structural optimization of materials using quantum ESPRESSO

by

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Abstract

I will briefly introduce the Quantum ESPRESSO (QE) code distribution. Then I will focus on the practical steps needed to perform an structural optimization of materials calcultion. I used element Niobium crystal in this project.these includes:
(1) Installed quantum Espresso and obtain pwscf code and doing scf calculation
(2) going from crystal structure to input file (done by setting in input file)
(3) written a shall script to find minimum energy by changing celldimension of unit cell
(4) finally, plot the graph celldimension vs energy and found minimum energy of crystal with their cell dimension

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➔ Introduction

➢ Quantum ESPRESSO

Quantum ESPRESSO is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.

The main goals of quantum ESPRESSO are

• innovation in methods and algorithms

• efficiency on modern computer architectures

We use the QUANTUM ESPRESSO which a computer package to study the electronic structure and optimization using the molecular dynamics simulation.This package contains two codes in addition with some auxiliary codes for the study of calculation of electronic structure properties within density functional theory,using the plane wave basis set and peudopotentials.

The two codes are

• PWscf(plane wave self-consistent field)

• CP(Car-Parinello)

and the auxiliary codes are

• PWgui (graphical user interface for PWscf): a graphical interface for producing input data files for Pwscf.

• atomic : a program for atomic calculations and generation of pseudopotentials.

• iotk : an input-output toolkit

The codes used in the package are capable of performing different kinds of calculations.The PWscf code can currently perform the following kinds of calculations :

• ground state energy and one electron (Kohn Sham)orbitals.

• atomic forces, stresses and structural optimization.

• IR and Raman (non-resonant) cross-section.

• effective charges and dielectric tensors etc...

CP can currently perform the following kinds of calculations :

• CP molecular dynamics simulation.

• geometry optimization by damped dynamics etc..

CP works with both norm-conserving and ultrasoft pseudopotentilas.

➢ INPUT file in PWscf

The input data for the various calculations listed above are organized as several namelists followed by the other fields introduced by keywords.The various namelists are:

• &control : the general variables controlling the run are specified here

• &system : structural information on the system under investigation is being specified in this namelist

• &electrons : electronic variable self-consistency,smearing.

• &ions (optional) : ionic variables,relaxation,dynamics

• &phonon(optional) : information required to produce data for phonon calculations.

• &cell(optional) : variable cell dynamics.

the following variables in &system must be always be specified.

ibrav : takes an integer value,it is the Bravais lattice index or the structure index.
celldm : it represents the crystallographic constants.

nat(integer) : indicates the number of atoms in the unit cell.

ntyp(integer) : number of types of atoms in the unit cell.

- **Solid-state physics**

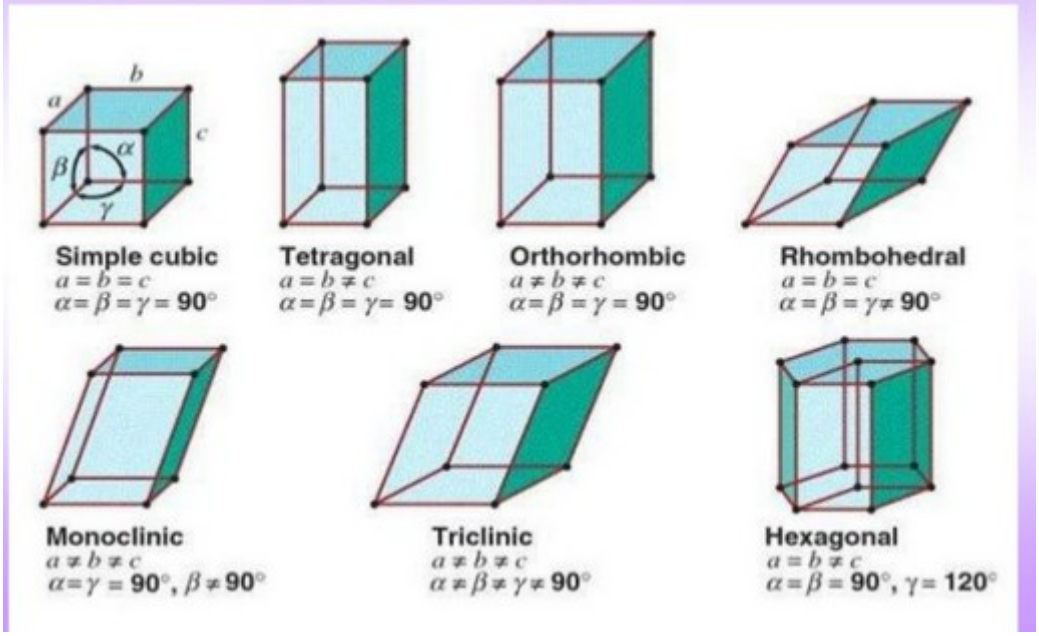
  Solid-state physics is the study of rigid matter, or solids, through methods such as quantum mechanics, crystallography, electromagnetism, and metallurgy. It is the largest branch of condensed matter physics. Solid-state physics studies how the large-scale properties of solid materials result from their atomic-scale properties. Thus, solid-state physics forms a theoretical basis of materials science. It also has direct applications, for example in the technology of transistors and semiconductors.

