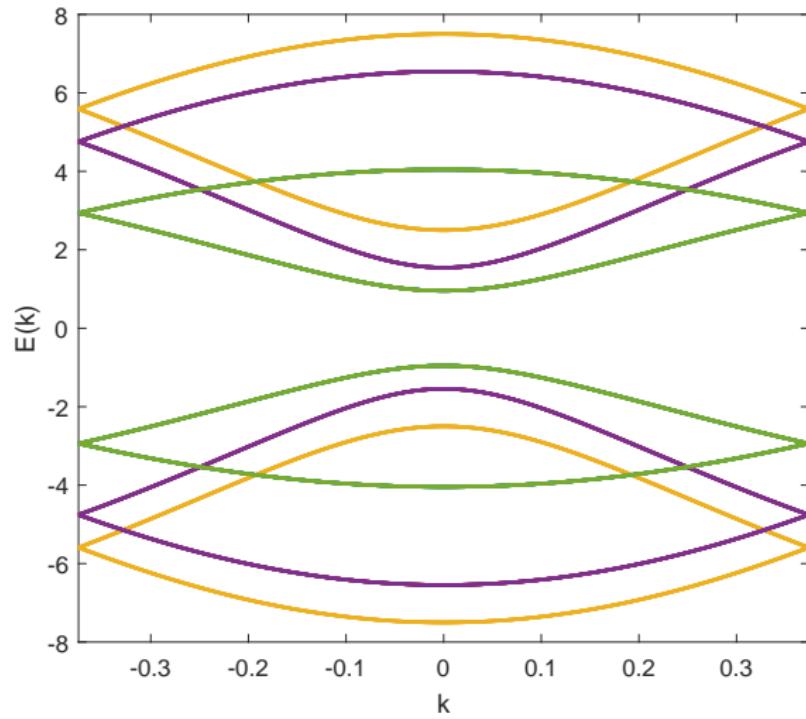
## Zig-zag for N = 3



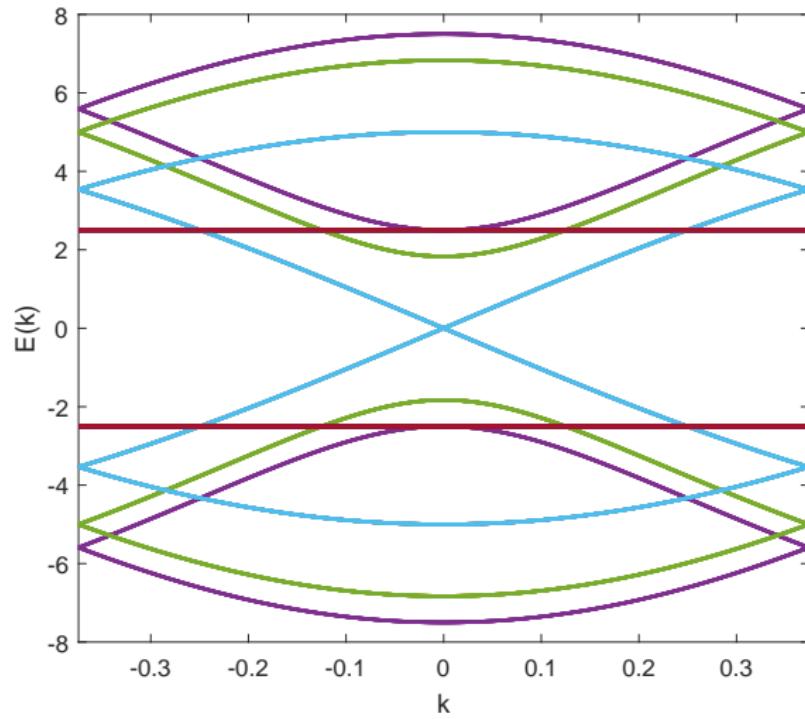
## Zig-zag for N = 4



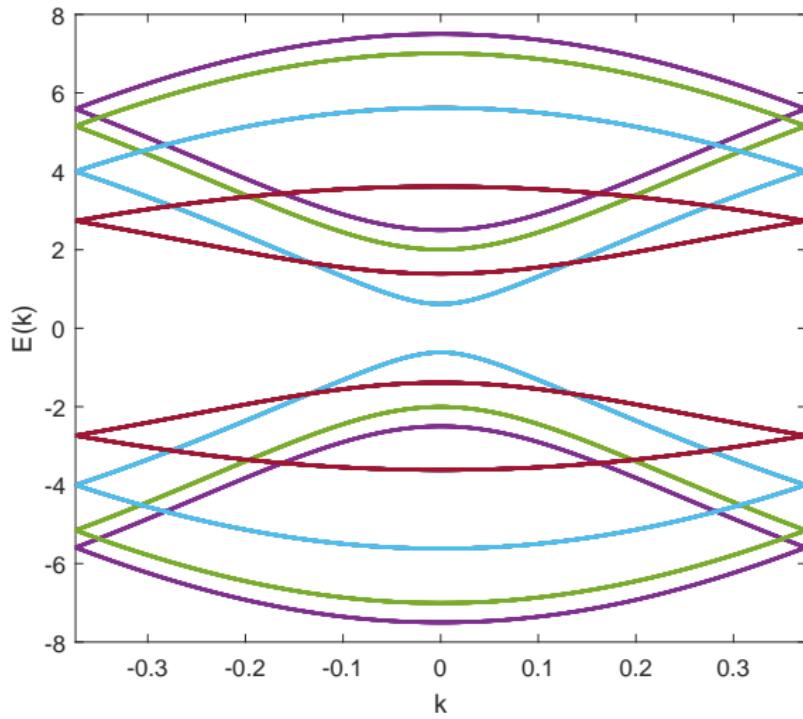
