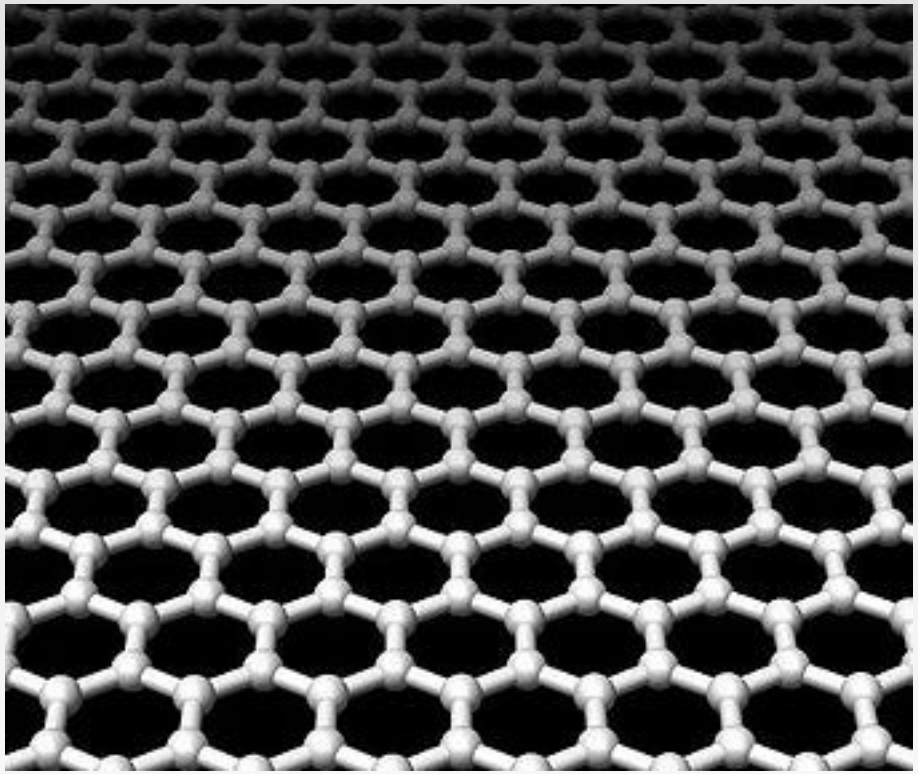
VASP exercises III

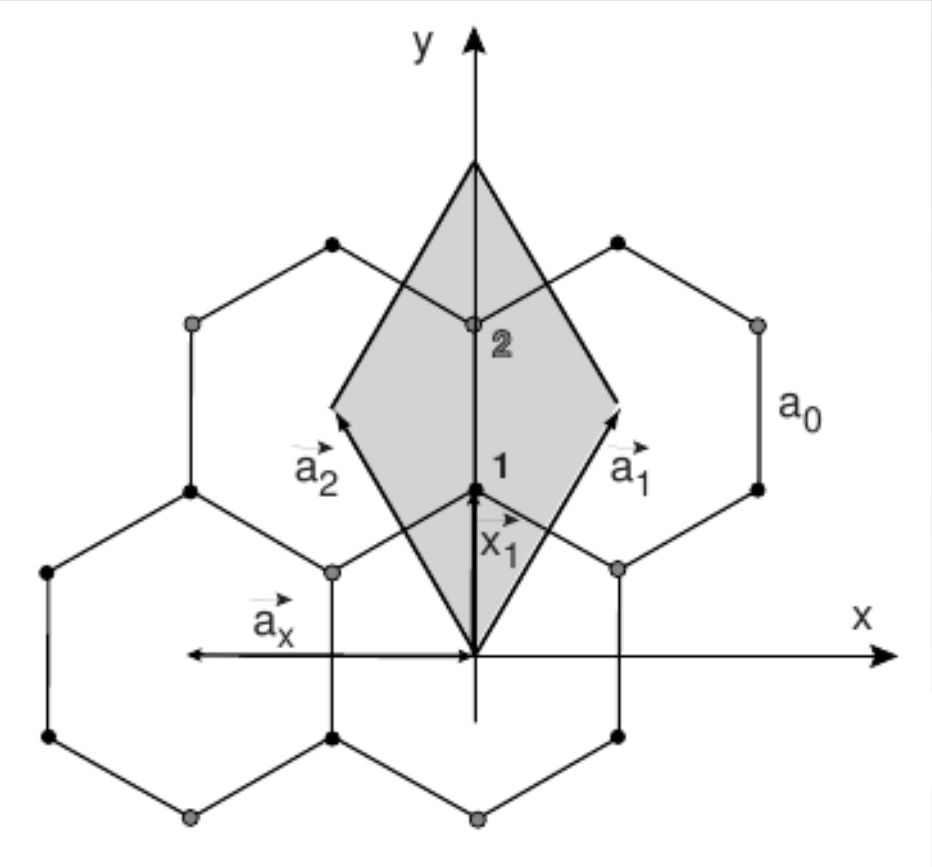
Outline

- Surface calculation – slab model
  - graphene sheet



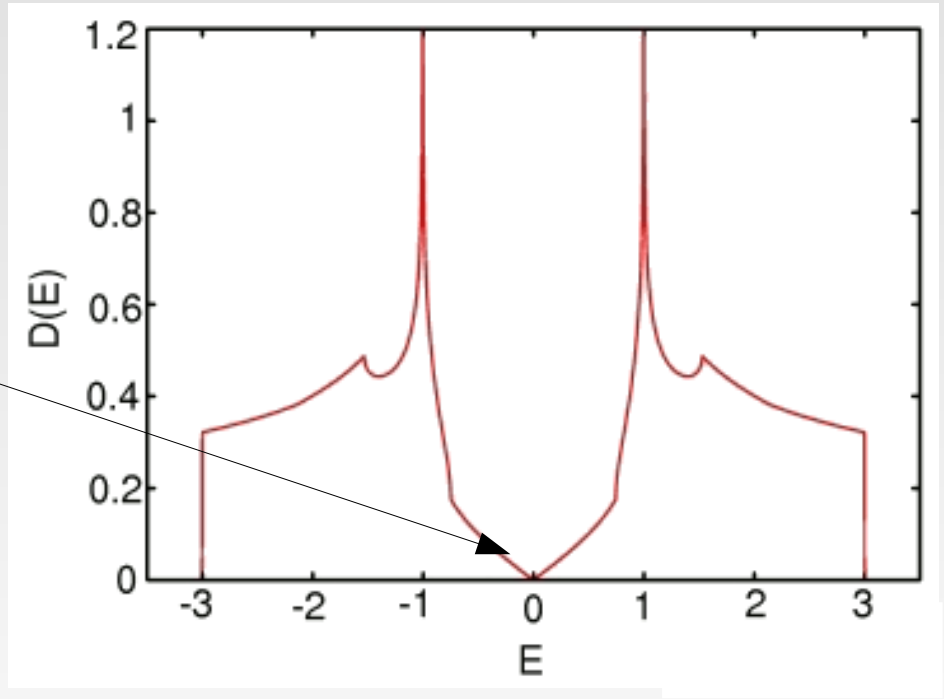
Graphene – free surface

- planar sheet of sp^2 carbons – honeycomb lattice
- building unit of graphite, nanotubes, fullerenes
- interesting properties



Graphene – free surface

- planar sheet of sp^2 carbons – honeycomb lattice
- building unit of graphite, nanotubes, fullerenes
- interesting properties
  - semi-metal or zero-gap semiconductor (ex. el_prop)
  - high electron mobility, low resistivity
  - strong material – breaking strength 200x higher than steel