- **crystal structure**

  A crystal structure is composed of a unit cell, a set of atoms arranged in a particular way; which is periodically repeated in three dimensions on a lattice.

  The “ibrav” parameter helps in selecting this. There are 14 possible choices

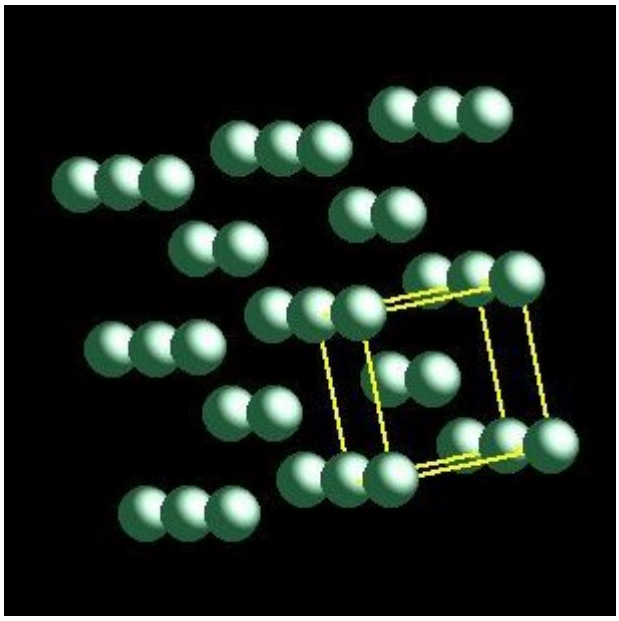
  There 14 types of Bravais Lattice.



Niobium: crystal structures

```
 &system
    ibrav= 6,celldm(1) = 6.28,
,nat= 2, ntyp= 1
/
ATOMIC_SPECIES
 Nb  92.90    nb_pbe_v1.uspp.F.UPF

ATOMIC_POSITIONS {crystal}
Nb  0.00 0.00  0.00
Nb  0.50  0.50 0.50
```

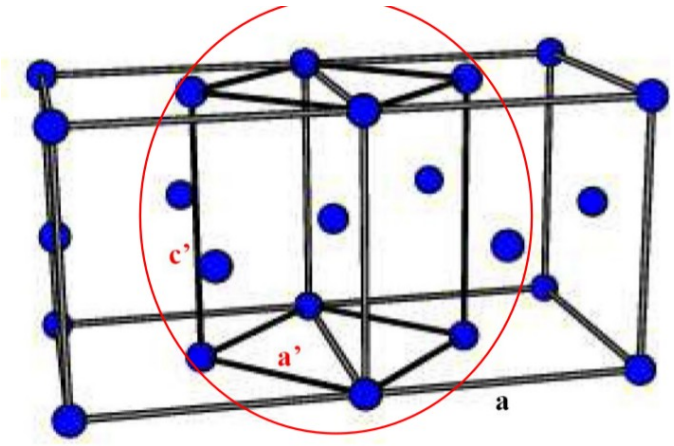


Nb: Tetragonal : ibrav = 6, the lattice parameter is 6.28 A.

If using

ibrav= 6, celldm(1) =6.28, celldm(3) =1.0

```
ATOMIC_POSITIONS {crystal}
Nb 0.00 0.00 0.00
Nb 0.50 0.50 0.50
```



simple tetragonal (p)

==========

v1 = a(1,0,0),

v2 = a(0,1,0),

v3 = a(0,0,c/a)

➔ **Procedure**

The Espresso 5.3.0 was downloaded from Quantum Espresso Website Download page and installed in linux system and used for this project.

