

## EXAM assignment

**Lecture:** Atomistic Computer Modeling of Materials (ÚFV/APMM/19)

**Student:** Matej Kecer

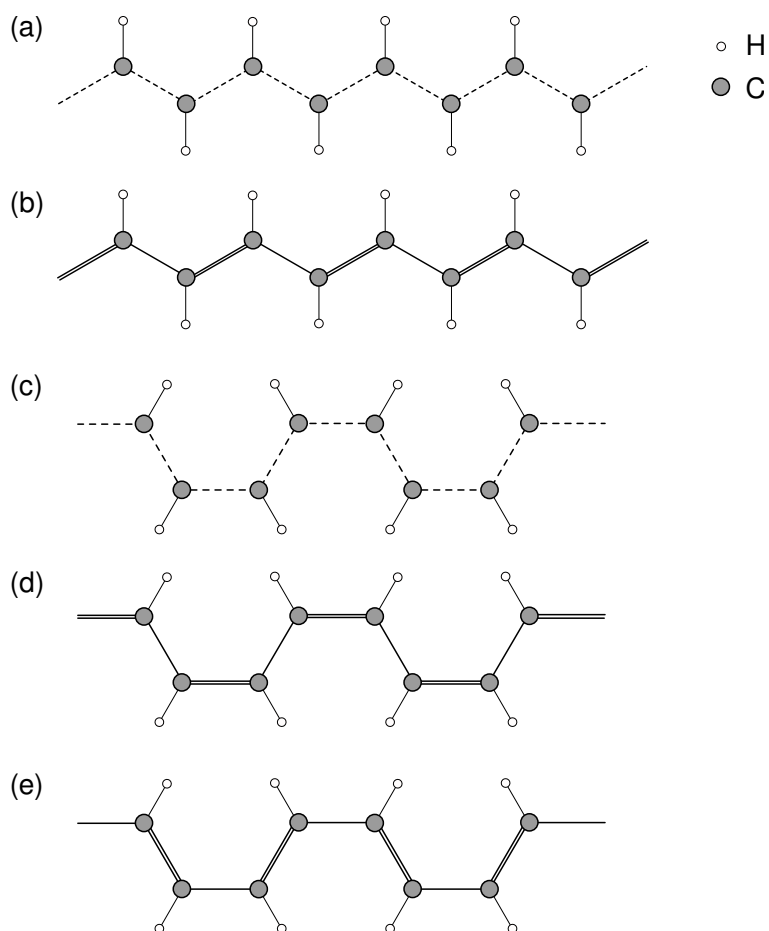
**Date:** April 16, 2021

**Submission Deadline:** April 30, 2021 via email: *martin.gmitra@upjs.sk*

### Assignment:

Calculate using density functional theory as implemented in Quantum Espresso code suite ground state properties of polyacetylene. Polyacetylene is a quasi one-dimensional organic polymer with repeated chemical unit  $(C_2H_2)_n$  in trans- or cis- isomer geometry of double bonds.

1. Find which of the five structures shown in the figure below is most stable.



For calculations assume for the single carbon-carbon bonds length  $1.54 \text{ \AA}$  (solid lines) and for the double bonds (double solid lines) length  $1.34 \text{ \AA}$ . For carbon-hydrogen bond length assume  $1.09 \text{ \AA}$ . For the cases with identical carbon-carbon bond (dashed lines) length assume  $1.40 \text{ \AA}$ . For exchange-correlation functional use PBESOL and for energy cutoffs use the largest values as can be found in headers of the pseudopotentials files:

[https://www.quantum-espresso.org/upf\\_files/C.pbesol-n-kjpaw\\_psl.1.0.0.UPF](https://www.quantum-espresso.org/upf_files/C.pbesol-n-kjpaw_psl.1.0.0.UPF)

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Optimize number of k-points on accuracy of the ground state energy for one chosen structure and use it for the other structures. Converge the ground state energy value with precision below 10 meV.

2. Calculate electronic band structures for the five structures and discuss possible electric properties in case of undoped and possible hole doping of the systems.

Note: to keep the system quasi one-dimensional, consider a vacuum in two remaining directions at least of about 6 Å to separate periodic images of the molecule. The unit cell can be specified as free structure (ibrav = 0).

**Evaluation:**

- 25% construction of the input files for self-consistent field calculations
- 45% self-consistent field calculations
- 20% calculation of the electronic band structures
- 10% discussion of the electric properties
- +20% bonus, online oral exam covering theory topics given on lectures, please submit the requested files 2 days before oral exam.

