National Supercomputing Mission Workshop on

Computational Desing of Electrocatalyst

(CDE-2024)

Module 1: Structure Optimization and SCF calculation using Quantum Espresso (QE).

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Tutor: Dr Prasenjit Ghosh

(Email: prasenjit.jnc@gmail.com & sourav_ghosh.srmap.edu.in)

What we will learn in today's hands-on:

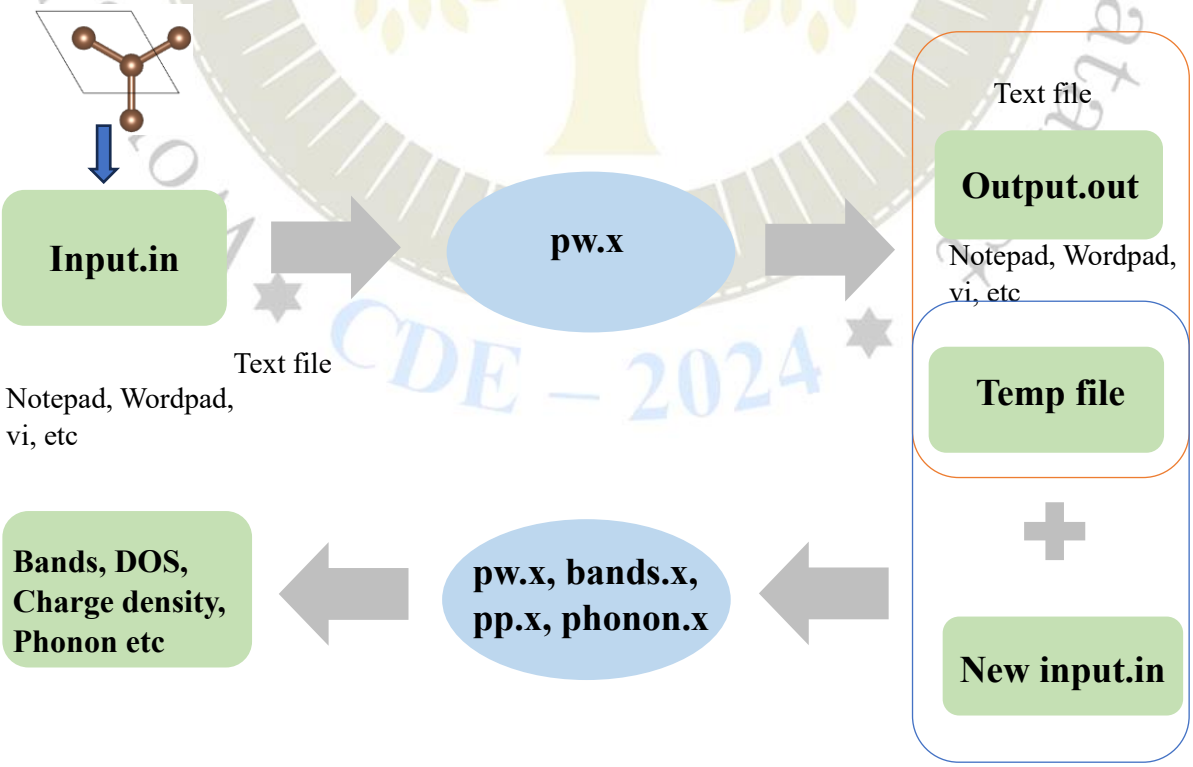
Hands-on #1: Total energy, Optimisation, Density of state (DOS) and Phonon frequency for Graphene

Exercise 1: Unit cell relaxation calculation for graphene.
Exercise 2: DOS calculation for graphene.
Exercise 3: Phonon frequency calculation for graphene.