Element used is Niobium(Nb) for this project.
We used Pwscf code from quantum espresso to do this project.
PWSCF (Plane Wave Self Consistent Field)

- We used this to perform total energy calculations.
- It uses both norm-conserving pseudopotentials(PP) and Ultrasoft pseudopotentials (US-PP) within the Density Functional Theory(DFT).

One can perform Plane Wave self consistent field calculations for DFT. The executable is called “pw.x”

Sample input for the pw.x code :

Input File In Pwscf

Element - Niobium(Nb)
File Name- relax.in
#####################

NBT,

Self Consistant calcualtion

occupations = 'smearing'

smearing = 'gaussian'

degauss = 0.01

####################

&control

calculation = 'scf'

restart_mode='from_scratch',

prefix='Nb',

pseudo_dir = '/home/akhilesh/Desktop/work/Si'

verbosity = 'default'

wf_collect = .FALSE.

etot_conv_thr = 1.0D-5

forc_conv_thr = 1.0D-4

```
   disk_io = 'default'
 /
 &system
   ibrav= 6,
   celldm(1) = 6.28,
   celldm(3) = 1.10
   nat= 2, ntyp= 1,
   ecutwfc =20, ecutrho=160
   occupations = 'smearing'
   smearing = 'gaussian'
   degauss = 0.01

 nspin =1

 /
 &electrons
   diagonalization='david'
   mixing_mode = 'plain'
   mixing_beta = 0.7
   conv_thr =  1.0d-7
 /
&IONS
/
&CELL
/
ATOMIC_SPECIES
```

```
 Nb  92.90    nb_pbe_v1.uspp.F.UPF

ATOMIC_POSITIONS {crystal}
Nb  0.00 0.00  0.00
Nb 0.50  0.50       0.50

K_POINTS {automatic}
  4 4 4 0 0 0

EOF
##running PWscf calcualtion
```

Meaning of variables used in input file realx.in

&control .../, &system .../, &electrons .../ are fortran-90 namelists

calculation='scf',

perform a self-consistent calculation, calculate forces and stress,Energy.

ibrav= 6, celldm(1)=6.28, celldm(3)=1.10

specify lattice: simple tetragonal with a = 6.28 a.u., c/a = 1.00

nat=2, ntyp=1 there are 2 atoms of 1 type in the unit cell

ecutwfc = 20, ecutrho=160

kinetic energy cutoffs in Ry for plane waves (one for wavefunctions, one for charge density with Ultrasoft pseudopotentials)

conv thr=1.0d-7

convergence threshold for self-consistency

ATOMIC POSITIONS (crystal)

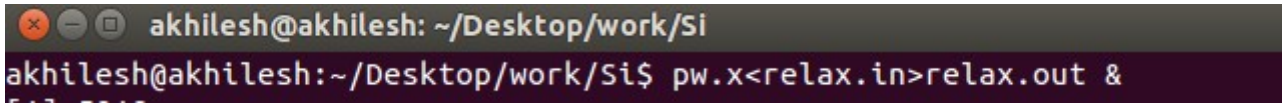
Nb 0.00 0.00 0.00

Nb 0.50 0.50 0.50

atomic positions (in terms of crystal lattice vectors)

