

# Stability of edge states and edge magnetism in graphene nanoribbons

## *NANOTR-VII, İstanbul, Sabancı University*

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- ZGNRs have magnetic edge states. Antiferromagnetic semiconductors.

# Introduction & Aim

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- Is the application of edge magnetism in spintronic devices feasible?

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- ZGNRs have magnetic edge states. Antiferromagnetic semiconductors.
- Is the application of edge magnetism in spintronics devices feasible?
- Outline:
  - Graphene & (A,Z)GNRs
  - Edge States
  - Stability - Edge Passivation
  - Stability - Edge Reconstruction & Closure
  - Stability - Edge Magnetism

- Method: Density Functional Theory.
- Exchange-correlation: GGA (PW91).
- Basis set: Plane waves. PAW Pseudopotential.
- Code: VASP
- **Edge Energy**; amount of energy needed (per edge atom) to cut out a ZGNR from infinite graphene

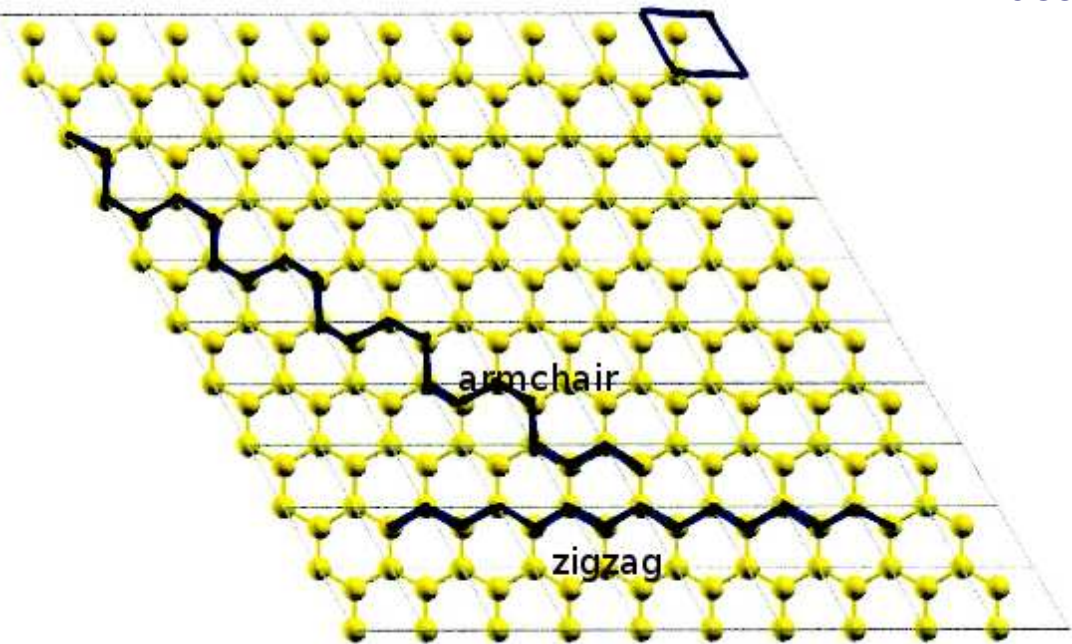
$$E_{edge}^{at} = (E_{tot}^{ZGNR} - N_C E_{coh}^{graphene} - N_H E_{coh}^{H_2}) / N_C^{edge} \quad (1)$$

- **Magnetic Stabilization Energy**; difference in total energy (per magnetic atom) of a magnetic state with respect to the magnetic ground state.

$$\Delta E_{mag} = (E_{tot} - E_{tot}^{GS}) / N_{MA}, \quad (2)$$

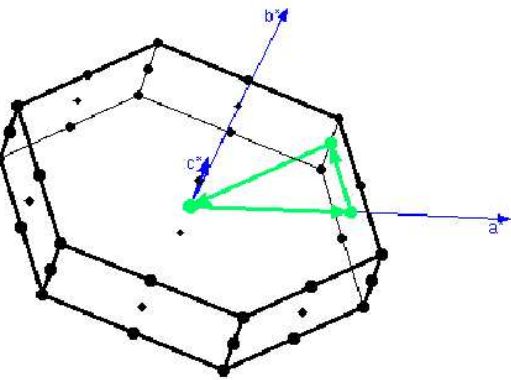
# Graphene & (A,Z)GNRs

- Crystalline lattice of graphene. Hexagonal. Ideal 2D system.

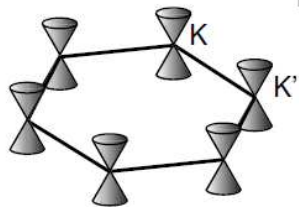


# Graphene & (A,Z)GNRs

Primitive Brillouin Zone

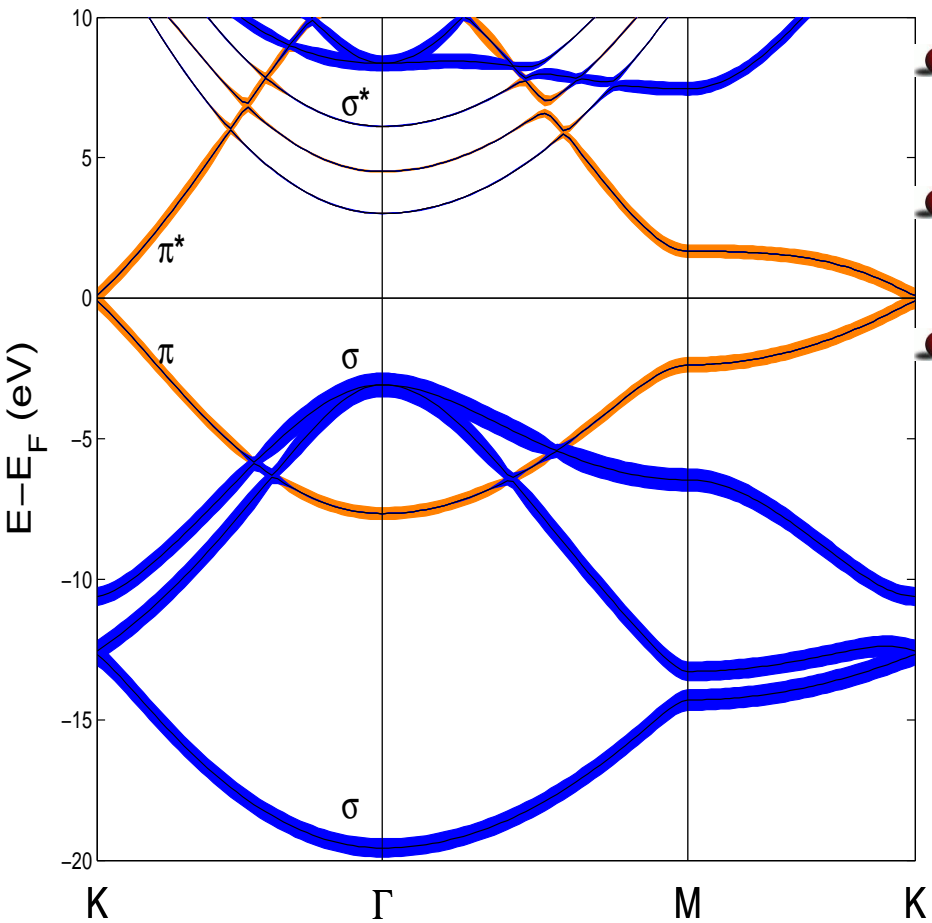


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3	0.50000	-0.00000 0.00000
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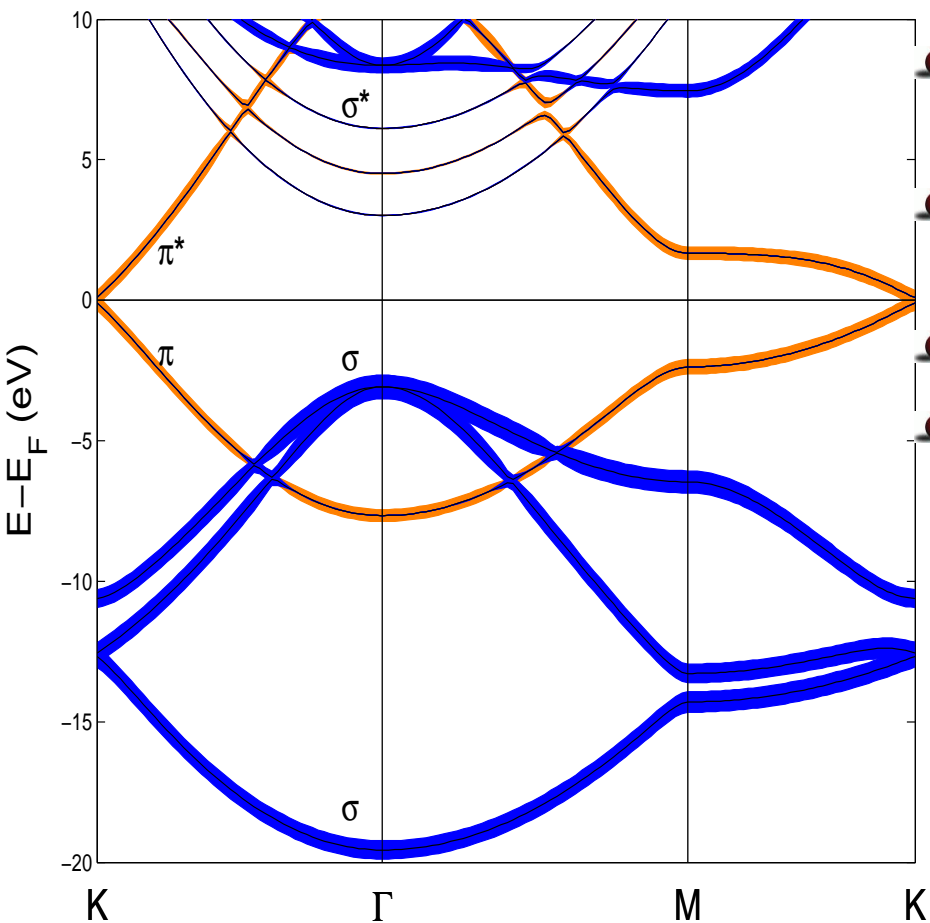
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- Hexagonal Brillouin zone. Two inequivalent points K and K'  $\Rightarrow$  Dirac cone. Linear bands.