## Zig-zag for N = 5



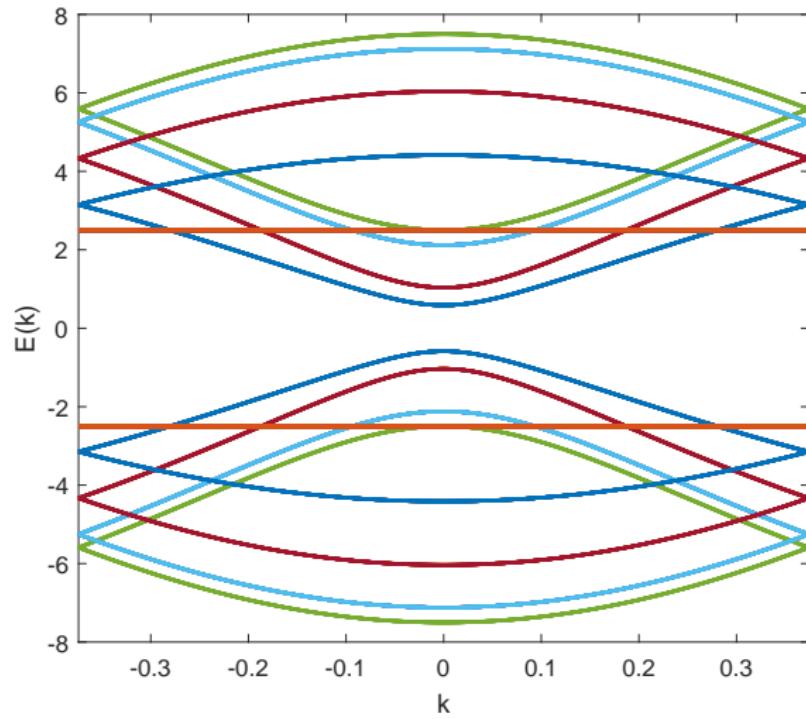
# Zig-zag for N = 6



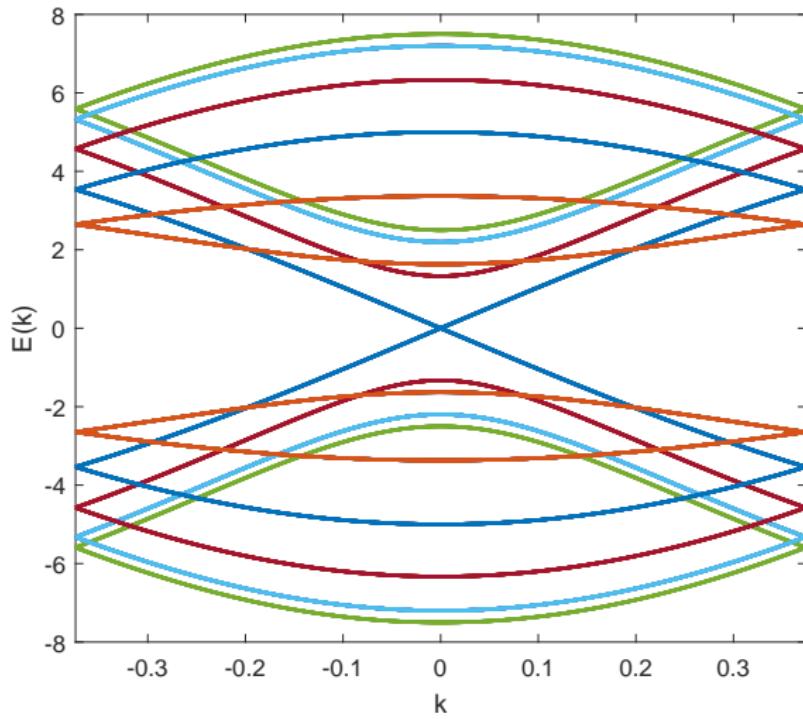
