

# Design Oriented Project Report

Computation of Properties in **Quantum Espresso** pertaining to  
**Density Functional Theory**

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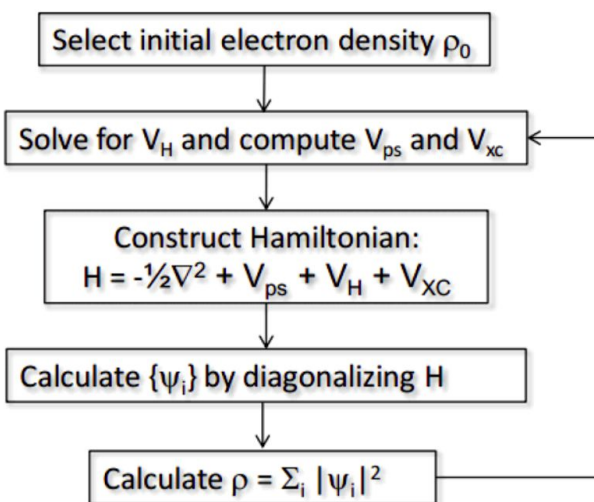
## ABSTRACT

Calculations based on the first-principles pseudopotential plane-wave method and density-functional theory are performed to investigate the properties of Silicon, metals like Iron, Nickel, copper, Aluminium, graphene and bilayer graphene. From an analysis of the electronic band structure close to the Fermi level, we have quantified the gradual change in the Fermi surface topology from the point-like structure for graphene

## DENSITY FUNCTIONAL THEORY AND ITS COMPUTATION:

Density Functional Theory is one approximate solution to the many-body theory of solids. Many-body theory is well known to be unsolvable analytically, so an approximation must be made. We will not be going into the details of the theory here. There are various approximations and computational methods that are used to give a good approximation to the solution of this problem.

Our computation methods use these approximations to measure the properties of the given materials as accurately as possible.



This flowchart shows the basic algorithm for calculating the **Density of States** according to the Kohn Sham theorem.

Similarly, the **Band Structure** is a visual representation of the energy levels that the electrons can have inside the solid. A band structure calculation is accomplished by calculating an integral over the Brillouin zone of the crystal. However, Quantum Espresso does the numerical integration in an earlier step so then all that is needed is to designate the points desired for plotting.

## A BRIEF INTRODUCTION TO QUANTUM ESPRESSO AND ITS METHODS USED IN THIS STUDY:

Each of the input parameters have meanings that need to be considered. It is important to understand these as they decide if a particular computation goes write or wrong.

Any of the sections that have an ampersand are described in the literature as "cards" and the rest are simple parameter specifications.

### Features of Input File:

The first card is CONTROL. The important parameter that it describes are:

1. Calculation, which determines the type of calculation, as in scf, nscf, band etc.
2. Restart mode = 0 from scratch0 this field tells the program to restart the calculations from scratch if there is a problem.
3. outdir: temporary directory for large files. Must be writable, will be created if not existent. outdir='./tmp' should be fine.
4. pseudo dir: directory where pseudopotential (PP) files are kept. It must exist, be readable, and contain the required PP file (in this example, Si.pz-vbc.UPF for Silicon). pseudo dir='./pseudo' should be fine

The SYSTEM card describes the structure of the system under calculation.

1. The field ibrav = 4 tells the type of bravais lattice to use for the calculation, example, 4 stands for the hexagonal lattice.
2. The field celldm(1) and celldm(3) give the lattice parameters for a, b and c respectively.
3. The parameter c is only included as the program requires it; it will be given a very large value to separate the layers and provide separation.
4. nat = 2 gives the number of atoms in the unit cell. T
5. ntyp = 1 tells the system how many types of atoms there are in the unit cell.
6. ecutwfc = 30 gives the energy cutoff for the wavefunction calculations in units of Rydberg. The cutoff energy for the wavefunction tells how much energy can be used for the dispersion relation of the plane-waves used to determine structure of the system.
7. occupations = tells the system to use the specified method
8. smearing = tells the system the type of distribution to use when smearing.

ELECTRONS card has only two key fields.

1. Conv thr = 1.D - 7 which gives the value for the convergence threshold of the energy of the final wavefunctions. The calculations will finish when the value of the self consistent calculation gives an energy difference less than the threshold.
2. The field mixing beta = 0.3D0 tells the system that when it gets results to feed them back into the calculations with a percent equal to the mixing beta parameter.

ATOMIC SPECIES card gives the information to be used by the machine for the atoms in the system. We specify the atomic weight, the name of the pseudopotential file to be used.

K POINTS give various ways to determine the number of K points and path used for various calculations like the band structure. All fields have been explained, except for the ones inside the

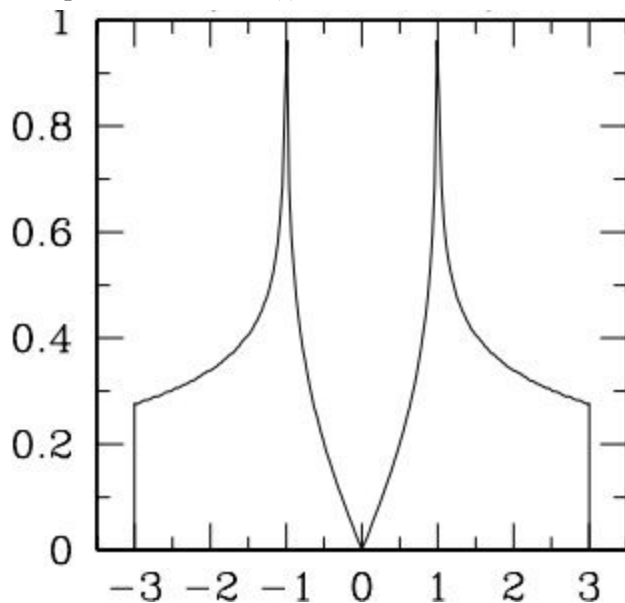
ATOMIC POSITIONS parameter. It is in units of lattice parameters (alat). We specify the positions of the atoms as required by the case.