# Graphene & (A,Z)GNRs



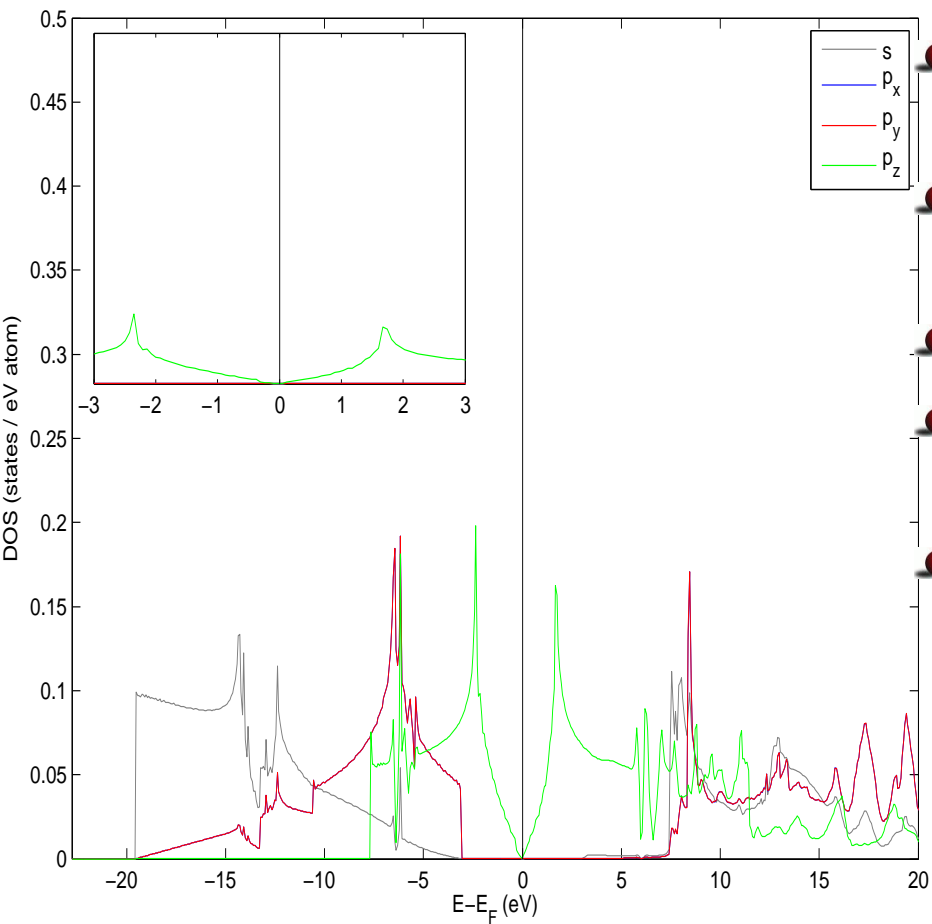
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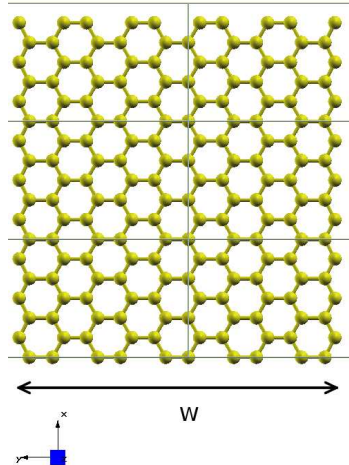
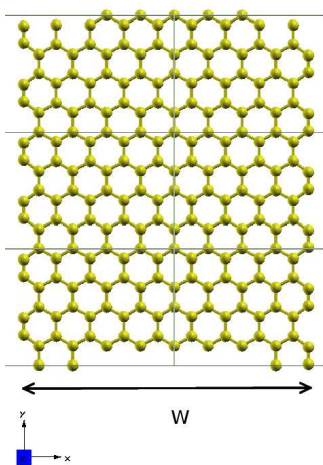
# Graphene & (A,Z)GNRs



Graphene nanoribbons (GNRs)

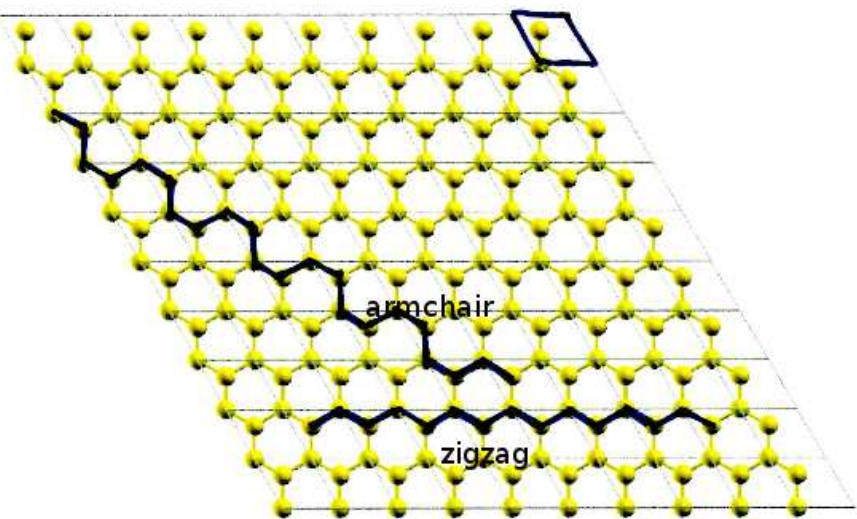
Armchair (AGNR)

Zigzag (ZGNR)



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- GNR. A graphene strip of finite width (W) and infinite length.

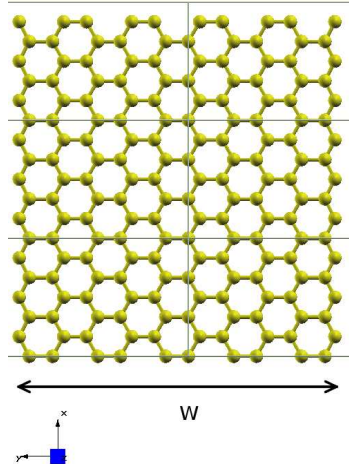
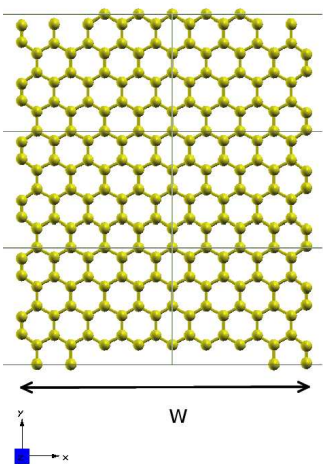
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- AGNR  $\Rightarrow$  Semiconducting

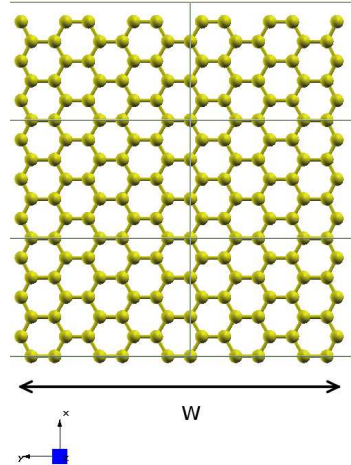
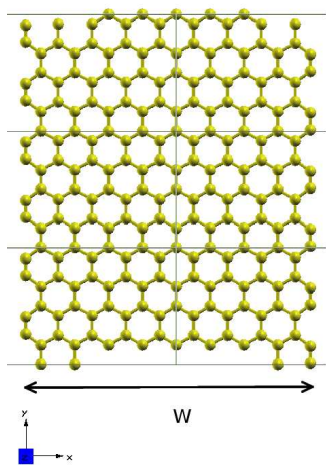
# Graphene & (A,Z)GNRs



Graphene nanoribbons (GNRs)

Armchair (9-AGNR)

Zigzag (10-ZGNR)



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- AGNR  $\Rightarrow$  Semiconducting
- ZGNR  $\Rightarrow$  Magnetic Edge States

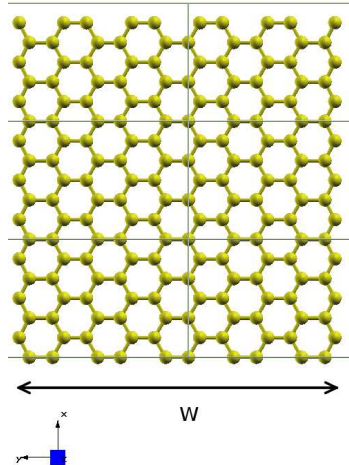
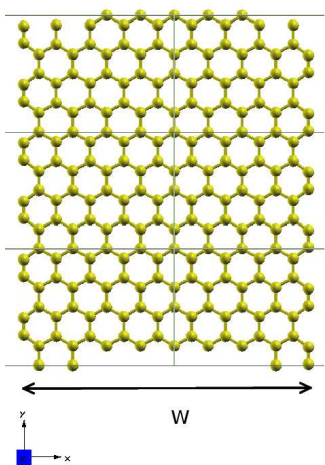
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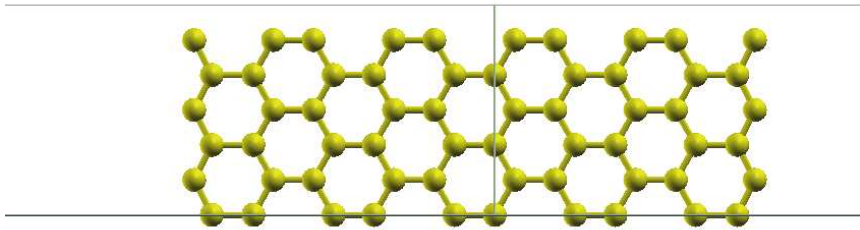
Armchair (AGNR)

Zigzag (ZGNR)



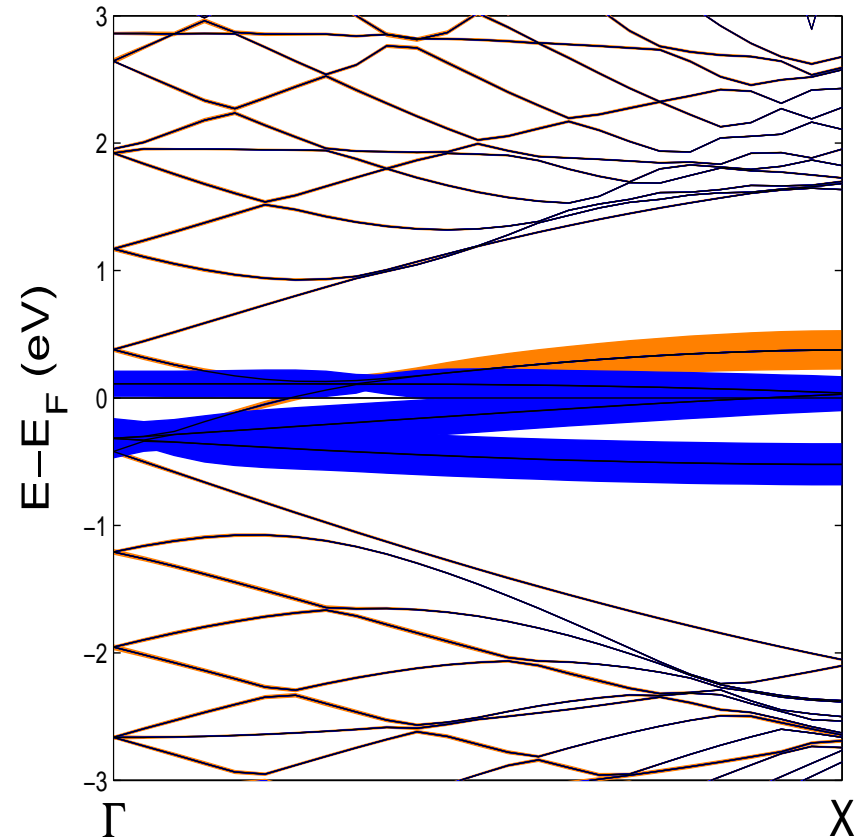
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- GNR. A graphene strip of finite width (W) and infinite length.
- AGNR  $\Rightarrow$  Semiconducting
- ZGNR  $\Rightarrow$  Magnetic Edge States
- ZGNR  $\Rightarrow$  Antiferromagnetic Semiconductor