Requirement to run any QE calculation:

i. QE software package.
ii. Relevant environment for QE calculation like HPCC (High Performance Computing Cluster)
iii. Model Structure (Geometric information like lattice vector, lattice type, atom positions and atom type)

Schematics steps for QE run:



Structure of QE input file:

Quantum expresso input file consist of **NAMELIST**, **FLAGS** and **CARDS**.

```
&NAMELIST_1
      Flag1 =.....,
      Flag2 =……..,
       .
      FlagX =…….,
  /

 &NAMELIST_2
      Flag1 =.....,
      Flag2 =……..,
       .
      FlagX =…….,
  /
 Input_Card1

 Input_Card2 …
```

More details of QE tags from QE websites: *https://www.quantumespresso.org/Doc/INPUT_PW.html*

One typical QE input file

&CONTROL (Here we define general variables that control the run)

calculation = "scf" (scf, nscf, realx, vc-relax, bands, dos, MD etc.)

pseudo_dir = "/home/samim/pseudo" (Location of pseudo potential file)

outdir = "/samim/temp" (Location where temporary output files (i.e charge file wave files))

prefix = "graphene" (Name of the temporary files)

/

&SYSTEM (Here we provide the input variables of the system)

ibrav= i (i=0-14, -12 & -13)

0= Free cell, 1= simple cubic, 2=FCC cubic, 3=BCC cubic, 4=Hexagonal …

a = x

b=y

c =z

cosAB = cosine of the angle between axis a and b (gamma)

cosAC = cosine of the angle between axis a and c (beta)

cosBC = cosine of the angle between axis b and c (alpha)

nat = n (Total numbers of atoms in system)

For ibrav=0 not need to specify any these parameters instead we need to use “CELL_PARAMETERS” this input card

CELL_PARAMETERS { alat | bohr | angstrom }
v1(1) v1(2) v1(3)
v2(1) v2(2) v2(3)
v3(1) v3(2) v3(3)

ntyp =m (Total number of types of atoms)

occupations = "smearing"

smearing = "gaussian"

degauss= 2.00000e-02

ecutwfc=2.50000e+01 (kinetic energy cutoff (Ry) for plane wave. The quality of a plane wave basis set can be systematically increased by increasing the cut-off energy.)

ecutrho=2.25000e+02 (Kinetic energy cutoff (Ry) for charge density and potential)

/

&ELECTRONS (Here we provide the details of electronic calculations.)

conv_thr =1.00000e-06 (Convergence threshold for self-consistency (desire accuracy).

electron_maxstep= 200 (maximum number of iterations for scf calculation.)

mixing_beta = 7.00000e-01 (mixing factor for self-consistency)

/

K_POINTS {automatic} (The Monkhosrt-Pack K- grid{automatic})

8 8 1 0 0 0

ATOMIC_SPECIES

C 12.01070 C.pbe-rrkjus.UPF

(atom mass pseudopotential)

ATOMIC_POSITIONS {angstrom}
C 0.000000 0.000000 3.950788
C -0.000012 1.424503 3.950788
That all about QE input file

C.pbe-rrkjus.UPF

pbe-- Type of the exchange correlation functional. Here it is PBE type.

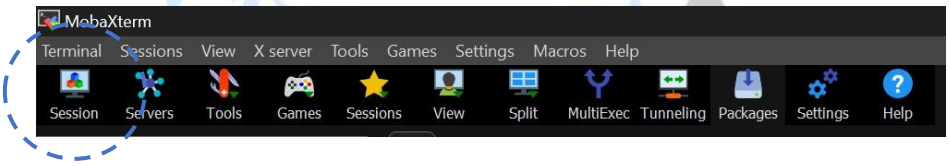
rrkjus-- Type of pseudopotential. Here it is a ultrasoft pseudopotential.

http://www.quantum-espresso.org/pseudopotentials/
You can download the pseudo potentials from these website

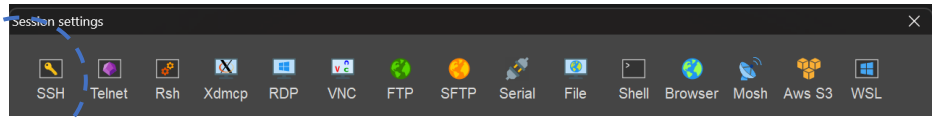
How to access the server:

i) Open "**mobaxterm"** application.

