Purdue, Norfolk State, Northwestern, MIT, Molecular Foundry, UC Berkeley, Univ. of Illinois, UTEP

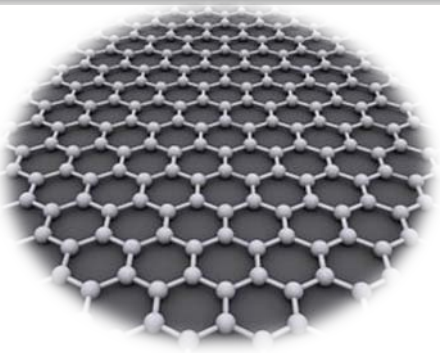
NEMO5 Tutorial: Graphene Nanostructures

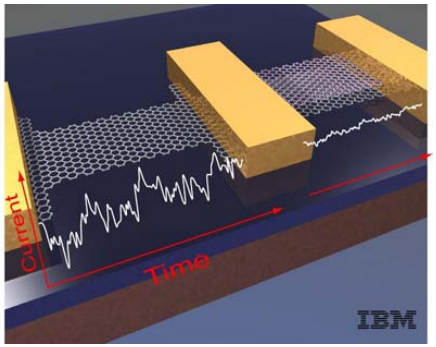
NCN Summer School 2012

Junzhe Geng, NEMO5 team

PURDUE UNIVERSITY

Graphene and transistor

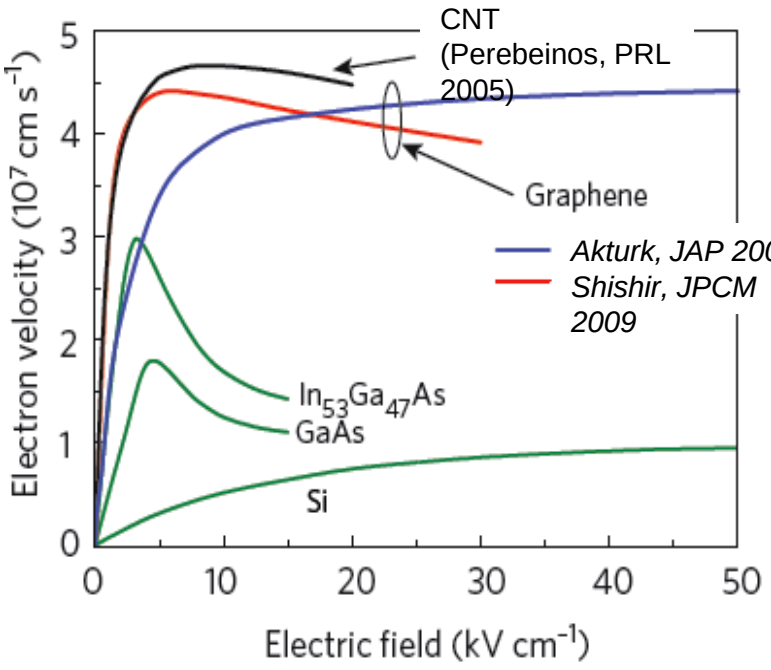




100GHz Graphene FET
Image credit: IBM

Advantages:

- High intrinsic mobility (Over 15,000 $cm^2/V\text{-}s$)
- High electron velocity ➔ Good transport
- 2D material → Good scalability



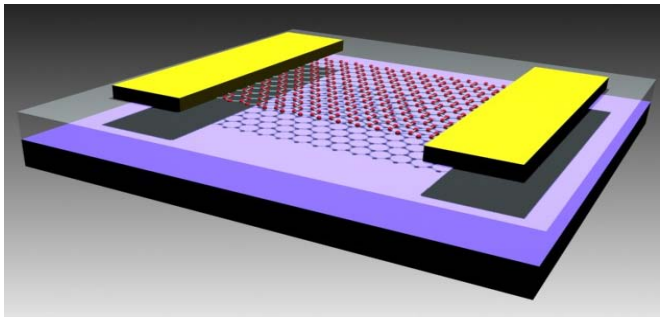


Image from: University of Maryland

Frank Schwierz, Nature Nano. **5**, 487 (2010)

Outline

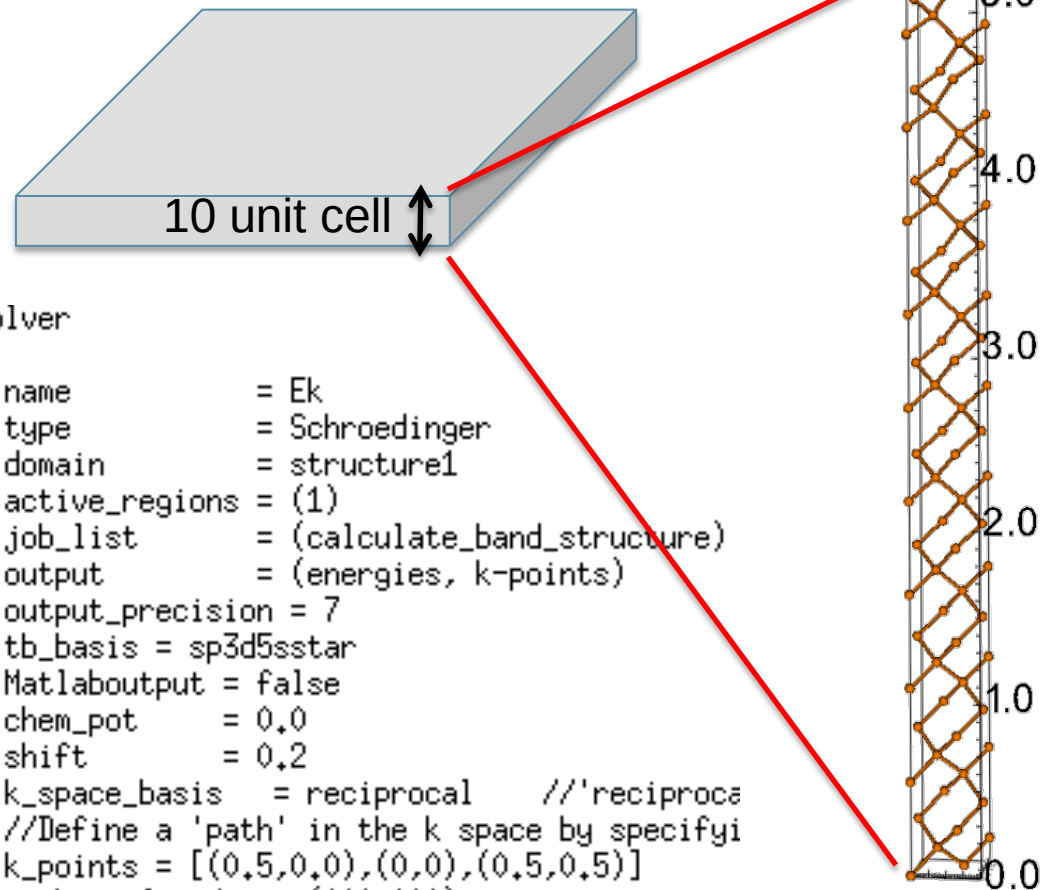
- Tutorial Outline:
  - » Tight binding surface treatment in NEMO5
  - » Graphene models, lattice, setup in nemo5
  - » Example 1: Graphene bandstructure, band model comparison
  - » Example 2: Armchair graphene nanoribbon
  - » Exercise: Zig-zag graphene nanoribbon
  - » Example 3: Graphene nanomesh with a circular hole
  - » Exercise: Graphene nanomesh with a rectangular hole

Surface Treatment In NEMO5

PURDUE UNIVERSITY J.Z Geng

Surface Passivation in NEMO5: example Si UTB

Example: Si_UTB_10uc_no_pass.in




```
solver
{
  name            = Ek
  type            = Schroedinger
  domain          = structure1
  active_regions  = (1)
  job_list        = (calculate_band_structure)
  output          = (energies, k-points)
  output_precision = 7
  tb_basis = sp3d5sstar
  Matlaboutput = false
  chem_pot      = 0.0
  shift         = 0.2
  k_space_basis   = reciprocal    //'reciproca
  //Define a 'path' in the k space by specifyi
  k_points = [(0.5,0.0),(0,0),(0.5,0.5)]
  number_of_nodes = (100,100)
}
```

```
Domain
{
    name = structure1
    periodic = (true, true, false)
    crystal_direction1 = (1,0,0)
    crystal_direction2 = (0,1,0)
    crystal_direction3 = (0,0,1)
    space_orientation_dir1 =  (1,0,0)
    space_orientation_dir2 =  (0,1,0)
    regions = (1)
    passivate= false    //this applies to
    geometry_description = simple_shapes
}
```

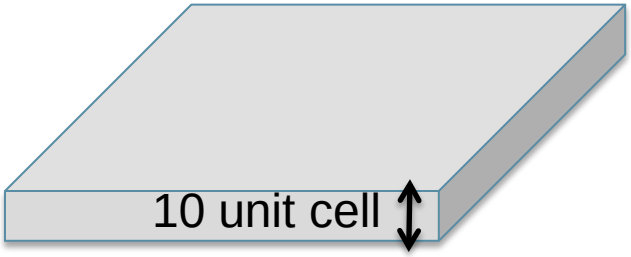
passivate = false

```
Geometry
{
    Region
    {
        shape          = cuboid
        region_number  = 1
        priority       = 1
        min            = (-15,-50,-50)
        max            = ( 15, 50, 50)
        tag = substrate
    }
}
```

Inputdeck: Bandstructure calculation of a Si UTB with default settings, no passivation used

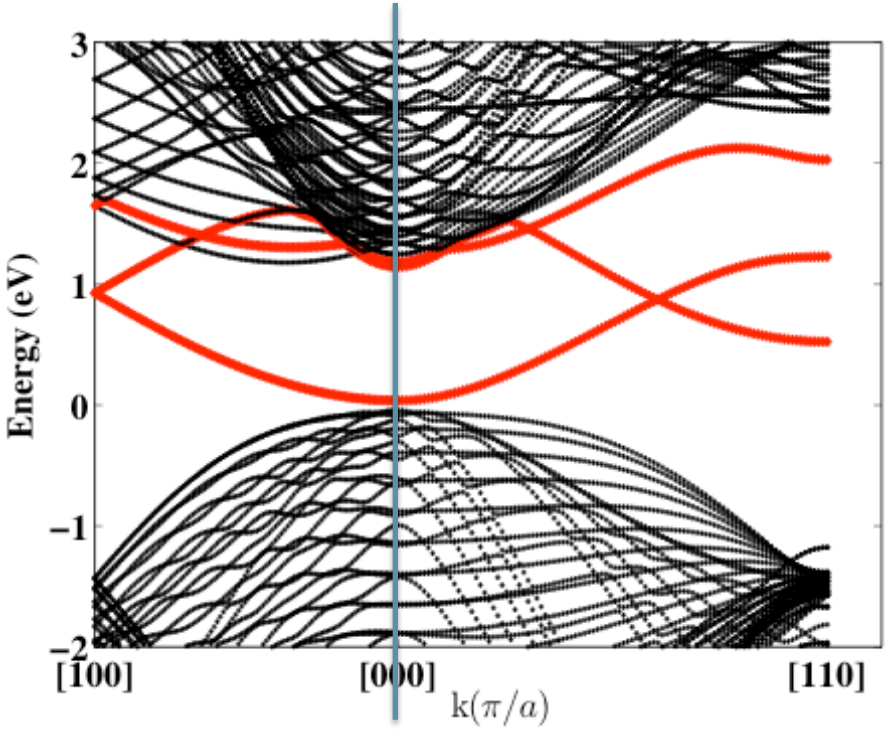
Surface Passivation in NEMO5

Example: Si_UTB_10uc_no_pass.in



UTB Bandstructure:
A few states span over the band gap

Identify the nature of band gap states:
Get the wave functions

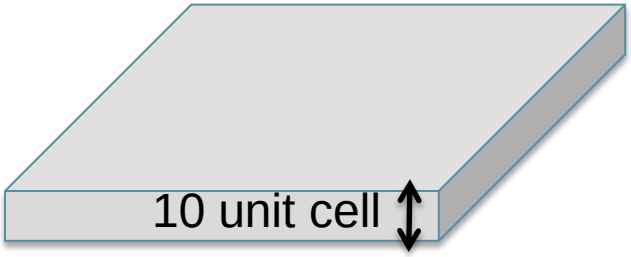



```
 solver
{
name            = Gamma
type            = Schroedinger
domain          = structure1
active_regions  = (1)
job_list        = (calculate_band_structure)
output          = (eigenfunctions, eigenfunctions_VTK)
output_precision = 7
tb_basis = sp3d5sstar
Matlaboutput = false
chem_pot      = 0.0
shift         = 0.2
k_space_basis    = reciprocal
k_points = [(0.0,0.0)]
number_of_nodes = 1
}
```