Graphene – free surface

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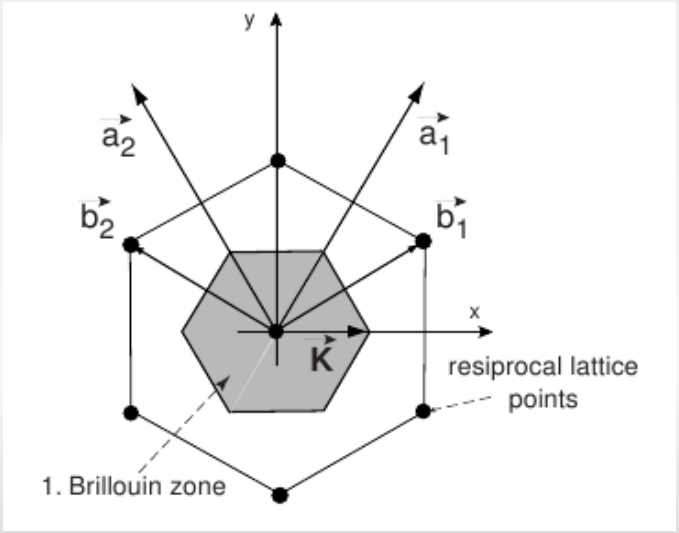
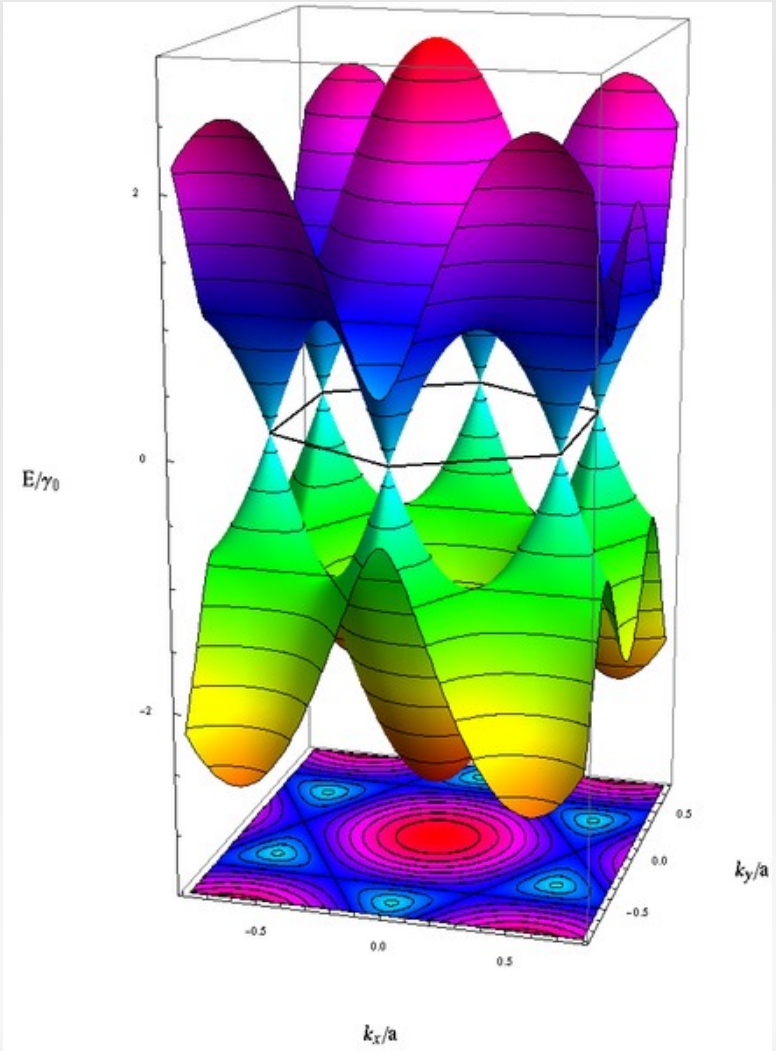
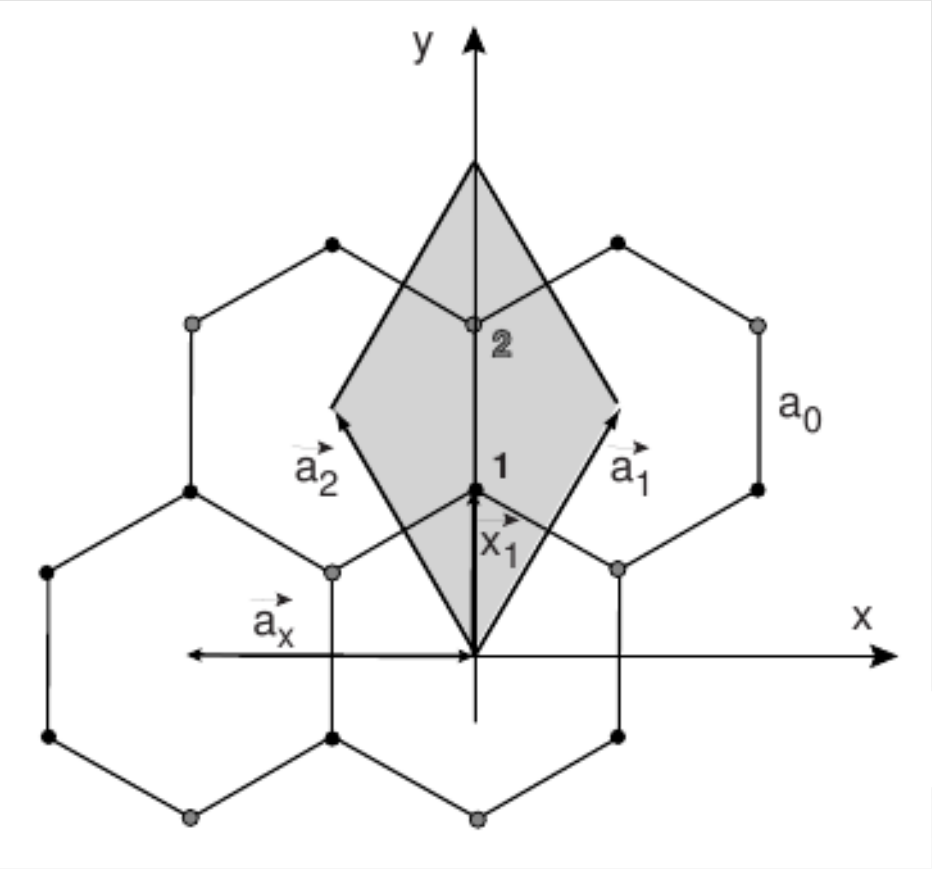




Graphene – free surface

- `cd cviceni_3/adsorption/gga/ex_1`
- POSCAR

```
Graphene
   1.00
     1.229756    2.130000    0.000000
    -1.229756    2.130000    0.000000
     0.000000    0.000000   20.000000
   C
   2
Direct
  0.333333  0.333333  0.000000
  0.666667  0.666667  0.000000
```

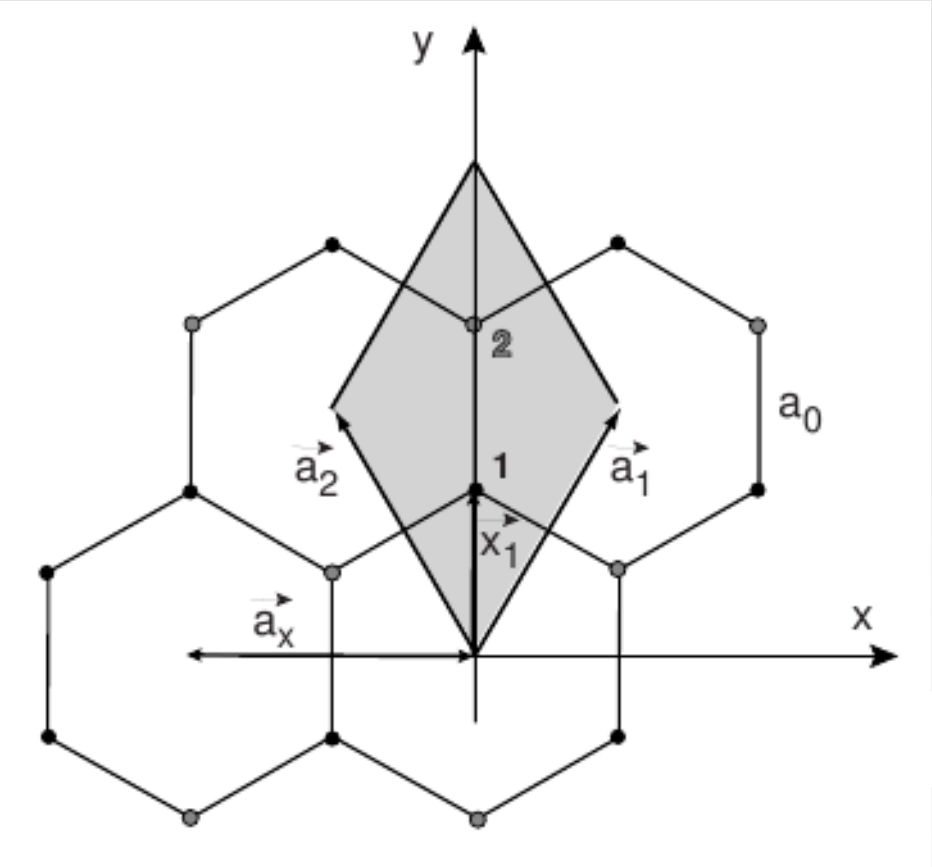


  - mind the large z component of last lattice vector - slab model – minimizing the interaction of plane images

Graphene – free surface

- POSCAR

```
Graphene
   1.00
     1.229756    2.130000    0.000000
    -1.229756    2.130000    0.000000
     0.000000    0.000000   20.000000
   C
   2
Direct
  0.333333  0.333333  0.000000
  0.666667  0.666667  0.000000
```



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Graphene – free surface

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   1.00
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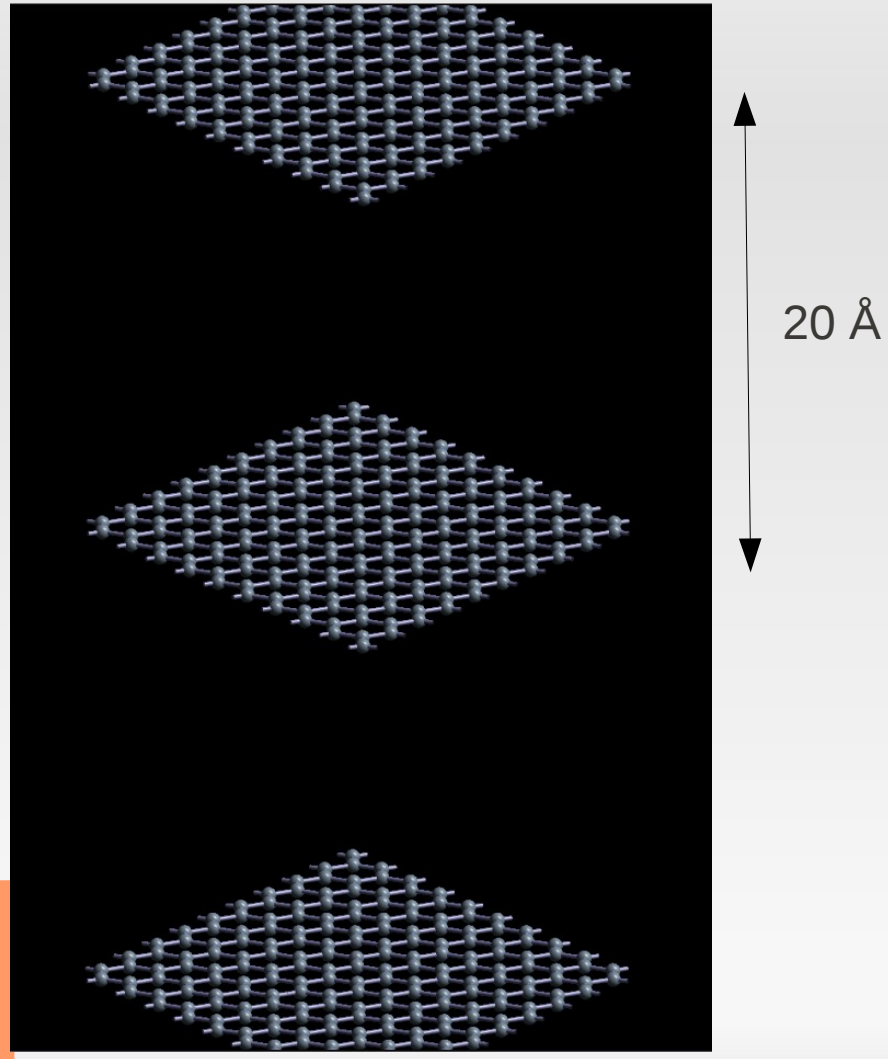
    -1.229756    2.130000    0.000000
     0.000000    0.000000   20.000000
   C
   2
Direct
  0.333333  0.333333  0.000000
  0.666667  0.666667  0.000000
```

  - mind the large z component of last lattice vector - slab model – minimizing the interaction of plane images

- KPOINTS