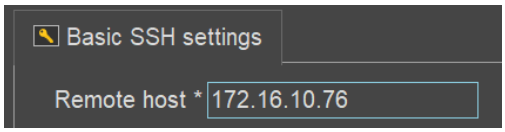
ii) Go to the session section.



iii) Click on SSH section.



iv) In the remote host put server address "172.16.10.76".



v) In specific user section give user name "**workshop** or **guest1** or **guest2** or **guest3**" (whichever is provided for you) and port will be 22.

vi) Now give the password.

vii) Go to node05 or node06 (which is provided for you) for running calculation. Command ssh node05 or ssh node06 (choose the command accordingly).

viii) Make a folder with your name in server. Command for making file
mkdir your_name.
Ex:- mkdir samim

ix) To see the files in server command is ls.

x) We have given all the input files in "hands_on_1" folder. Then copy hands_on_1 to your folder. Command for copying file
cp -r hands_on_1 your_folder
Ex:- cp -r hands_on_1 samim

xi) Go to your folder. Command
cd your_folder_name.
Ex:- cd samim

xii) Then go to hands_on_1 folder. Command cd hands_on_1. So, this is your working directory. Here in this directory, we have provided all the input file for the exercise 1 in this folder.

Sl no.	Calculation type	Folder name
Exercise 1	Relaxation	relax
Exercise 2	DOS	dos
Exercise 3	Phonon frequency	phonon

Note: To go to a directory command cd<space>directory_name
To go out from the from a directory command cd<space>..
To view a input file command vi<space>input file name
To go out from a input file command esc(button) :q
To edit input file press " I (button)" then edit
After editing to save the input file command esc(button):wq

To Run the calculation with this command

mpirun<space>-np<space>4<space>pw.x<space>
-i<space>input_file<space>|<space>tee<space>relax.out

Follow these commands properly.

Exercise 1: Relaxation calculation for Graphene unit cell.

- For optimised calculation go to relax directory.
  Command cd relax
- Here we have provided the sample input file for a primitive graphene cell using experimental lattice constant. To view input file
  Command vi relax.in

This is the Input file for relaxation calculation for graphene unit cell:

```
&CONTROL
   calculation = 'relax',
   outdir = './',
   pseudo_dir = '/home/samim/QE/upf_files',
   prefix = 'graphene',
   nstep        = 200 ──► Number of structural optimization steps performed in this run.
   etot_conv_thr=1.0e-04 ──► Convergence threshold on total energy (a.u) for ionic minimization
/
&SYSTEM
   ibrav      = 4
   a          = 2.47
   c          = 1.50000e+00
   ecutrho  = 5.50000e+02
   ecutwfc  = 5.50000e+01
   nat          =  2
   ntyp        =  1
   occupations = "smearing"
   smearing    = "gaussian"
   degauss     = 1.00000e-02
/
&ELECTRONS
   conv_thr            =   1.00000e-06
   electron_maxstep =   200
   mixing_beta        =   0.7 ,
/
&IONS
   ion_dynamics = "bfgs" ──►
/
K_POINTS {automatic}
 7 7 1 0 0 0
ATOMIC_SPECIES
C     12.01070  C.pbe-rrkjus.UPF
ATOMIC_POSITIONS {angstrom}
C      1.240000   0.721561   7.500000
C      0.000012   1.431695   7.500000
```

Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm is an iterative method for solving unconstrained nonlinear optimization problems.

- To go out from the input file.
  Command esc(button):q

- Run the calculation with this command --

mpirun -np 4 pw.x -i relax.in | tee relax.out

Output:

To open the output file.

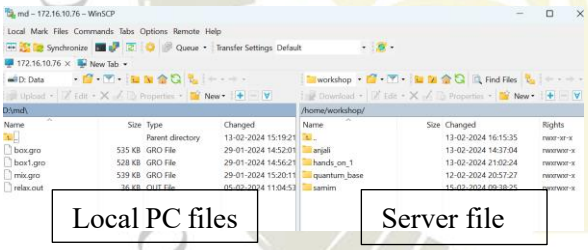
Command vi relax.out

```
     bfgs converged in   3 scf cycles and   1 bfgs steps
     (criteria: energy <  1.0E-04 Ry, force <  1.0E-03 Ry/Bohr)

     End of BFGS Geometry Optimization

     Final energy            =     -22.7919744735 Ry

     File ./graphene.bfgs deleted, as requested
Begin final coordinates

ATOMIC_POSITIONS (angstrom)
C               1.2375011647        0.7201071119        7.5000000000
C               0.0025108353        1.4331488881        7.5000000000
End final coordinates
```