All the input and output files can be found on <https://github.com/28shambhavi/Quantum-Espresso-DOP> in case any reference is required.

## DOS Calculation:

This calculation provides us with the Density of States for a given set of K points.

DOS plot: DOS vs E-E(f) in eV



Shown in the figure above is the DOS calculation for Single Layer Graphene. The ones with negative energy represent the HOLES and the ones with positive energy represent the ELECTRONS.

To increase the accuracy of the calculation the number of empty bands and the mesh of k-points must be increased. For example, by setting nbnd=16, the mesh of k-points to 48 48 1 for scf calculation and 96 96 1 for nscf calculation, we get a more accurate DOS as in the figure below (we set degauss=0.02 in the projwfc input). Executed by projwfc.x library.

## Band Structure Calculation:

We perform again a non self-consistent calculation (nscf) where k-point mesh is substituted with paths along the lines connecting the high symmetry points in the Brillouin zone.

```

K_POINTS crystal_b
4
-0.333333333 0.666666667 0.000000000 50 ! K
0.000000000 0.000000000 0.000000000 50 ! G
0.000000000 0.500000000 0.000000000 50 ! M
-0.333333333 0.666666667 0.000000000 50 ! K

```

The code above shows how we describe a K-path for the nscf calculation in band structure calculation

To do it, we need to run pw.x with another input file, which will be called "graphene.band.in". The file looks similar to "graphene.scf.in" that we have used previously. The main difference is that the 'band' is used for the parameter "calculation". The number of bands to be drawn is set to be 16 (nbnd=16). Here, K\_POINTS is given differently. The points are specified in units of  $2\pi/a$ , where  $a$  is equal to the one given in celldm(1). Note that the points are described in cartesian coordinates.

Those points are connected by straight lines and the band is calculated along the line. The integer given in the fourth column indicates that each line is divided by 50 mesh points and at those points the band is calculated.

**Plotting:** Graphs have been plotted using xmgrace software. To attain the upspin and downspin both in the same graph, we plotted one with the transformation  $y=-y$ . Similarly to achieve a graph of  $E-E(f)$ , we have done the transformation on all the data sets.

## Xcrysden view of sample:

Use Xcrysden to view the structure in the sample file:  
`$ xcrysden --pwi Al.sample.in`

## Convergence tests with respect to plane-wave cut-off:

To find out how the total energy changes when we vary the plane wave cut-off  $ecutwfc$ , we can either do this by copying the sample file Si.sample.in to other input files and editing them, and running pw.x using each of these input files in turn, or by running the sample shell script Si.sample.sh. We can easily find the values of the total energy by searching for an exclamation mark, e.g., using the grep command. Plot the data.

## Convergence with respect to Brillouin zone sampling:

Fix the value of  $ecutwfc$  convergence value. Differences in energy matters rather than the absolute value of the total energy, hence an approximate value will also work perfectly.

Let the lattice constant celldm(1) remain at the experimental value. Vary the Monkhorst-Pack grid parameters  $nk_1$ ,  $nk_2$  and  $nk_3$ . We can do this either by manually editing input files, or by creating a shell script. Use  $nk_1=nk_2=nk_3=1, 2, 3, 4, 5, 6$ . Leave the offset at  $k_1=k_2=k_3=1$ .

Run pw.x (with correct path) for each of the input files and plot the data.

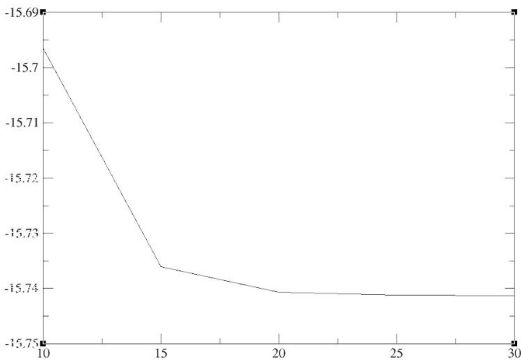
## Equilibrium lattice constant of Si:

Fix values of `ecutwfc` and `nk1=nk2=nk3`. I chose `ecutwfc` and `nk1=nk2=nk3=6`, but you can choose other values if you feel that they are more appropriate. Make input files in which you vary the lattice constant, i.e., `celldm(1)`, in steps. Then run the scf calculations.

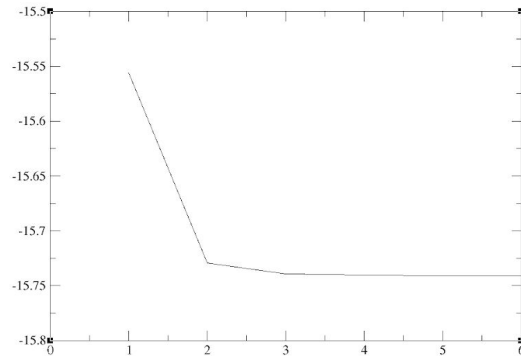
By plotting the Total energy in Ry VS Lattice const in Bohr , We can observe that the energy is symmetric about the minimum value. This minimum value corresponds to the equilibrium lattice constant

# Silicon:

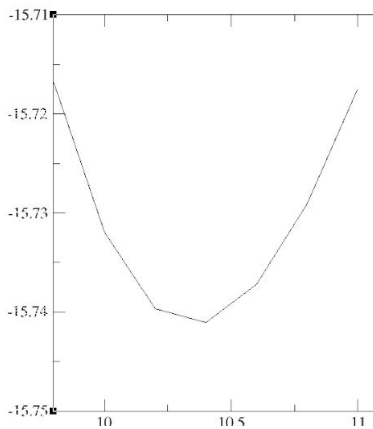
A. Total energy vs value of  $ecutwfc$  for Si