```
Graphene
0
Monkhorst
7 7 2
0 0 0
```

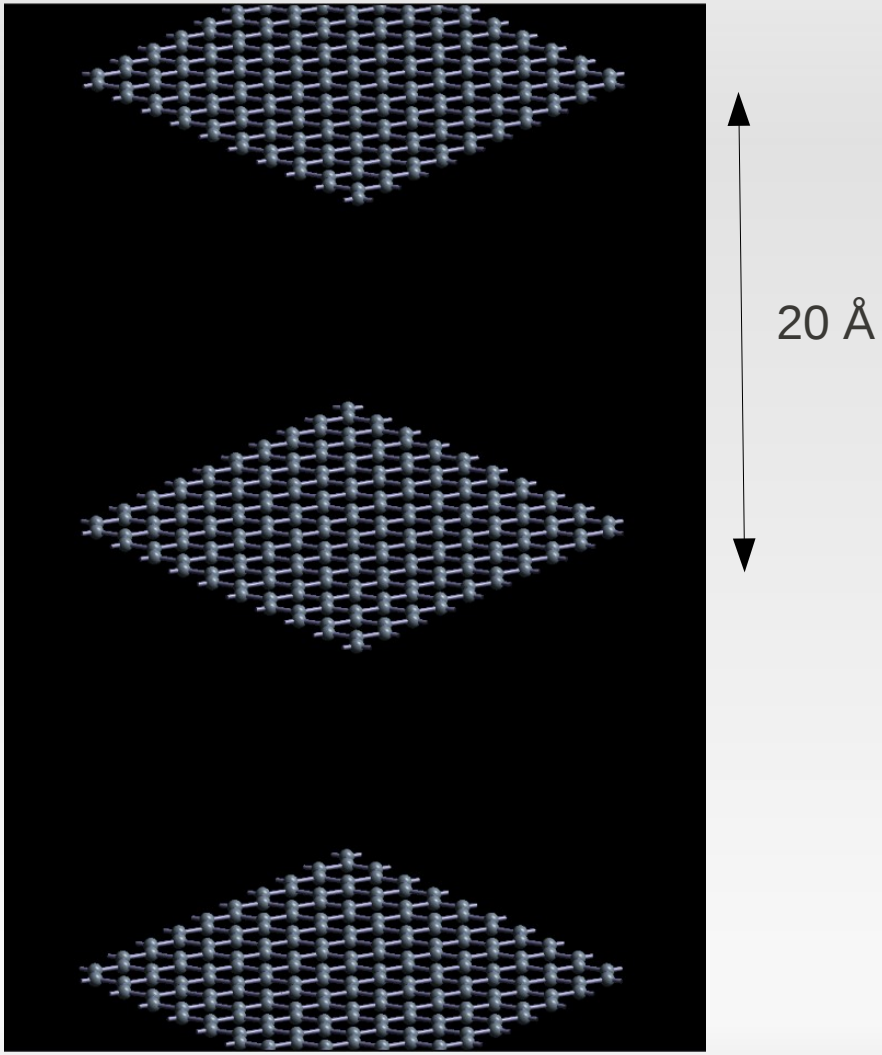
  - in z-direction only few k-points – no interaction in this direction



Graphene – free surface

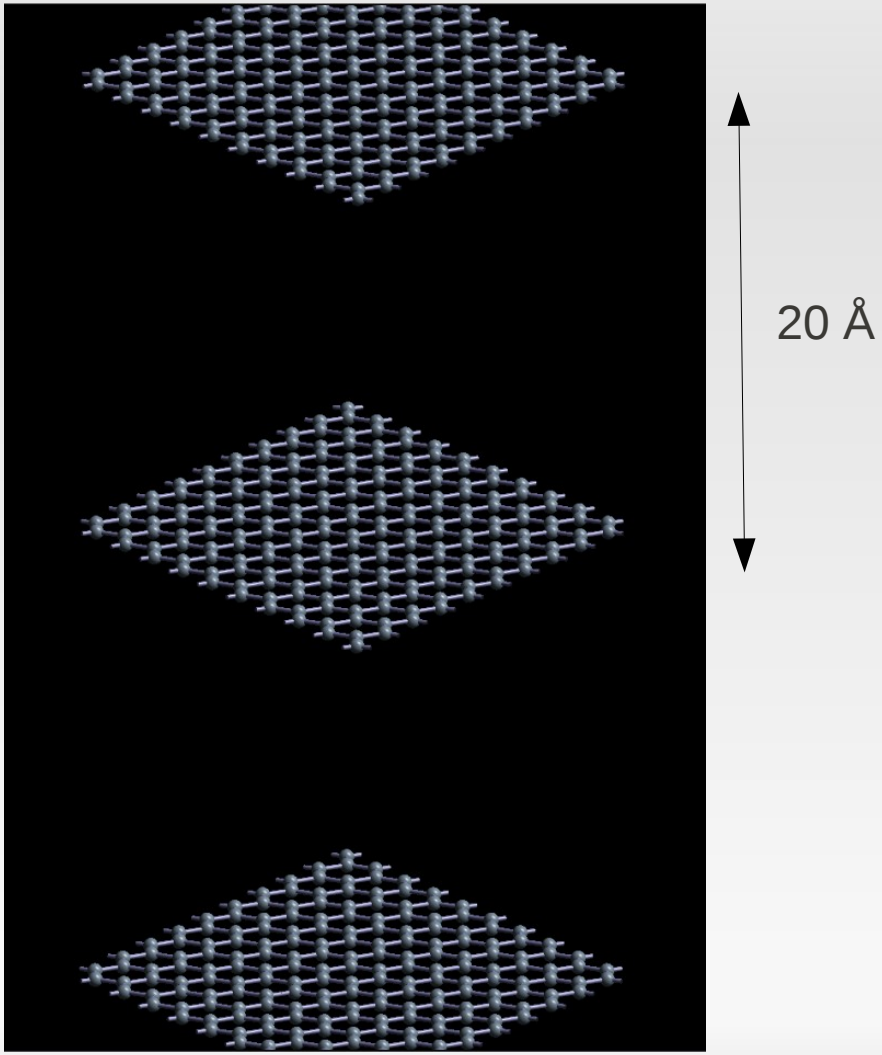
- POSCAR
  - mind the large z component of last lattice vector - slab model – minimizing the interaction of plane images
- KPOINTS
  - in z-direction only few k-points – no interaction in this direction
- POTCAR

  PROVIDED



Graphene – free surface

- POSCAR
  - mind the large z component of last lattice vector - slab model – minimizing the interaction of plane images
- KPOINTS
  - in z-direction only few k-points – no interaction in this direction
- INCAR and run VASP




```
SYSTEM = graphene
NSW = 100
IBRION = 2
ISIF = 2
ENCUT = 400
ISMEAR = 0
SIGMA = 0.05
```

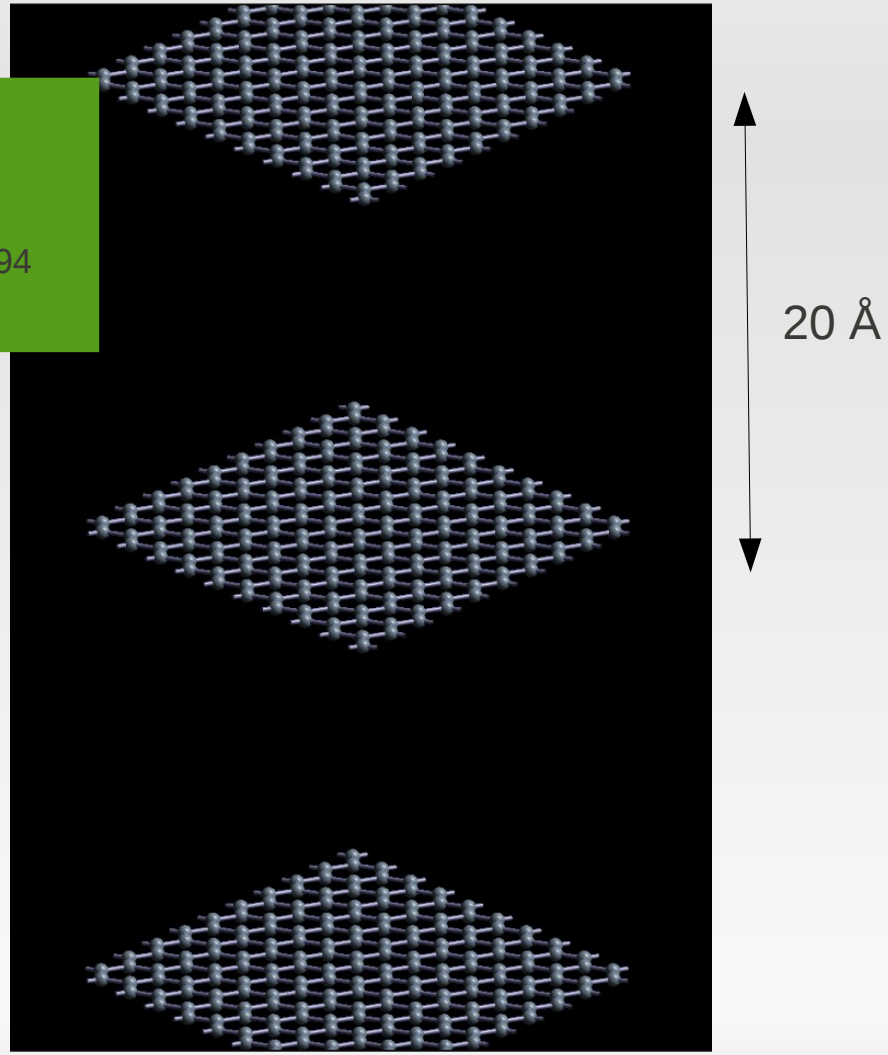
Graphene – free surface

- OUTCAR

```
FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)
---------------------------------------------------
free  energy   TOTEN  =       -18.471794 eV

energy  without entropy=      -18.471794  energy(sigma->0) =      -18.471794
```

- E(graph) = -18.471794 eV



Graphene – H_2 adsorption

- how to calculate adsorption on the surface?
  - E_{ads} = E(graph..H_2) – E(graph) - E(H_2)
- mind that the each energy contribution has to be calculated at the same level (ideally with the converged values of parameters) – cutoff value, k-points number, cell size, relaxed geometries
- `cd ../ex_2;` copy KPOINTS and INCAR
- POSCAR
- POTCAR
  - catenate the C and H POTCARs
- run VASP