## 10-zgnr Non-Magnetic (NM)

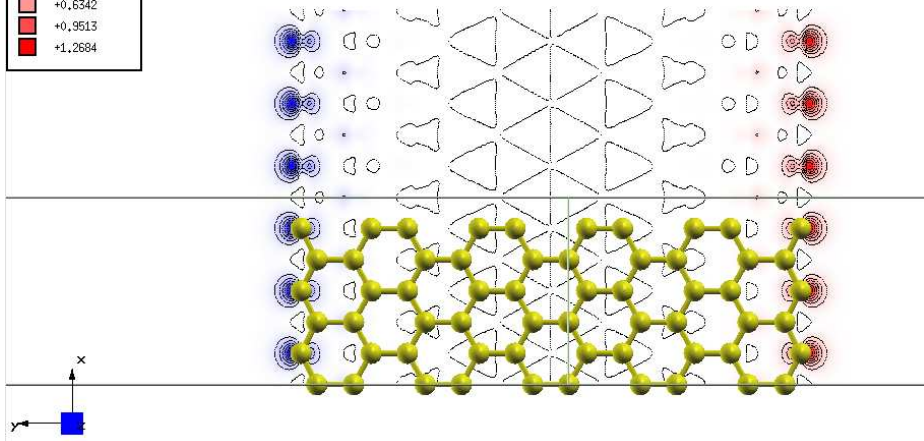
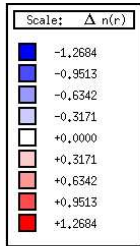


Edge states are localized at the edges of the ZGNR

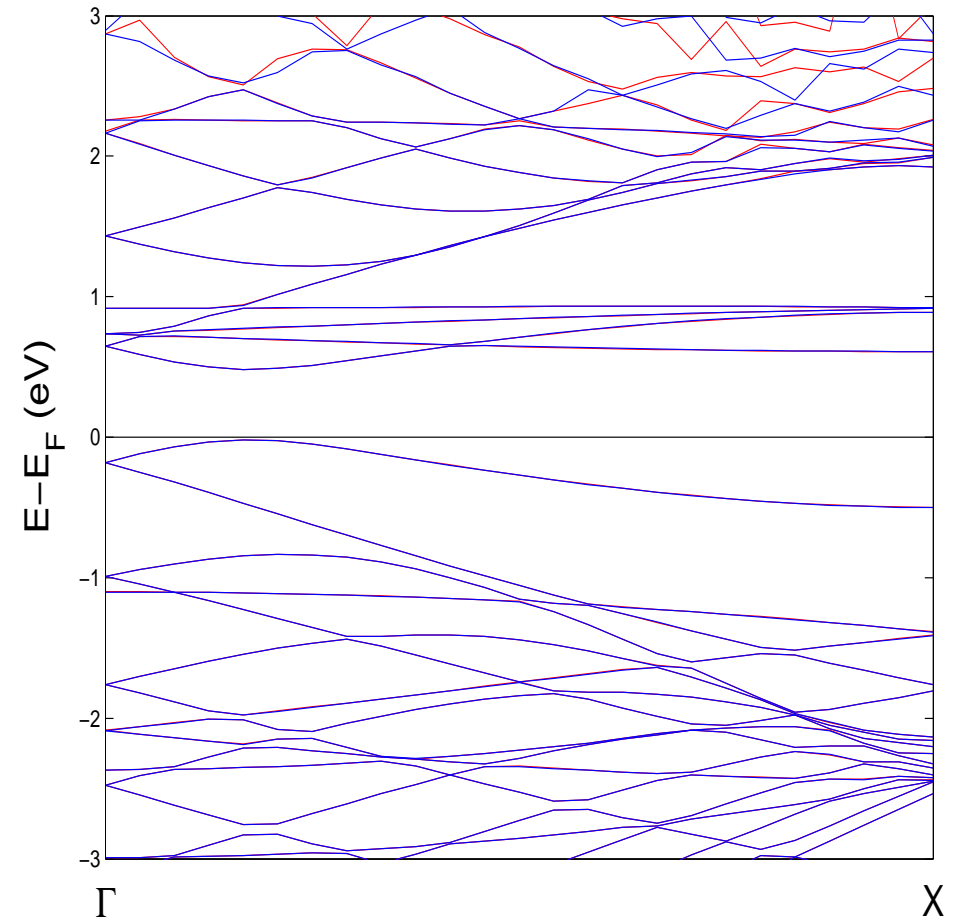
## Edge States. $\sigma$ - $\pi$ states



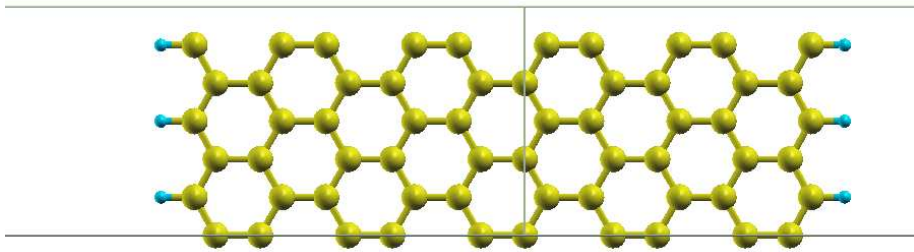
## 10-zgnr Magnetic (AFM)



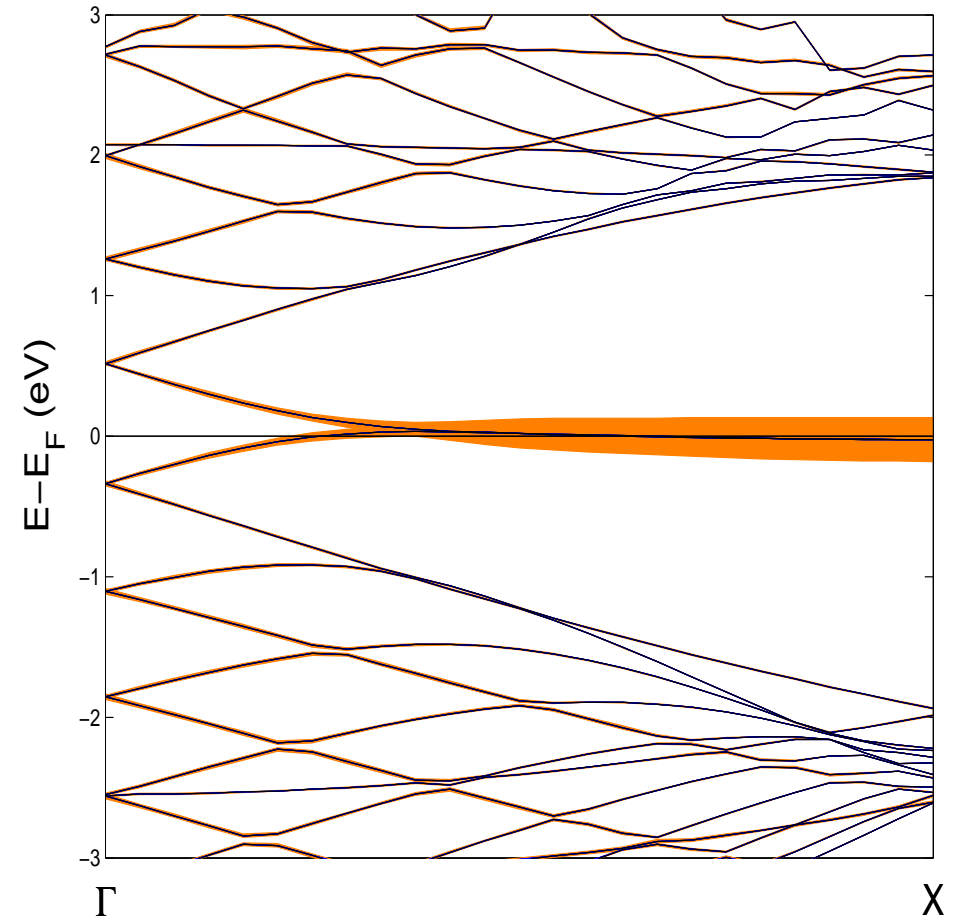
Semi-conducting



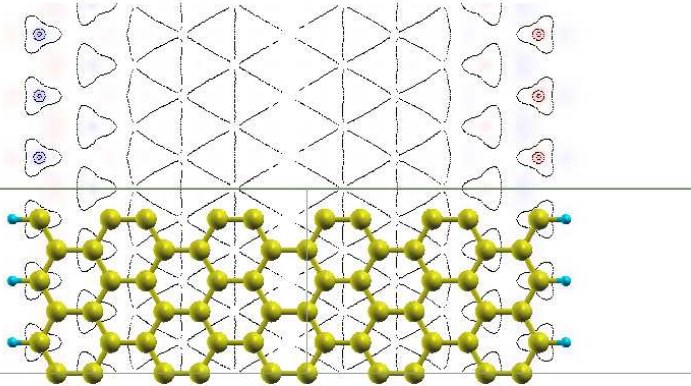
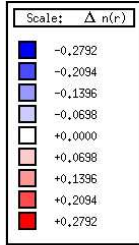
10-zgnr+H NM