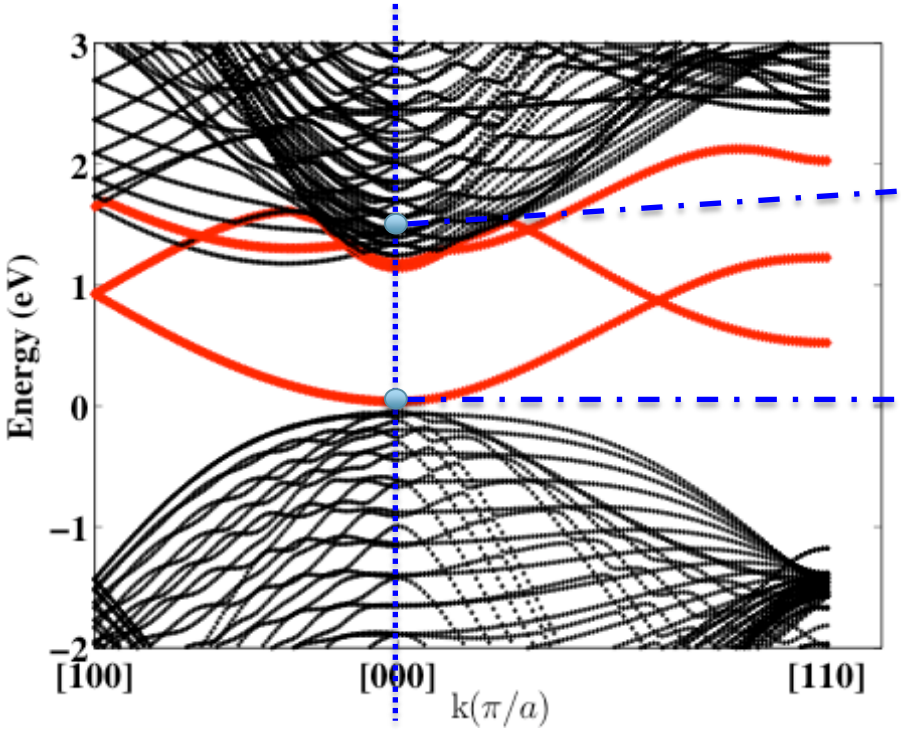
Calculate the wave functions at the Γ point

Surface Passivation in NEMO5

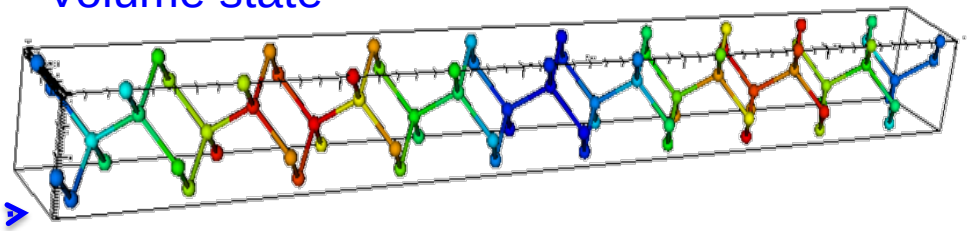
Example: Si_UTB_10uc_no_pass.in



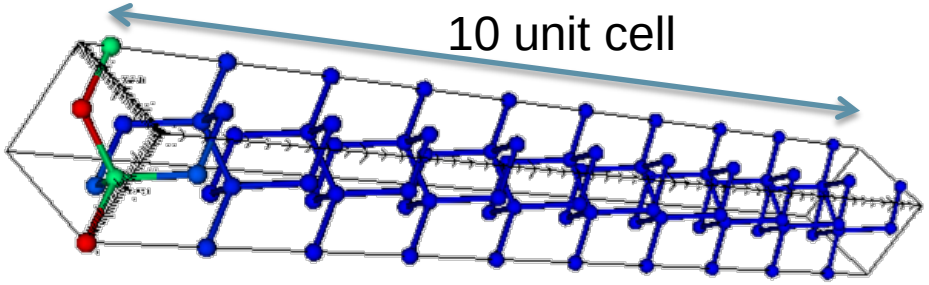
States in the bandgap are surface states
They are produced by dangling bonds



Volume state

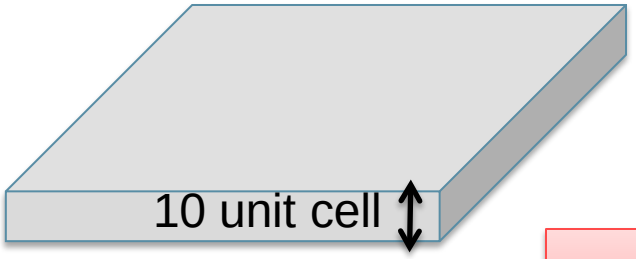


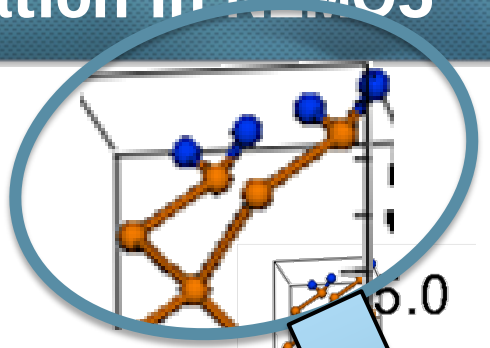
Surface state

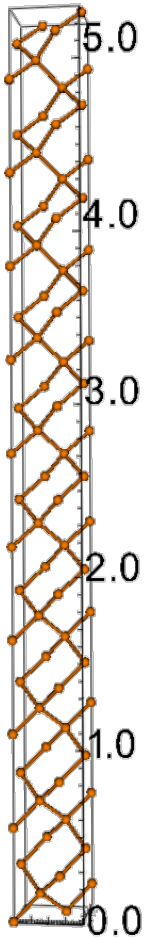


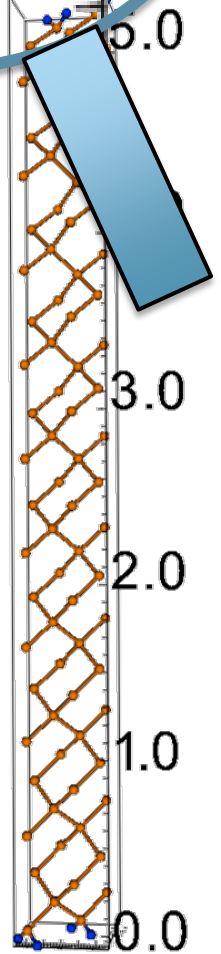
Surface Passivation in NEMO5

Example: Si_UTB_10uc_pass.in









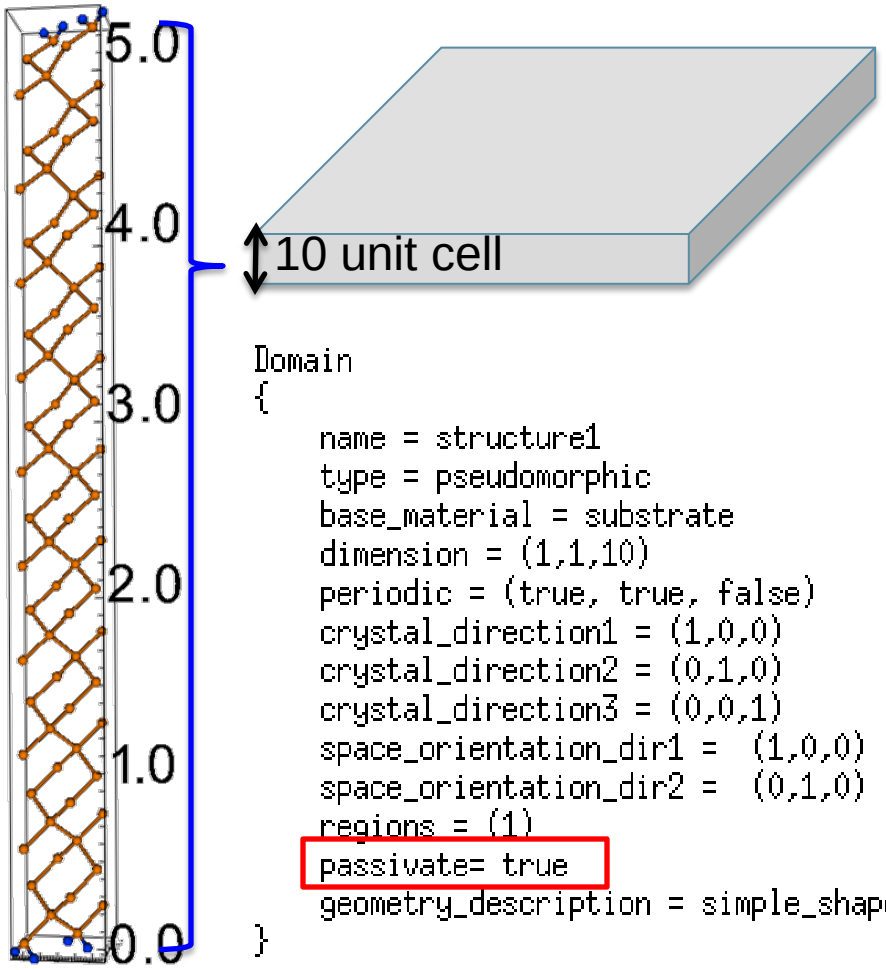
"passivate = true"

Adds H-atoms at the surface

```
Domain
{
    name = structure1
    type = pseudomorphic
    base_material = substrate
    dimension = (1,1,10)
    periodic = (true, true, false)
    crystal_direction1 = (1,0,0)
    crystal_direction2 = (0,1,0)
    crystal_direction3 = (0,0,1)
    space_orientation_dir1 =  (1,0,0)
    space_orientation_dir2 =  (0,1,0)
    regions = (1)
    passivate= false     //this applies to
    geometry_description = simple_shapes
}
```