```
Graphene and H2
   1.00
     1.229756    2.130000    0.000000
    -1.229756    2.130000    0.000000
     0.000000    0.000000   20.000000
   C H
   2 2
Direct
  0.333333  0.333333  0.000000
  0.666667  0.666667  0.000000
  0.666667  0.666667  0.157500
  0.666667  0.666667  0.194500
```

Graphene – H_2 adsorption

- how to calculate adsorption on the surface?
  - E_{ads} = E(graph..H_2) – E(graph) - E(H_2)
- mind that the each energy contribution has to be calculated at the same level (ideally with the converged values of parameters) – cutoff value, k-points number, cell size, relaxed geometries
- `cd ../ex_2;` copy KPOINTS and INCAR
- POSCAR
- POTCAR
  - catenate the C and H POTCARs
- run VASP and look at the OUTCAR
  - E(graph...H_2) = -25.090832 eV

```
Graphene and H2
   1.00
     1.229756    2.130000    0.000000
    -1.229756    2.130000    0.000000
     0.000000    0.000000   20.000000
   C H
   2 2
Direct
  0.333333  0.333333  0.000000
  0.666667  0.666667  0.000000
  0.666667  0.666667  0.157500
  0.666667  0.666667  0.194500
```

Graphene – H_2

- how to calculate adsorption on the surface?
  - E_{ads} = E(graph..H_2) – E(graph) - E(H_2)
- mind that the each energy contribution has to be calculated at the same level (ideally with the converged values of parameters) – cutoff value, k-points number, cell size, relaxed geometries
- `cd ../ex_3;` copy KPOINTS and INCAR
- POSCAR
- POTCAR
  - only H POTCAR
- run VASP and look at the OUTCAR
  - E(H_2) = -6.617838 eV

```
Graphene and H2
   1.00
     1.229756    2.130000    0.000000
    -1.229756    2.130000    0.000000
     0.000000    0.000000   20.000000
   H
   2
Direct
  0.666667  0.666667  0.157500
  0.666667  0.666667  0.194500
```

E_{ads} = -0.0012 eV => -0.1 kJ/mol - very weak interaction

Graphene – GGA vs. LDA

- the experimental value of the H_2 adsorption ~ -5 kJ/mol
- large discrepancy for DFT/GGA used (~ -0.1kJ/mol) due to incapability to correctly describe weakly (VdW) bound complexes
- but it was observed that DFT/LDA gives in this case much more satisfying results although due to some error compensation
- copy needed files (or all) to `cviceni_3/adsorption/lda/`
- only use different POTCARs
  - `~grajciar/School/QCH_VASP_exercises/potpaw_LDA/`
- run VASP and check the OUTCARs/OSZICARs
-

Graphene – DOS

- analogous to previous DOS calculation with fcc Si
- `cd exercises_3/dos/ex_1`; copy POSCAR and POTCAR from previous graphene runs
- INCAR
- KPOINTS – finer grid used
- run VASP
- copy input files along with CHGCAR to ../ex_2/
- change INCAR and use even fined k-point grid
- rerun VASP
- visualize

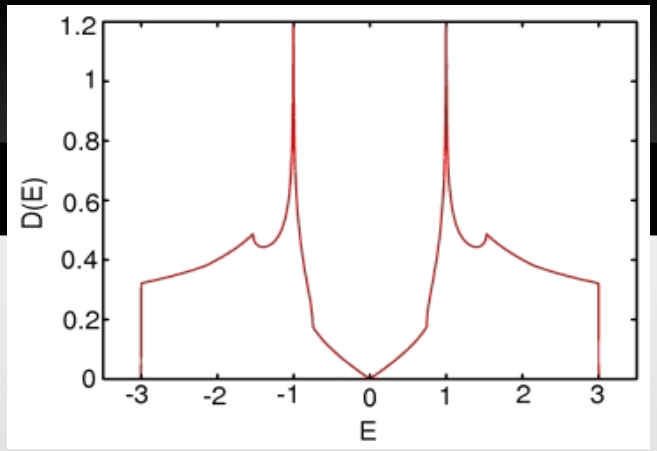
```
SYSTEM = graphene
ENCUT = 400
ISMEAR = -4
SIGMA = 0.05
```

```
Graphene
0
Monkhorst
11 11 1
0 0 0
```

```
SYSTEM = graphene
ICHARG = 11
ENCUT = 400
ISMEAR = -4
SIGMA = 0.05
```

```
Graphene
0
Monkhorst
21 21 1
0 0 0
```

Graphene – DOS



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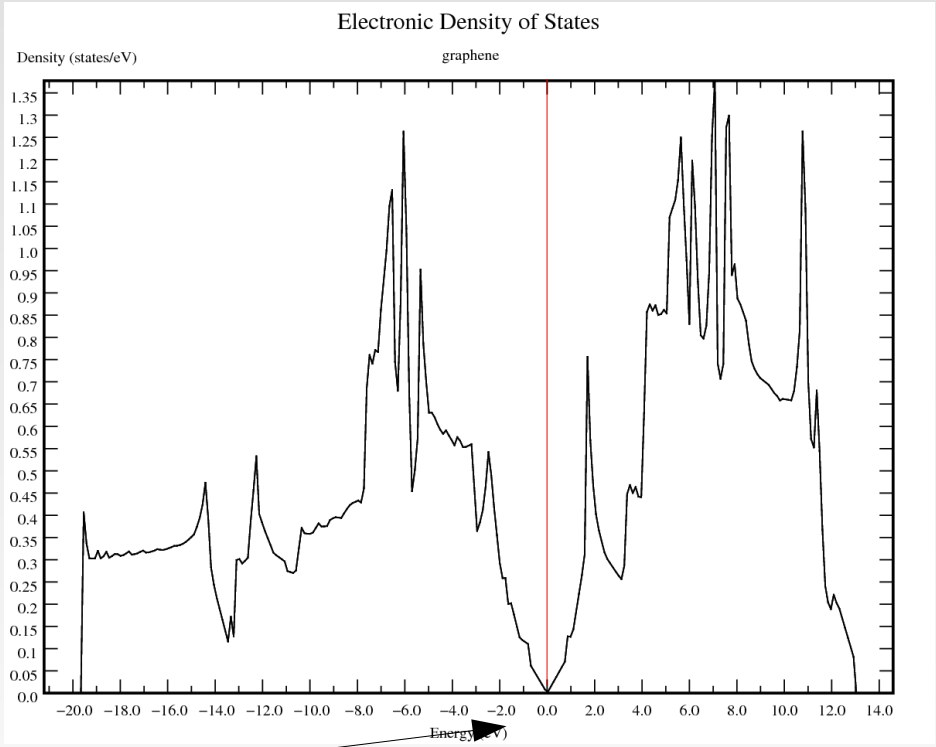


Graphene – band-structure

- analogous to previous band-structure calculation with fcc Si
- `cd exercises_3/band/ex_1`; copy POSCAR, POTCAR and CHGCAR from previous run (dos/ex_1)
- INCAR
- KPOINTS
  - k-points along x and y axis of k-space
-

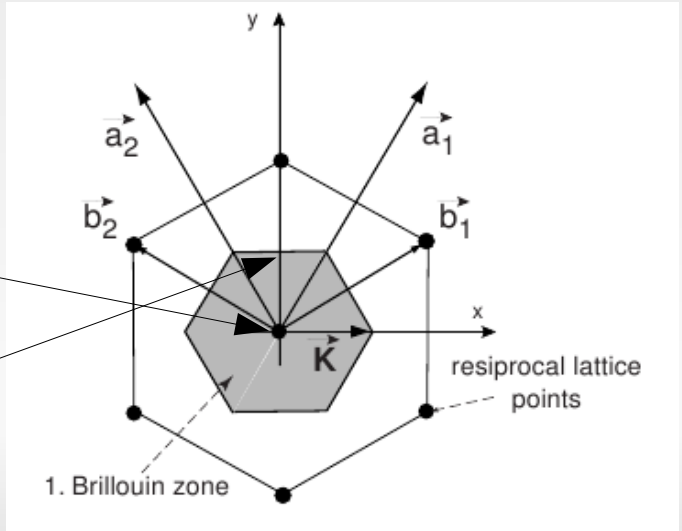
```
SYSTEM = graphene
ICHARG=11
ENCUT = 400
ISMEAR = 0
SIGMA = 0.05
```

```
Graphene
20
line
cartesian
-0.384900179  0  0 1     !-kx
 0.000000000  0  0 1     !Gamma

0.000000000  0  0  1     !Gamma
0.384900179  0  0  1     !+kx

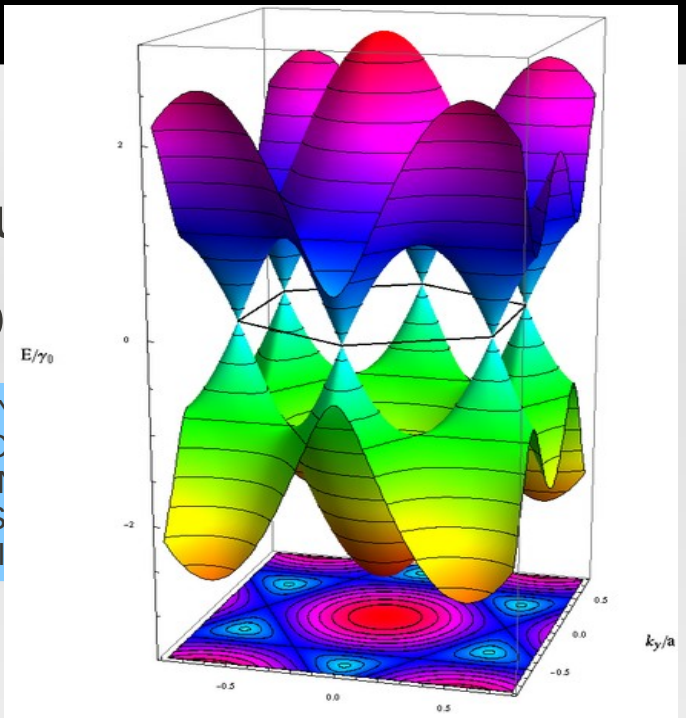
0  -0.384900179  0  1     !-ky
0   0.000000000  0  1     !Gamma