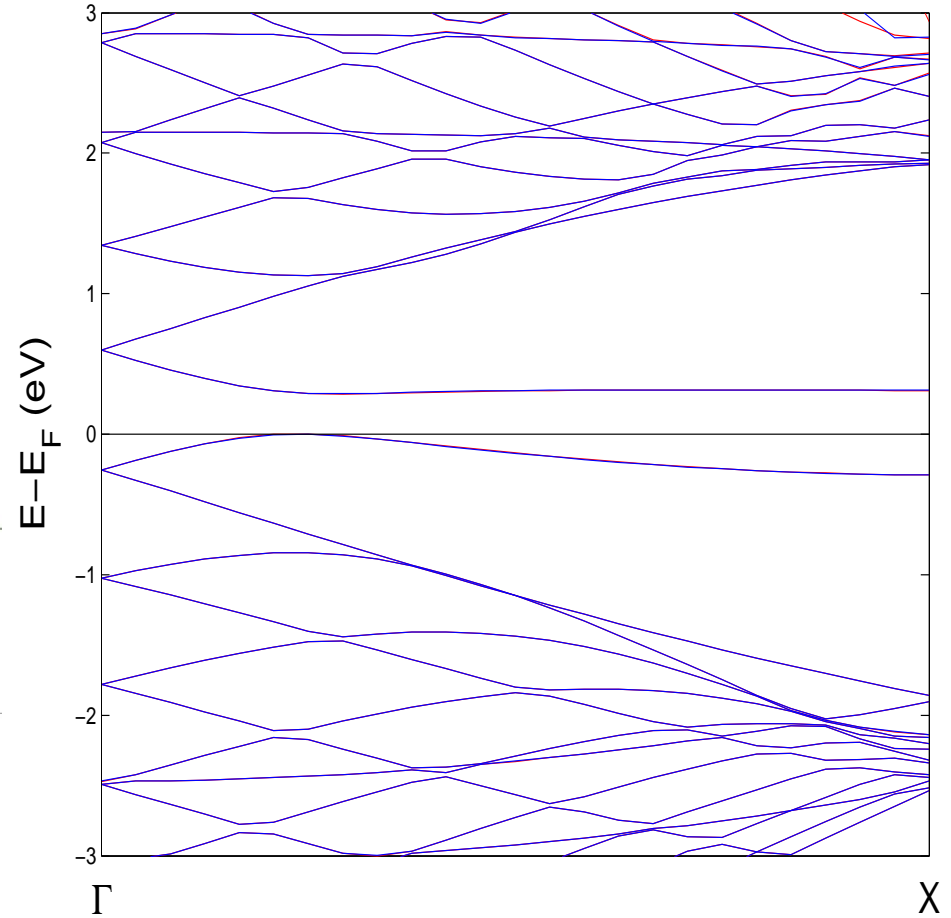
Edge States.  $\pi$  states



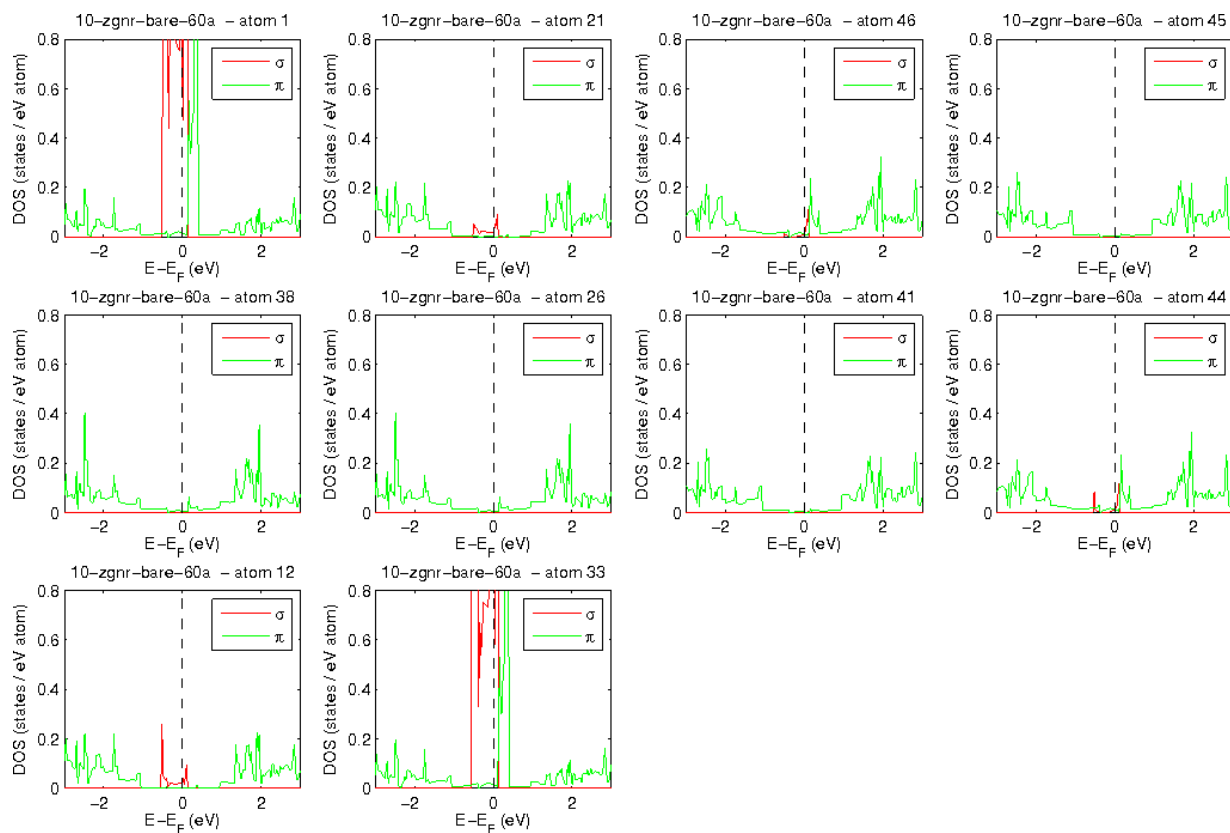
## HP 10-zgnr AFM



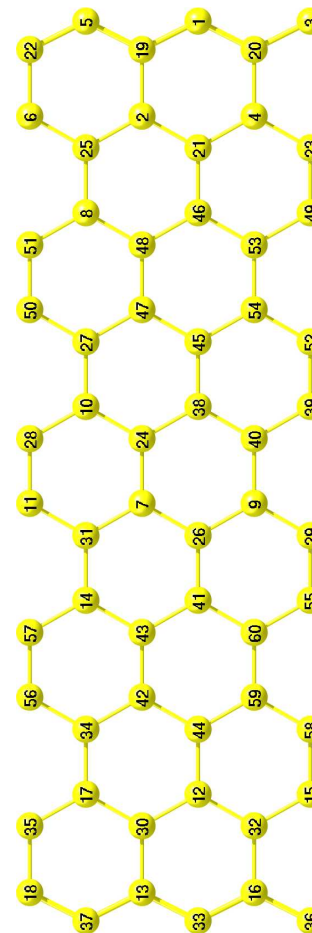
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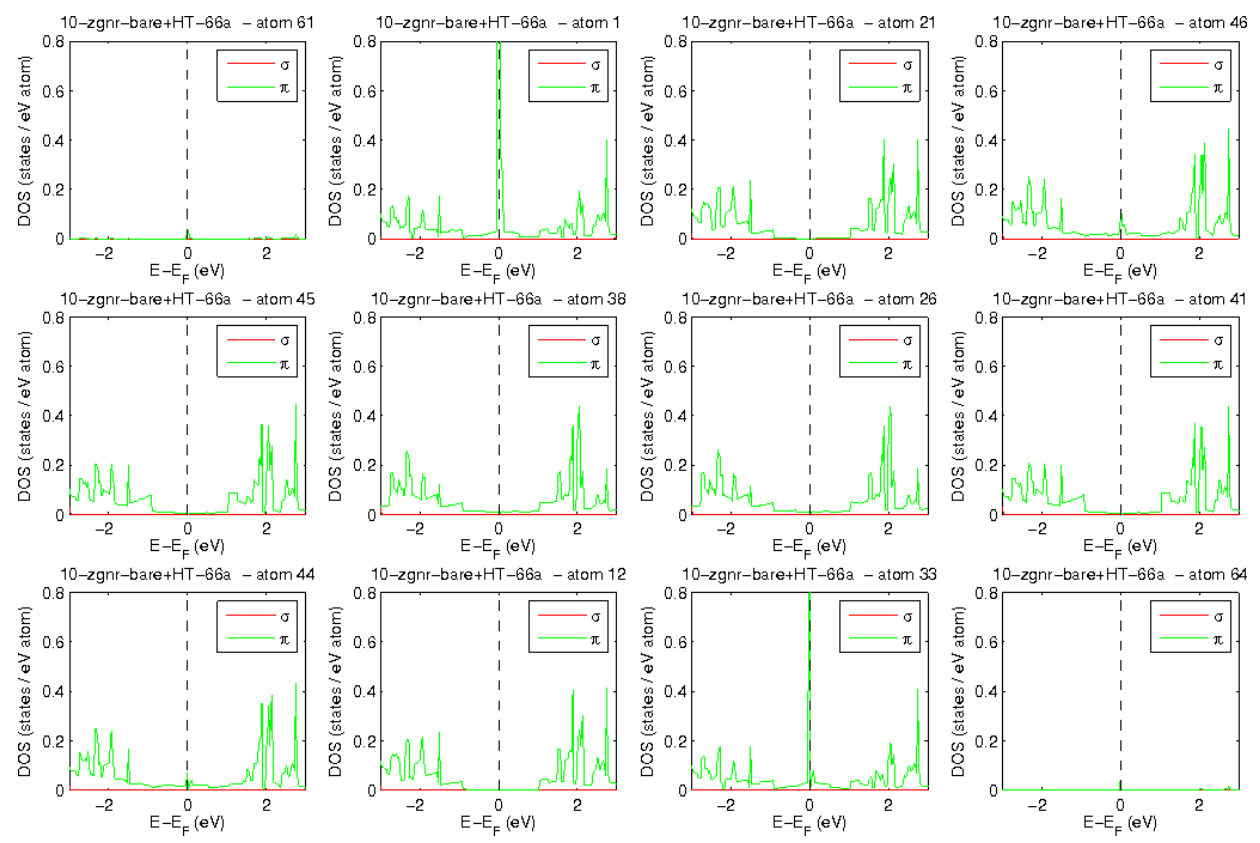
## Unpassivated 10-zgrn. Projected DOSs for atoms 1-33



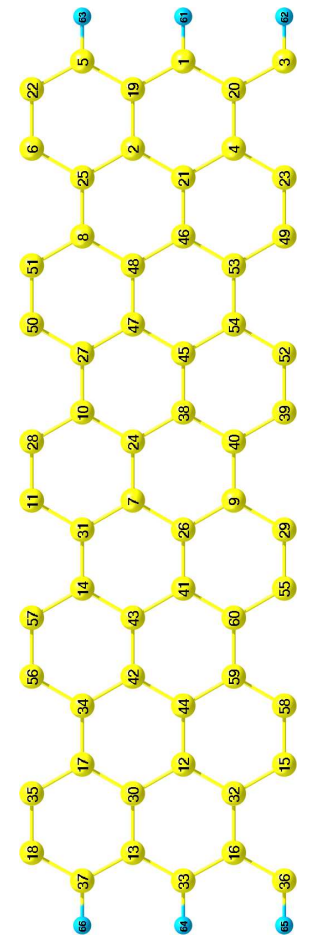
## Geometry



## Passivated 10-zgnr. Projected DOSs for atoms 61-64

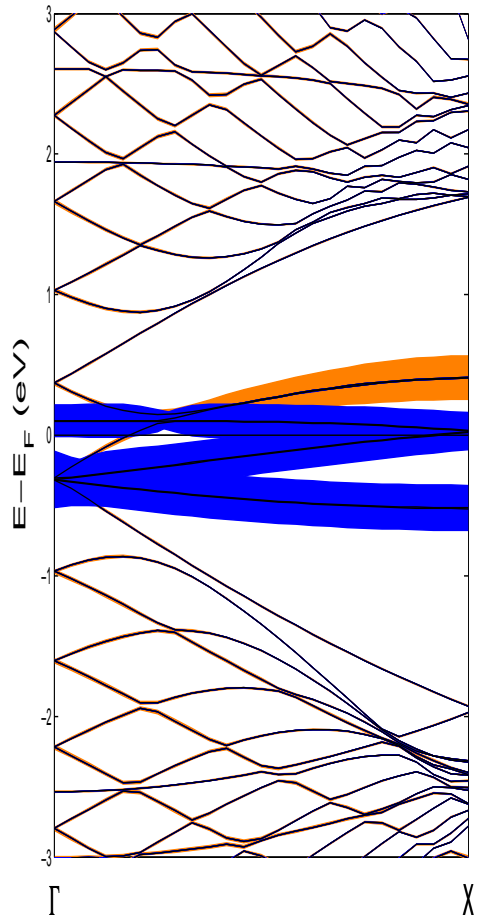
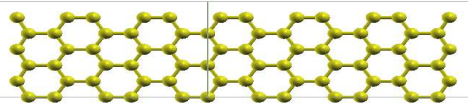