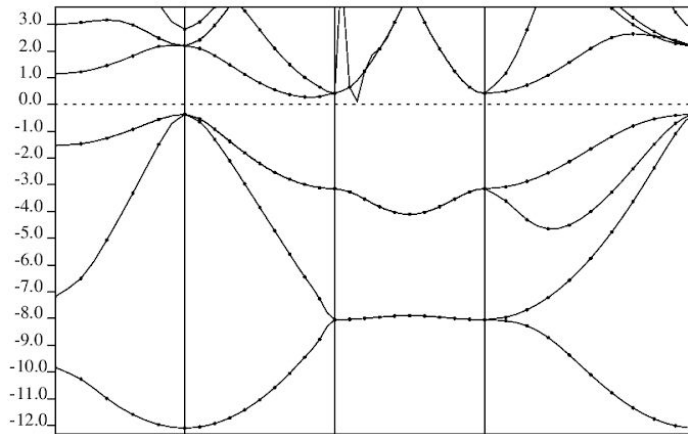
B. Total Energy vs  $nk1$  for Si



C. Total Energy vs lattice constant for Si



D. Band structure diagram for Silicon (E vs  $k$ )



Total energy vs value of  $ecutwfc$  for Si graph helps us find the convergence value for  $E_{cut}$ , here we can take it to be 20 or 25. Total Energy vs  $nk1$  for Si, illustrates how Total Energy varies by varying the K point mesh. Total Energy vs lattice constant for Si is obtained by the graph C and figure D shows the Band structure diagram for Silicon.

# Metallic And Magnetic Materials:

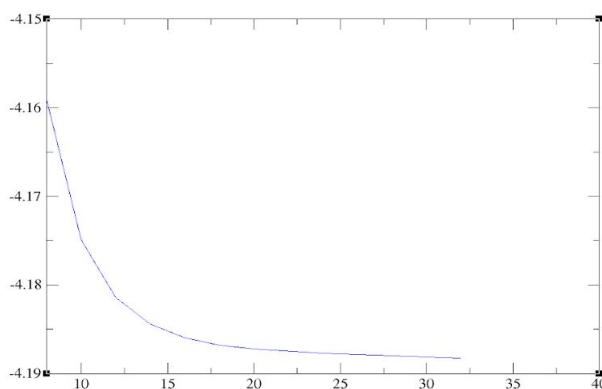
Now, we will be computing a metallic material and finding the Convergence value of “Ecut” through the Total Energy vs Ecut-wave function graph shown below. The limit obtained is then written in the file to obtain the Equilibrium Lattice constant or the celldm(1).

Procedure is described above in the section for these calculations

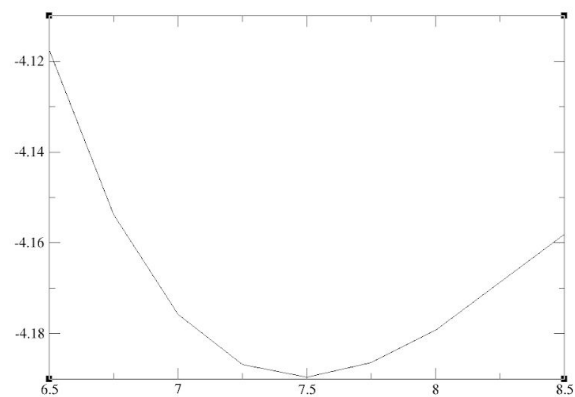
Input files can be found on <https://github.com/28shambhavi/Quantum-Espresso-DOP>.