0   0.000000000  0  1     !Gamma
0   0.384900179  0  1     !+ky
```



Graphene – band-structure

- analogous to previous band-structure calcu
- `cd exercises_3/band/ex_1`; copy PO
  CHGCAR from previous run (dos/ex_1)
- INCAR
- KPOINTS
  - k-points along x and y axis of k-space
-

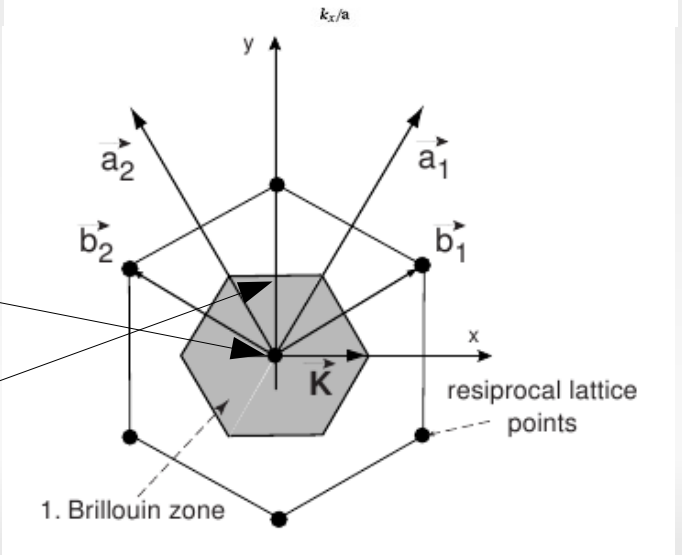



```
Graphene
20
line
cartesian
-0.384900179  0  0 1     !-kx
 0.000000000  0  0 1     !Gamma

0.000000000  0  0  1     !Gamma
0.384900179  0  0  1     !+kx

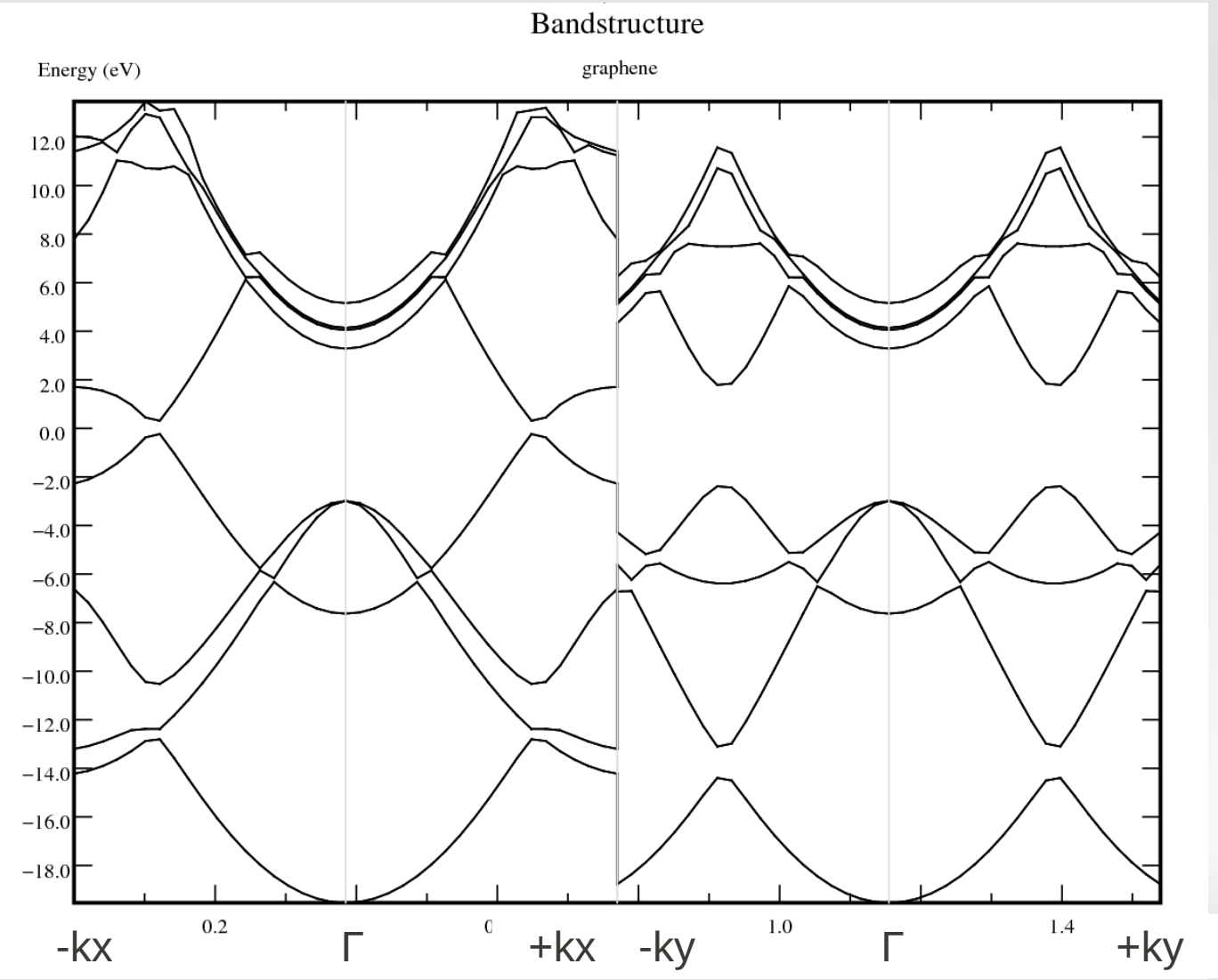
0  -0.384900179  0  1     !-ky
0   0.000000000  0  1     !Gamma