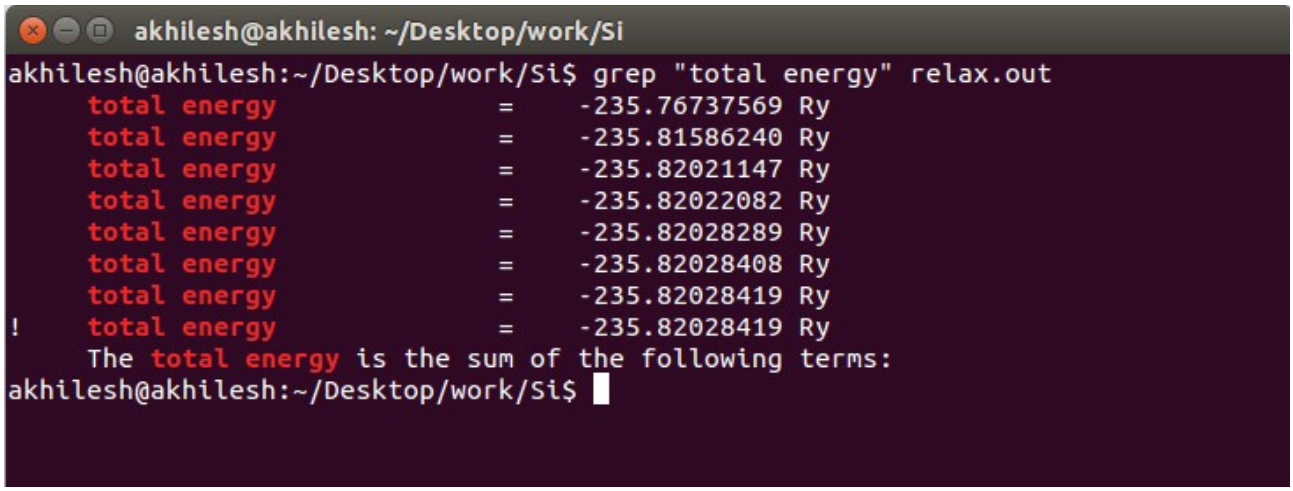
➔ Data/Observations

The syntax to run this files
pw.x <input_file >output_file
operator & can be used to make the code run in background
using This inputfile(relax.in) Pwscf is executed by the following command on the terminal .



Output file named relax.out is generated in the same directory.

Now by using grep command we can get final Energy from the Outputfile .



Problem:

When the crystal has strain in a plain(i.e when two cell dimensions are fixed) then it would change the third dimension to have the minimum possible energy. So my task was to calulate the third dimension for which the system has minimum energy.
To achieve this a shell script is written in linux system.

Used programming language : Bash shell programming
used linux utility command like grep,awk,sed etc..

Shall Script code :

bash shell script is written in linux system to solve this problem.

relax.in × s.sh ×

```
#AKHILESH KUMAR
#EP14BTECH11002
#shall script code

c1=0.01
c2=-0.01

echo -e "Celldim(3) \t Energy"

pw.x<relax.in>relax.out &&                                          #pw.x command used for pwscf calculation

mv relax.out relax.out_1                                            #to move energy from relax.out  to relax.out_1 file
E1=$(echo "$(awk '/!/ {print $5}' relax.out_1)" |bc)                # variable E1 contains last final energy


Cell_dim=$(echo "$(awk '/celldm/{a=$3} END{print a}' relax.in)" |bc)        #Cell_dim contains value of cell dimension (3)

temp=$(echo "$Cell_dim + $c1" |bc)                                   #temp variable changes cell dim by 0.01

sed -i '/    celldm(3) =/c \    celldm(3) = '$temp'' relax.in               #sed command used for to chnage cell dim from relax.in file

pw.x<relax.in>relax.out &&

E2=$(echo "$(awk '/!/ {print $5}' relax.out)" |bc)                  #E2 variable contains new final energy with new cell dim value

if(($(bc <<<"$E2>$E1")))                                             # if E2 >E1
then
    c1=$c2                                                  # set c1 equals to c2 that decides where minimum Energy value we can find
fi


sed -i '/    celldm(3) =/c \    celldm(3) = '$Cell_dim'' relax.in

E1=$(echo "$(awk '/!/ {print $5}' relax.out_1)" |bc)

temp=$(echo "$Cell_dim + $c1" |bc)

sed -i '/    celldm(3) =/c \    celldm(3) = '$temp'' relax.in

pw.x<relax.in>relax.out &&

E2=$(echo "$(awk '/!/ {print $5}' relax.out)" |bc)

while(($( bc <<<"$E2 < $E1" )))             #while loop condition to get minimum energy
do

    Cell_dim=$(echo "$(awk '/celldm/{a=$3} END{print a}' relax.in)" |bc)
    temp=$(echo "$Cell_dim + $c1" |bc)
    sed -i '/    celldm(3) =/c \    celldm(3) = '$temp'' relax.in

    mv relax.out relax.out_1
    E1=$(echo "$(awk '/!/ {print $5}' relax.out_1)" |bc)

    echo -e "$Cell_dim \t\t $E1"
    pw.x<relax.in>relax.out &&

    E2=$(echo "$(awk '/!/ {print $5}' relax.out)" |bc)

done

echo "Final minimum energy with respective celldim"

echo -e "$Cell_dim \t\t $E1"                                                #printing final energy and cell dimension value


