Materials Simulation - Bandstructure, Density of States, Phonon Dispersions

Summer Research Project

by

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Abstract

Over the past few decades, innovation in materials simulation and modeling has resulted from the concerted efforts of many individuals and groups worldwide, often of small size [1]. The combination of methodological and algorithmic innovations and ever-increasing computer power is delivering a simulation revolution in materials modeling, starting from the nanoscale up to bulk materials and devices [2]. This revolution has been extremely beneficial for both theorists as well as experimentalists in a way that it gave a direction to experimentalists to carry out experiments and a shorter route to theorists to get the numerical results from their theory.

Over the years, various software packages have been developed to simulate the bulk behavior of crystals using first principles. Density Functional Theory (DFT) has been crucial in enabling this development as it provides a computationally efficient approach towards solving many body quantum systems.

In this Summer Project, an open source software which is widely used for materials simulation is utilised to simulate various properties of Aluminium and Silicon. Quantum opEn Source Package for Research in Electronic Structure, Simulation, and Optimization or Quantum Espresso [1] is a DFT simulation package based on Density Functional Theory, plane waves, and pseudopotentials.

In this project, Quantum Espresso's pw.x, ph.x, bands.x, dos.x, projwfc.x and few other modules are used to simulate bandstructure, phonon dispersions, density of states of Aluminum and Silicon. The rest of the report is structured in the following way : A brief introduction to Density functional theory and how Espresso makes use of Kohn Sham equations. Convergence tests with resrpect to K points, lattice parameters, cutoff energy followed by results of Aluminum and Silicon.

Density Functional Theory

1. **Problem with many body Hamiltonian**

In order to find the energy levels for electrons crystal, we will need to solve the time independent Schrodinger Equation for the energy eigenvalues. The equation is given by

$$\left(-\frac{\hbar^2}{2m} \sum_i \nabla^2_{\vec{r}_i} + V(r,R) \right) \Psi(r|R) = E(R)\Psi(r|R) \tag{1}$$

$\Psi(r|R)$ is the many electron wave function, R is Here, we have already applied the Born Oppenheimer approximation or the adiabatic approximation by keeping the nuclei fixed. In other words, R is just a parameter in the equation. The potential energy $V(r,R)$ is the contribution of the following terms.

$$V(r,R) = \sum_{I \neq J} \frac{e^2}{2} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \tag{2}$$

The first term is the nuclei potential energy, which is a constant as far as our electron wave function is concerned (Born Oppenheimer approximation). The second term is the potential energy of electrons due to the nuclei. The third term is the self interaction energy of the electrons. This term is the one which creates computational problems, as the number of electrons in a crystal are of the order of 10^{23}. To tackle this problem, the many electron wave function is reduced to a hypothetical single electron wave function using Density Functional Theory [3].

2. **Hohenberg Kohn Theorem**[4]

Here, we state the theorem without proof. It states *the ground state of any interacting many particle system with a given fixed inter-particle interaction is a unique functional of the electron density $\rho(r)$*. In quantum mechanical terms, we have the density operator, $\hat{\rho}(\vec{r}) = \delta(\vec{r'} - \vec{r})$. Electron density for one electron is given by $\langle \psi^* | \hat{\rho(r)} | \psi \rangle = \int \psi^*(\vec{r'})\psi(\vec{r'})\delta(\vec{r'} - \vec{r})d\vec{r'} = |\psi(\vec{r})|^2$ For many body electrons, the electron density is simply the sum of individual single electron wavefunctions. Essentially, the many n body $3n$ variable problem is reduced to find $\rho(r)$ which is a 3 variable problem. We now turn to understand the Kohn Sham equations in which, we make use of the Hohenberg Kohn theorem.

3. **Kohn Sham Method**[5]

Although the original form of the Schrodinger equation is retained, the meaning of

each terms, changes in the new approach. The modified Kohn Sham Hamiltonian of (fictitious) non interacting electrons is given by

$$H\psi_i = \left(-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + V_R(\vec{r}) \right)\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \tag{3}$$

The effective potential is a functional of charge density $\rho(\vec{r})$.

$$V_R(\vec{r}) = -\sum_I \frac{Z_I e^2}{|\vec{r} - \vec{R}_I|} + v[\rho(\vec{r})], \ \ \rho(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2 \tag{4}$$

The form of the effective potential is unknown but approximate forms are known. DFT, in principle is valid only for ground state properties.