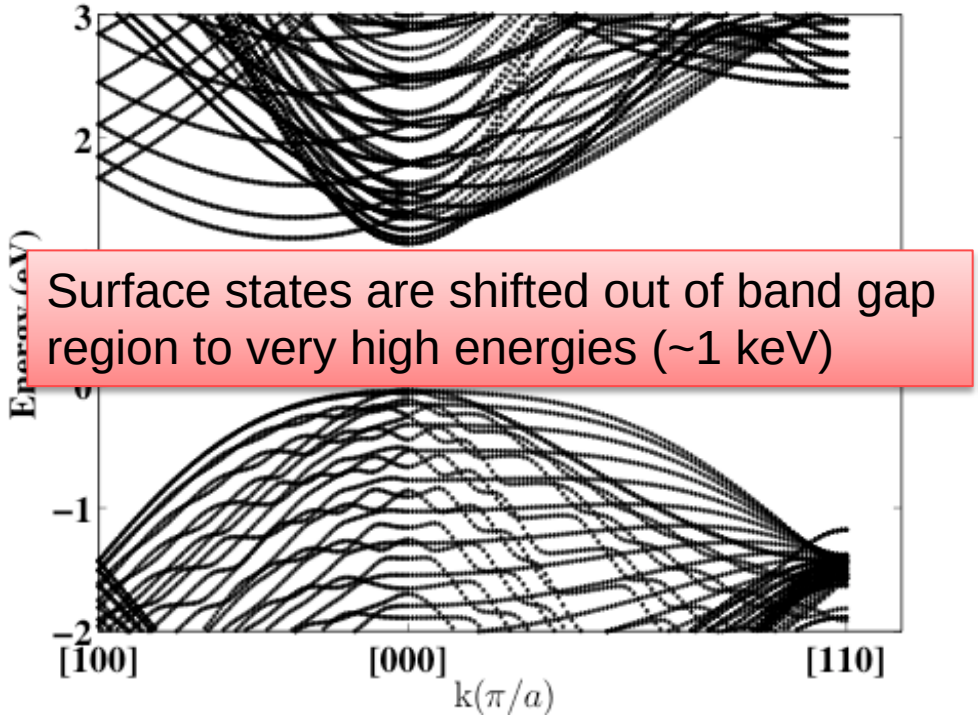
Surface Passivation in NEMO5

Example: Si_UTB_10uc_pass.in

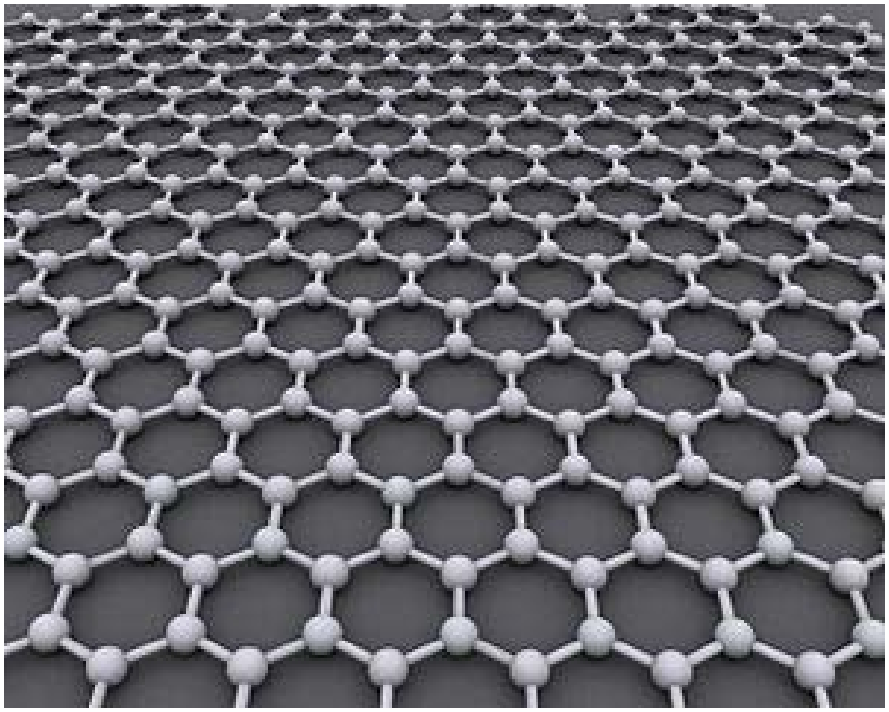



```
Domain
{
    name = structure1
    type = pseudomorphic
    base_material = substrate
    dimension = (1,1,10)
    periodic = (true, true, false)
    crystal_direction1 = (1,0,0)
    crystal_direction2 = (0,1,0)
    crystal_direction3 = (0,0,1)
    space_orientation_dir1 =  (1,0,0)
    space_orientation_dir2 =  (0,1,0)
    regions = (1)
    passivate= true
    geometry_description = simple_shapes
}
```

```
solver
{
  name            = Ek
  type            = Schroedinger
  domain          = structure1
  active_regions  = (1)
  job_list        = (passivate_H,calculate_band_structure)
  output          = (energies, k-points)
}
```



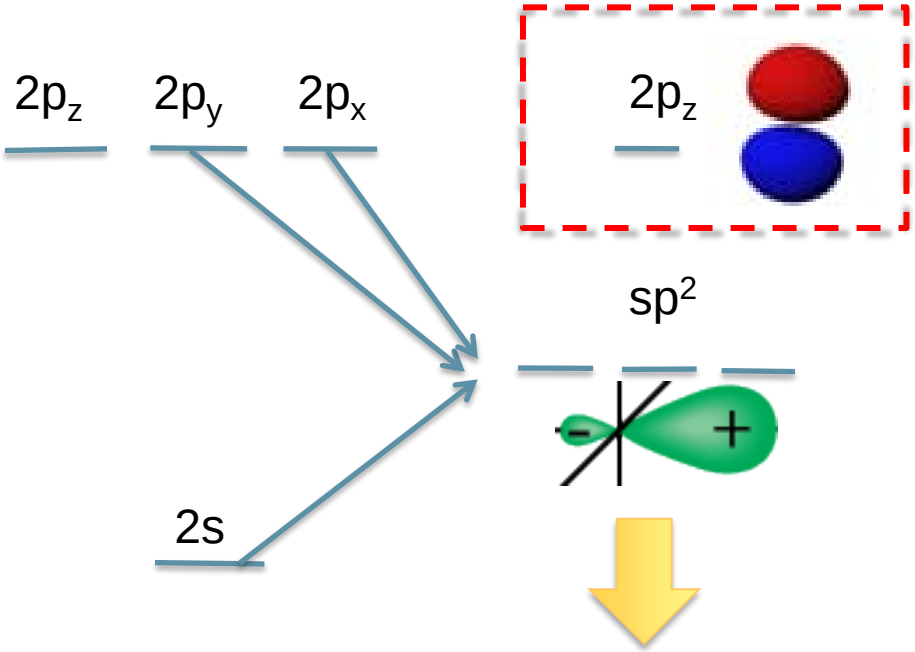
Surface states are shifted out of band gap region to very high energies (~1 keV)

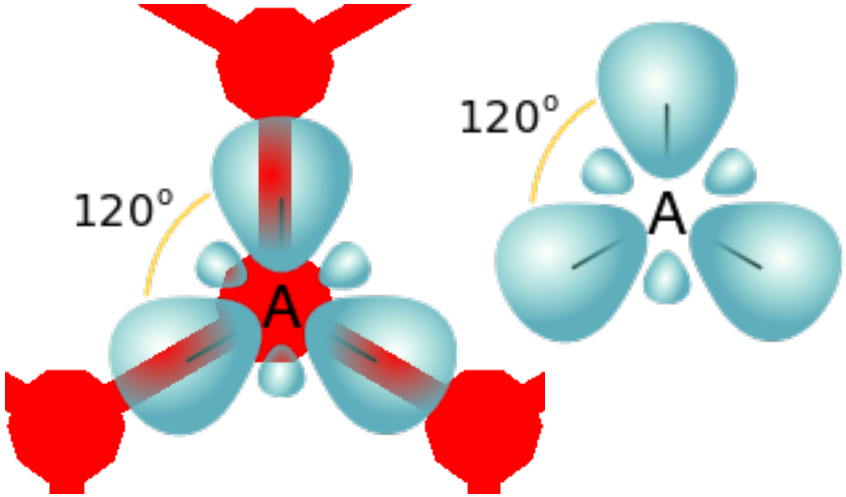


http://en.wikipedia.org/wiki/Graphene

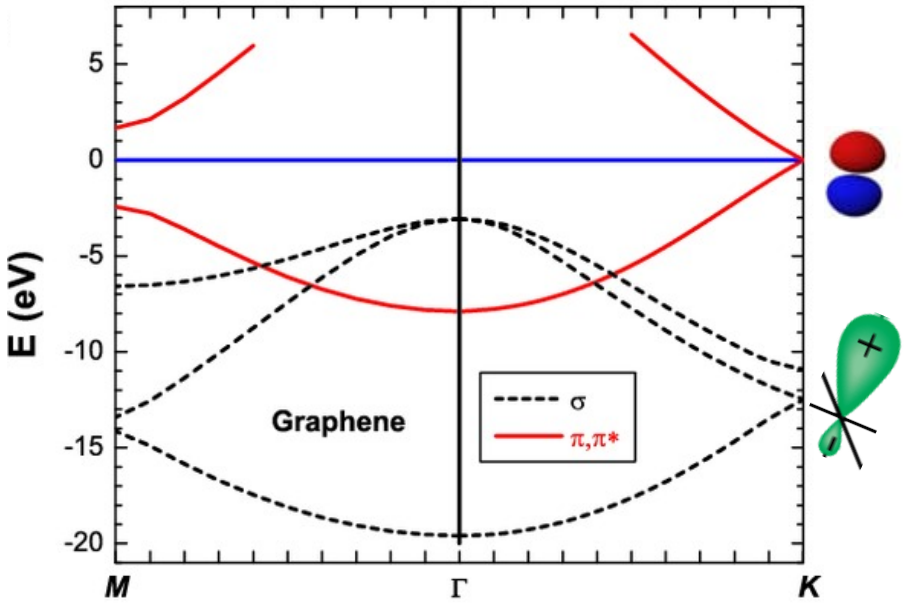
Graphene

Tight-binding Model





Y. Zhang and R.Tsu, Nanoscale Research Letters Vol. 5 Issue 5



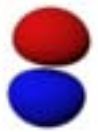
- p_z orbital is well separated in energy from the sp^2 orbitals
- More importantly, only the p_z electron is close to the Fermi level
- Therefore, the common tight-binding method for graphite/graphene considers only the p_z orbital (P.R. Wallace, PRB 1947)

Passivation in PD and Pz tight binding model

NEMO5: two models for Graphene bandstructure

1) Standard model of tight binding literature "Pz"

- Includes just one p_Z orbital per atom
- Does not allow for hydrogen passivation
  Because p_z orbital of C has zero coupling to s orbital in H



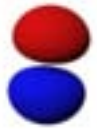
p_Z

2) Recently developed model "PD" (J. Appl. Phys. **109**, 104304 (2011)

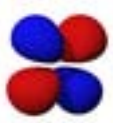
- Includes {p_z d_{yz} d_{zx}} orbital set on each C atom and H atom
- Hydrogen atoms included explicitly (realistic treatment)

"passivate_H" not required in job_list
BUT
Make H atoms "active", i.e. include them explicitly:

```
Domain
{
   activate_hydrogen_atoms = true (default = false)
```