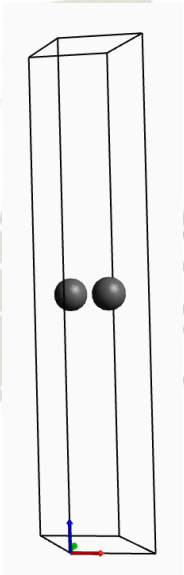
Going down you can find this section where final coordinates from your DFT calculation**. Use these atomic positions for further calculation.**

For visualization of the optimised structure, you can use **Avogadro** or XCrysden. Here we'll use Avogadro.

Open WinSCP . Login to server. New Site / My Workspace / 172.16.10.76 Click on the server address 172.16.10.76. Enter user ID then password. RHS box is for server and LHS box is for local PC.



- Go to your folder on the server box.
- Go to hands_on_1 folder.
- Go to relax folder.
- Copy the relax.out file and paste it to local PC box (i.e LHS box).
- Minimise WinSCP
- Now open Avogadro
- Now again open WinSCP and drag the relax.out file from LHS



Optimised structure viewed with Avogadro

Exercise 2: Density of state calculations:

For total DOS calculation first go into dos folder. Command cd ../dos
For DOS calculation we need to perform

- 1st scf calculation
- 2nd nscf calculation
- 3rd dos calculation.

Scf calculation:

Copy the relax.in file from the "relax" directory and name it as scf.in
cp ../relax/relax.in scf.in

Open the "scf.in" file using vi editor and make the following changes:

(a) Set calculation='scf'
(b) Replace the atomic positions with the optimized positions obtained from the relax calculation.
(c) Remove & IONS Namelist.

To run the scf calculation. command
mpirun -np 4 pw.x -i scf.in |tee scf.out

nscf calculation:

Copy "scf.in" and name it as "nscf.in"

cp scf.in nscf.in

Do the following changes in the "nscf.in" file:

(a) Set calculation='nscf'
(b) In &SYSTEM part set occupations='tetrahedra'
(c) nbnd=16
(d) Remove the flag degauss & smearing
(e) Increase the k-grid to 51×51×1. **Note we are using a much denser k-grid. Why?**

To save the input file command esc(button):wq

Run the calculation with this command
mpirun -np 4 pw.x -i nscf.in |tee nscf.out

DOS calculation:

This input file is given already in this directory.

Dos input file:

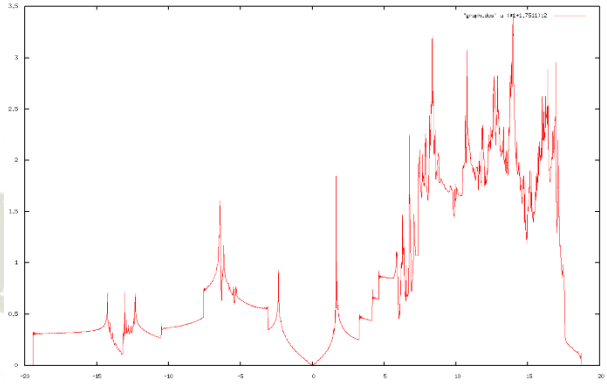
```
&DOS
    outdir='./',
   prefix='graphene',
   fildos='graph.dos'
 /
```

→ Output file for DOS data

Run the calculation with this command
mpirun -np 4 dos.x -i dos.in |tee dos.out

Plotting of data :

For plotting DOS use any plotting software such as **gnuplot** (origin, qtiplot, matlab etc.)
We use here gnuplot. First note the fermi energy value which is required for DOS plotting. You can find this value in scf output file. Check with this command vi scf.out and note down the fermi energy value.
For plotting in gnuplot you need to come to masternode.
Command exit