The total energy is also a functional of electron density, $E \implies E[\psi, R]$

$$E[\psi, R] = -\frac{\hbar^2}{2m}\sum_i \int \psi_i^*(r)\nabla^2\psi_i(r)d\vec{r} + \int V_R(\vec{r})\rho(\vec{r})d\vec{r} + \frac{e^2}{2}\int \frac{n(\vec{r})n(\vec{r'})}{|\vec{r}-\vec{r'}|} + E_{xc}[n(\vec{r})]$$
$$+ \sum_{I\neq J} \frac{e^2}{2}\frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \tag{5}$$

The Kohn Sham equations from the minimization of energy functional

$$E(R) = minE[\psi, R], \ \ \int \psi_i^*(r)\psi_i(r)d\vec{r} = \delta_{ij}$$

Hellman-Feynman theorem is used to get the forces on atoms which are used to get the phonon frequencies.

$$\vec{F}_I = -\nabla_{\vec{R}_I}E(R) = -\int n(\vec{r})\nabla_{\vec{R}_I}V_R(r)d\vec{r}$$

4. **DFT using Quantum Espresso** [1]
From the KS equations, we can see that $n(\vec{r})$ is crucial in calculating the physical properties like energies and forces. Quantum Espresso uses Self Consistent Field (SCF) method to get the ground state electronic charge densities. Initially, it guesses some ground state electronic density, constructs the effective potential (eqn 4), solves KS equation (eqn 3), again uses eqn 4 to get the ground state density and compares it with the initial guess. If they are almost the same (the difference is less than some threshold) or in other words, the density is self consistent, then the calculation terminates and we get the ground state electronic density. All this SCF calculation is included in the pw.x module of Quantum Espresso. Futher, to calculate bandstructure, phonons, density of states, other modules like bands.x, ph.x, dos.x are available.

Silicon

1. **SCF Convergence Tests**

   Image below shows the general structure of a Quantum Espresso input file for SCF calculation using pw.x

```
 1  &control
 2      prefix='silicon',
 3      calculation='scf',
 4      restart_mode='from_scratch',
 5      ! this is a comment: you can comment out variables
 6      ! set pseudo_dir and outdir to suitable directories
 7      pseudo_dir = '.',
 8      outdir='./tmp',
 9  /
10  &system
11      ibrav=2, celldm(1) =10.2,
12      nat=2, ntyp=1,
13      ecutwfc=50
14  /
15  &electrons
16      conv_thr=1e-10
17  /
18  ATOMIC_SPECIES
19  Si  28.086  Si.pz-vbc.UPF
20
21  ATOMIC_POSITIONS (alat)
22  Si 0.00 0.00 0.00
23  Si 0.25 0.25 0.25
24  K_POINTS (automatic)
25    6 6 6 1 1 1
```

Figure 1: Sample Input File for SCF calculation

A brief description of each term :
&control, &system, &electons are called namelists. They specify type of calculation, the crystal structure, and electron convergence threshold respectively. In the &control namelist, *pseudo_dir* gives the address of the directory containing pseudopotentials. Pseudopotentials is used as an approximation for the simplified description of complex systems, in this case our crystal. &system namelist contains the crystal structure specifications. ibrav specifies type of unit cell (2 imples FCC), celldm(1) gives length of unit cell in direction 1, nat gives number of atoms

in the unit cell, ntyp gives number of types of atoms and ecutwfc is a cutoff values used during calculating total energy. The Atomic_species namecard specifies all the atoms present in the unit cell. The text infront of the atom is the name of the pseudopotential file of that particular element. Atomic_positions specifies the locations of the atom species in the crystal defined in &system. K_points is an important concept used by Espresso. K points are points in reciprocal space which have dimensions of inverse length. One point in k space represents infinite points in the real crystal space. Mathematically, reciprocal space is the fourier transform of the real space. In k space, the periodicities of the crystal in real space are captured by discrete points. Quantum esresso, uses discrete points in the first brilloiun zone, to get the wavefunction. More the number of k points used, more accurate wavefunction we get. There are certain special high symmetry points in the K space (Chadi Cohen, Monkhorst) around which it is easy to get the wavefunction. Automatic specifies that it will use Monkhorst-Pack set of k points [6].