p_Z

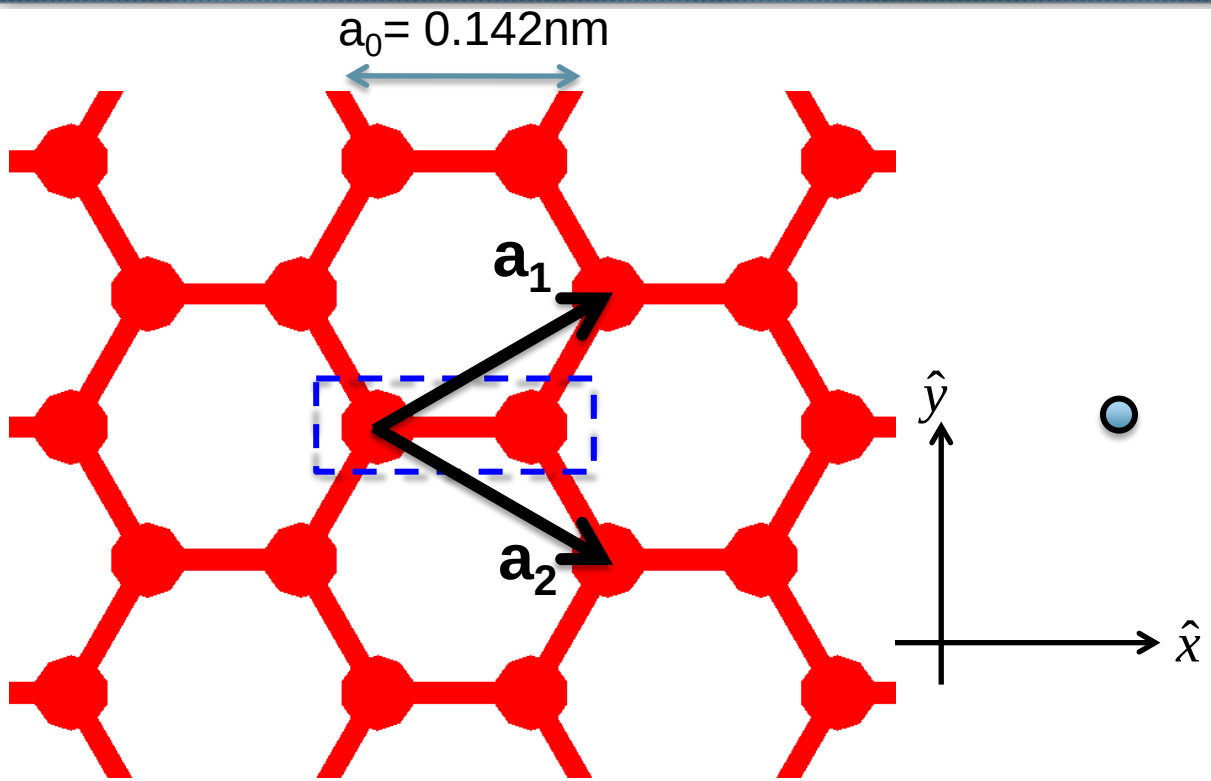


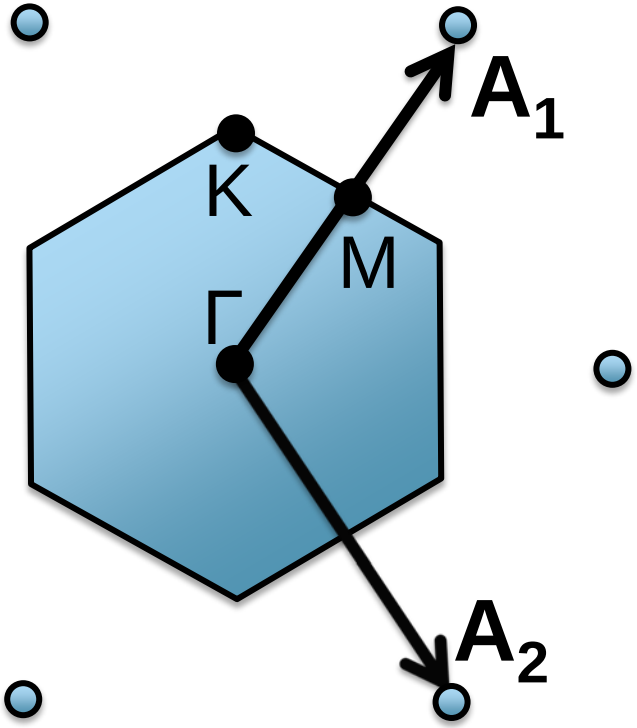
d_{yz}

d_{zx}

Always have passivate = true in the domain section (default)

Graphene: Primitive Basis





Lattice basis:

$$\vec{a}_1 = \frac{3a_0}{2}\hat{x} + \frac{\sqrt{3}a_0}{2}\hat{y}$$

$$\vec{a}_2 = \frac{3a_0}{2}\hat{x} - \frac{\sqrt{3}a_0}{2}\hat{y}$$

Reciprocal lattice basis:

$$\vec{A}_1 = \frac{2\pi}{3a_0}\hat{x} + \frac{2\pi}{\sqrt{3}a_0}\hat{y}$$

$$\vec{A}_2 = \frac{2\pi}{3a_0}\hat{x} - \frac{2\pi}{\sqrt{3}a_0}\hat{y}$$

Symmetry points:

$$K : \frac{1}{3}\vec{A}_1 - \frac{1}{3}\vec{A}_2$$

$$M : \frac{1}{2}\vec{A}_1$$

Given in NEMO5

User defined points

Defining the Structure

```
Material
{
    name = Carbon
    tag = substrate
    crystal_structure = graphene
    regions = (1)
    Bands:TB:Pz:param_set = param_default
}

Geometry
{
    Region
    {
        shape          = cuboid
        region_number  = 1
        priority       = 1
        min            = (-5,-5,-5) // in nm
        max            = ( 5, 5, 5)
    }
}
```

Define the material

With a large enough region, device is limited by dimension only

```
Domain
{
    name = structure1
    type = pseudomorphic
    base_material = substrat
    dimension = (1,1,1)

    origin = (0,0,0)
    activate_hydrogen_atoms = true

    periodic = (true, true, false)

    miller_index_basis = primitive
    crystal_direction1 = (1,0,0)
    crystal_direction2 = (0,1,0)
    crystal_direction3 = (0,0,1)

    space_orientation_dir1 =  (1,0,0)
    space_orientation_dir3 =  (0,0,1)

    regions = (1)
    geometry_description = simple_shapes
    FEM_mesh_creation = false
```

Dimension in number of unit cells

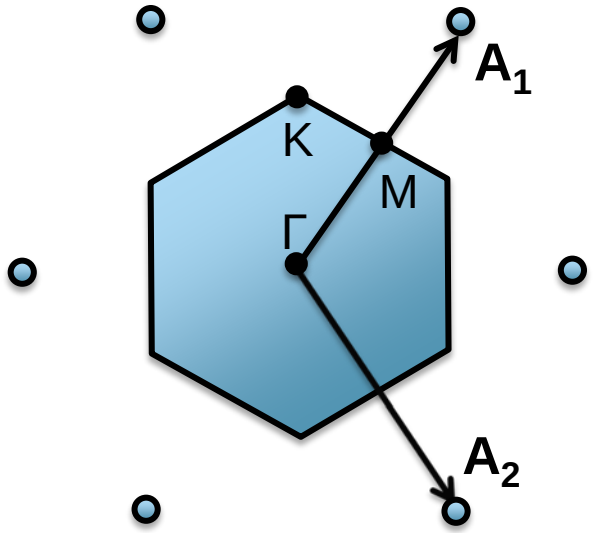
Have “true” only for PD model

‘primitive’ or ‘Cartesian’

Defining Solver

```
solver
{
    name              = Ek
    type              = Schroedinger
    domain            = structure1
    active_regions = (1)

    eigen_values_solver = krylovschur
    preconditioner  =mumps
    output            = (energies,k-points)
    output_precision = 7

    job_list          = (calculate_band_structure)

    tb_basis = PD

    k_space_basis    = reciprocal
    number_of_eigenvalues = 20
    k_points          = [ (0.0,0.0), (0.333,-0.333), (0.5,0), (0.0,0.0)]
    number_of_nodes = (100,50,40)

}
```

'Pz' or 'PD'



Symmetry points:

$$K:\frac{1}{3}\vec{A}_1-\frac{1}{3}\vec{A}_2$$

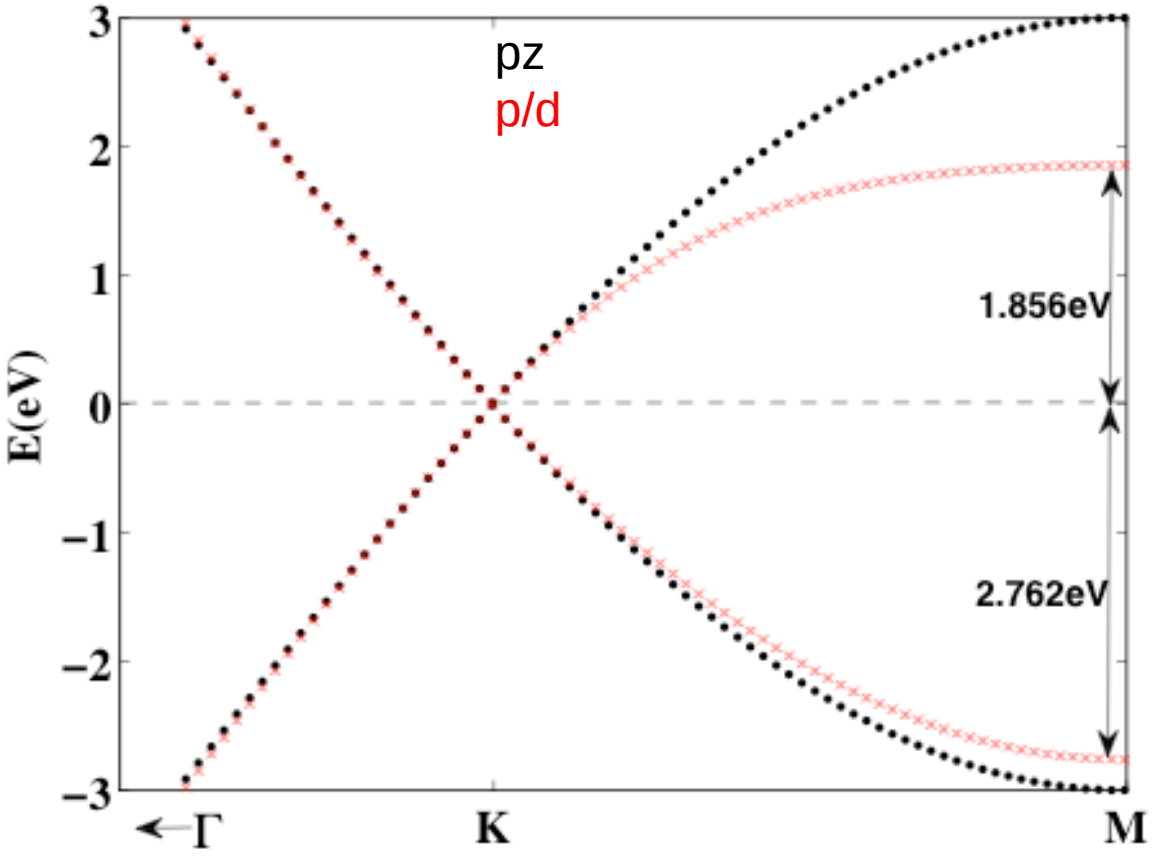
$$M:\frac{1}{2}\vec{A}_1$$

Γ → K → M → Γ

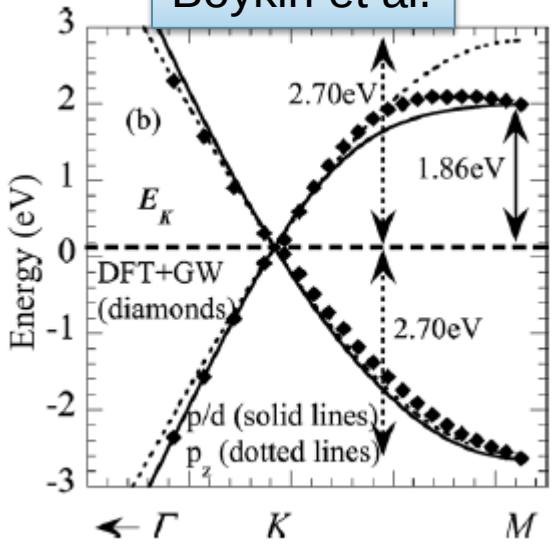
Expressed in units of **A_1** and **A_2**

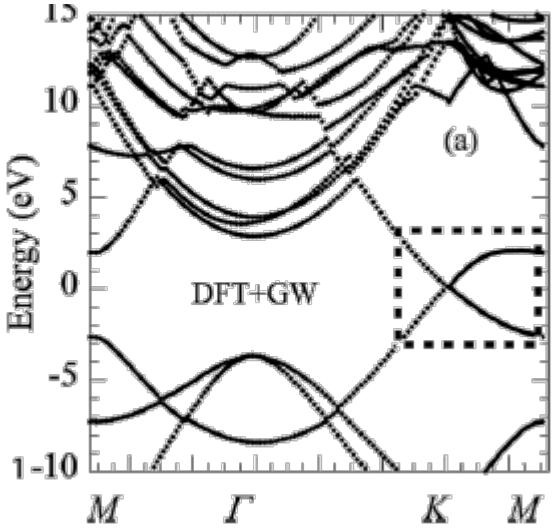
Graphene Bandstructure: P_z vs. P/D

NEMO5



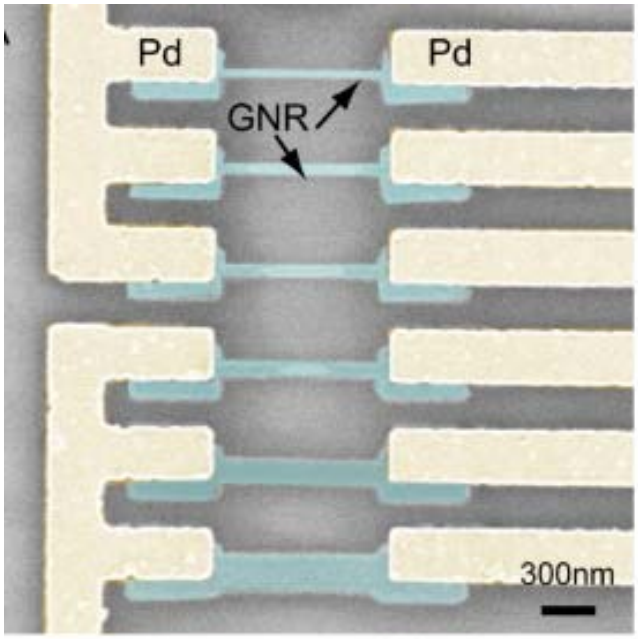
Boykin et al.