## 1. Aluminium

Total Energy vs Ecut-wave function



Total Energy vs Lattice constant

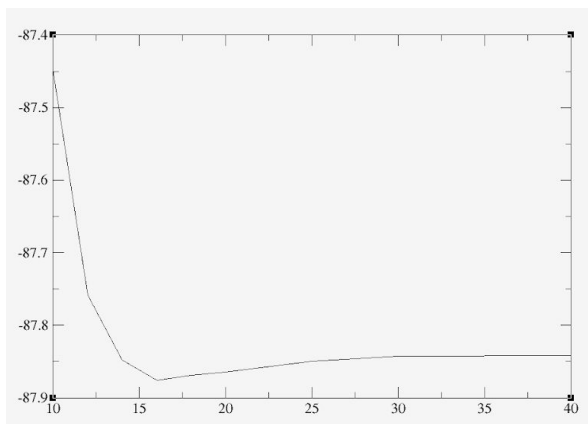


Ecut =20

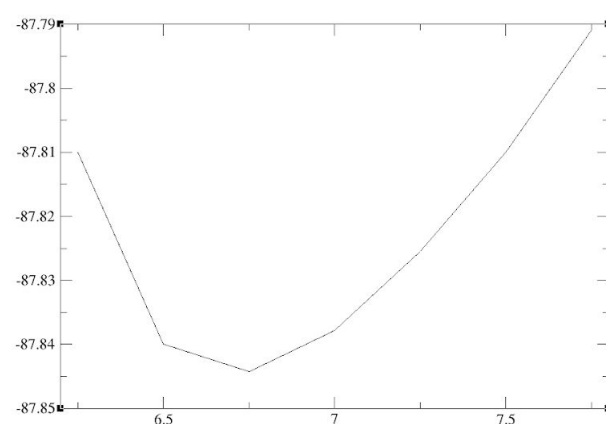
Celldm=7.65

## 2. Copper

Total Energy vs Ecut-wave function



Total Energy vs Lattice constant



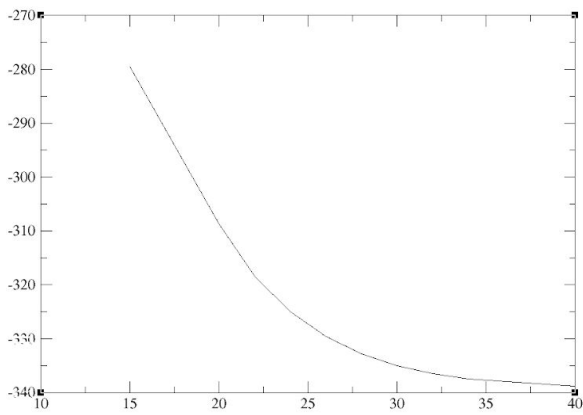
Ecut=30

Celldm=6.83

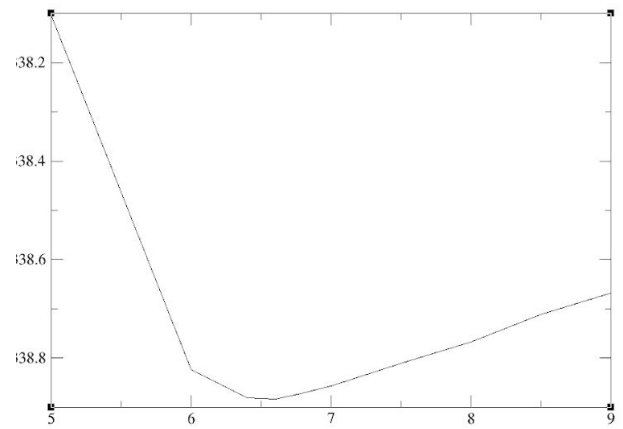


### 3. Nickel

Total Energy vs Ecut-wave function



Total Energy vs Lattice constant

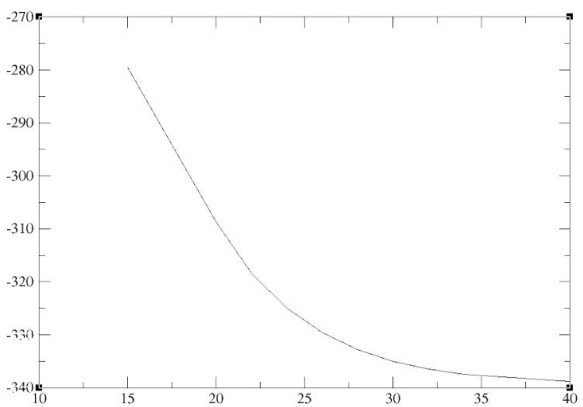


Ecut=40

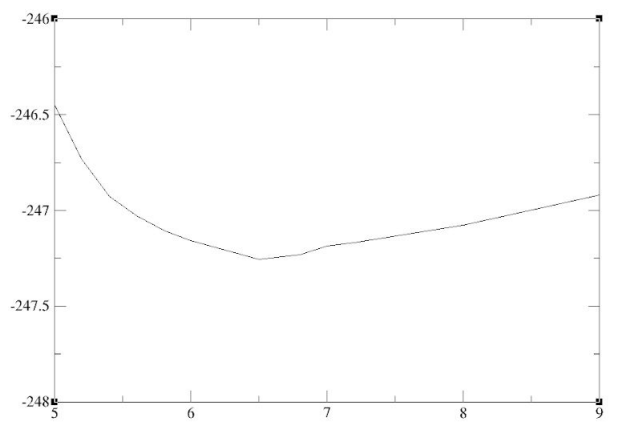
Celldm=6.65

### 4. Iron

Total Energy vs Ecut-wave function



Total Energy vs Lattice constant

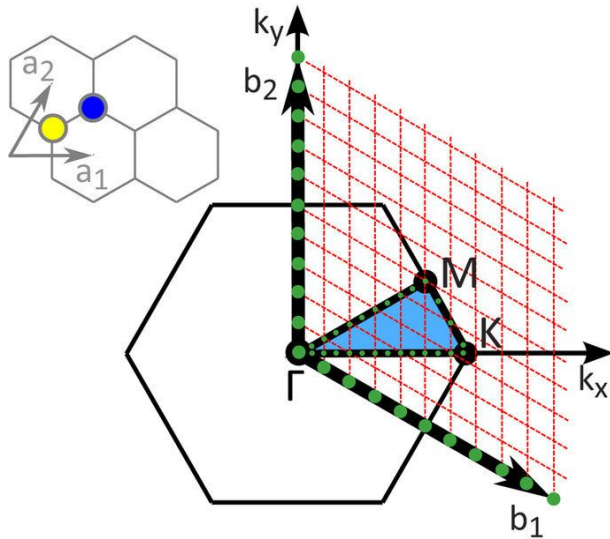


Ecut=37

Celldm=6.59

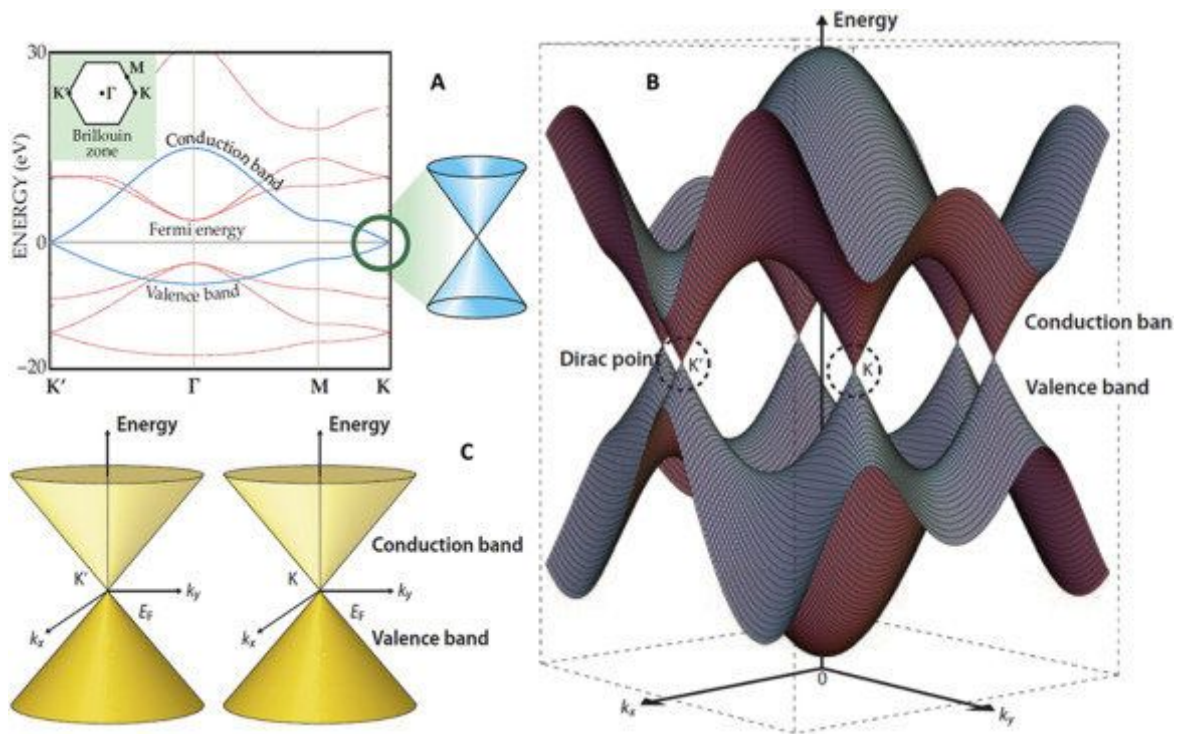
# GRAPHENE:

First Brillouin Zone of Graphene is shown in this figure:



The path of most our calculations follow the of K- $\Gamma$ - M-K

The Brillouin zone of graphene, is a two dimensional hexagon.



## Commands for Calculations of Graphene:

Following are the commands for the various calculations for the AA bilayer case.

Command for running the scf calculation: `pw.x < gr_scf.in > gr_scf.out`