We now turn to the actual convergence tests. To run a scf file, we use the pw.x module. We use the terminal to type $pw.x < scf\_filename.in > scf\_filename.out$. In the .out file, we get the total energy values and values at the discrete k points which we have specified. We see how energies converge to a value as we increase number of k points, ecutwfc and see how energy achieves a minima at the equlibrium lattice paratmeter (celldm(1)). We run several instances of pw.x with varying ecutwfc from 12 to 32 in steps of 4. We see the following convergence
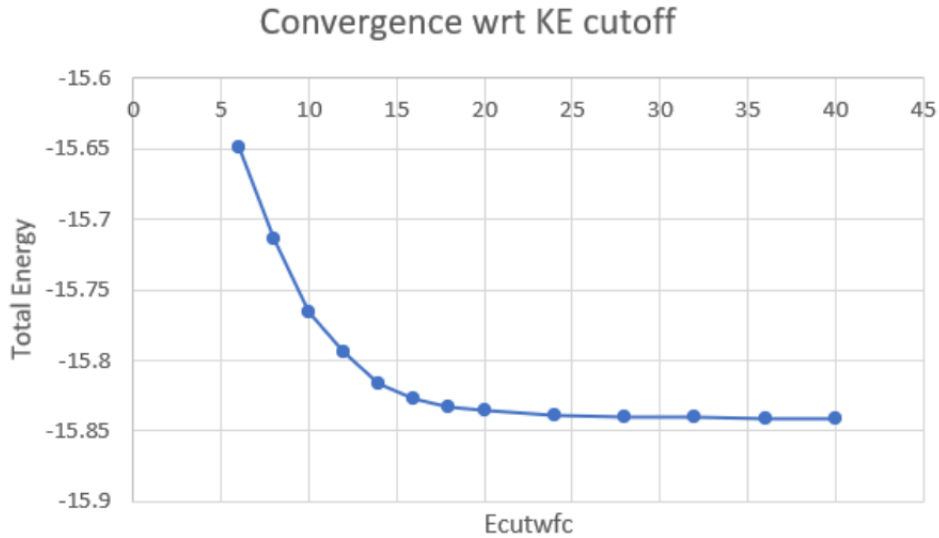

Figure 2: Covergence w.r.t. ecutwfc

Next, we vary the lattice parameter from 9.8 a.u. to 10.7 in steps of 0.1. We get an almost parabolic curve as shown below.
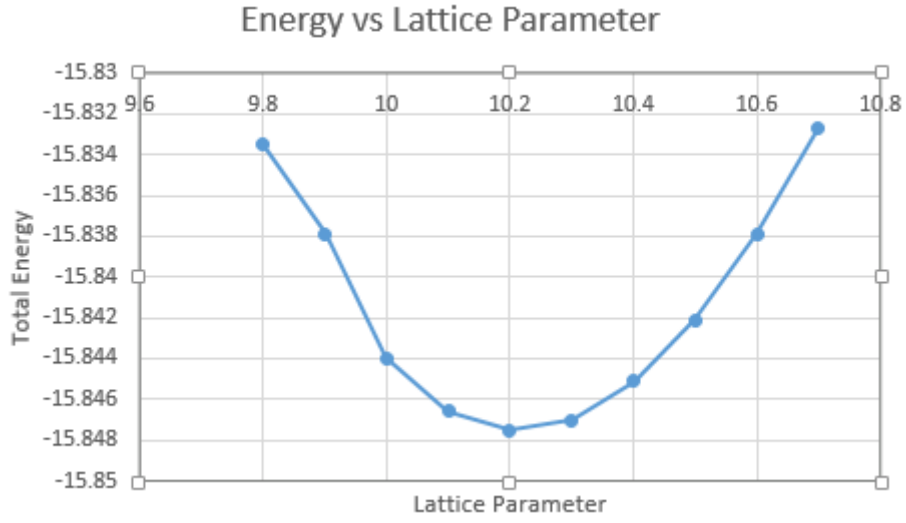

Figure 3

We can see that minimum energy occurs at 10.2 a.u. which is the equilibrium lattice parameter for Silicon.

Next we try to obtain convergence w.r.t. K points by increasing the grid from 2 x 2 x 2 to 8 x 8 x 8. We obtain convergence as shown below