## Geometry



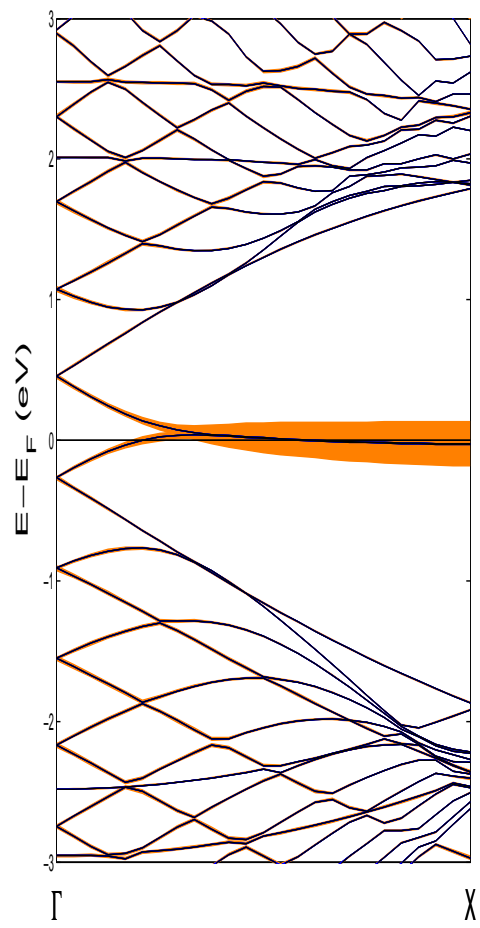
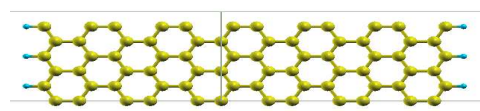
# Stability - Edge Passivation

12-zgnr NM



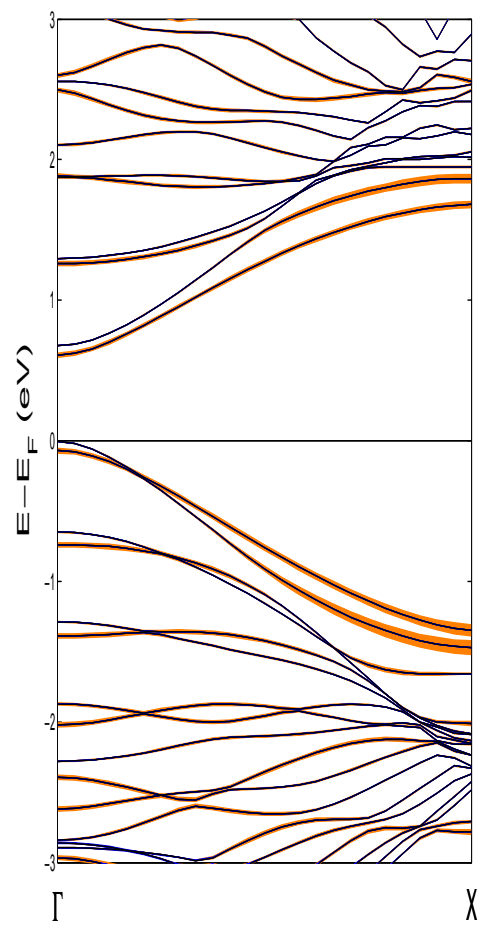
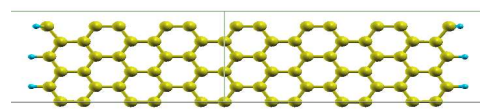
$E_{edge}^{at} = 3.00 \text{ eV/at}$   
(Eqn. 1)

12-zgnr+H NM



$E_{edge}^{at} = 0.28 \text{ eV/at}$

12-zgnr+H ( $z_{211}$ ) NM

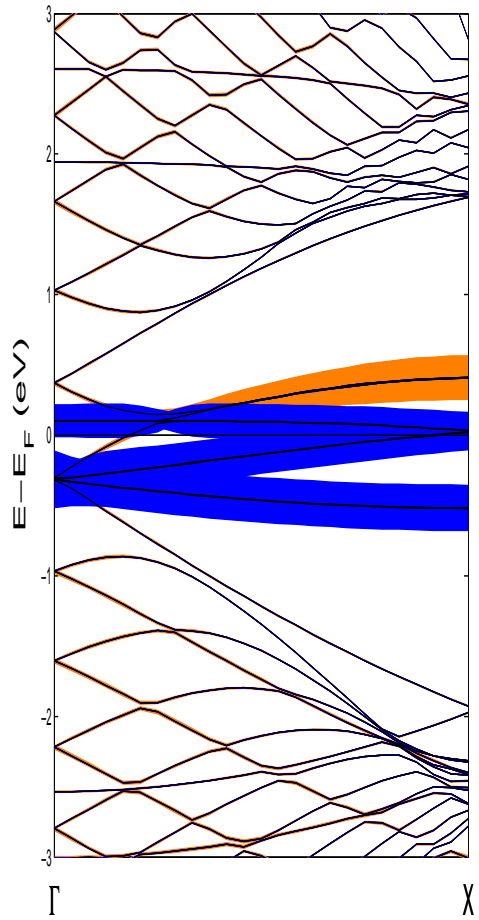
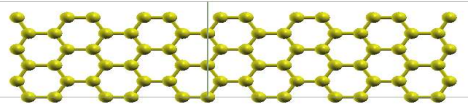


$E_{edge}^{at} = 0.08 \text{ eV/at}$

● 12-zgnr  $\Rightarrow \sigma$ - $\pi$  states around  $E_F$ .

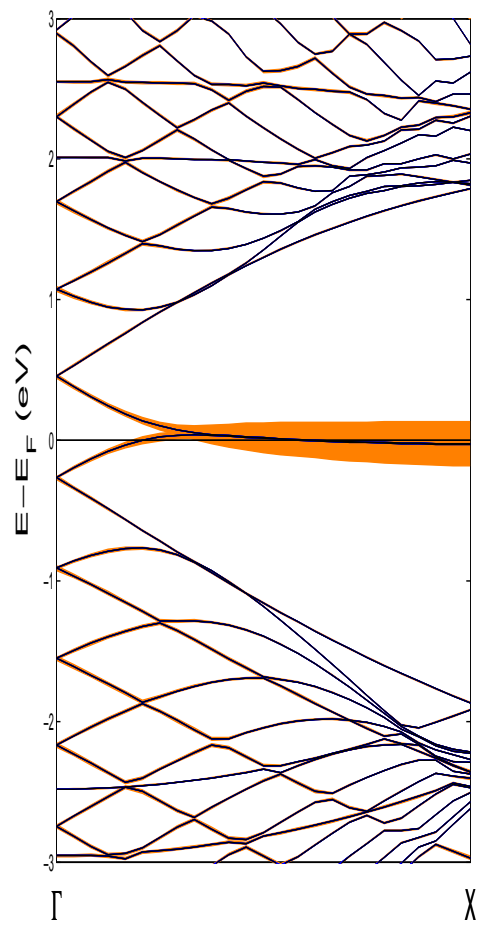
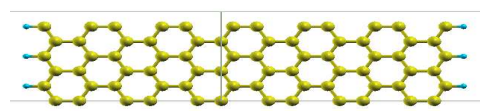
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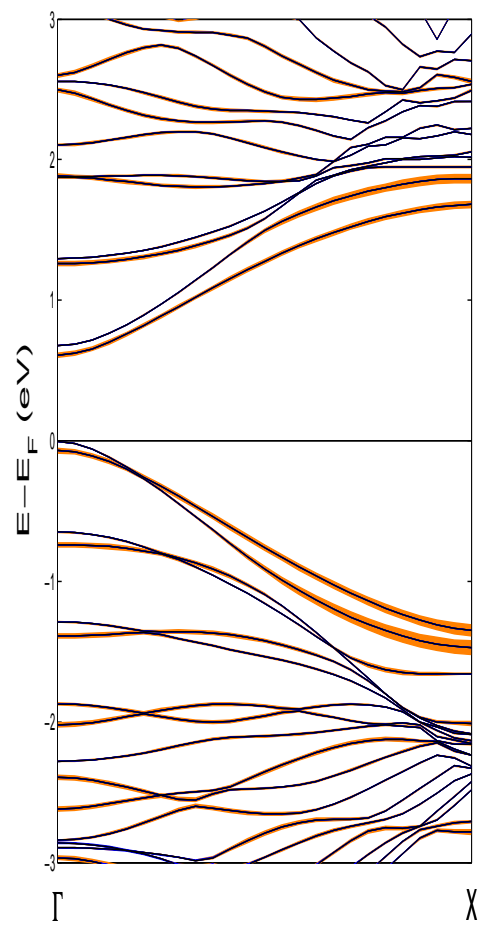
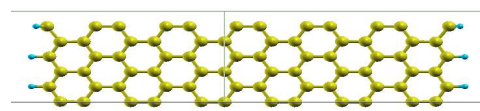
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12-zgnr+H ( $z_{211}$ ) NM

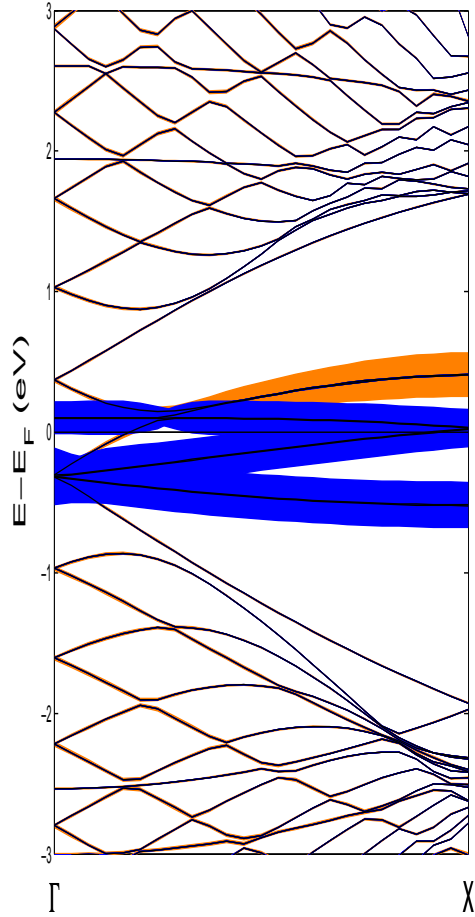
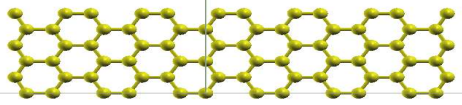


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- 12-zgnr  $\Rightarrow \sigma$ - $\pi$  states around  $E_F$ .
- 12-zgnr+H  $\Rightarrow$  Flat bands ( $\pi$ ).