DFT results are much better reproduced with the PD model

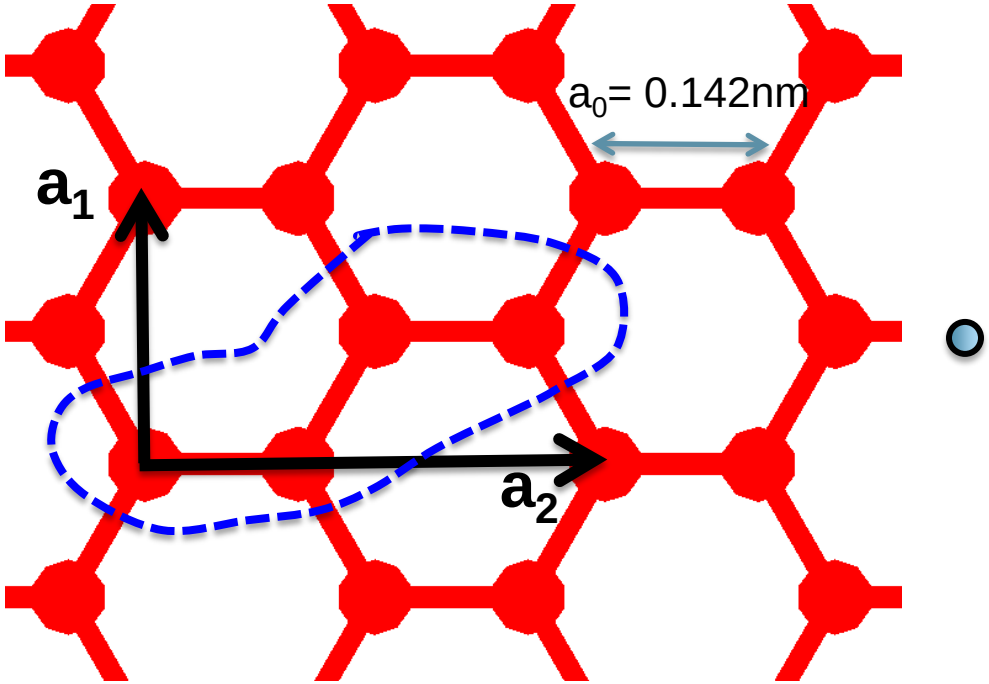
J. Appl. Phys. **109**, 104304 (2011)

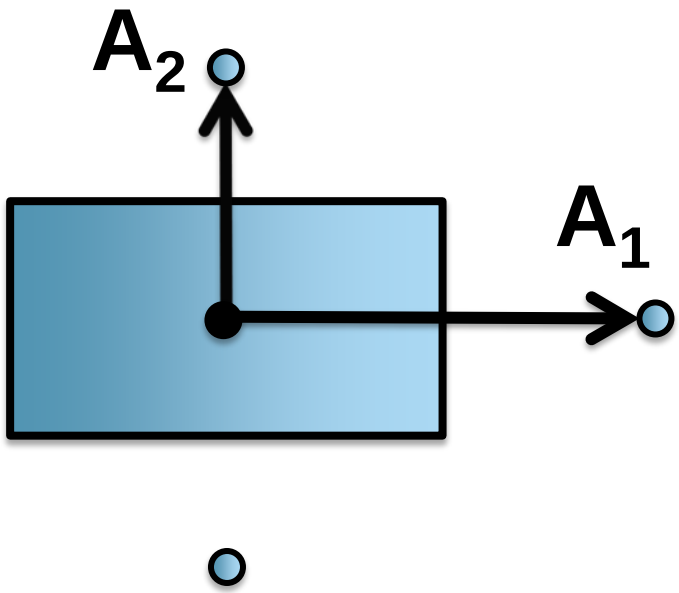


Z.Chen, *et al.* Physica **40**, 228-232 (2007)

Graphene Nanoribbons

Graphene: Cartesian Basis





Lattice basis:

$$\vec{a}_1 = \sqrt{3}a_0\hat{y}$$

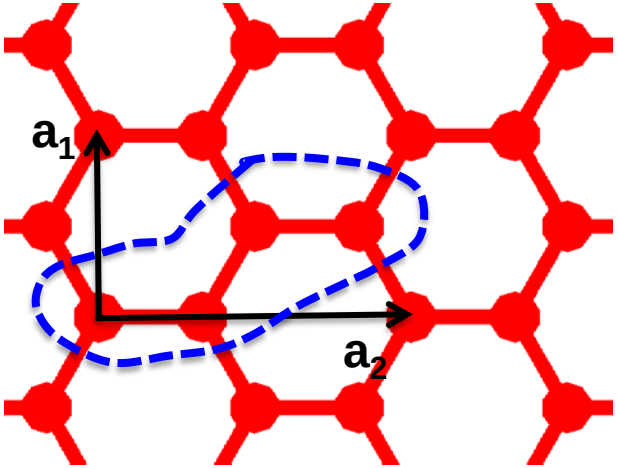
$$\vec{a}_2 = 3a_0\hat{x}$$

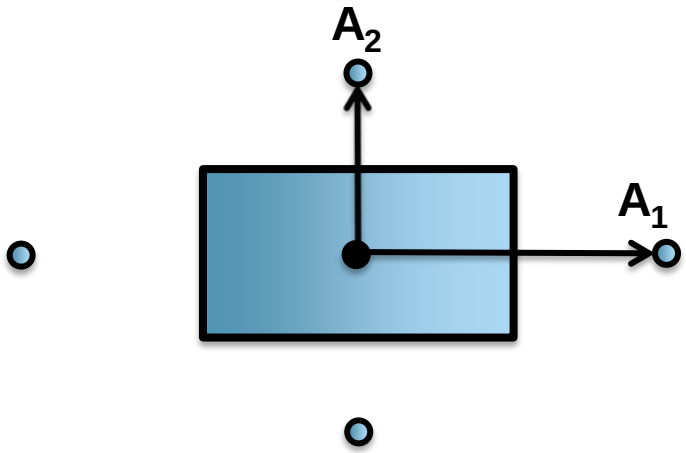
Reciprocal lattice basis:

$$\vec{A}_1 = \frac{2\pi}{\sqrt{3}a}\hat{x}$$

$$\vec{A}_2 = \frac{2\pi}{3a}\hat{y}$$

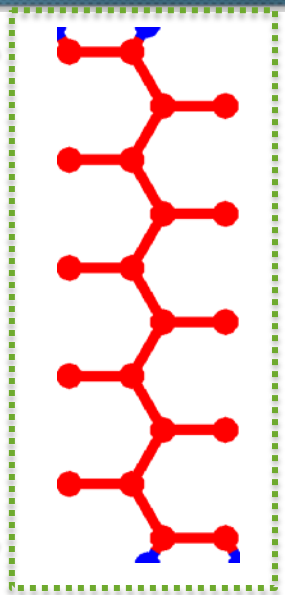
Structure



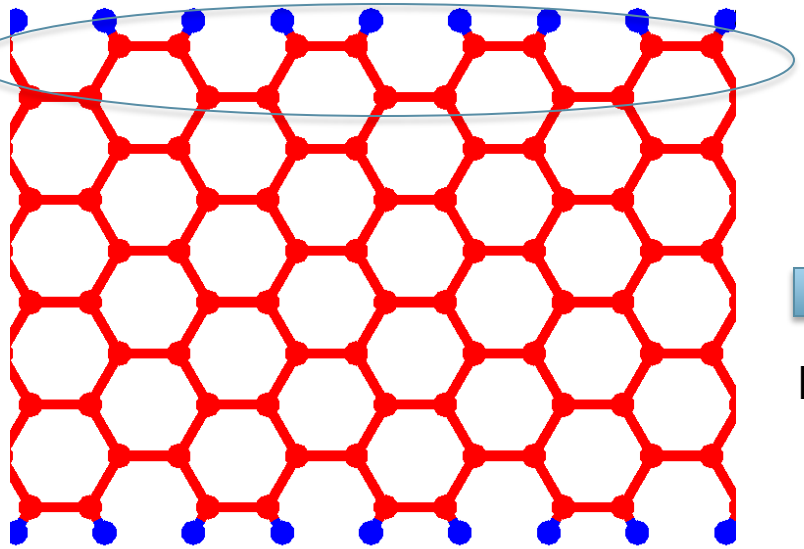



```
Domain
{
    name = structure1
    type = pseudomorphic
    base_material = substrate
    dimension = (1,1,1)

    origin = (0,0,0)
    activate_hydrogen_atoms = true

    periodic = (true, true, false)

    miller_index_basis = cartesian
    crystal_direction1 = (1,0,0)
    crystal_direction2 = (0,1,0)
    crystal_direction3 = (0,0,1)

    space_orientation_dir1 =  (1,0,0)
    space_orientation_dir3 =  (0,0,1)

    regions = (1)
    geometry_description = simple_shapes
    FEM_mesh_creation = false
}
```

Example 1 : 10-AGNR



10 atomic layers wide



"Armchair"

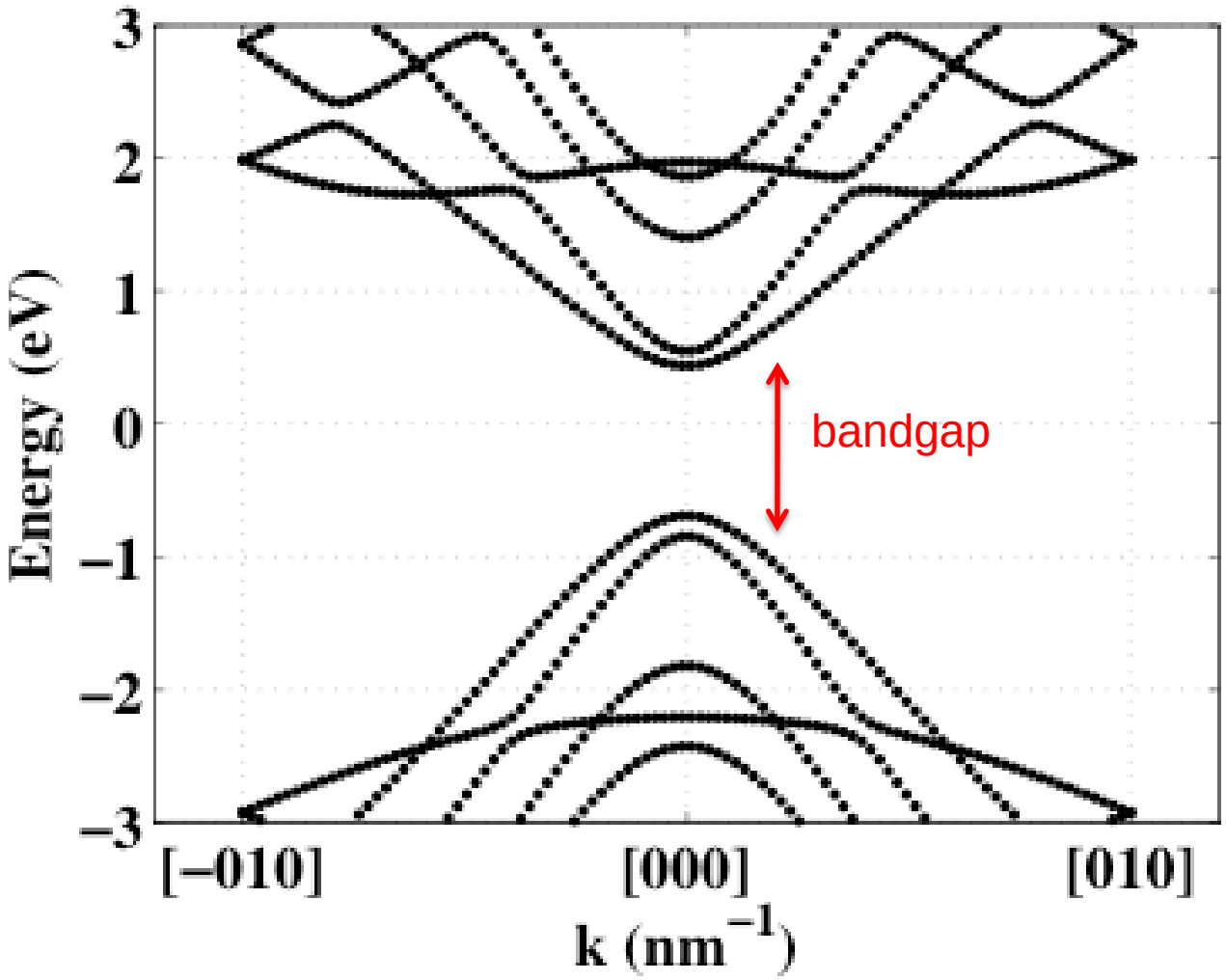
Periodic

```
Domain
{
    name = structure1
    type = pseudomorphic
    base_material = substrate
    dimension = (10,1,1)

    origin = (0,0,0)
    activate_hydrogen_atoms = true

    periodic = (false, true, false)

    miller_index_basis = cartesian
    crystal_direction1 = (1,0,0)
    crystal_direction2 = (0,1,0)
    crystal_direction3 = (0,0,1)
```