```

sh Tab Width: 4 Ln 34, Col 26 INS

this code can be run by using this command in same working directory by terminal

./s.sh // s.sh is shall script file name

final output of this shell script

stored all energy value with their celldimension value in a file and used gnuplot software to plot graph between celldimension vs energy

Final minimum energy = -235.84501101 Ry

final celldim (c/a) = 1.00

a = 6.28 A (this value set to in relax.in input file for pwscf calculation)

then c = 6.28 A

```
akhilesh@akhilesh:~/Desktop/work/Si$ ./s.sh
Celldim(3)       Energy
Note: The following floating-point exceptions are signalling: IEEE_UNDERFLOW_FLAG IEEE_DENORMAL
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
1.09             -235.82441708
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
1.08             -235.82817711
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
1.07             -235.83164765
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
1.06             -235.83486652
Note: The following floating-point exceptions are signalling: IEEE_UNDERFLOW_FLAG IEEE_DENORMAL
1.05             -235.83762827
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
1.04             -235.84013466
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
1.03             -235.84205278
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
1.02             -235.84357276
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
1.01             -235.84453016
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
1.00             -235.84501101
Note: The following floating-point exceptions are signalling: IEEE_DENORMAL
Final minimum energy with respective celldim
1.00             -235.84501101
akhilesh@akhilesh:~/Desktop/work/Si$
```

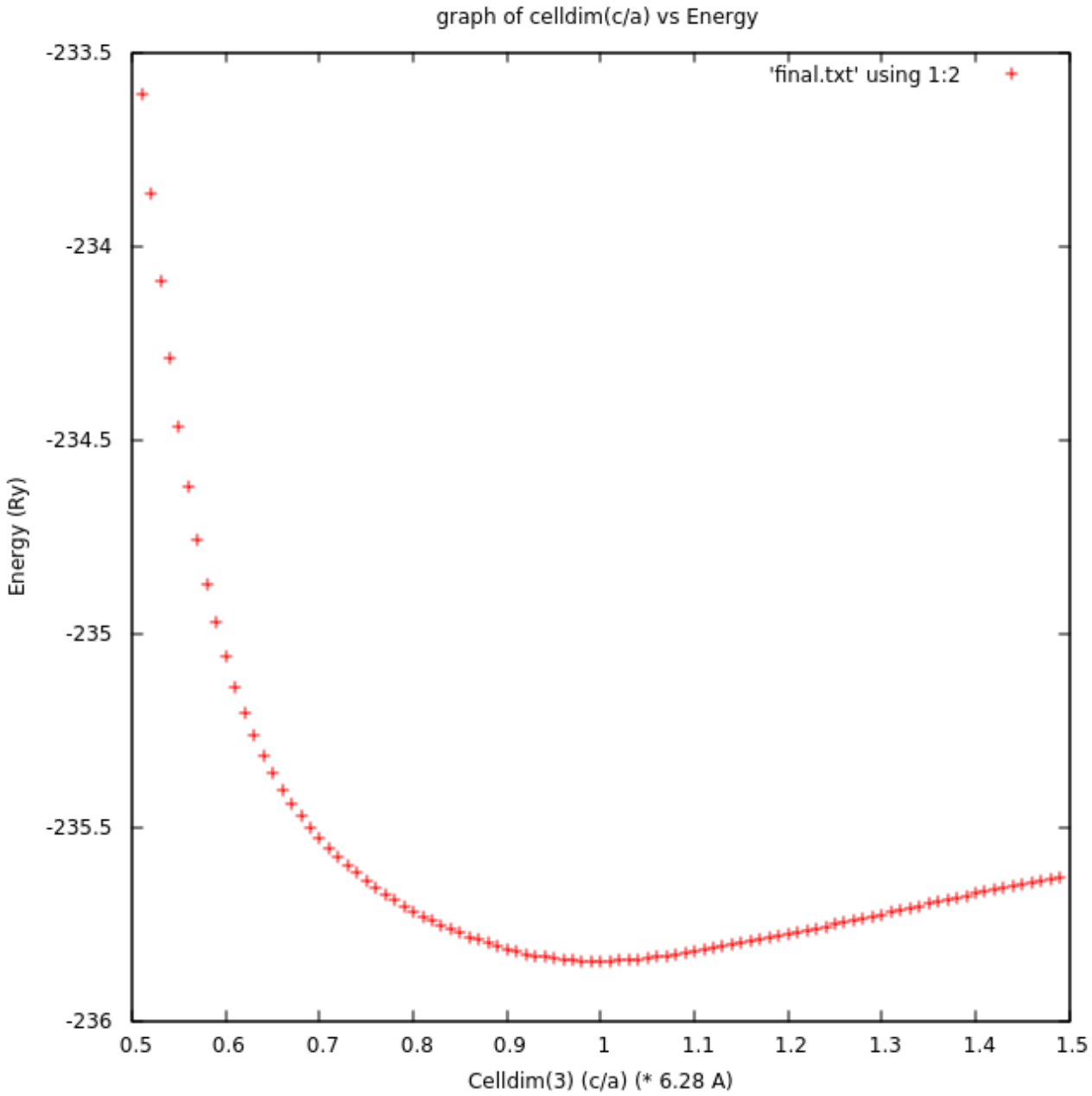
screenshot of output from shall script code