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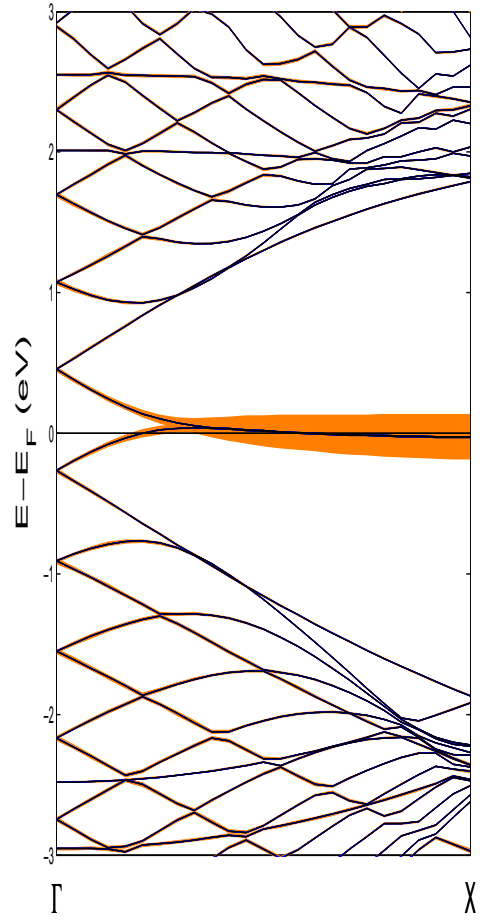
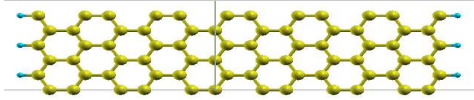
12-zgnr NM



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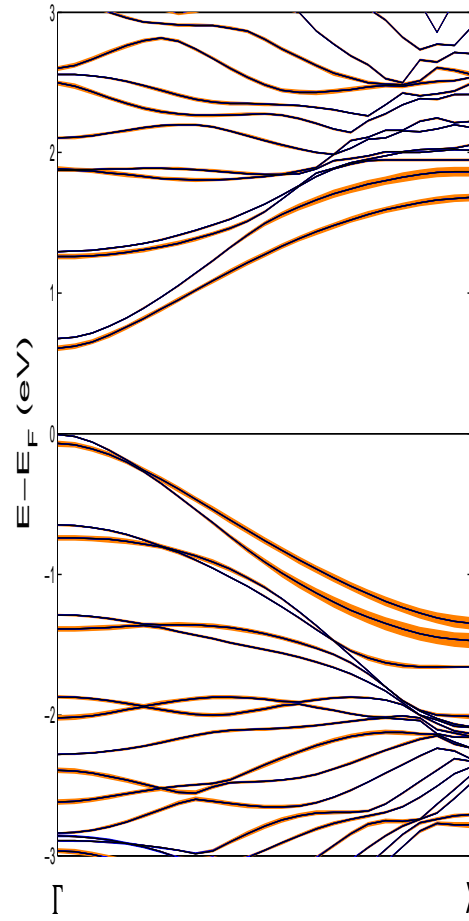
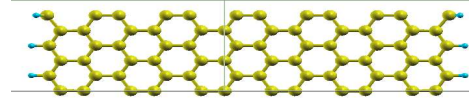
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12-zgnr+H ( $z_{211}$ ) NM

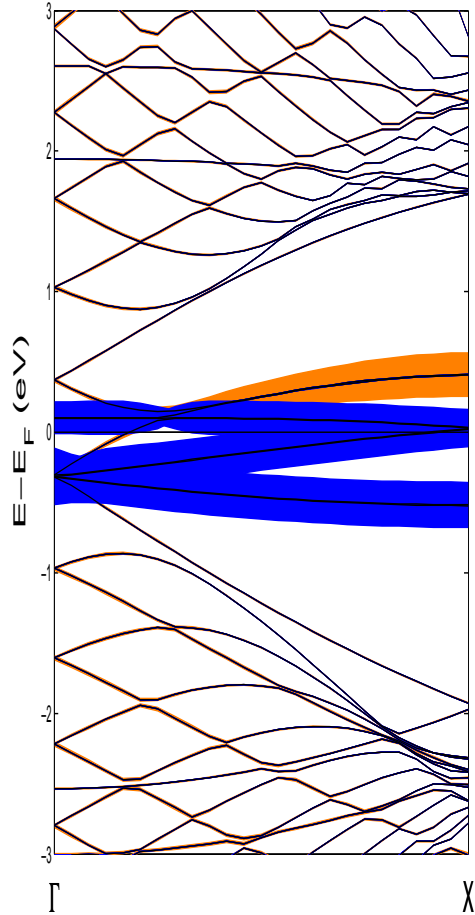
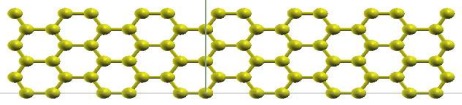


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- 12-zgnr  $\Rightarrow \sigma$ - $\pi$  states around  $E_F$ .
- 12-zgnr+H  $\Rightarrow$  Flat bands ( $\pi$ ).
- $z_{211}$  edge is the most stable edge.

# Stability - Edge Passivation

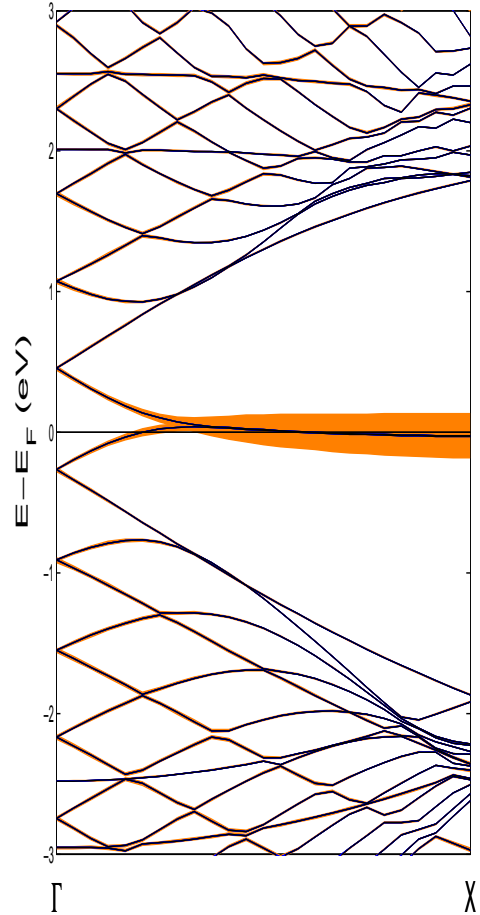
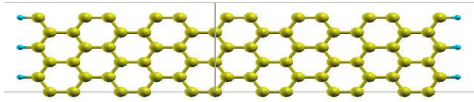
12-zgnr NM



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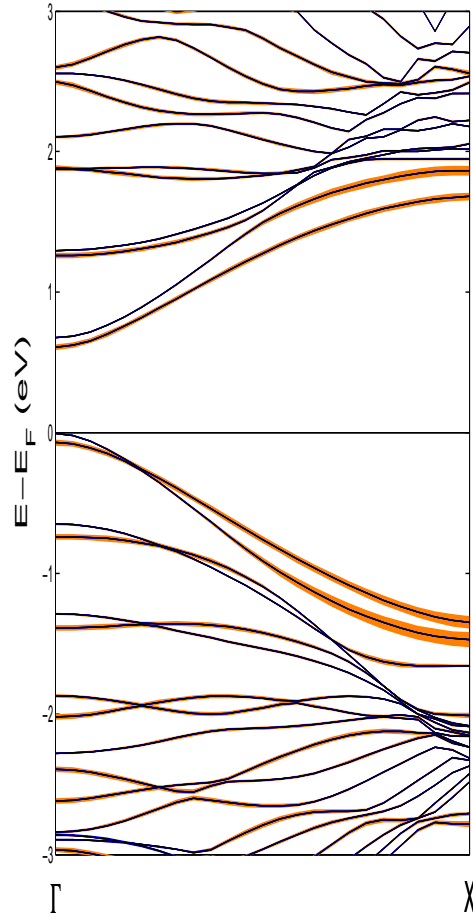
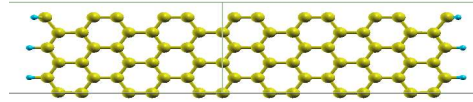
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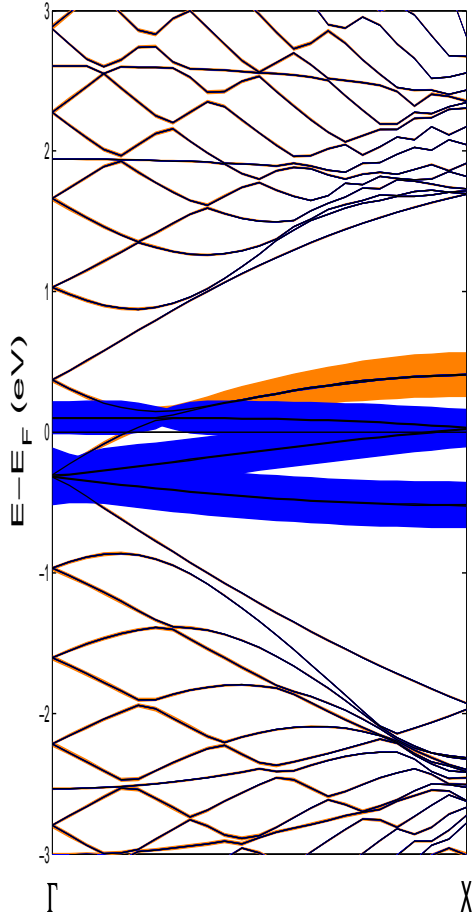
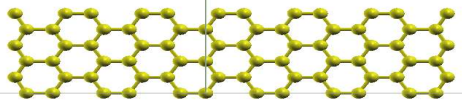


$$E_{edge}^{at} = 0.08 \text{ eV/at}$$

- 12-zgnr  $\Rightarrow \sigma$ - $\pi$  states around  $E_F$ .
- 12-zgnr+H  $\Rightarrow$  Flat bands ( $\pi$ ).
- $z_{211}$  edge is the most stable edge.
- Semiconducting (band gap 0.61 eV).