A big domain

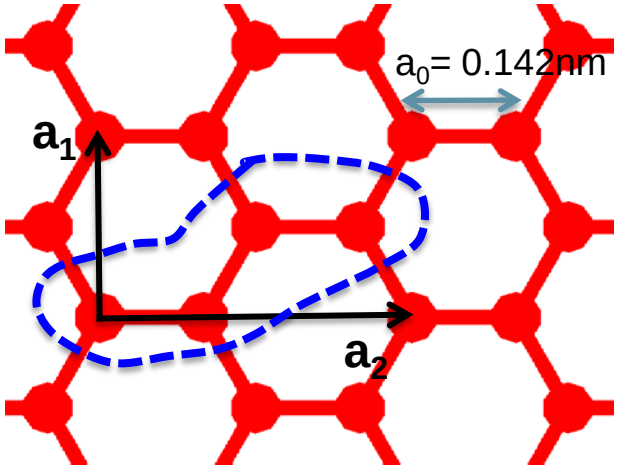
```
Geometry
{
    Region
    {
        shape          = cuboid
        region_number  = 1
        priority       = 1
        min            = (-0.0,-20,-5) // in nm
        max            = ( 1.15,20, 5)
        tag = substrate
    }
}
```

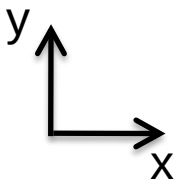
10-AGNR Bandstructure

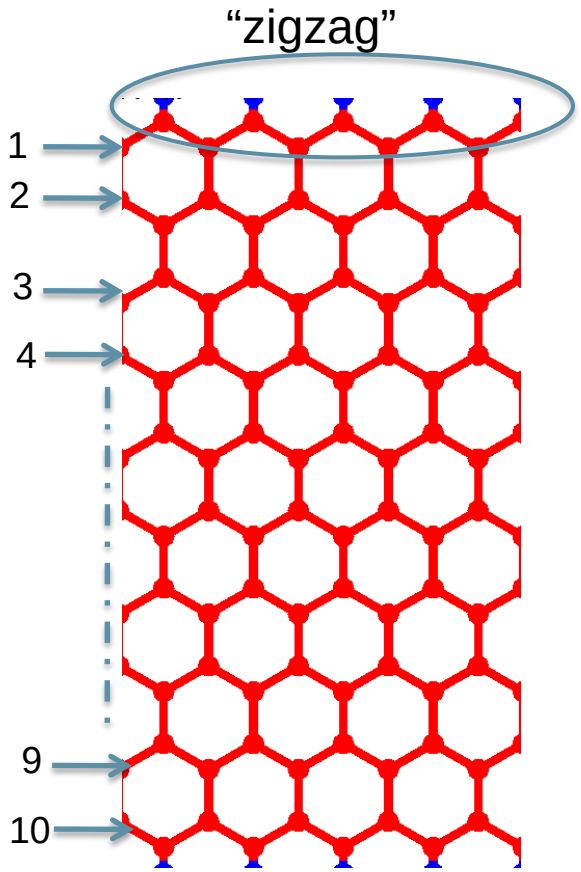


Armchair edges allow opening up a bandgap

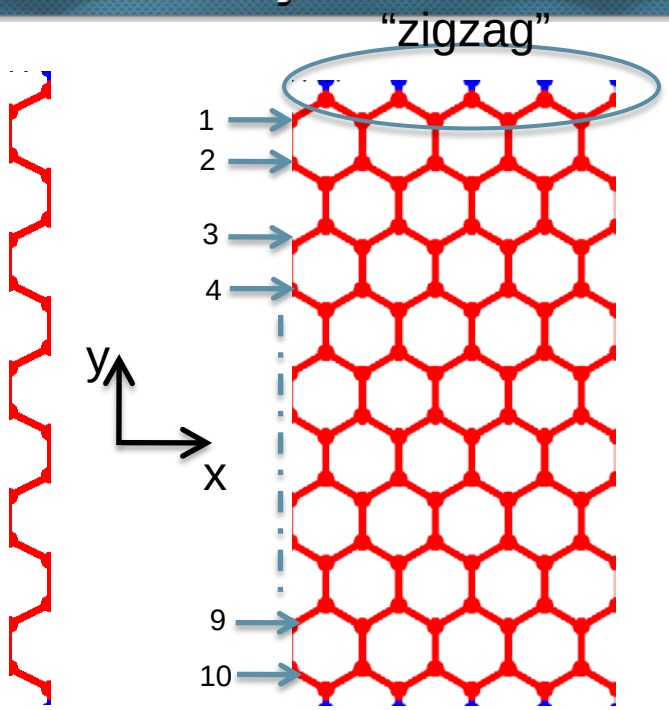
- Exercise: Define a “10-ZGNR” in NEMO5 and calculate its bandstructure along x direction ([100])







Exercise1 : 10-ZGNR

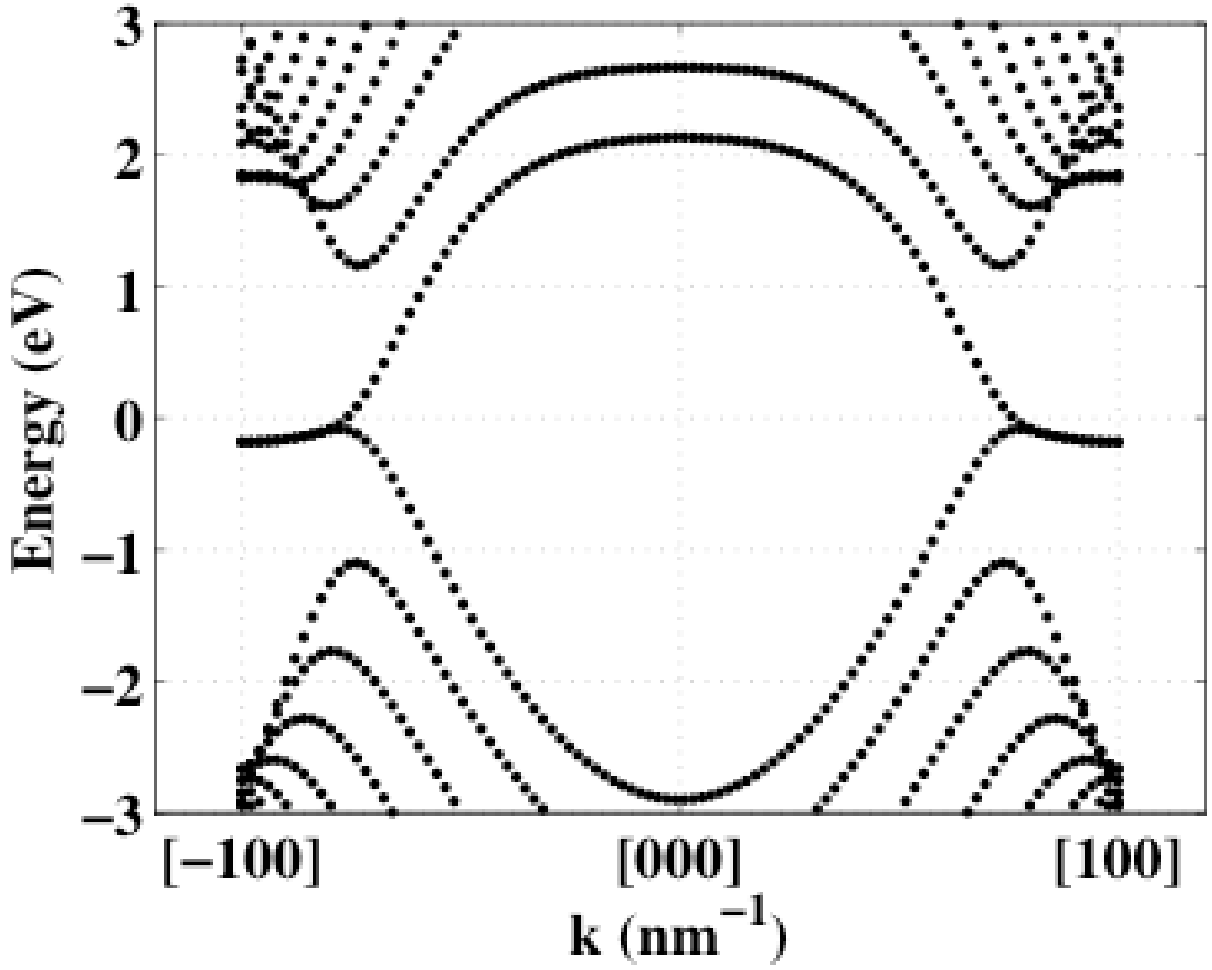



```
Domain
{
    name = structure1
    type = pseudomorphic
    base material = substrate
    dimension = (1,6,1)

    origin = (0,0,0)
    activate_hydrogen_atoms = true // gra

    periodic = (true, false, false)

    miller_index_basis = cartesian
    crystal_direction1 = (1,0,0)
    crystal_direction2 = (0,1,0)
    crystal_direction3 = (0,0,1)
```

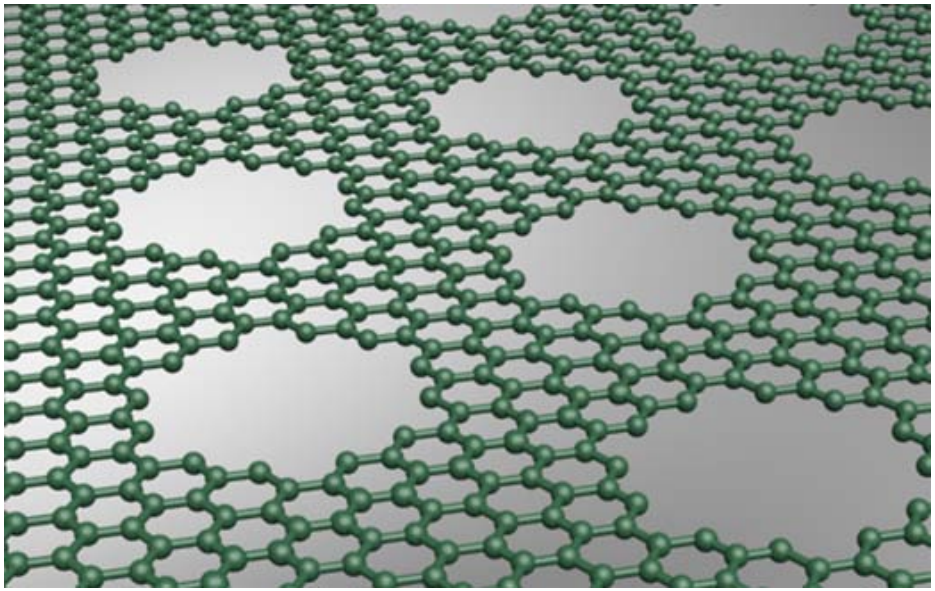
```
solver
{
    k_points        = [ (-0.5) , (0.5)]
    number_of_nodes = (100)
}
```

```
Geometry
{
    Region
    {
        shape         = cuboid
        region_number = 1
        priority      = 1
        min           = (-20,0.35,-5)
        max           = ( 20,2.35, 5)
        tag = substrate
    }
}
```