# Zig-zag for N = 7



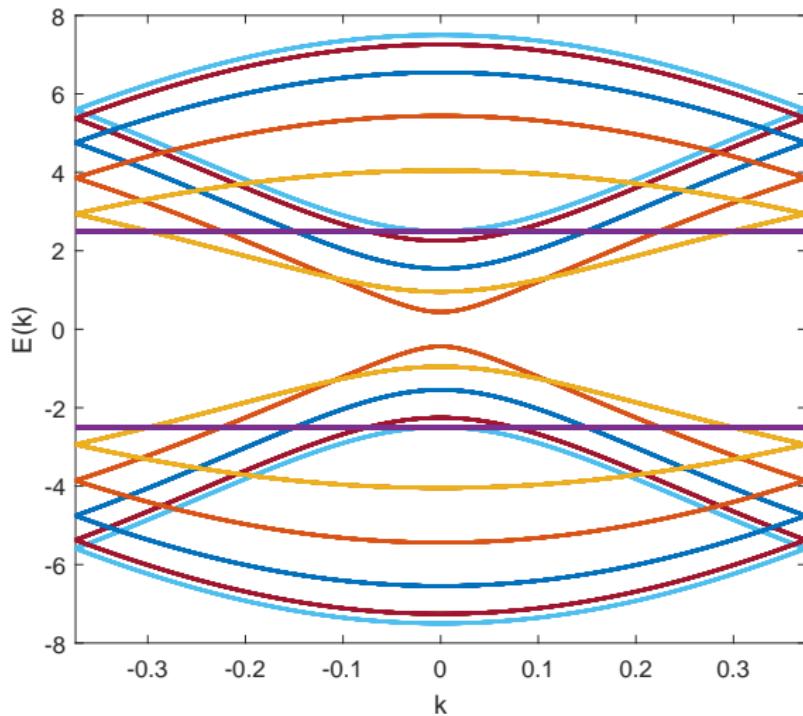
# Zig-zag for N = 8



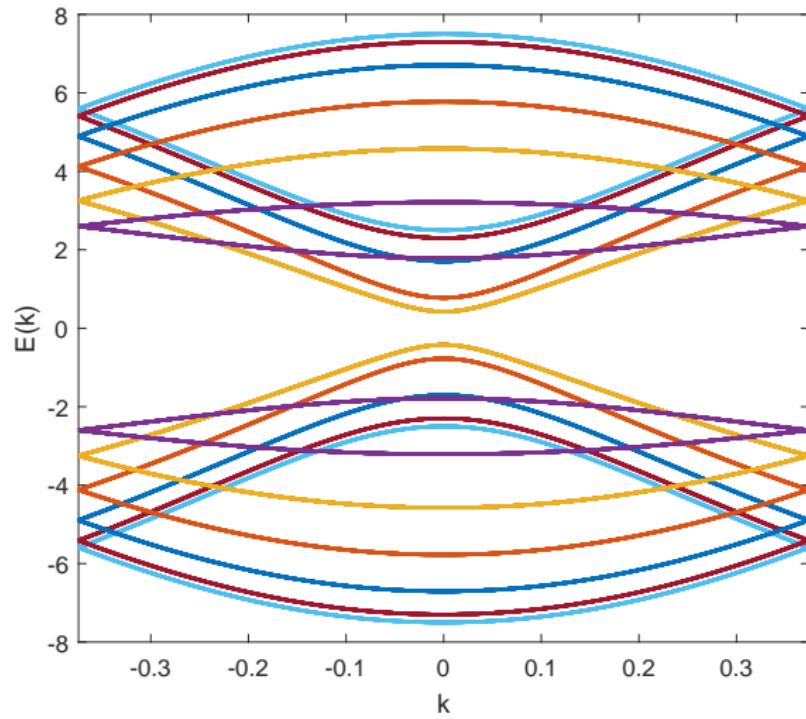
## Zig-zag for N = 9