**Submit:**

- input files, output files of self-consistent field calculations
- a short text report (pdf/odt/doc) with results figures/tables demonstrating obtained results

**Exam evaluation scale:**

A: 100% - 90% B: 89% - 75% C: 74% - 60% D: 59% - 40% E: 39% - 20% FX: 19% - 0

# Report

Matej Kecer

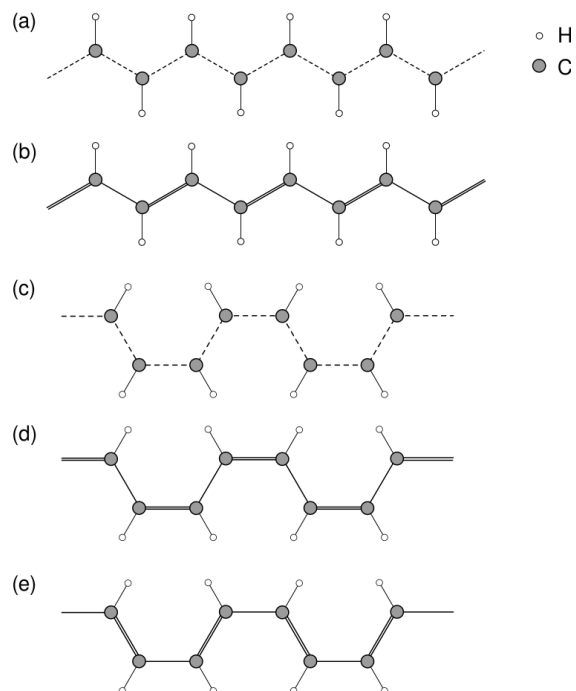
April 25, 2021

## 1 Part I.

### 1.1 Assignment

The first problem was the following: Calculate using density functional theory as implemented in Quantum Espresso code suite ground state properties of polyacetylene. Polyacetylene is a quasi one-dimensional organic polymer with repeated chemical unit  $(C_2H_2)_n$  in trans- or cis- isomer geometry of double bonds.

Find which of the five structures shown in the figure below is most stable.



For calculations assume for the single carbon-carbon bonds length 1.54 Å (solid lines) and for the double bonds (double solid lines) length 1.34 Å. For carbon-hydrogen bond length assume 1.09 Å. For the cases with identical carbon-carbon bond (dashed lines) length assume 1.40 Å. For exchange-correlation functional use PBESOL and for energy cutoffs use the largest values as can be found in headers of the pseudopotentials files:

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Optimize number of k-points on accuracy of the ground state energy for one chosen structure and use it for the other structures. Converge the ground state energy value with precision below 10 meV.

## 1.2 Solution

The first task to perform is to build given structures. For that, we use the ase package in python. As an example, we show the code for structure a) here:

```
#!/usr/bin/python3

import numpy as np
import ase.io as io
from ase import Atoms, Atom
from ase.build import bulk
from ase.visualize import view

cc = 1.4 #length of C-C bond
ch = 1.09 #length of C-H bond
z = 6 #size of PUC perpendicular to direction of chain
cx = cc*(np.cos(np.pi/6)) #displacement of second C atom inside PUC in x-direction
cy = cc*(np.sin(np.pi/6)) #displacement of second C atom inside PUC in y-direction
a = 2*cx #size of PUC along the chain

atoms = Atoms([Atom('C', (0.0, (z/2), 0.0)),
               Atom('C', (cx, (z/2)-cy, 0.0)),
               Atom('H', (0.0, (z/2)+ch, 0.0)),
               Atom('H', (cx, (z/2)-cy-ch, 0.0))])

cell = [(a, 0, 0),
        (0, z, 0),
        (0, 0, z)]

atoms.set_cell(cell)

view(atoms)
```