Bandstructure: 10-ZGNR

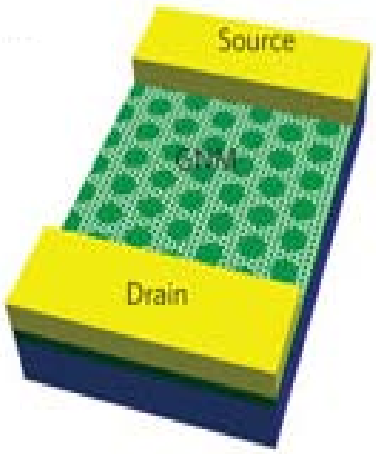


Zigzag edges give metallic behavior



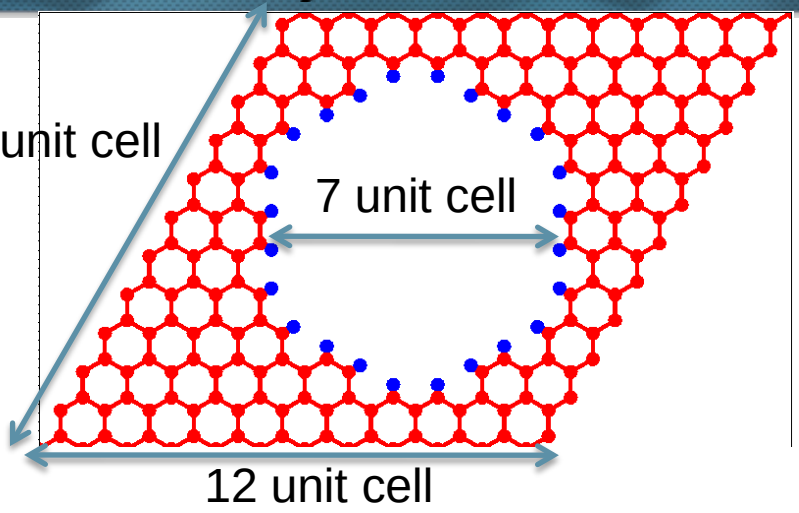
http://today.ucla.edu/

Graphene Nanomeshes



J. Bai *et al.* Nature Materials 5, 190-194 (2010)

Example 2: Graphene Nanomesh




```
Domain
{
    name = structure1
    type = pseudomorphic
    base_material = substrate
    dimension = (12,12,1)

    origin = (0,0,0)
    activate_hydrogen_atoms = true
    periodic = (true, true, false)

    miller_index_basis = primitive
    crystal_direction1 = (1,0,0)
    crystal_direction2 = (0,1,0)
    crystal_direction3 = (0,0,1)

    space_orientation_dir1 =  (1,0,0)
    space_orientation_dir3 =  (0,0,1)

    regions = (1)
    geometry_description = simple_shapes
    FEM_mesh_creation = false
}
```

Only include region 1 in the domain

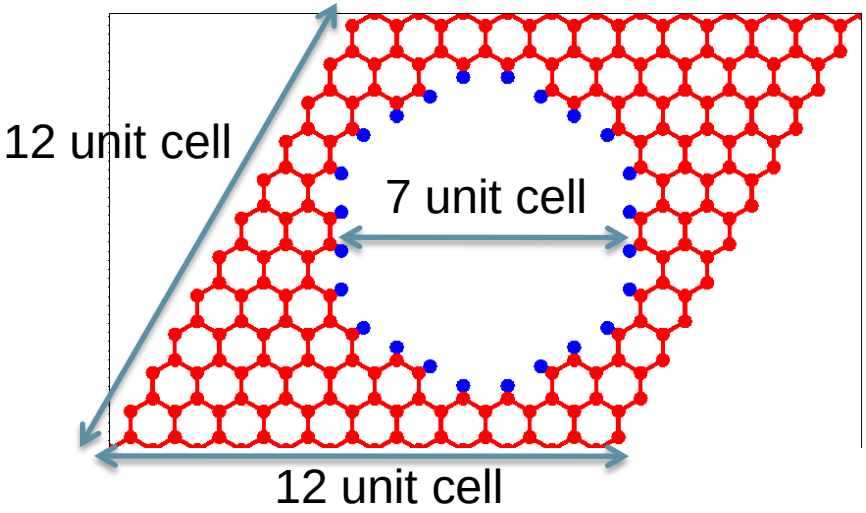
```
Geometry
{
    Region
    {
        shape          = cuboid
        region_number  = 1
        priority       = 1
        min            = (-10, -10,-5) // in
        max            = ( 10, 10, 5)
        tag = substrate
    }
    Region
    {
        shape          = cylinder
        region_number  = 2
        priority       = 2
        min            = ( 1.230, 0.346, -5)
        max            = ( 2.952, 2.068, 5)
        tag = substrate
    }
```

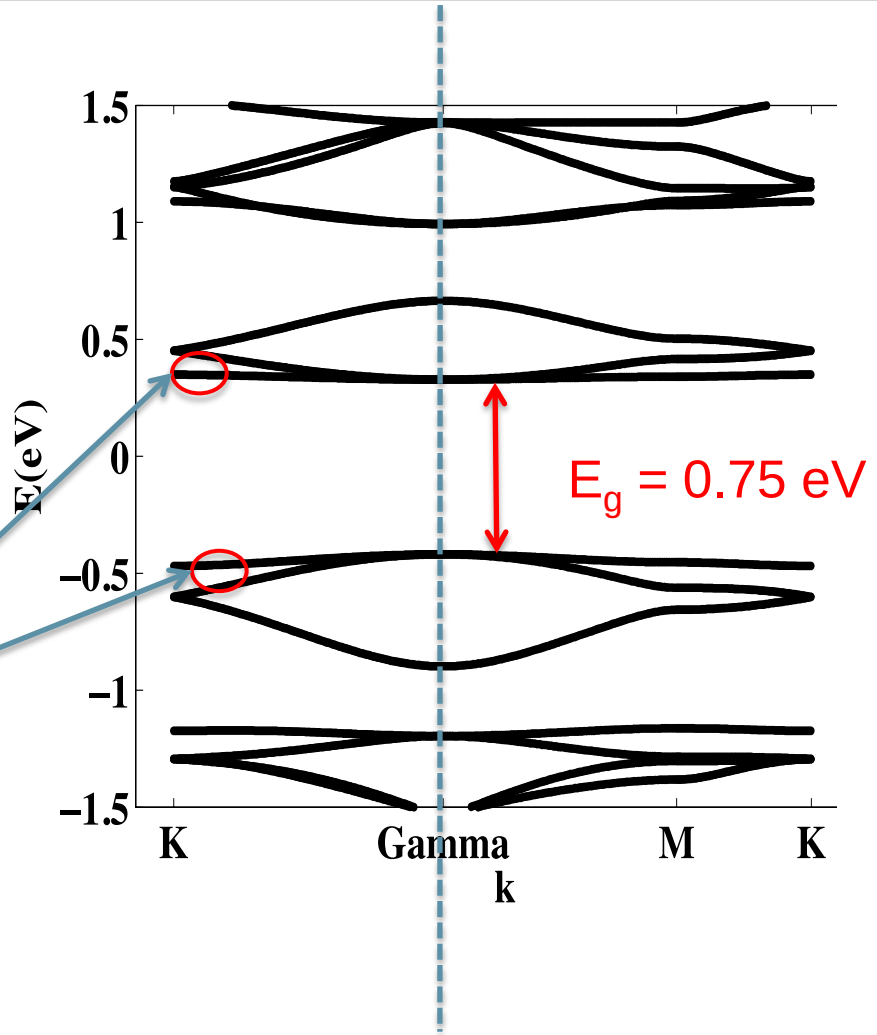
Region 1 defines the graphene supercell

Region 2 defines a hole

Higher priority in the hole region

Bandstructure: GNM





Flat bands in the middle of the bandgap

Need to visualize the wavefunction at the Γ point

Wavefunction Visualization

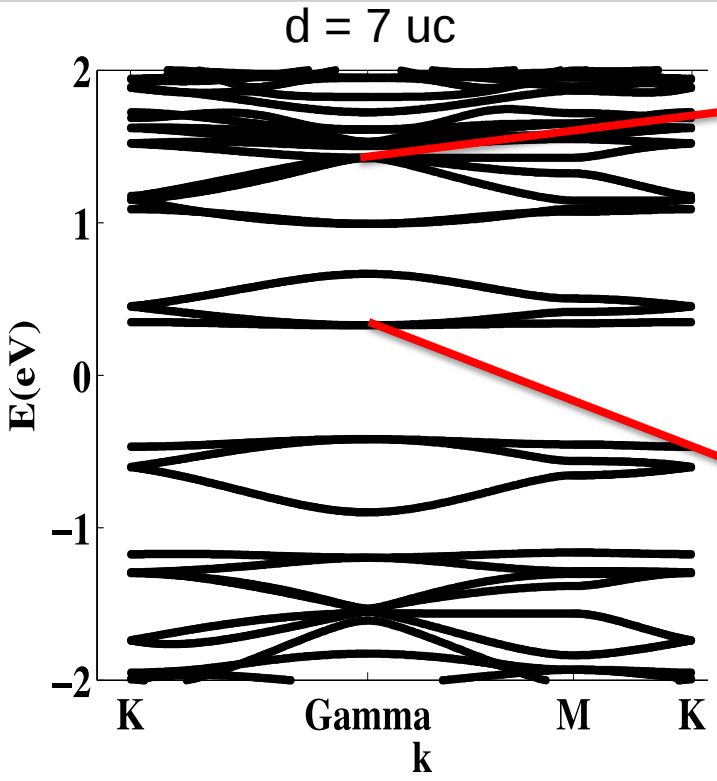
```
solver
{
    name            = Gamma
    type            = Schroedinger
    domain          = structure1
    active_regions = (1)

    eigen_values_solver    = krylovschur
    preconditioner  = mumps
    output          = (eigenfunctions, eigenfunctions_VTK)
    output_precision = 7

    job_list        = (passivate_H, calculate_band_structure)

    tb_basis = PD
    k_space_basis    = reciprocal
    number_of_eigenvalues = 120
    shift = 0.1
    k_points         = [(0.0,0.0,0.0)]
    number_of_nodes = 1
}


Global
{
//  solve     = (visualizer, BZ, gnm)
    solve     = (Gamma)
    database = /autohome/u121/jgeng/NEMO5/prototype/ma
    messaging_level = 5
}
```

```
[jgeng@rossmann-fe02 AL_12_5]$ ls
BZ.vtk          BZ_points.txt   gnm.err   gnm.out   gn
BZ_facets.txt   eigenfunctions  gnm.in    gnm.silo  gn
```

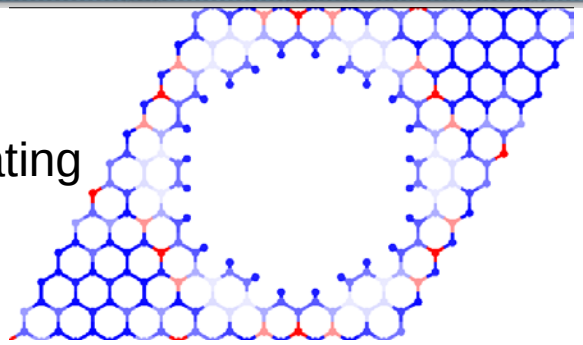
A new directory
That stores all
wavefunction files