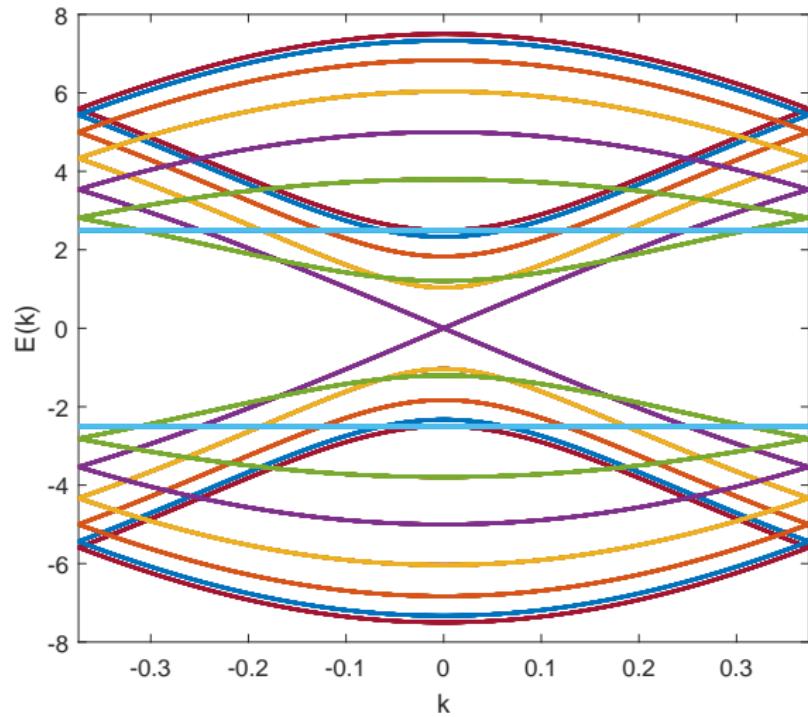
## Zig-zag for N = 10



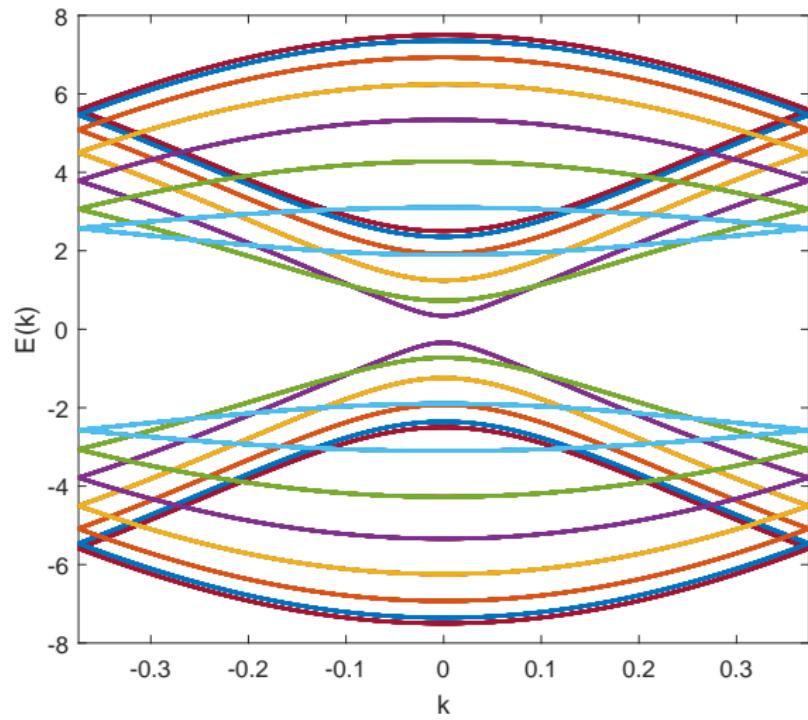
# Zig-zag for N = 11



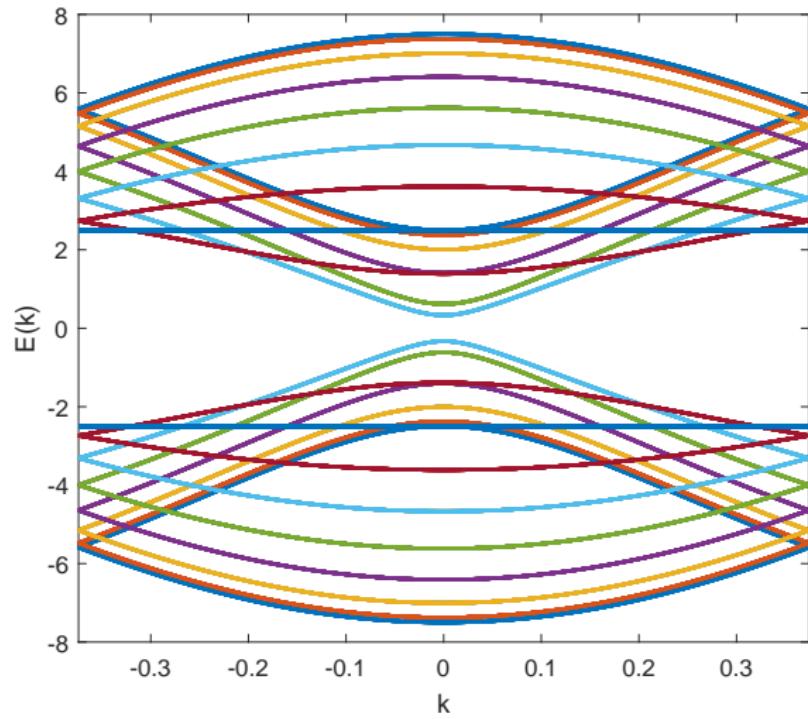