Then again go to your working directory.
Command cd your_name/hands_on_1/dos

Now plot DOS with these Commands:
i) gnuplot
ii) plot "graph.dos" u ($1-fermi energy value):2 w l
iii) To come out from gnuplot command is exit

Exercise 3: Phonon Calculation:

As in Exercise2 you have logged out form your working node so, again you need to enter your prescribed node for phonon calculation. Command for logging your working node ssh node05 or ssh node06 (choose whichever is provided for you) give this command

Now go to phonon folder in your working directory.
Command cd your_name/hands_on_1/phonon

For phonon frequency calculation we need to perform first scf calculation and then ph calculation.

For scf calculation copy the "scf.in" file in the "dos" directory to the current working directory.
cp ../dos/scf.in scf.in

Increase the scf convergence threshold to 1.0d-12

Run the calculation with this command
mpirun -np 4 pw.x -i scf.in |tee scf.out

Ph input file:
This input file is given already in this directory.

```
&inputph
 outdir="./",
 prefix="graphene",
 tr2_ph = 1d-12,
 ldisp = .false.,
 amass(1)=12.01070,
 fildyn='graph.dyn',
 asr=.true.
/
0.0d0 0.0d0 0.0d0
```

Run the calculation with this command
mpirun -np 4 ph.x -i ph.in |tee ph.out

Dynmat input file:
This input file also is given already in this directory.
&input
fildyn='graph.dyn'
asr='crystal'
/

Run the calculation with this command
mpirun -np 4 **dynmat**.x -i dynmat.in |tee dynmat.out

Output:

```
#  mode    [cm-1]    [THz]      IR
     1      -0.00    -0.0000    0.0000
     2       0.00     0.0000    0.0000
     3       0.00     0.0000    0.0000
     4     882.11    26.4449    0.0000
     5    1580.78    47.3905    0.0000
     6    1581.67    47.4172    0.0000

     DYNMAT        :       0.00s CPU       0.04s WALL
```

Open the excel sheet to calculate ZPE & TS.

ZPE &TS Calculation Sheet

		kT	4.11*10^(-2 in J	0.025 in meV		h	6.62607015*10^(-34) m2 kg / s			################		
			A	B	C	D	E	F	G	H	I	J
			"A"	"B"	C="-B"	"D=exp(B)-1"	"E=1/D"	"F= exp (C)"	"G=1-F"	"H=ln(G)"	"I=B*E"	"J=I-H"
f (THz)	hf(eV)	hf(meV)	hf(J)	hf/KT	"-hf/KT"	exp(hf/KT)-1	1/(exp(hf/KT)-1)	exp(-hf/KT)	1-exp(-hf/KT)	ln(1-exp(-hf/KT))	hf/kT*(1/(exp(hf/KT)-1))	hf/kT*exp(hf/KT) -ln(1-exp(-hf/KT))
1	0.00414	4.138576779	6.63E-22	0.161313869	-0.161313869	0.17505372	5.712532018	0.851024919	0.148975081	-1.90397623	0.921510639	2.825486869
2	0.00828	8.277153558	1.326E-21	0.322627737	-0.322627737	0.38075125	2.62638663	0.724243413	0.275756587	-1.288236734	0.847345175	2.135581909
3	0.01242	12.41573034	1.989E-21	0.483941606	-0.483941606	0.6224569	1.606536932	0.616349192	0.383650808	-0.958022494	0.777470063	1.735492557
		24.83146067										6.696561336
	ZPE	0.012416 eV									TS	0.167414033 in eV

Copy your output frequency in f (THz) column. And you will get your ZPE and TS Energy.

$$ZPE=\frac{1}{2}\sum_{i,k} h f_{i,k} \qquad TS=\sum_i \frac{h f_{i,k}}{kT(\exp\left(\frac{h f_{i,k}}{KT}\right)-1)} - \ln(1-\exp(-hf_{i,k}/KT))$$

Note: The above mention formulas are for extended system but we can use these formulas for localized system also.

Note: The instruction given in the manual may change slightly depending on the software and the platform used.