Find out the final value of fermi energy from the output file `gr_scf.out`

Command for running the non scf calculation: `pw.x < gr_bands.in > gr_bands.out`

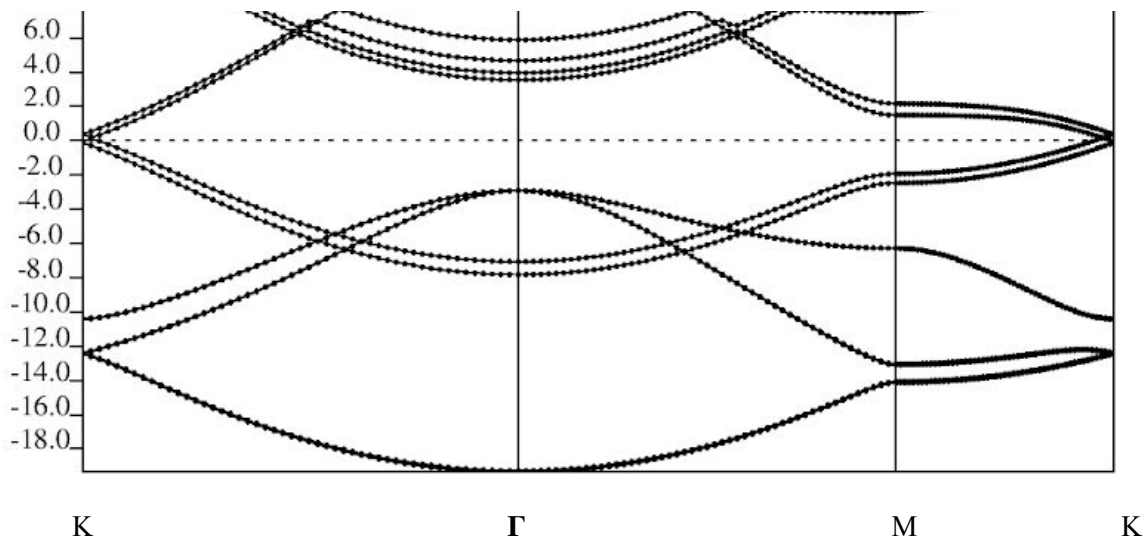
Command for band calculation: `bands.x < bandplots.in > bandplots.out`

Plotting the band: `plotband.x < plotband.in > plotband.out`

All the input and output files can be found on <https://github.com/28shambhavi/Quantum-Espresso-DOP>

## Single layer Band Structure:

The band structure and outline of the Brillouin zone is well known. Shown below is the band structure for a single layer of graphene. It is actually the conduction and valence band that get plotted in the band structure diagrams.



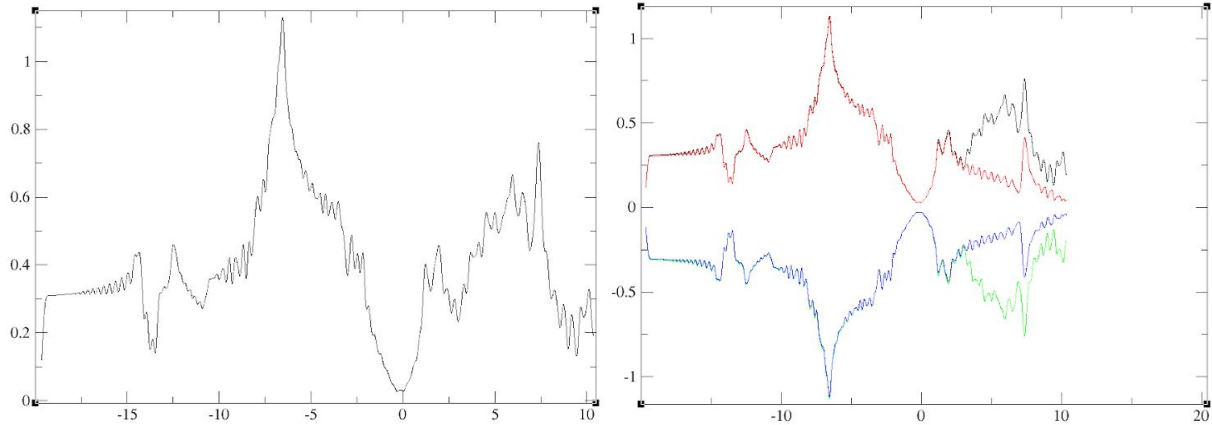
In order to verify the effectiveness of Quantum Espresso, the band structure needs to be compared to a well known accurate band structure model. When we compare we see, the graphing styles are slightly different but one can see that the graphs are very similar. In the one calculated by Quantum Espresso, the lines do not appear to cross, but instead meet at points. This is just due to the graphical style of plotting.