# Stability - Edge Passivation

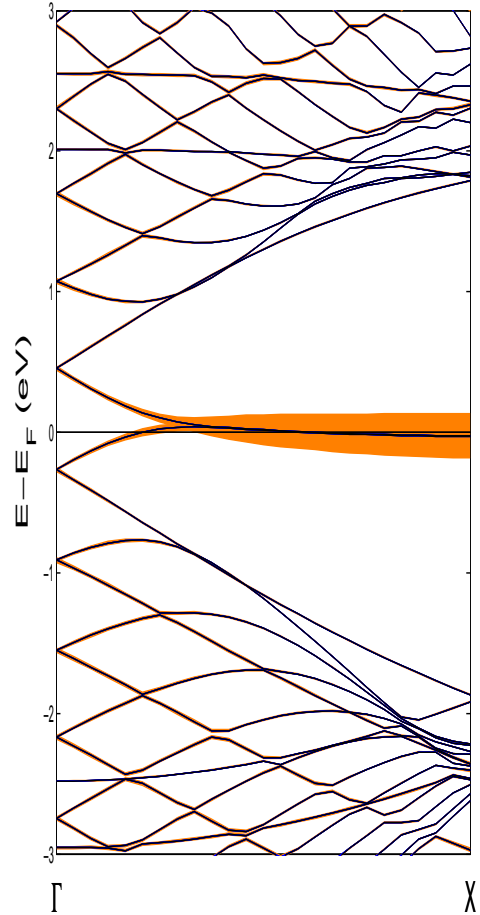
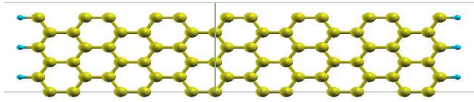
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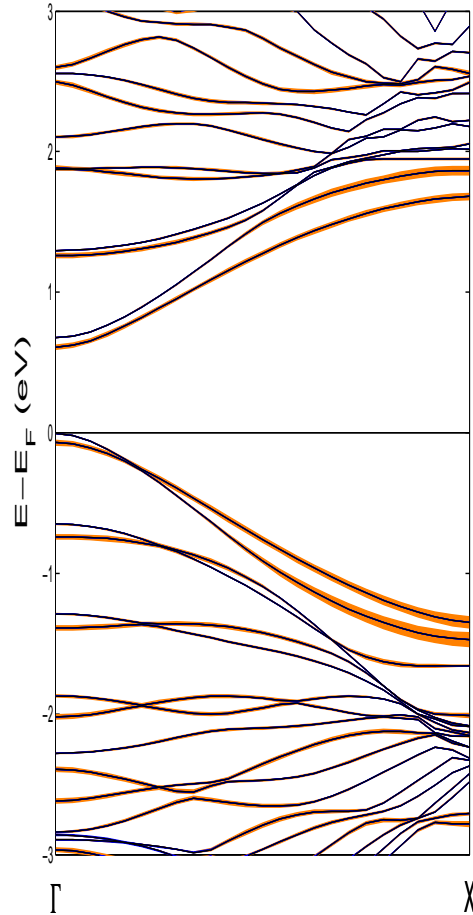
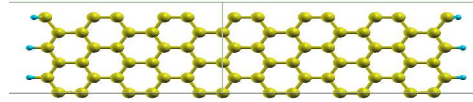
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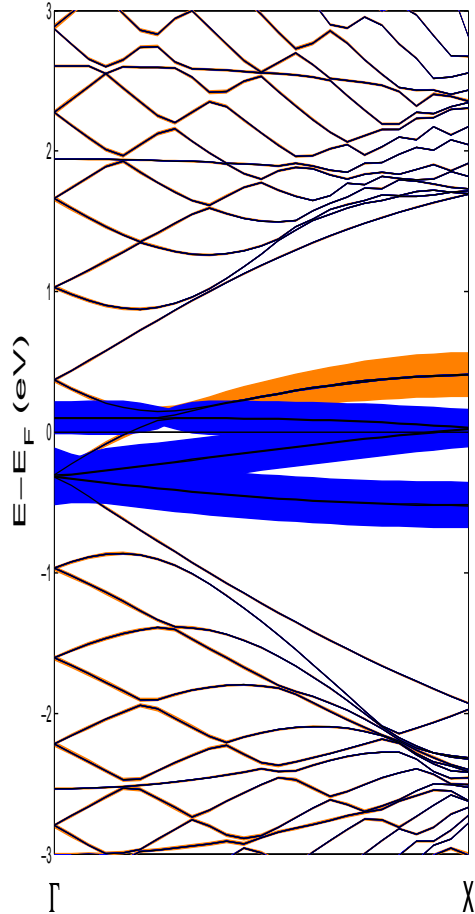
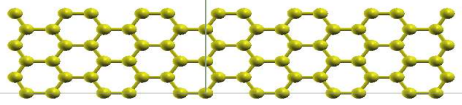


$$E_{edge}^{at} = 0.08 \text{ eV/at}$$

- 12-zgnr  $\Rightarrow \sigma$ - $\pi$  states around  $E_F$ .
- 12-zgnr+H  $\Rightarrow$  Flat bands ( $\pi$ ).
- $z_{211}$  edge is the most stable edge.
- Semiconducting (band gap 0.61 eV).
- Non-magnetic. No edge states.

# Stability - Edge Passivation

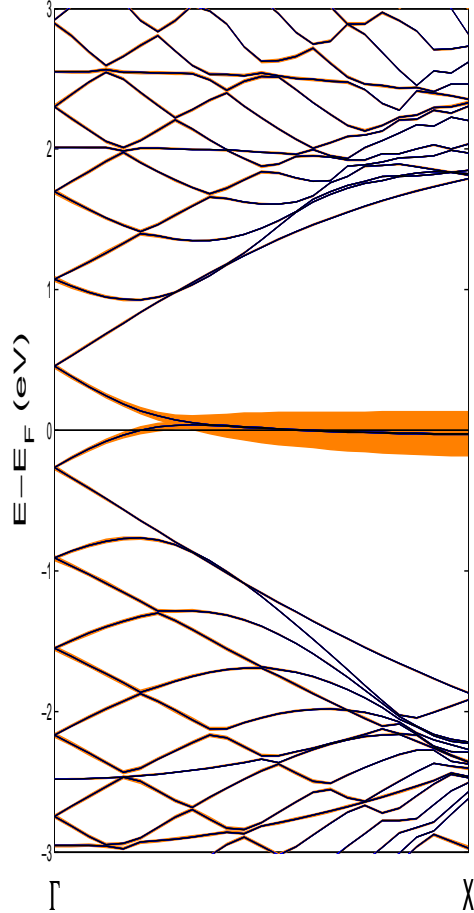
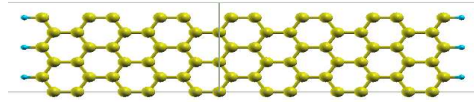
12-zgnr NM



$$E_{edge}^{at} = 3.00 \text{ eV/at}$$

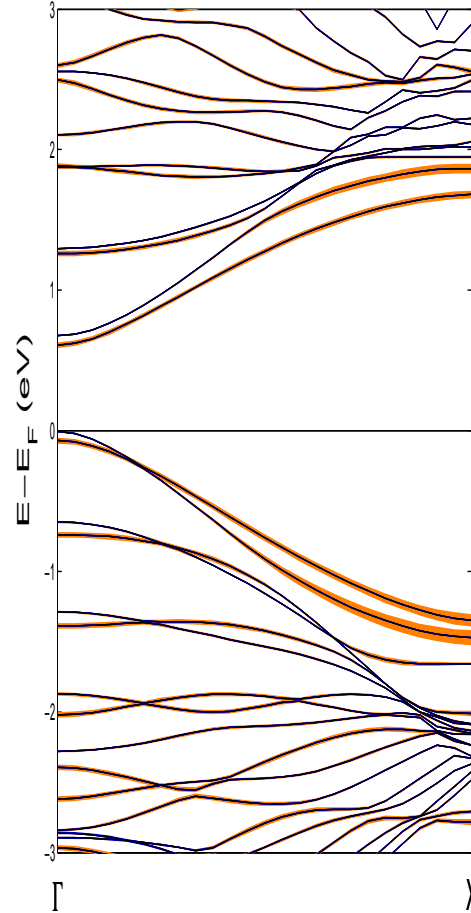
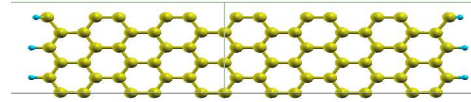
(Eqn. 1)

12-zgnr+H NM



$$E_{edge}^{at} = 0.28 \text{ eV/at}$$

12-zgnr+H ( $z_{211}$ ) NM

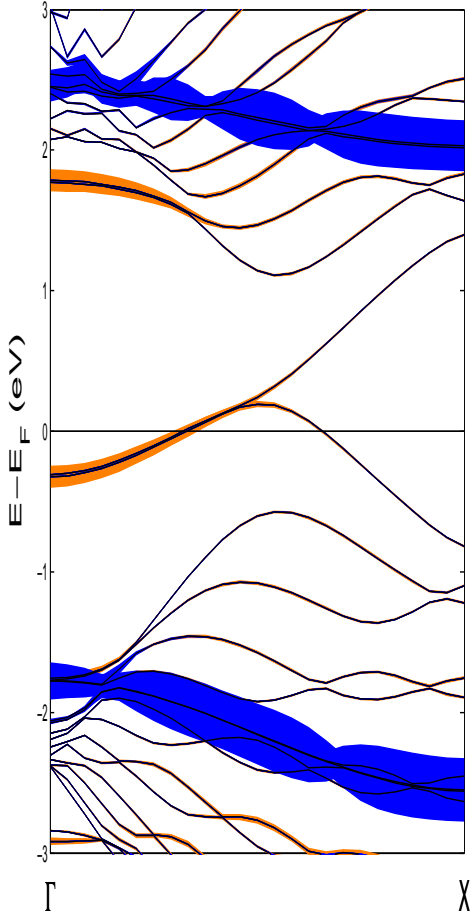
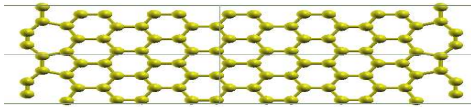


$$E_{edge}^{at} = 0.08 \text{ eV/at}$$

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- 12-zgnr+H  $\Rightarrow$  Flat bands ( $\pi$ ).
- $z_{211}$  edge is the most stable edge.
- Semiconducting (band gap 0.61 eV).
- Non-magnetic. No edge states.
- Wassmann et al., PRL **101**, 096402 (2008) (Theo.).

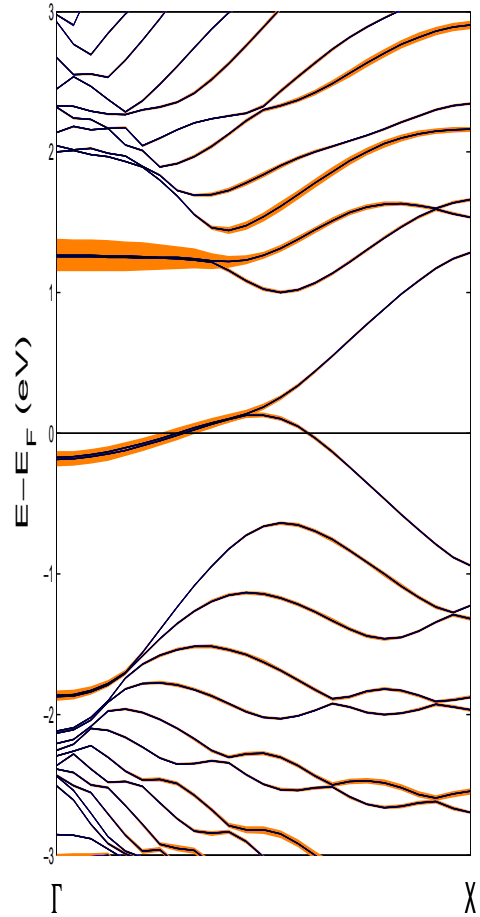
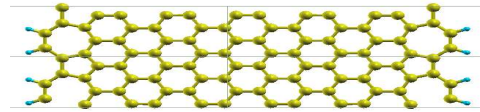
# Stability - Edge Reconstruction & Closure

12-zgnr (57) NM.



$$E_{edge}^{at} = 2.39 \text{ eV/at}$$

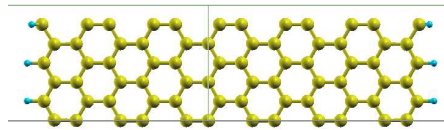
12-zgnr+H (57) NM.