work is going on to optimise the code in efficent way for more complex system.

➔ Discussion & Results

- **graph of Celldimension vs Energy**

  plotted graph at different energy value at their celldimension value.



from the graph its clear that crystal energy had minimum at -235.84501101 Ry

and Celldimension (c/a) = 1.00 angstrom

now ,

c = 1.00 * 6.28 angstrom

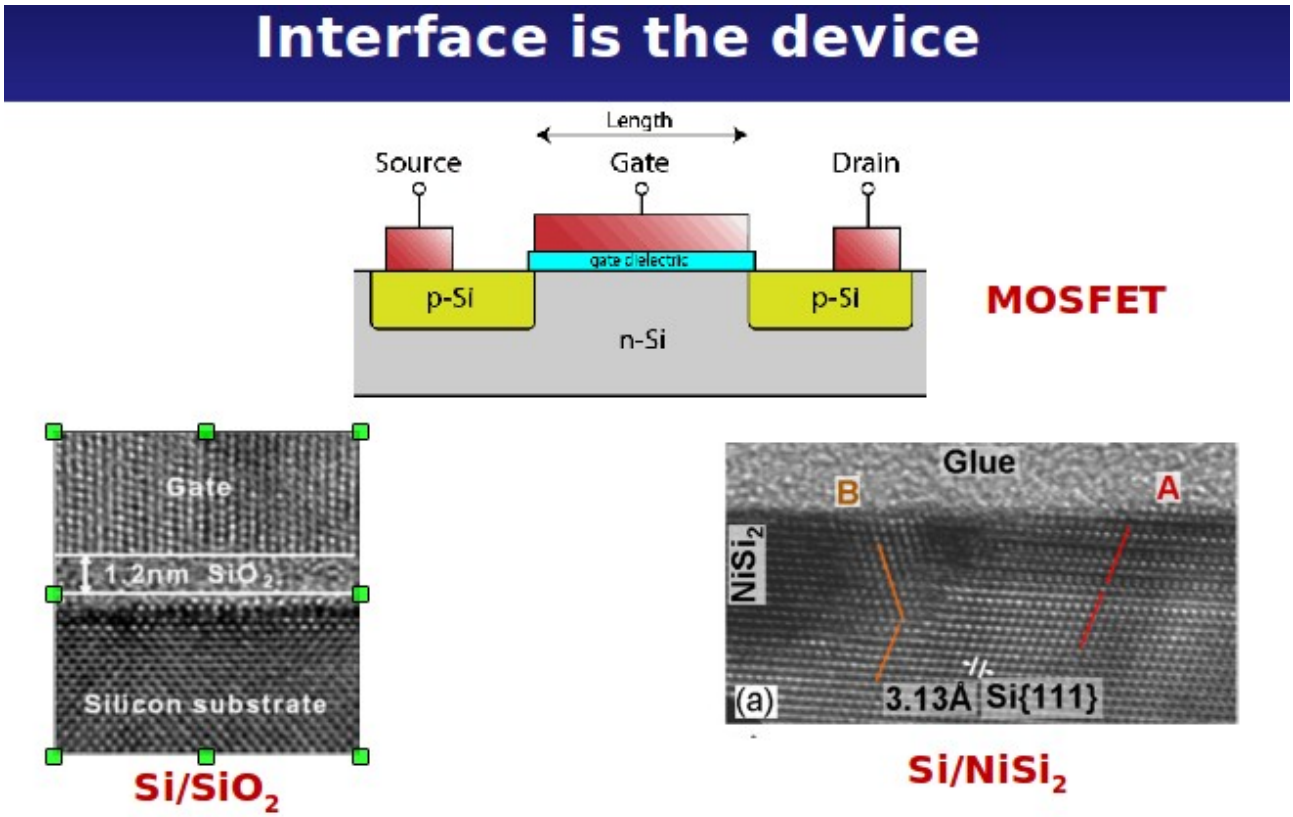
c = 6.28 angstrom

- i am done this project for element Niobium. Now working on silicon element and doing some other calculation related to pwscf calculation.

➔ Conclusion :

- for a large system this computational method is very helpful.

- In nanoscale devices, Interfaces are most important Components .When a material is deposited on another material a strain is developed on the surface and hence the material can relax only in another direction in order to attain a minimum energy and using the above procedure the extent of relaxtion can be calculated.