The Fermi level is confirmed by looking at the output file of the scf calculation. Fermi level is located at the point denoted as K.

## AA Bilayer:

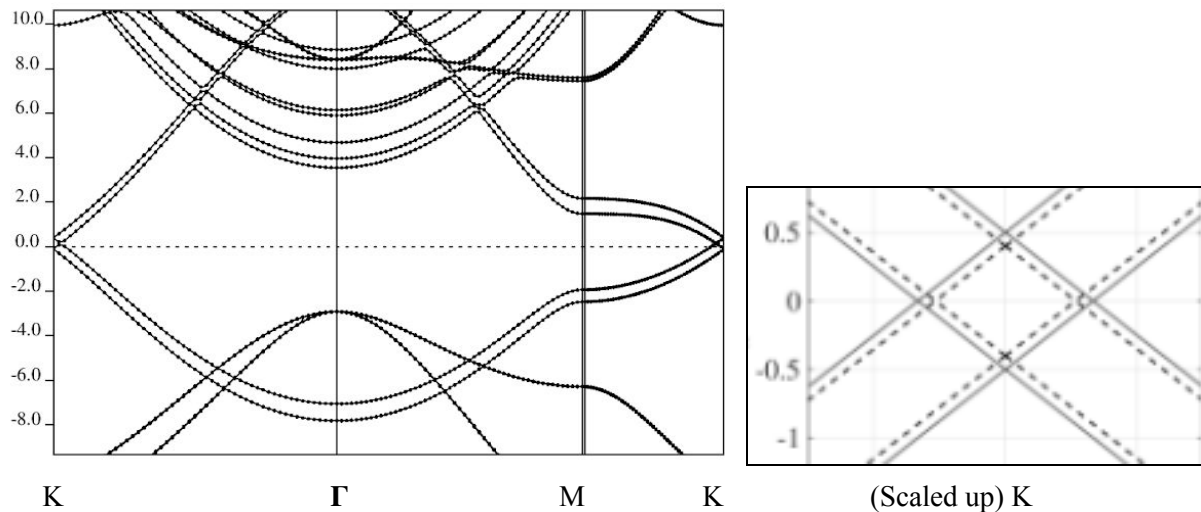
DOS vs E-E(f)

DOS vs E-E(f) for up(black) and down(green) spin  
Red and blue show the pdos for up and down spin



The graphs are symmetric in the neighbourhood of the 0 along the x axis, i.e, the point where  $E=E(f)$ . The graph on the right, presents the DOS plot for up spin and down spin; we can verify the magnetic properties of Graphene by exploiting this technique.

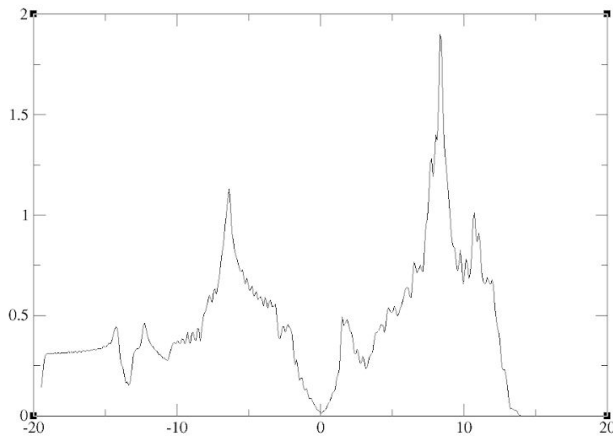
Band Structure: Energy per eV vs K points in momentum space



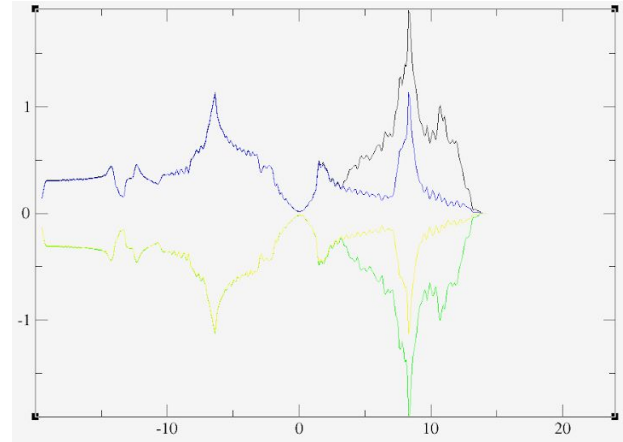
The band structure at the Wave vector K, gives us the graph on the right side. Here, we can see that the Band structure of the bilayers cross each other in AA Bilayer

# AB bilayer

DOS vs E-E(f)