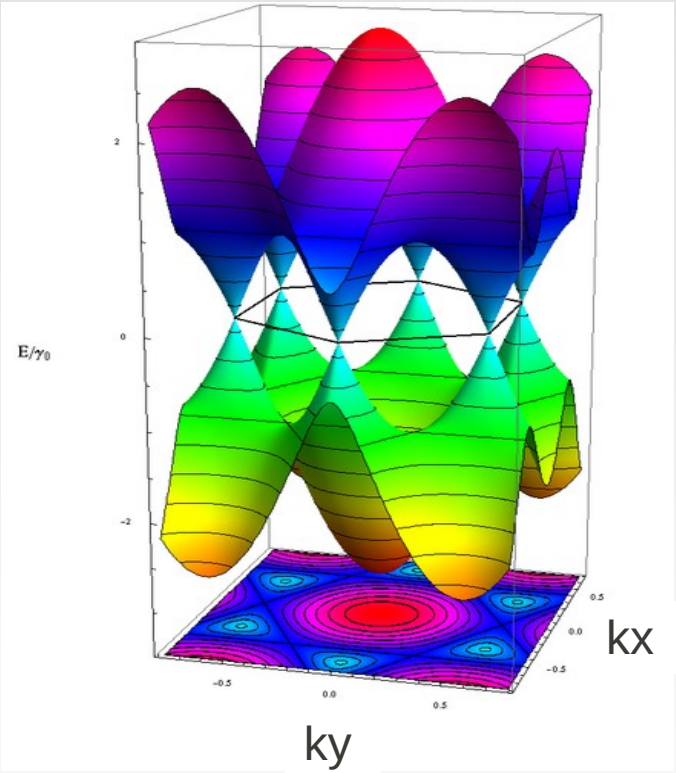
0   0.000000000  0  1     !Gamma
0   0.384900179  0  1     !+ky
```



Graphene – band-structure

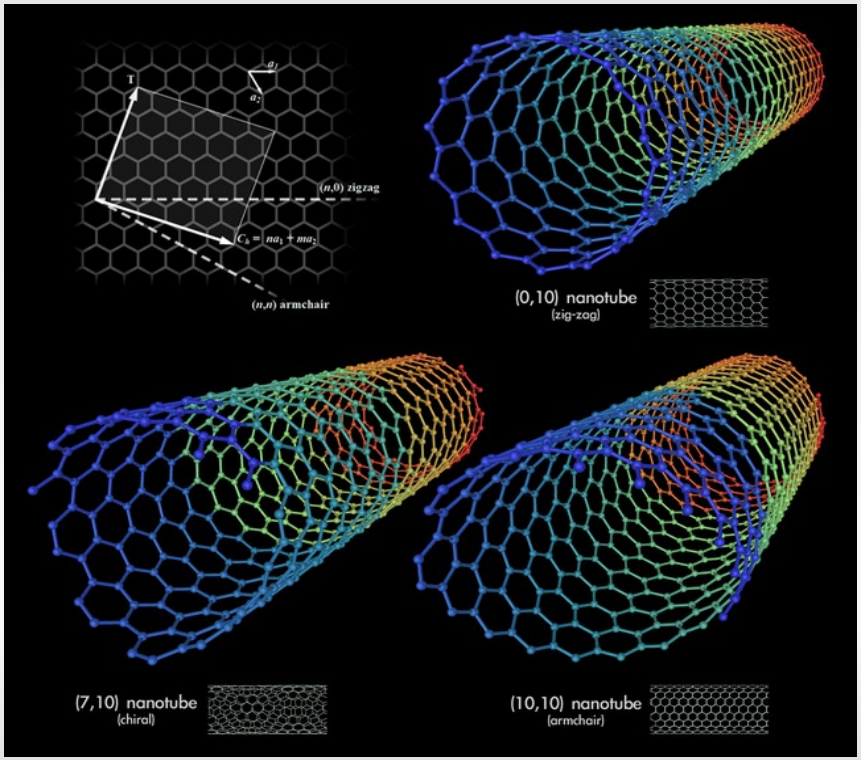
- run VASP and visualize





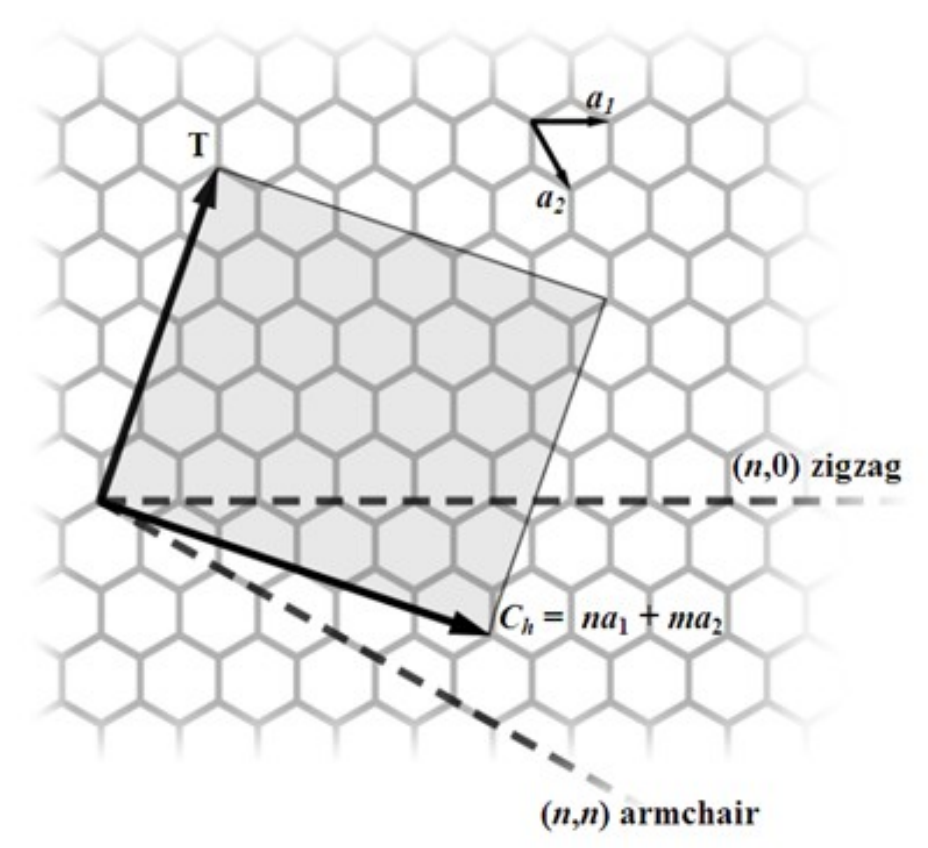
Outline

- Surface calculation – slab model
  - graphene sheet
- Optional – carbon nanotubes



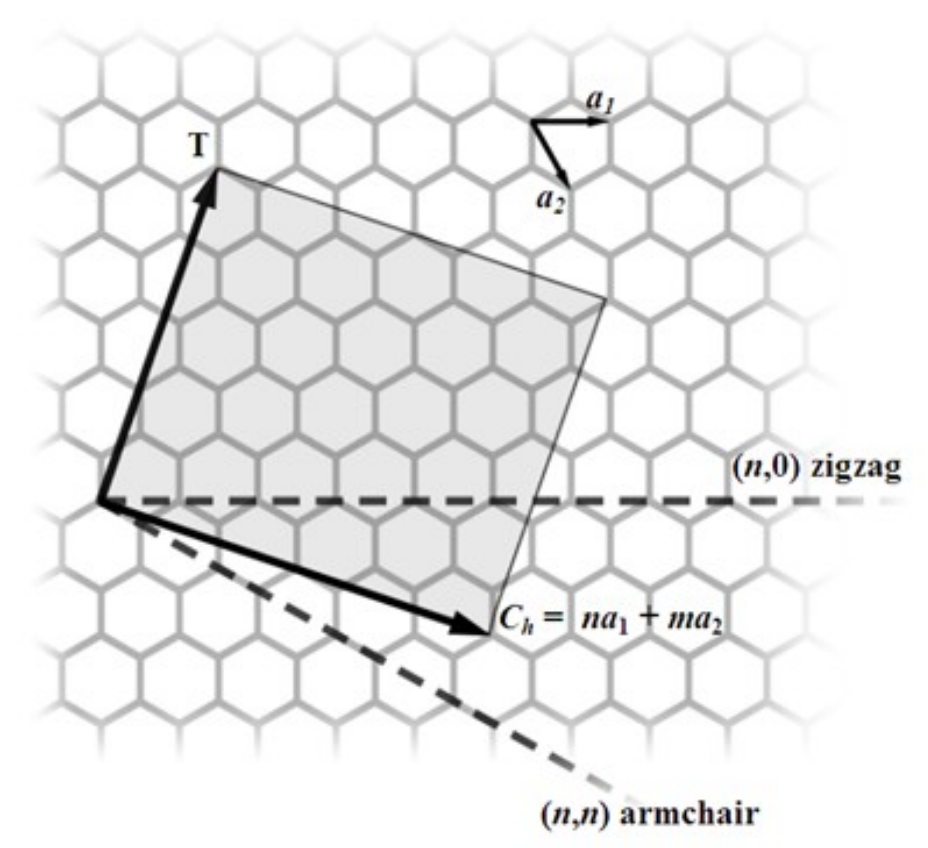
Carbon nanotubes

- wrapping the graphene sheet to seamless cylinder
- different ways to wrap a graphene leading to nanotubes with different properties – metallic/semiconductor
-



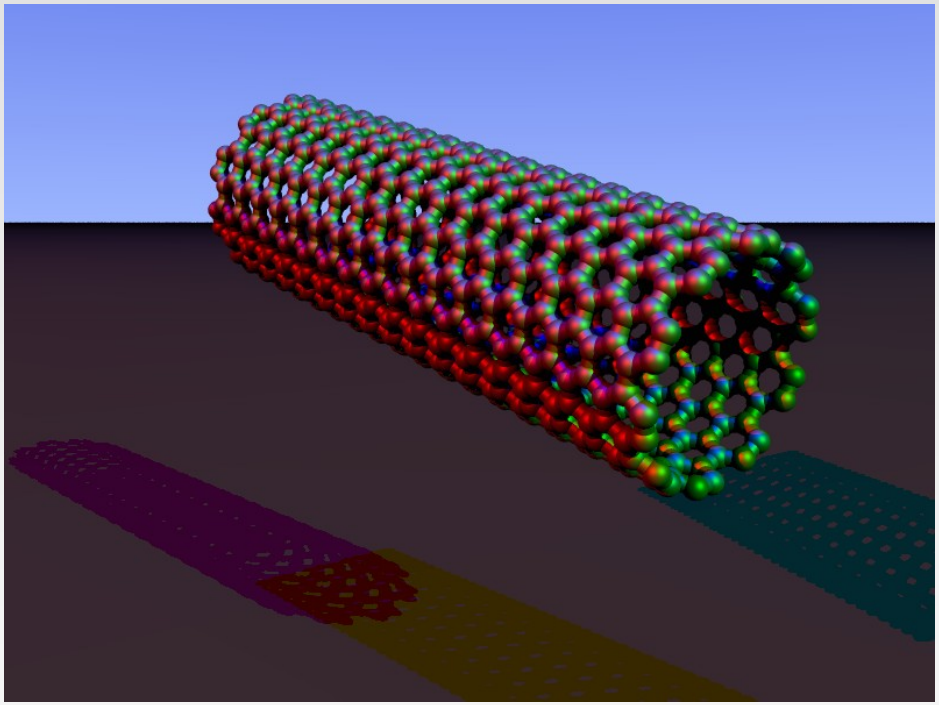
Carbon nanotubes

- wrapping the graphene sheet to seamless cylinder
- different ways to wrap a graphene leading to nanotubes with different properties – metallic/semiconductor