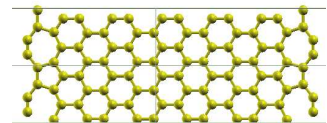
$$E_{edge}^{at} = 0.87 \text{ eV/at}$$

Moderate stability

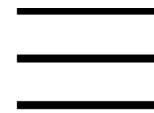
Edge Passivation



Edge Reconstruction



Edge Closure

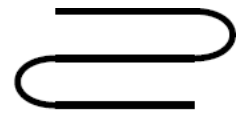


few-layers graphene

T=2000 °C



thermal treatment



folded layers with closed edges

- 5-7 edge reconstruction.
- No flat bands Metallic. Non-magnetic.
- Koskinen et al., PRL **101**, 115502 (2008) (Theo.); Koskinen et al., PRB **90**, 073401 (2009) (Exp.).
- Edge Closure ⇒ NO edge/state/magnetism.
- Liu et al., PRL **102**, 015501 (2009) (Exp.).

**Overview 1: Magnetic edge states are not likely exists.**

# Stability - Edge Magnetism I

- Different magnetic states; NM, FM, AFM.

## Normal Magnets

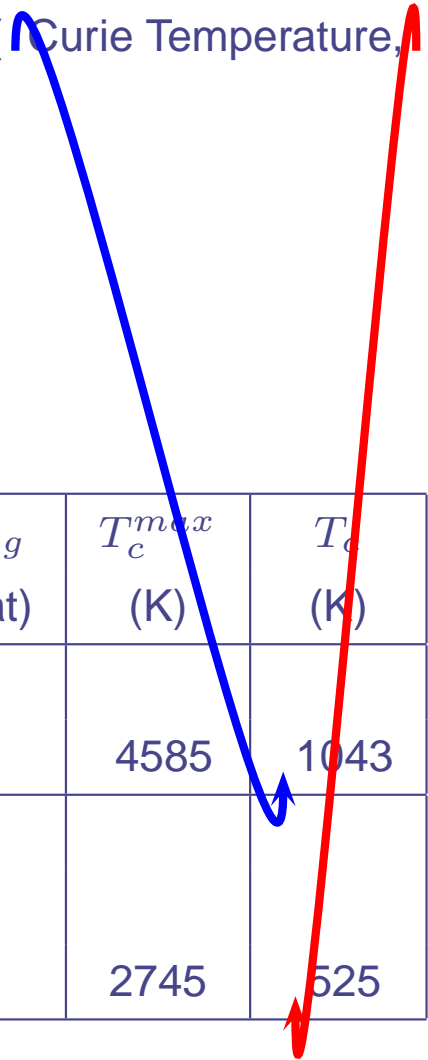
System	State	$\Delta E_{mag}$ (meV/at)	$T_c^{max}$ (K)	$T_c$ (K)
bcc Fe	NM	395		
	FM	0	4585	1043
NiO	NM	244		
	FM	237		
	AFM	0	2745	525

## Ideal ZGNRs

System	State	$\Delta E_{mag}$ (meV/at)	$T_c^{max}$ (K)
10-ZGNR+H	NM	27	
	FM	6	
	AFM	0	70
12-ZGNR+H	NM	29	
	FM	4	
	AFM	0	46

# Stability - Edge Magnetism I

- Different magnetic states; NM, FM, AFM.
- Critical temperature (Curie Temperature, Néel temperature)



## Normal Magnets

System	State	$\Delta E_{mag}$ (meV/at)	$T_c^{max}$ (K)	$T_c$ (K)
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# Stability - Edge Magnetism I

- Different magnetic states; NM, FM, AFM.
- Critical temperature ( Curie Temperature, Néel temperature)
- Magnetic stabilization energy;  $\Delta E_{mag}$  (Eqn. 2). (Spontaneous magnetization)

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System	State	$\Delta E_{mag}$ (meV/at)	$T_c^{max}$ (K)	$T_c$ (K)
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# Stability - Edge Magnetism I

- Different magnetic states; NM, FM, AFM.
- Critical temperature ( Curie Temperature, Néel temperature)
- Magnetic stabilization energy;  $\Delta E_{mag}$  (Eqn. 2). (Spontaneous magnetization)
- Upper bound for the critical temperature;  $\Delta E_{mag}^{GS+1} = kT_c^{max}$

Normal Magnets

System	State	$\Delta E_{mag}$ (meV/at)	$T_c^{max}$ (K)	$T_c$ (K)
bcc Fe	NM	395		
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# Stability - Edge Magnetism I

- Different magnetic states; NM, FM, AFM.
- Critical temperature ( Curie Temperature, Néel temperature)
- Magnetic stabilization energy;  $\Delta E_{mag}$  (Eqn. 2). (Spontaneous magnetization)
- Upper bound for the critical temperature;  $\Delta E_{mag}^{GS+1} = kT_c^{max}$
- **Overview 2: Edge magnetism is not stable at room temperature.**

Normal Magnets

System	State	$\Delta E_{mag}$ (meV/at)	$T_c^{max}$ (K)	$T_c$ (K)
bcc Fe	NM	395		
	FM	0	4585	1043
NiO	NM	244		
	FM	237		
	AFM	0	2745	525

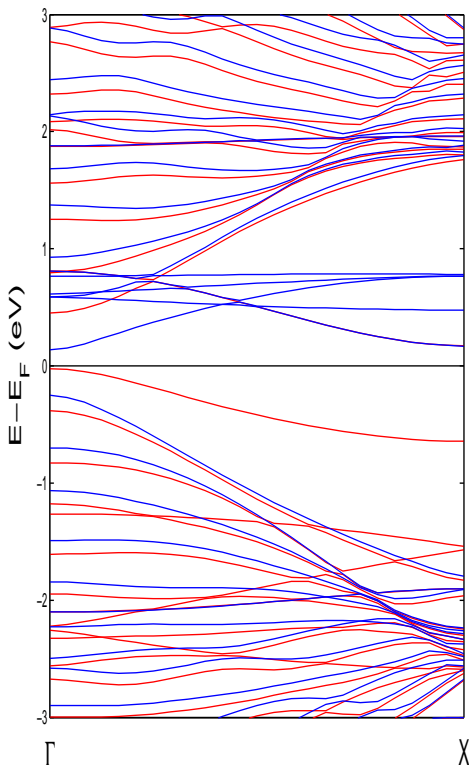
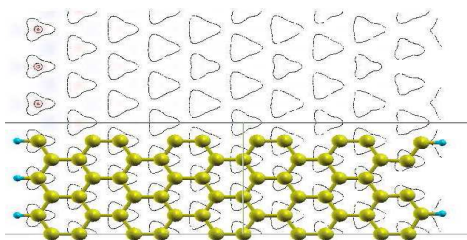
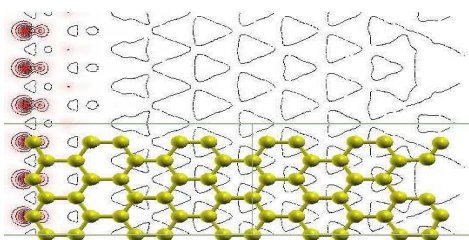
Ideal ZGNRs

System	State	$\Delta E_{mag}$ (meV/at)	$T_c^{max}$ (K)
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	FM	4	
	AFM	0	46

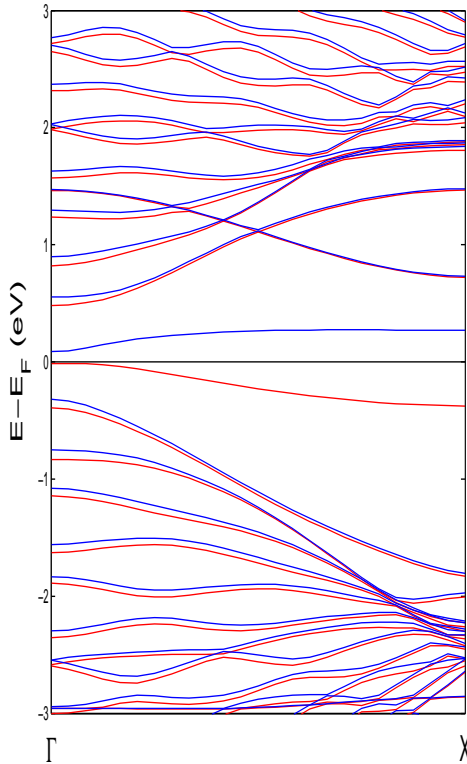
# Stability - Edge Magnetism II

Defect; Edge Vacancy (EV)  
10-zgnr+H FM.

10-zgnr FM.



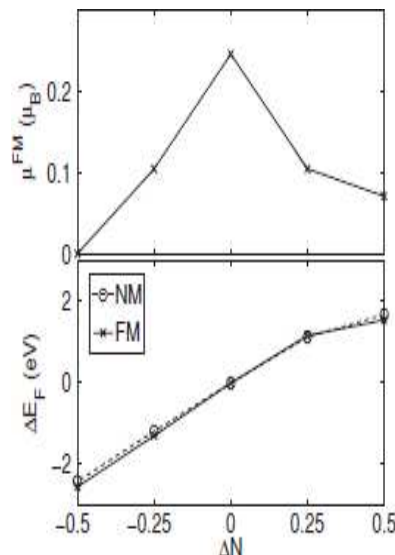
$$E_{edge}^{at} = 2.88 \text{ eV/at}$$



$$E_{edge}^{at} = 0.86 \text{ eV/at}$$

Moderate stability

Charge Doping.  
12-zgnr+H FM (NM).



Critical doping is 0.5 electrons/holes per edge atom (Exp.  $\Delta N_{max} = 0.06$ ).

- Structures have defects; edge vacancy.
- Destroy magnetic moments at defective edge.
- Charge doping further weaken the magnetism.

- In real graphene systems the edges are likely to be passivated, reconstructed, or closed  $\Rightarrow$  No / very little magnetic edge states.

Kunstmann, J., Özdoğan, C., Quandt, A., Fehske, H., PRB, **83**, 045414 (2011).

- In real graphene systems the edges are likely to be passivated, reconstructed, or closed  $\Rightarrow$  No / very little magnetic edge states.
- Edge defects (vacancy) and electron/hole doping weaken the magnetism.

Kunstmann, J., Özdoğan, C., Quandt, A., Fehske, H., PRB, **83**, 045414 (2011).

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- **Overview 1: Magnetic edge states are not likely exists.**

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- In real graphene systems the edges are likely to be passivated, reconstructed, or closed  $\Rightarrow$  No / very little magnetic edge states.
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- **Overview 1: Magnetic edge states are not likely exists.**
- **Overview 2: Even if they exist, edge magnetism is not stable at room temperature.**

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- In real graphene systems the edges are likely to be passivated, reconstructed, or closed  $\Rightarrow$  No / very little magnetic edge states.
- Edge defects (vacancy) and electron/hole doping weaken the magnetism.
- Overview 1: Magnetic edge states are not likely exists.
- Overview 2: Even if they exist, edge magnetism is not stable at room temperature.
- Result: NO spintronics applications of edge magnetism for ideal ZGNR?

Kunstmann, J., Özdoğan, C., Quandt, A., Fehske, H., PRB, **83**, 045414 (2011).

# Thanks

# Thanks for your attention.

Available at

[http://siber.cankaya.edu.tr/ozdogan/sunum/nanotr7\\_2011.pdf](http://siber.cankaya.edu.tr/ozdogan/sunum/nanotr7_2011.pdf)