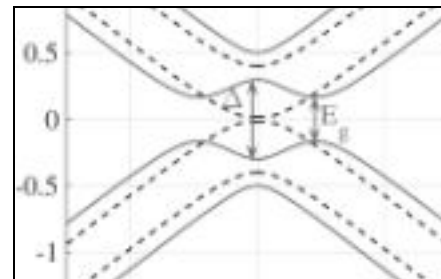
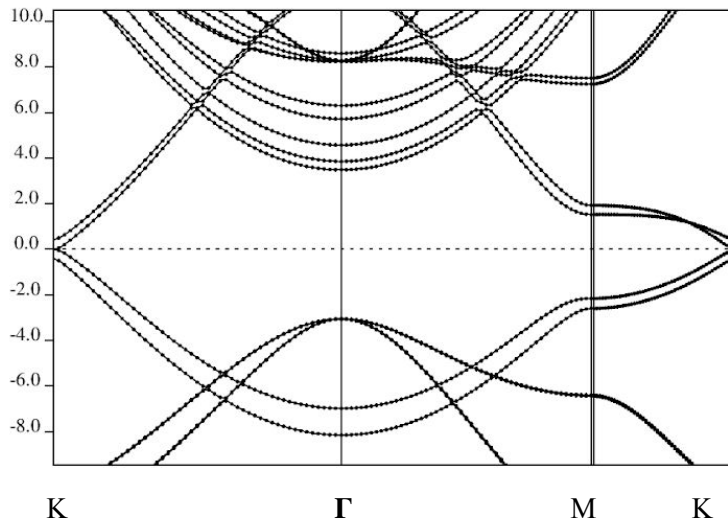


DOS vs E-E(f) for up(black) and down(green) spin  
Blue & yellow show the pdos for up and down spin



The graphs are symmetric in the neighbourhood of the 0 along the x axis, i.e, the point where  $E=E(f)$ . The graph on the right presents the DOS plot for up spin and down spin; we can verify the magnetic properties of Graphene by exploiting this technique.

Band Structure: Energy per eV vs K points in momentum space

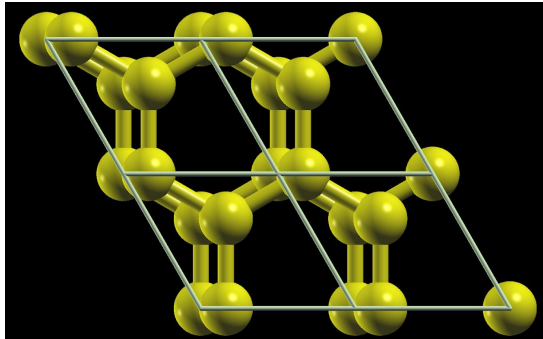


The band structure at the Wave vector K, gives us the graph on the right side. Here, we can see that the Band structure of the bilayers do not cross each other in AB Bilayer. There is a band gap that develops between the valence and conduction band.

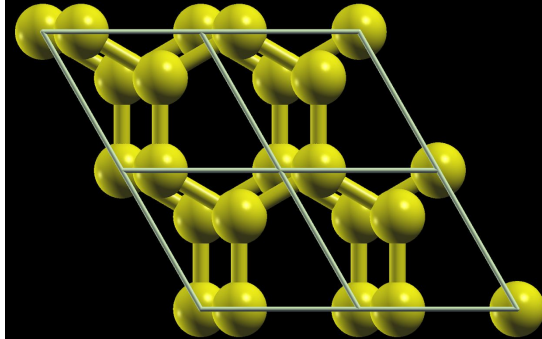
## Sliding AA Bilayer along the zz direction:

Here are the xcrsden views of the bilayer at six different stages of sliding,

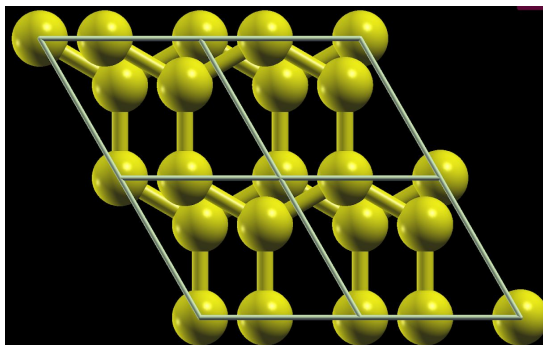
0.4



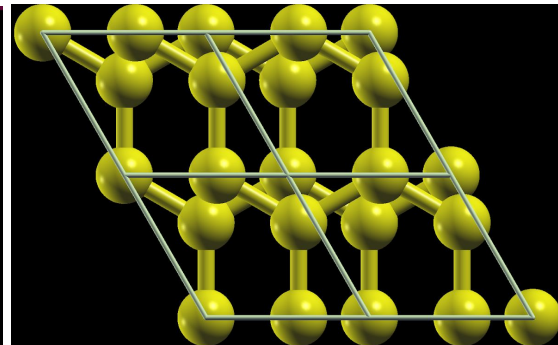
0.6



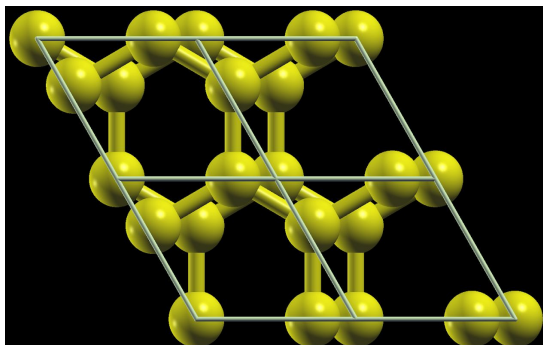
1



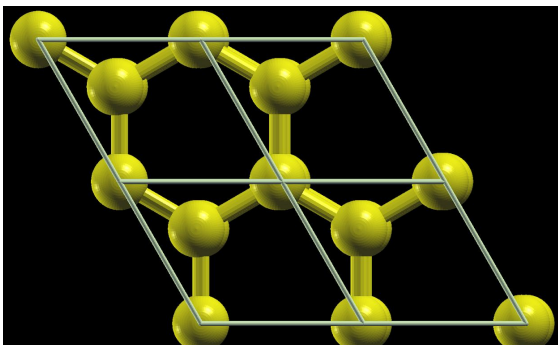
1.4



1.8



2.4



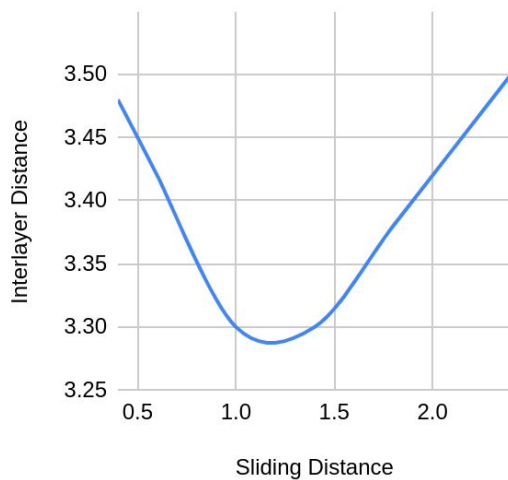


The configuration can be said to move from AA bilayer to AB bilayer and then back to AA bilayer as we change the sliding distance along the specified path. The fermi energy obtained has been presented and plotted as follows:

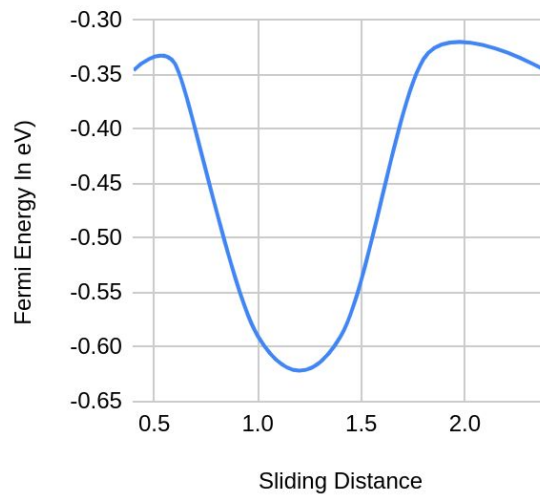
Sliding Distance (in A)	Interlayer Distance (in A)	Fermi Energy (In eV)
0.4	3.48	-0.3458
0.6	3.42	-0.3397
1	3.3	-0.5899
1.4	3.3	-0.5903
1.8	3.38	-0.3355
2.4	3.5	-0.3471

The value interlayer distance changes along with changing the value if sliding distance

Interlayer Distance vs. Sliding Distance



Fermi Energy In eV) vs. Sliding Distance



**BAND Plots at different sliding distances:** The band structure remains exactly the same. No difference is observed.

**DOS Plots at different sliding distances:** All the DOS plots come out to be exactly identical when applying the above given data of Sliding Distance VS Interlayer Distance(not derived originally). The Fermi Energy given in the table is obtained through scf calculation at these different points.

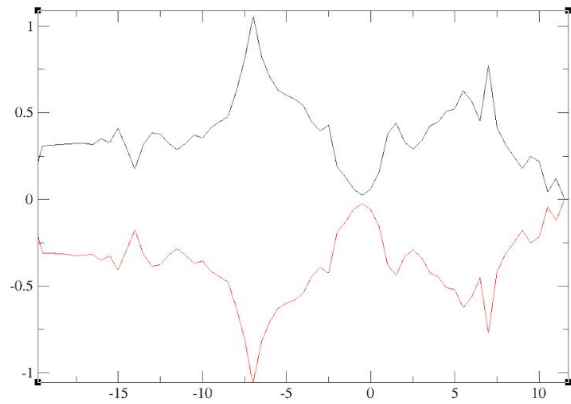
All that can be said about the DOS graphs, is that due to shift in Fermi Energy, the relative graphs shift. However, the E-E(f) graph remains the same, for each of these configurations. (Please refer to appendix 1 for the graph).

## APPENDIX 1:

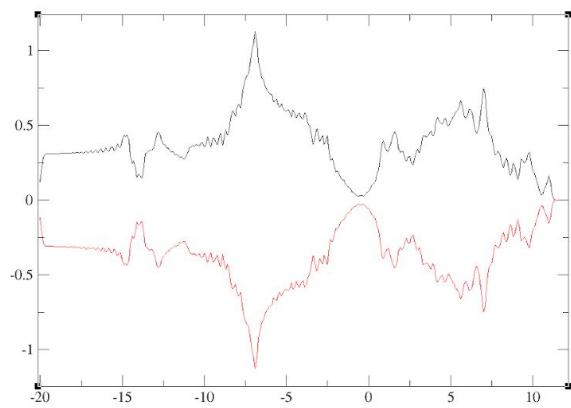
Difference in DOS plots of the sliding AA bilayers of Graphene by varying K points:

Following are graphs showing DOS vs E-E(f)

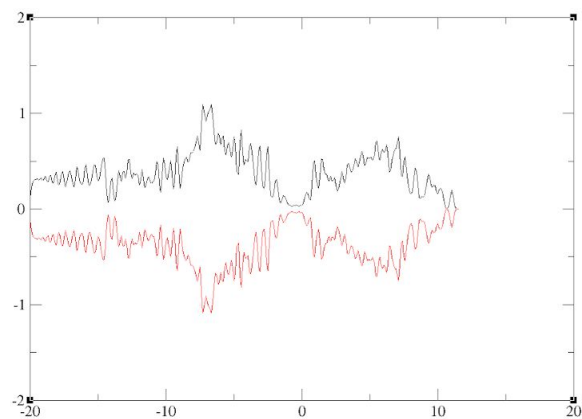
A.



B.



C.



Since I had tried many different combinations of K-points, these 3 graphs show very clearly how the accuracy grows by increasing the mesh of K-points.