- the (n,m) naming adopted – the integer prefactors for the unit vectors a_1 and a_2
- T – the tube axis
- C_h – the “roll up” vector



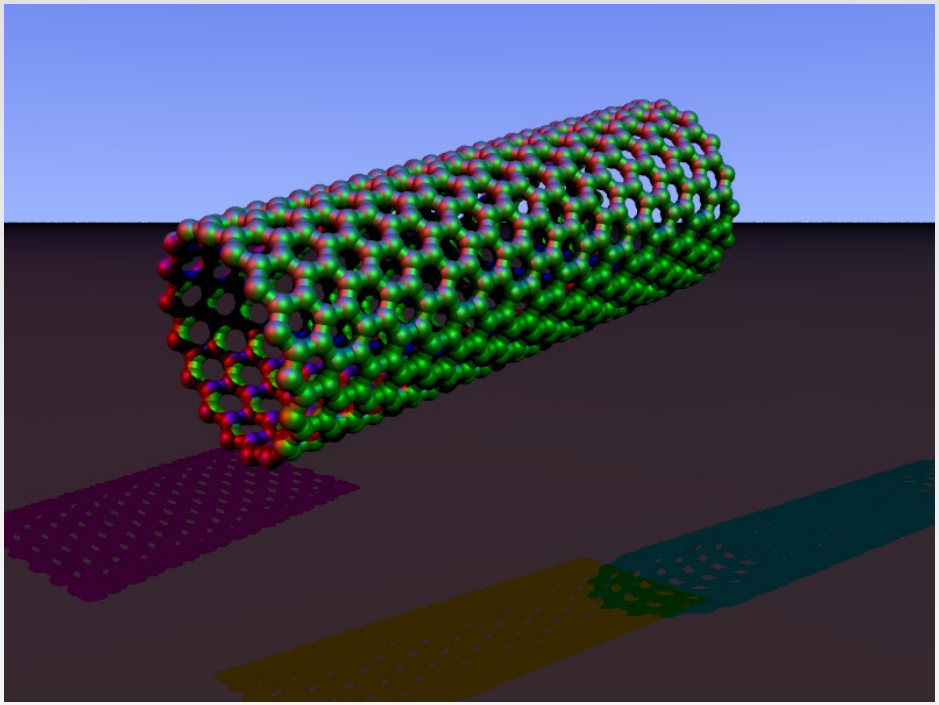
Carbon nanotubes

- wrapping the graphene sheet to seamless cylinder
- different ways to wrap a graphene leading to nanotubes with different properties – metallic/semiconductor
- the (n,m) naming adopted – the integer prefactors for the unit vectors a_1 and a_2
- T – the tube axis
- C_h – the “roll up” vector
- n=m – the armchair – metallic behaviour



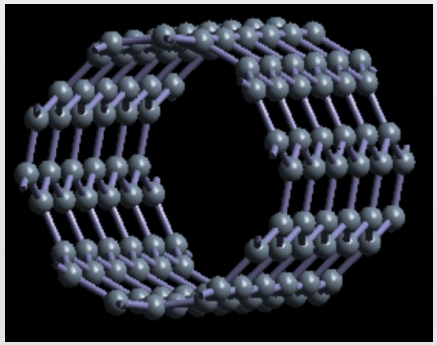
Carbon nanotubes

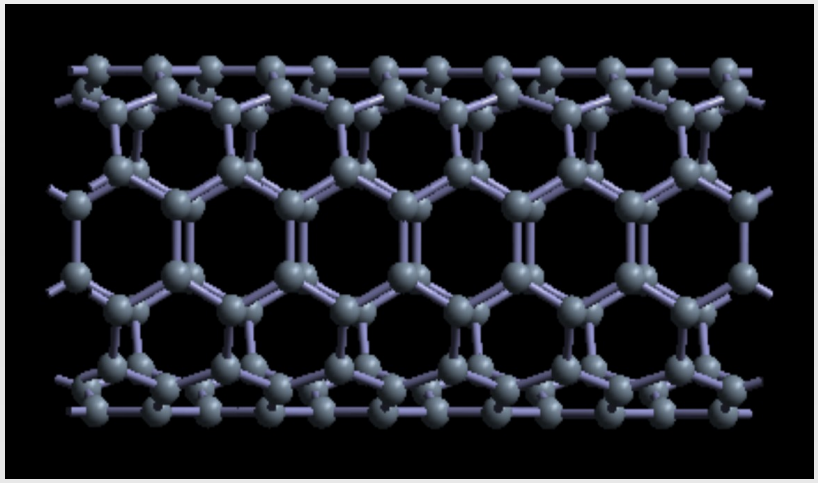
- the (n,m) naming adopted – the integer prefactors for the unit vectors a_1 and a_2
- T – the tube axis
- C_h – the “roll up” vector
- m=0 – the zigzag(otherwise – the chiral)