Few comments are in order. As only the bond lengths and not the angles between different bonds were provided, we were lacking a necessary parameter - the angle. We thus assumed all the angles be equivalent  $120^\circ$  in all the structures a) - e). In reality, the angles might differ because the bonds themselves are not necessarily equivalent. Under equal angle assumption, it was possible to define unit cells for all structures (except b)) as rectangular ones in 3D space, where we picked lattice parameter in a direction perpendicular to the linear chain to be 6 Å. Structure b) is a little special, as the lattice vector in the direction of the chain had to become "tilted" as a result of different bond lengths, yet equal angles. (see definition of a cell in previous code and in the following code for structure b))

```
#!/usr/bin/python3

import numpy as np
import ase.io as io
from ase import Atoms, Atom
from ase.build import bulk
from ase.visualize import view

cc = 1.54 #length of C-C bond
cc2 = 1.34 #length of C=C bond
ch = 1.09 #length of C-H bond
z = 6 #size of PUC perpendicular to direction of chain
cx1 = cc*(np.cos(np.pi/6)) #displacement of second C atom inside PUC in x-direction
cy1 = cc*(np.sin(np.pi/6)) #displacement of second C atom inside PUC in y-direction

#position of 3rd C atom w.r.t. 2nd, 3rd C atom is first in the next unit cell
cx2 = cc2*(np.cos(np.pi/6))
cy2 = cc2*(np.sin(np.pi/6))
a = cx1+cx2 #size of PUC along the chain

#position of 3rd C atom w.r.t. 1st,
c3x = a
c3y = -cy1+cy2

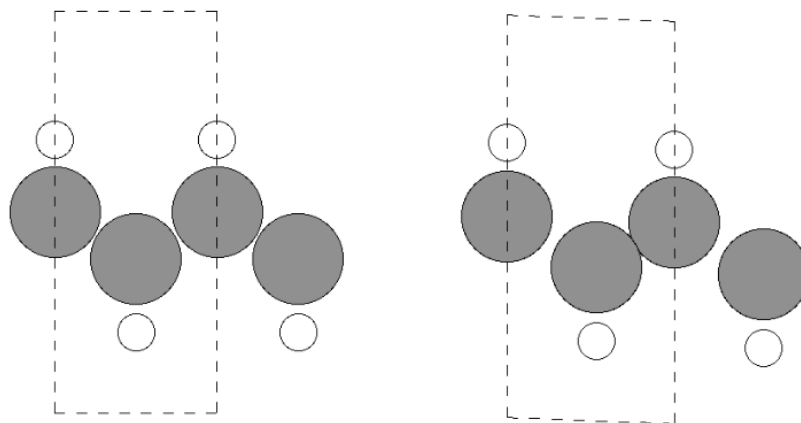
atoms = Atoms([Atom('C', (0.0, (z/2), 0.0)),
               Atom('C', (cx1, (z/2)-cy1, 0.0)),
               Atom('H', (0.0, (z/2)+ch, 0.0)),
               Atom('H', (cx1, (z/2)-cy1-ch, 0.0))])

cell = [(a, c3y, 0),
        (0, z, 0),
        (0, 0, z)]

atoms.set_cell(cell)
```

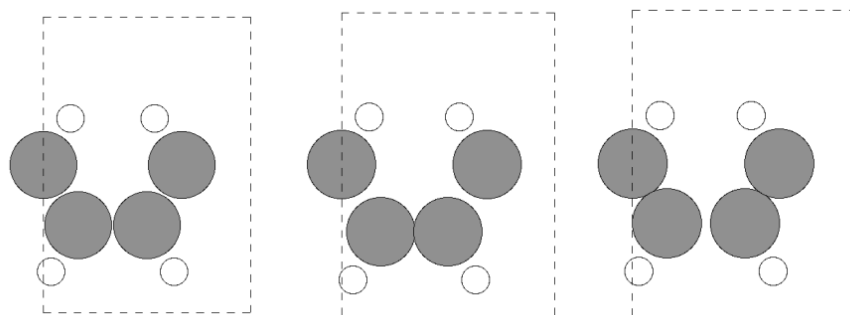
```
view(atoms)
```

One obtains following structures (unit cell repeated twice along the direction of the chain for visualisation purposes):



Structure a) on the left, and structure b) on the right.

Unit cells for these structures enclose 2 H atoms and 2 C atoms. When it comes to cis- structure, however, the unit cell has to be taken larger, such as to encompass 4 H and 4 C atoms. (All the files for generating the structures, also scripts, input and output files for scf calculations are enclosed in the email.)



Structures c), d), e) respectively.

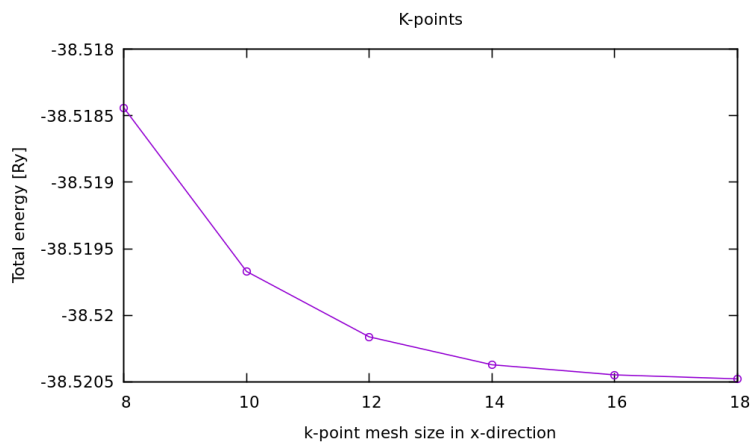
To find the most stable structure, we propose conducting self-consistent field calculation and identifying a structure with minimal total energy. In the input files, we have chosen cutoffs to be maximal values as given in pseudopotentials, that is