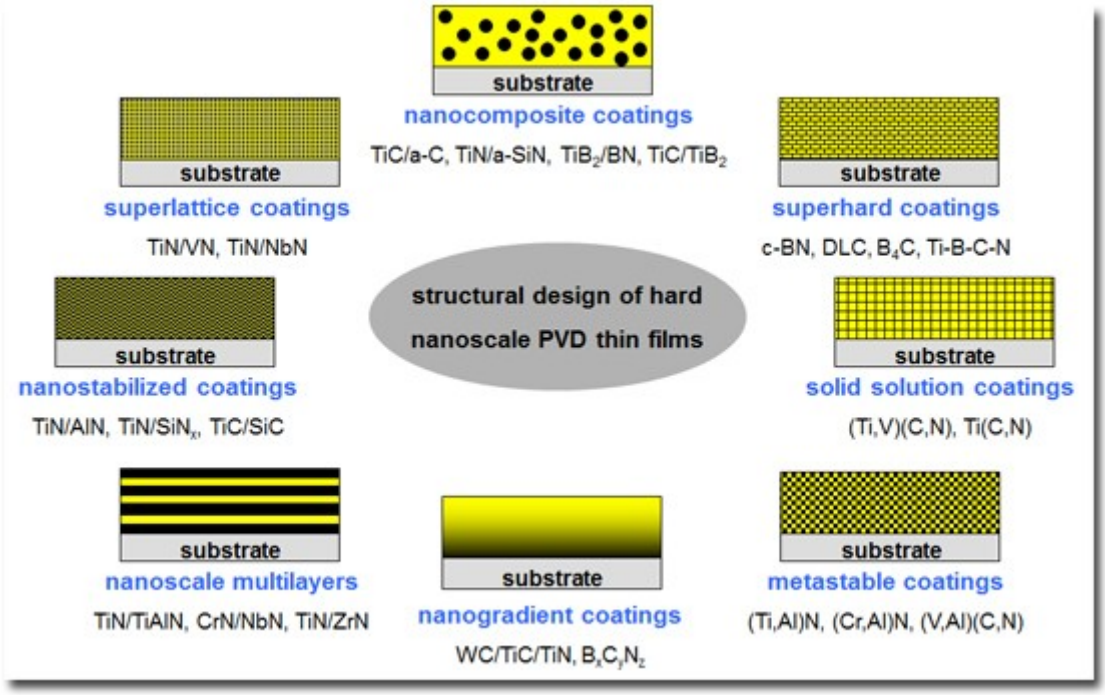
➔ Practical Application:

. This type of optimisation is useful in

- Thin film deposition

  Thin Film Deposition is the technology of applying a very thin film of material – between a few nanometers to about 100 micrometers, or the thickness of a few atoms – onto a “substrate” surface to be coated, or onto a previously deposited coating to form layers. Thin Film Deposition manufacturing processes are at the heart of today’s semiconductor industry, solar panels, CDs, disk drives, and optical devices industries.

- Nanoscale system



➔ References

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. https://en.wikipedia.org/wiki/Crystal_structure

.Solid State Electronic Devices by Ben Streetman