- if n-m = 3*Z, Z is integer => tiny-gap semiconductor
- otherwise large-gap semiconductor
- the gaps decreases with the tube diameter

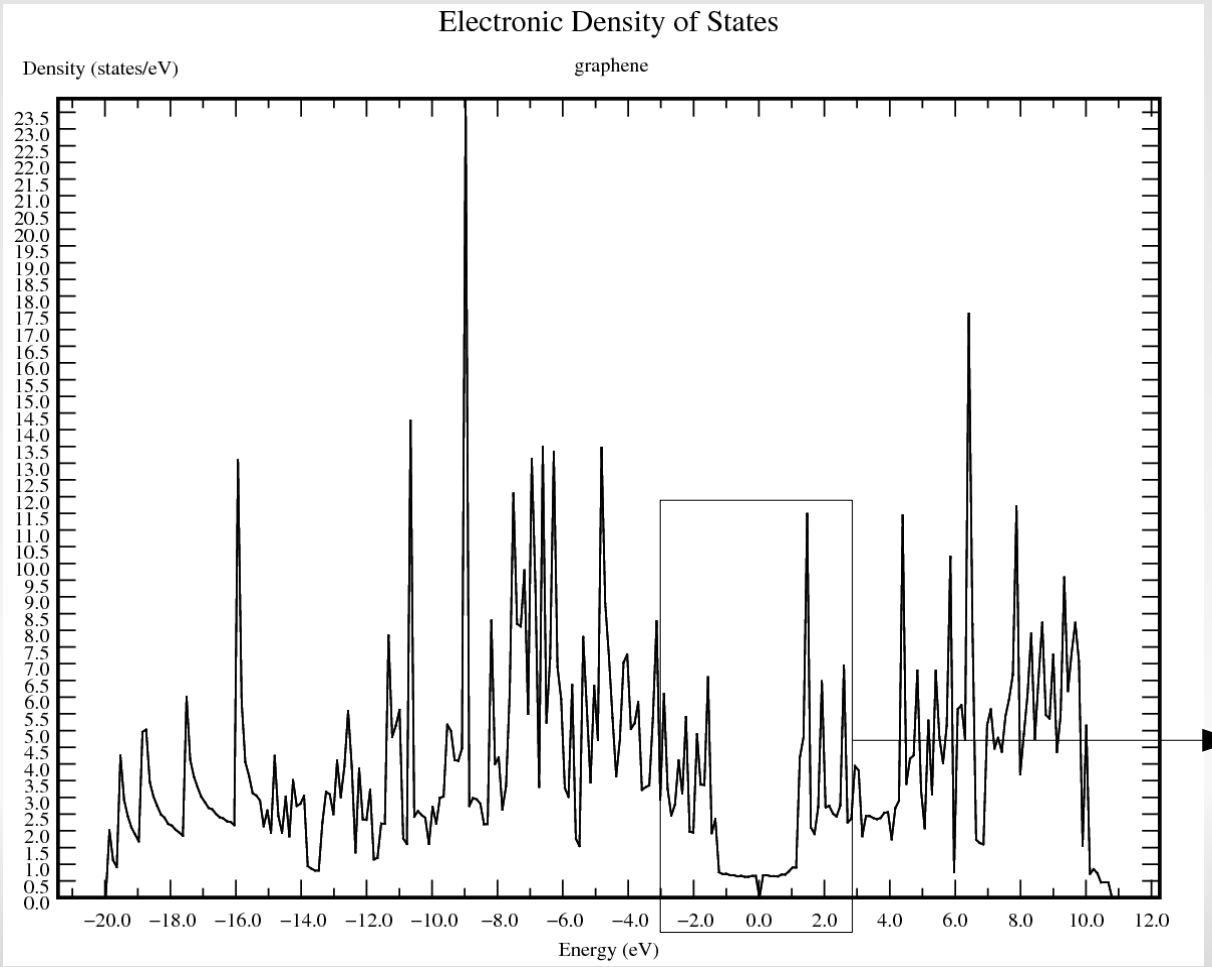


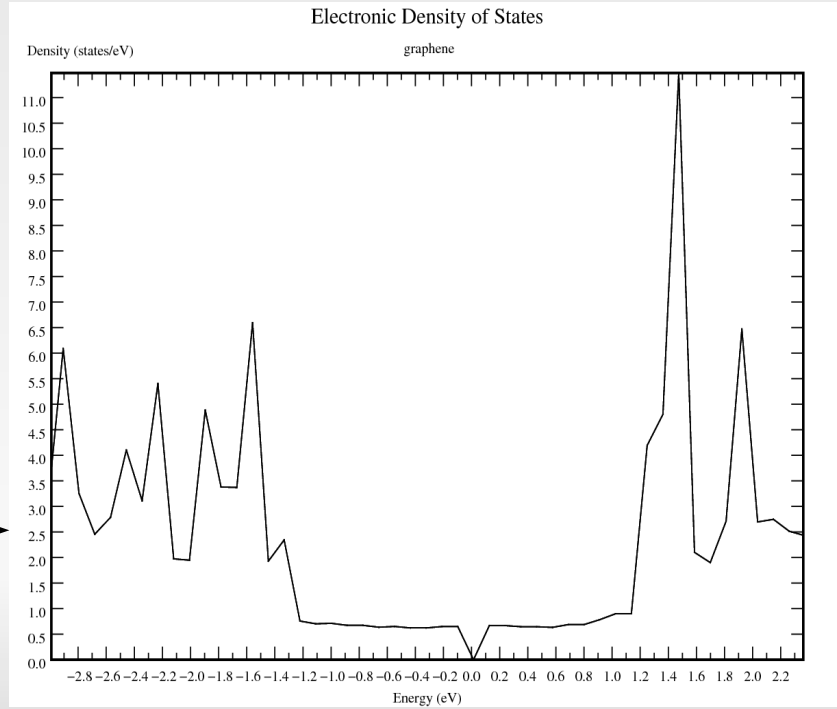
Examples – (5,5) SWNT

- VASP calculation
- DOS - metallic



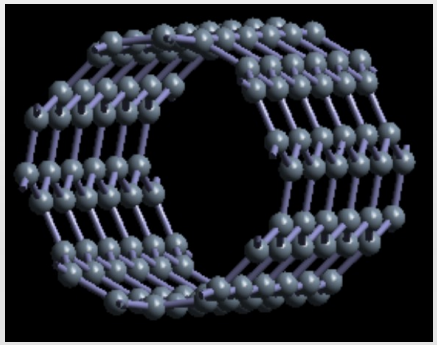


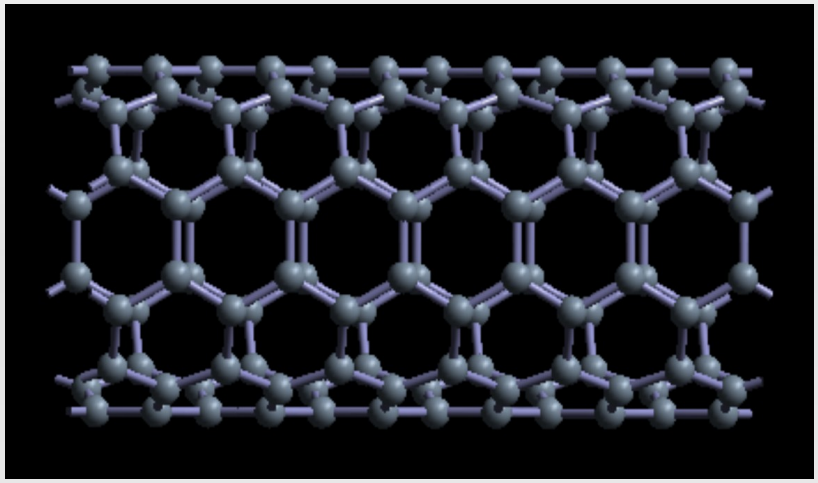


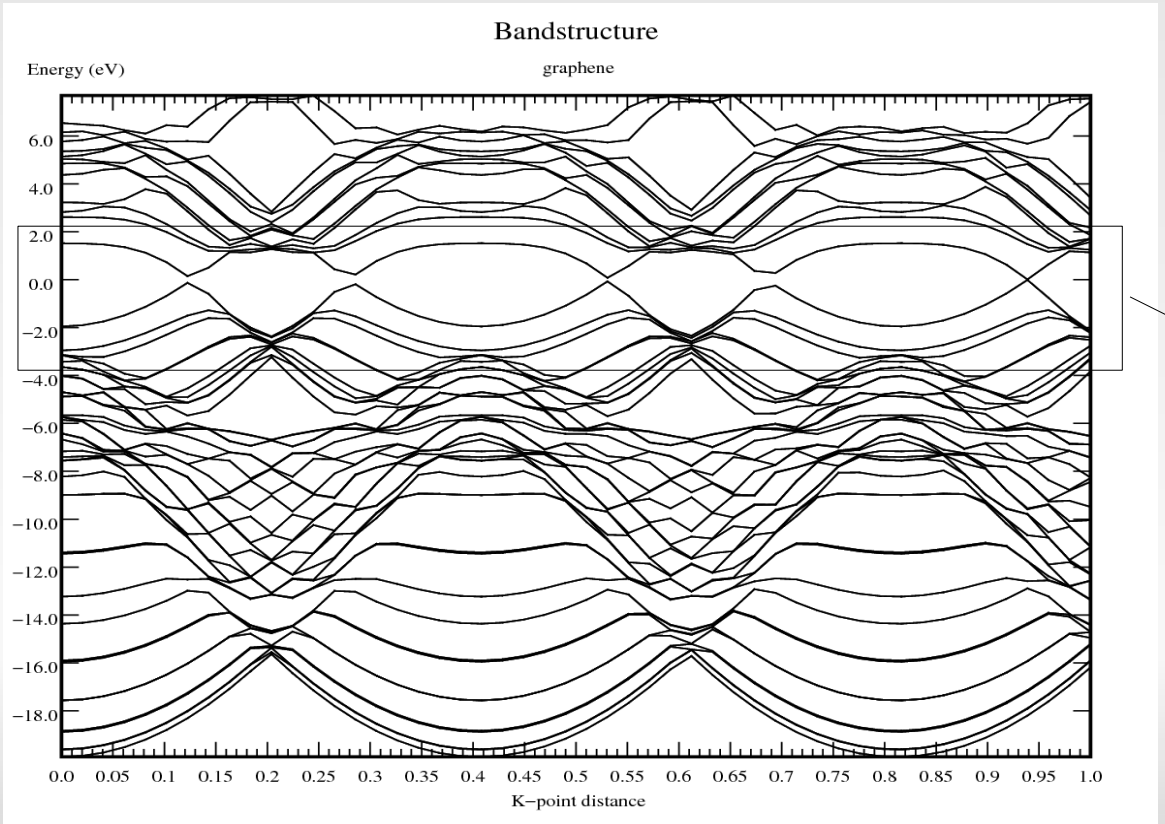


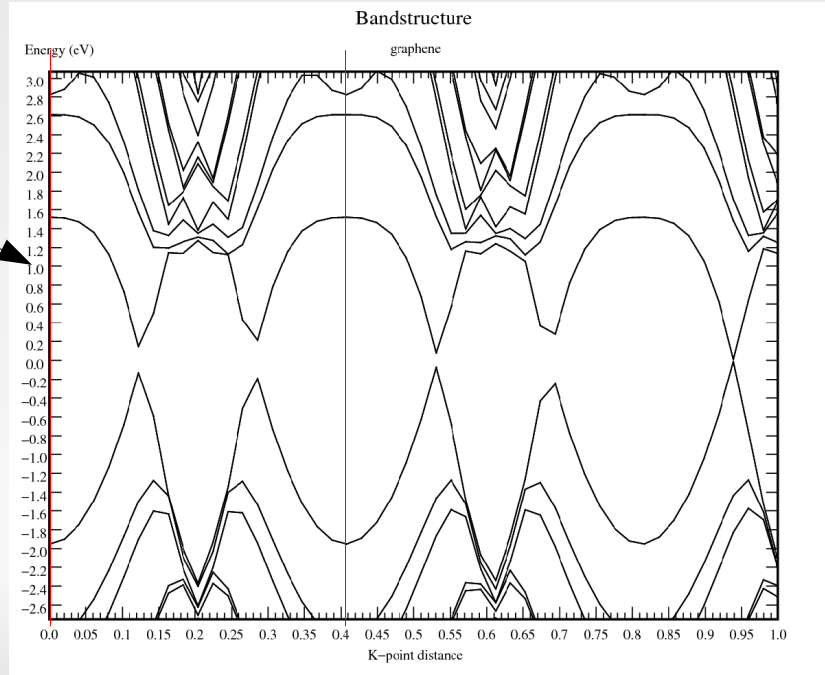
Examples – (5,5) SWNT

- VASP calculation
- Band-stucture
  - scan along the z-direction - k_z





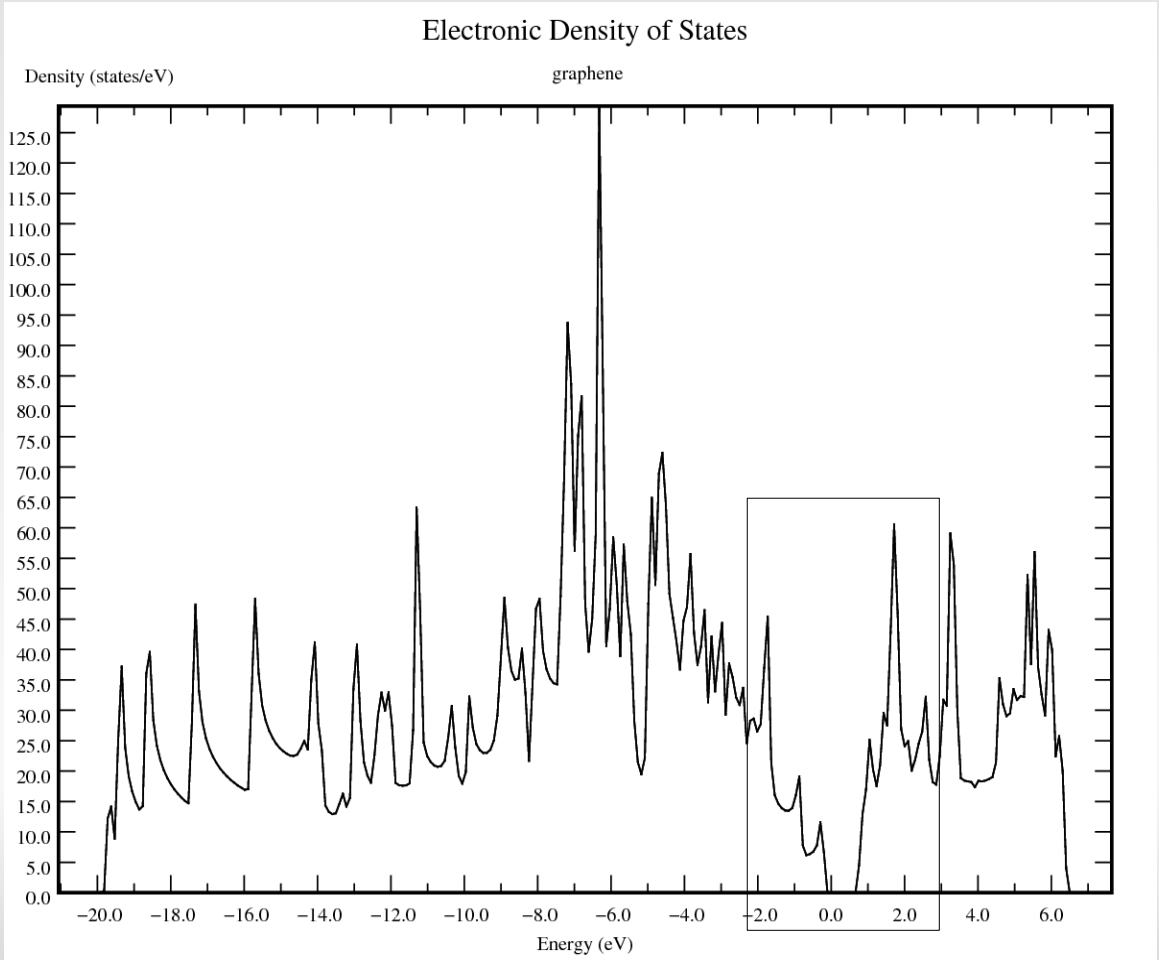


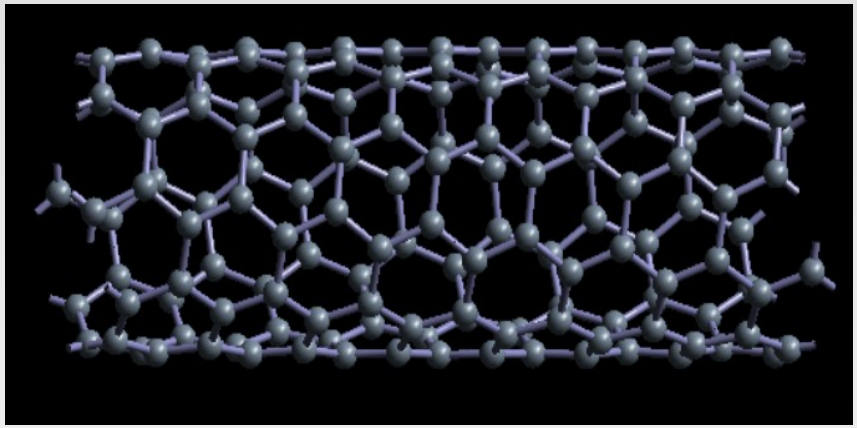


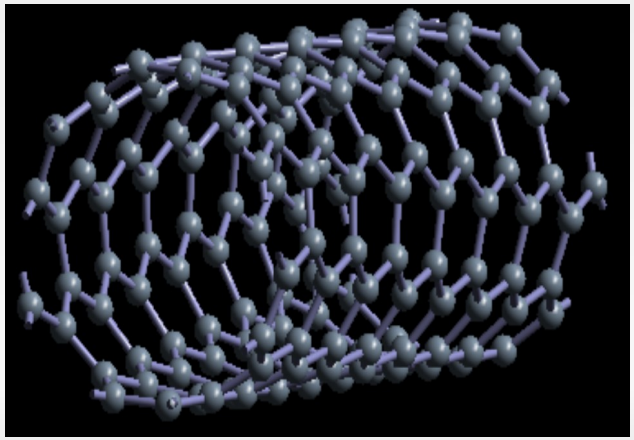
1. BZ

Examples – (6,4) SWNT

- VASP calculation
- DOS - semi-conductor







Examples – (6,4) SWNT

- VASP calculation
- Band-stucture – band-gap present