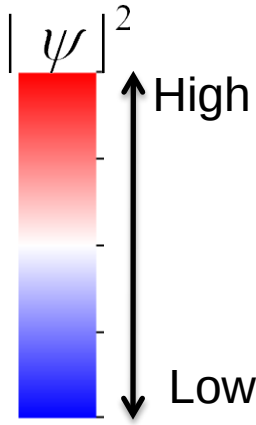
```
Gamma_f2.dat    Gamma_f33.dat
Gamma_f2.vtk    Gamma_f33.vtk
Gamma_f20.dat   Gamma_f34.dat
Gamma_f20.vtk   Gamma_f34.vtk
Gamma_f21.dat   Gamma_f35.dat
Gamma_f21.vtk   Gamma_f35.vtk
Gamma_f22.dat   Gamma_f36.dat
```

GNM: Edge state

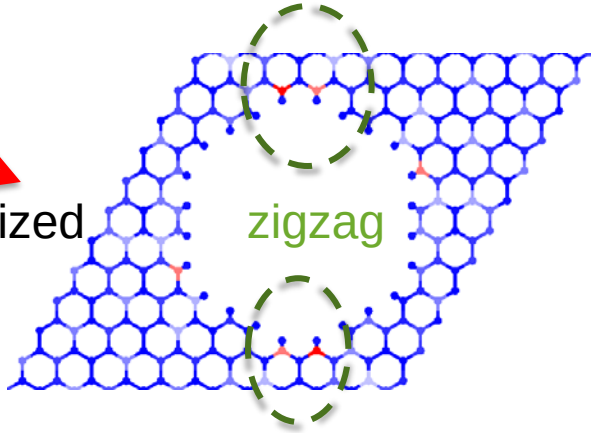


Propagating state





Localized state

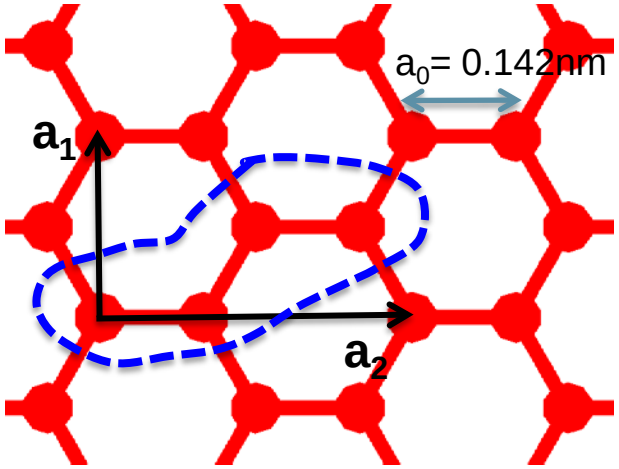


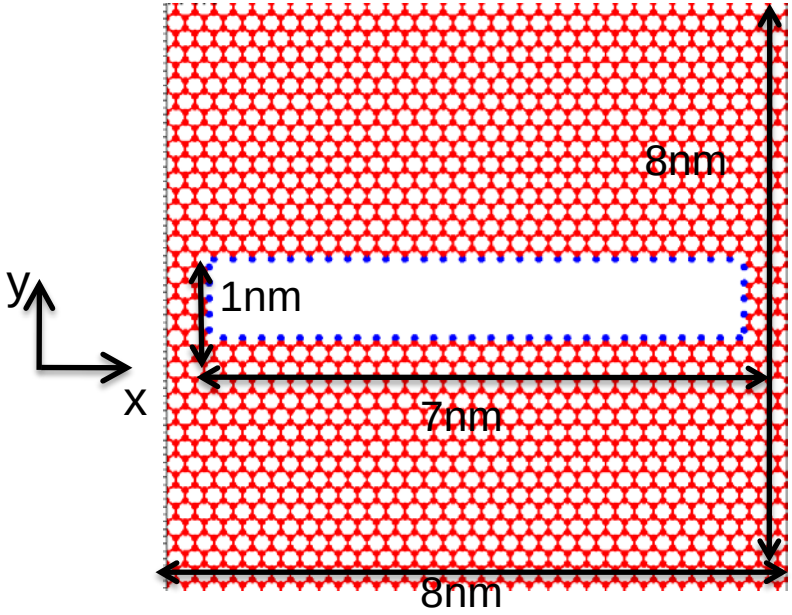
Wavefunctions on the flat band are localized at the zigzag edges

Exercise 2: Graphene Nanomesh

Exercise:

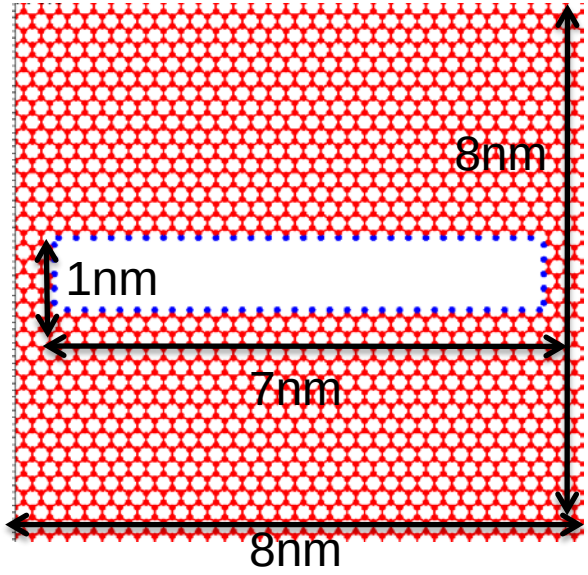
- Define a graphene nanomesh of 8nm x 8nm with rectangular hole 7nm x 1nm.
- Plot bandstructure along x and y.
- Obtain and visulize wavefunctions at Γ point





Exercise 2: Graphene Nanomesh

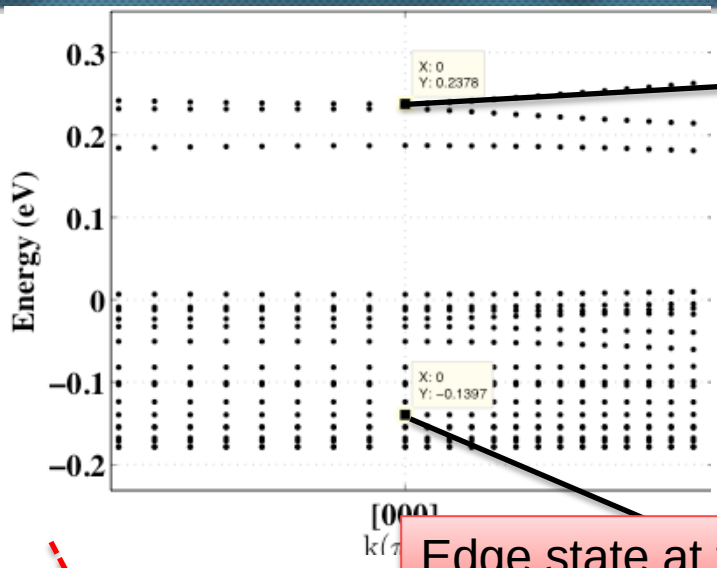
Structure:

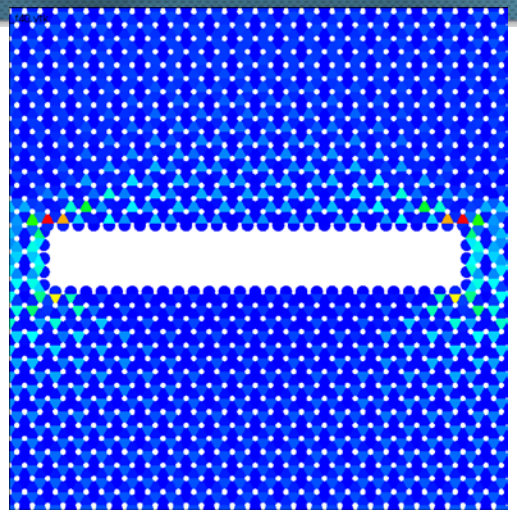


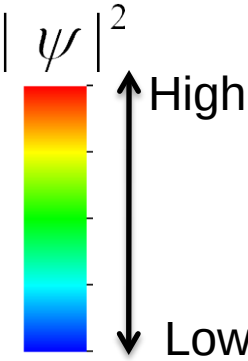

```
solver
{
    k_points        = [(0,0.5), (0.0,0.0) , (0.5,0)]
    number_of_nodes = (80,80)
}
```

```
18      Domain
19      {
20          name = structure1
21          type = pseudomorphic
22          base_material = substrate
23          dimension = (33,19,1)
24
25          origin = (0,0,0)
26          activate_hydrogen_atoms = true
27          periodic = (true, true, false)
28
29          miller_index_basis = cartesian

42      Geometry
43      {
44          Region
45          {
46              shape         = cuboid
47              region_number = 1
48              priority      = 1
49              min           = (-50,-50,-5)
50              max           = ( 50, 50, 5)
51              tag = substrate
52          }
53          Region
54          {
55              shape         = cuboid
56              region_number = 2
57              priority      = 2
58              min = (0.5919, 3.5, -5)
59              max = (7.3785, 4.5, 5)
60              tag = substrate
61          }
```

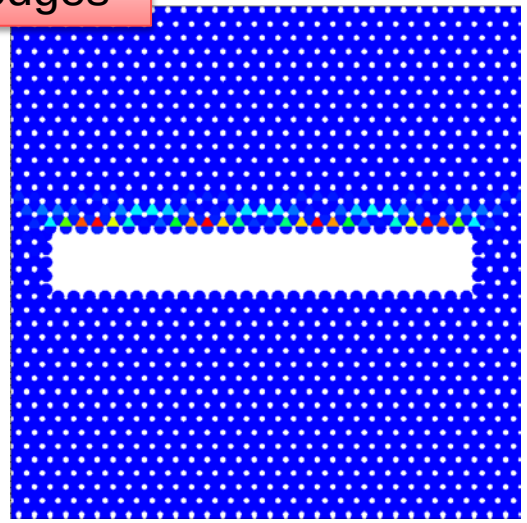
Bandstructure and Wavefunctions

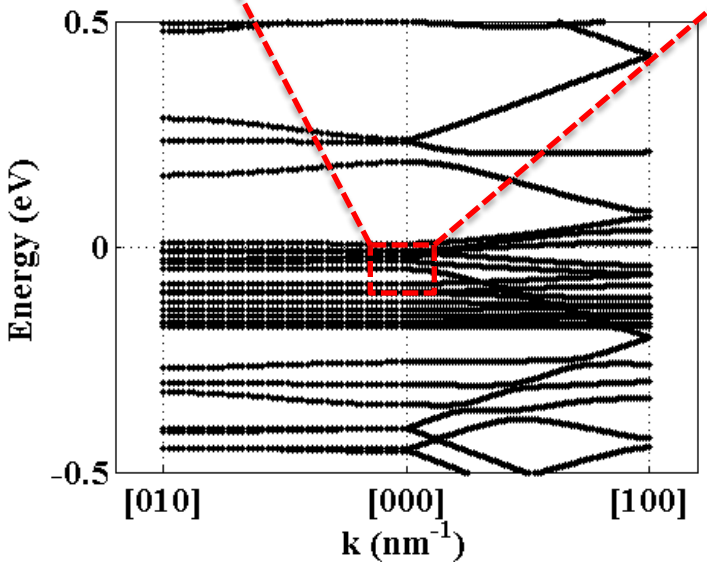


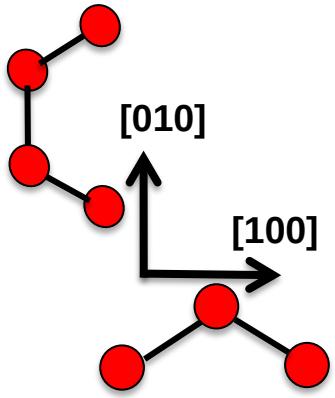




Edge state at the zigzag edges







Thank you !