# Zig-zag for N = 12



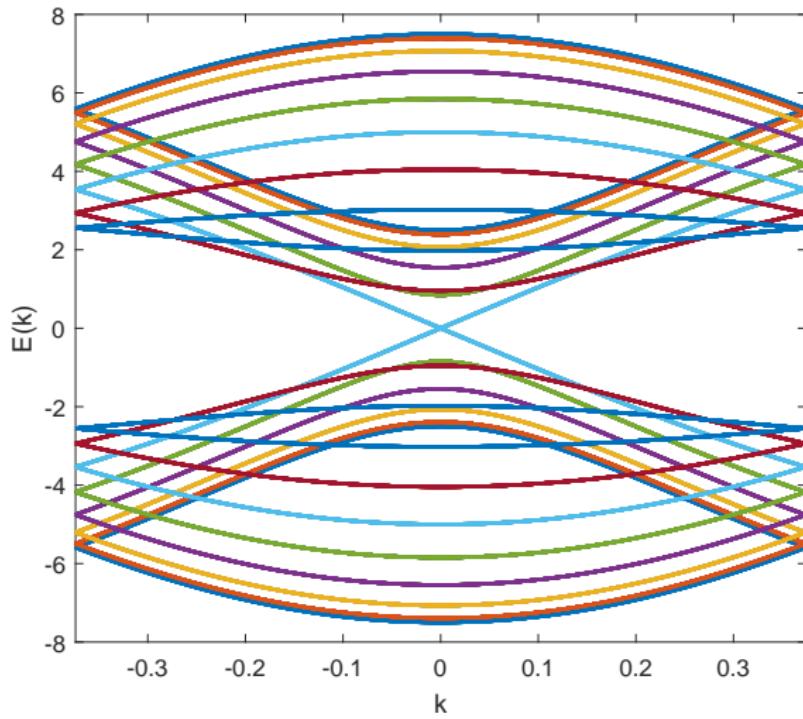
# Zig-zag for N = 13



## Zig-zag for N = 14



# Zig-zag for N = 15



# The Real End