NEMO5 Tutorial: Graphene Nanostructures

NCN Summer School 2012
Junzhe Geng, NEMO5 team
Advantages:
• High intrinsic mobility (Over 15,000 cm²/V-s)
• High electron velocity $\Rightarrow$ Good transport
• 2D material $\Rightarrow$ Good scalability

• 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
Example: Si_UTB_10uc_no_pass.in

Input deck: Bandstructure calculation of a Si UTB with default settings, no passivation used.
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.

Calculate the wave functions at the $\Gamma$ 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

10 unit cell

Energy (eV)

[100]  k(π/a)  [110]

-2  -1  0  1  2  3
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 = false   //this applies to
  geometry_description = simple_shapes
}
```

“passivate = true”
Adds H-atoms at the surface
Example: Si_UTB_10uc_pass.in

Surface states are shifted out of band gap region to very high energies (~1 keV)
http://en.wikipedia.org/wiki/Graphene
Tight-binding Model

- $2p_z$, $2p_y$, and $2p_x$ orbitals
- $2p_z$ 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)
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

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)
}
Always have passivate = true in the domain section (default)
Graphene: Primitive Basis

Lattice basis:

\[ \vec{\alpha}_1 = \frac{3a_0}{2} \hat{x} + \frac{\sqrt{3}a_0}{2} \hat{y} \]

\[ \vec{\alpha}_2 = \frac{3a_0}{2} \hat{x} - \frac{\sqrt{3}a_0}{2} \hat{y} \]

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
Define the material

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

Have “true” only for PD model

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

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

```json
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 = 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

‘primitive’ or ‘Cartesian’
J.Z Geng

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

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

    job_list = (calculate_band_structure)

    tb_basis = PD
    'Pz' or 'PD'

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

Symmetry points:

- $K: \frac{1}{3} A_1 - \frac{1}{3} A_2$
- $M: \frac{1}{2} A_1$

Expressed in units of $A_1$ and $A_2$
DFT results are much better reproduced with the PD model.
Graphene Nanoribbons

Graphene: Cartesian Basis

Lattice basis:
\[ \vec{a}_1 = \sqrt{3} a_0 \hat{y} \]
\[ \vec{a}_2 = 3 a_0 \hat{x} \]

Reciprocal lattice basis:
\[ \vec{A}_1 = \frac{2\pi}{\sqrt{3}a} \hat{x} \]
\[ \vec{A}_2 = \frac{2\pi}{3a} \hat{y} \]
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

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)
}

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

“Armchair”

Periodic
Armchair edges allow opening up a bandgap
Exercise: Define a “10-ZGNR” in NEMO5 and calculate its bandstructure along x direction ([100])

\[a_0 = 0.142\text{nm}\]

The diagram illustrates a structure with labeled vectors and points labeled 1 through 10 along the y-axis and a_0=0.142nm along the x-axis. The term “zigzag” is also marked on the diagram.
Exercise 1: 10-ZGNR

Domain
{
    name = structure1
    type = pseudomorphic
    base_material = substrate
    dimension = (1, 6, 1)
    origin = (0, 0, 0)
    activate_hydrogen atoms = true
    periodic = (true, false, false)
    miller_index_basis = cartesian
    crystal_direction1 = (1, 0, 0)
    crystal_direction2 = (0, 1, 0)
    crystal_direction3 = (0, 0, 1)
}

Geometry
{
    Region
    {
        shape = cuboid
        region_number = 1
        priority = 1
        min = (-20.0, 0.35, -5)
        max = (20.0, 2.35, 5)
        tag = substrate
    }
}

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

"zigzag"
Zigzag edges give metallic behavior
Graphene Nanomeshes

http://today.ucla.edu/
Example 2: Graphene Nanomesh

Region 1 defines the graphene supercell

Region 2 defines a hole

Higher priority in the hole region

Only include region 1 in the domain

```
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
}
```

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
    }
```
Flat bands in the middle of the bandgap

Need to visualize the wavefunction at the $\Gamma$ point

$E_g = 0.75$ eV
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)]
  number_of_nodes = 1
}

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

A new directory
That stores all wavefunction files
Wavefunctions on the flat band are localized at the zigzag edges.
Exercise:
• Define a graphene nanomesh of 8nm x 8nm with a rectangular hole 7nm x 1nm.
• Plot bandstructure along x and y.
• Obtain and visualize wavefunctions at Γ point.
Exercise 2: Graphene Nanomesh

Structure:

```
Domain
{
  name = structure1
  type = pseudomorphic
  base_material = substrate
  dimension = (33,19,1)
  origin = (0,0,0)
  activate_hydrogen_atoms = true
  periodic = (true, true, false)
  miller_index_basis = cartesian
}

Geometry
{
  Region
  {
    shape = cuboid
    region_number = 1
    priority = 1
    min = (-50,-50,-5)
    max = (50,50,5)
    tag = substrate
  }
  Region
  {
    shape = cuboid
    region_number = 2
    priority = 2
    min = (0.5919, 3.5, -5)
    max = (7.3785, 4.5, 5)
    tag = substrate
  }
  solver
  {
    k_points = [(0,0,5), (0,0,0), (0.5,0)]
    number_of_nodes = (80,80)
  }
```
Bandstructure and Wavefunctions

Edge state at the zigzag edges
Thank you !