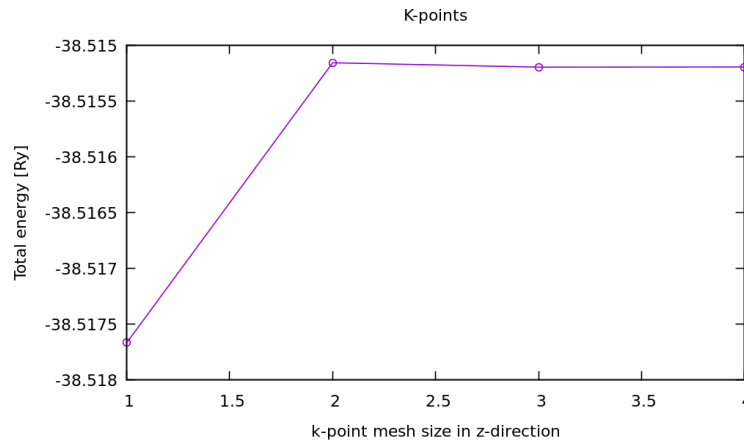
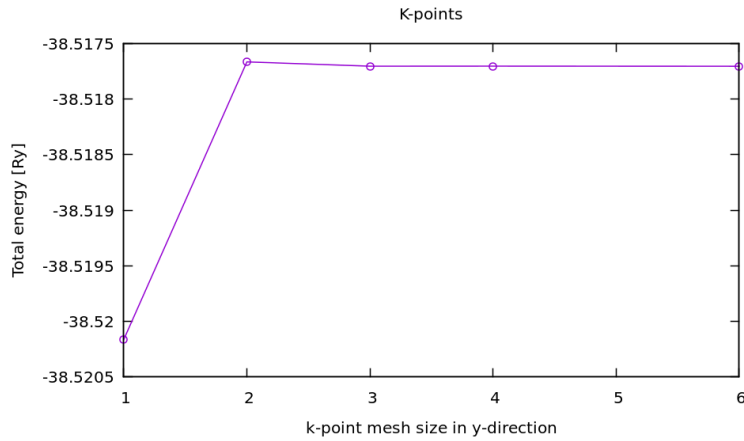
- $ecutwfc = 46 \text{ Ry}$ ,
- $ecutrho = 325 \text{ Ry}$ .

First off, we need to do series of calculations for optimizing k-point mesh size. As shown in lectures for the case of graphene, the k-points value in the z-direction was chosen to be 1. This was the case since graphene is a two-dimensional structure, and the z-axis was chosen as the one perpendicular to the graphene plane. Since we have chosen x-direction to be a direction along the polyacetylene chain, we can readily make such arguments here also. We, therefore, expect total energy to converge rather quickly in y and z directions. We further employ the following search pattern for finding optimal k-point values:

1. Optimize number of k-points in x-direction. We use values (8\_1\_1), (10\_1\_1), (12\_1\_1), (14\_1\_1), (16\_1\_1), (18\_1\_1)
2. Using the acceptable value in x-direction, optimize k-points in y-direction. We use values (12\_1\_1), (12\_2\_1), (12\_3\_1), (12\_4\_1), (12\_6\_1)
3. Using the acceptable values for x and y directions, optimize k-point values in the z-direction, i.e. (12\_2\_1), (12\_2\_2), (12\_2\_3), (12\_2\_4)

We kept offset values to be 0\_0\_0 during the entire process. For the calculation, we have chosen structure a). The optimized values were chosen such that the difference in total energy in two successive steps was  $< 10\text{meV} \approx 0.0007 \text{ Ry}$ . The values for mesh size have been considered for this accuracy independently in all directions, therefore to "sum up" all the errors, we test perform one more calculation for k-points (14\_3\_3) and compare it with the optimized values (12\_2\_2). We find given accuracy ( $< 10\text{meV}$ ) is satisfied.





However, in upcoming calculations, we are to compare energies of structures with different number of atoms inside the unit cell. To make such direct comparison possible, we propose doubling the size of a unit cell in structures a), b) so that these too encompassed 8 atoms in general.

We have performed a test calculation on a doubled unit cell with structure a) for two different k-points values. These were again (12\_2\_2) and (14\_3\_3). We found k-points values (12\_2\_2) can still be used, even in the doubled cell. We further perform the scf calculations on all the remaining structures. The resulting total energies are written in the table below.



Structure	Total energy
Structure a)	-77.03097152 Ry
Structure b)	-76.99841083 Ry
Structure c)	-76.99979863 Ry
Structure d)	-76.97772972 Ry
Structure e)	-76.97132712 Ry

From the table it follows, that structure a) has the lowest total energy. However, as we researched on the internet, in reality, polyacetylene creates quasi-linear chain of alternating single and double C bonds. These must have different lengths, thus structures a) and c) are not physical. Therefore, the physical structure with lowest energy is structure b) - trans- geometry of alternating single and double bonds, that is