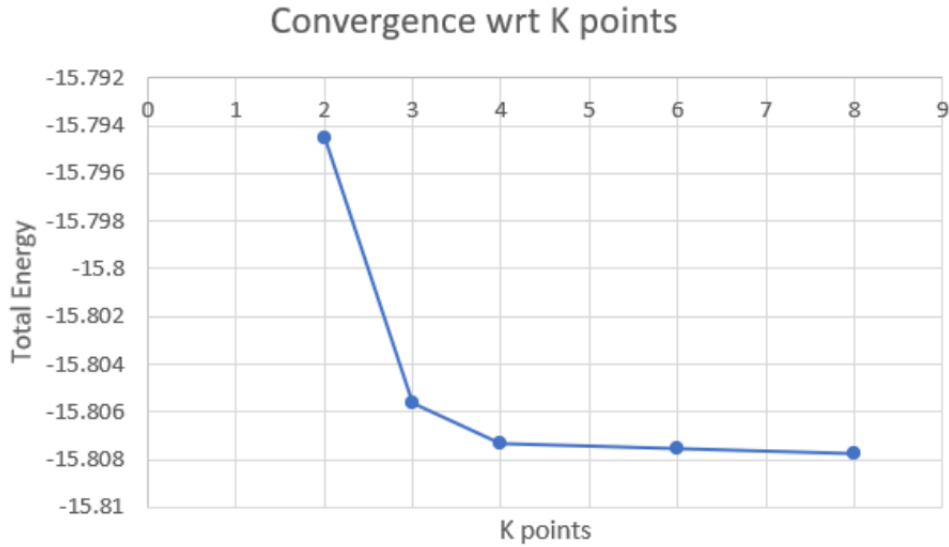We see that at about 6 x 6 x6 or 8 x 8 x 8 k point grid, the total energy values

Figure 4: Convergence w.r.t. K points

converge. Note, that as we increase k point grid, time required to complete the

SCF calculations increase, hence there is a trade off between computational time and accuracy. Once, convergence is obtained, we use those parameters to make the final SCF calculation and bulding up on that, we simulate bands, phonons, dos, etc.

2. **Bandstructure of Silicon**

We first do an SCF calculations to get the ground state electronic charge density. Then, we prepare a bands.in file for pw.x module. It has a similar structure, but in calculations, we set bands instead of scf. And we also provide the K path over which we wish to evaluate the band structure. Then we use bands.x module and prepare another bands2.in to get the plot values of the bandstructure. Two files are produced: sibands.dat.gnu, directly plottable with gnuplot, and sibands.dat, for further processing by auxiliary command plotband.x. After using plotband.x, we obtain the bandstructure shown below :
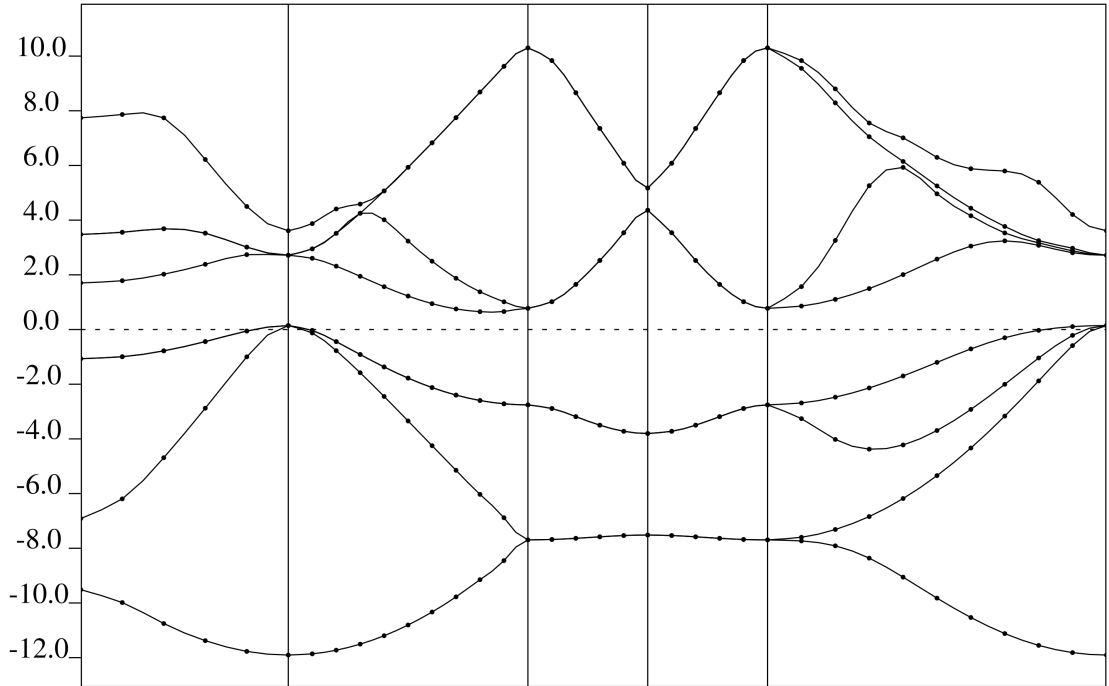
Figure 5: Bandstructure of Silicon

The k path followed here is L - Γ - X - K - Γ .From the SCF file, we also get the highest occupied energy level, (or fermi level). We plot the fermi level in the

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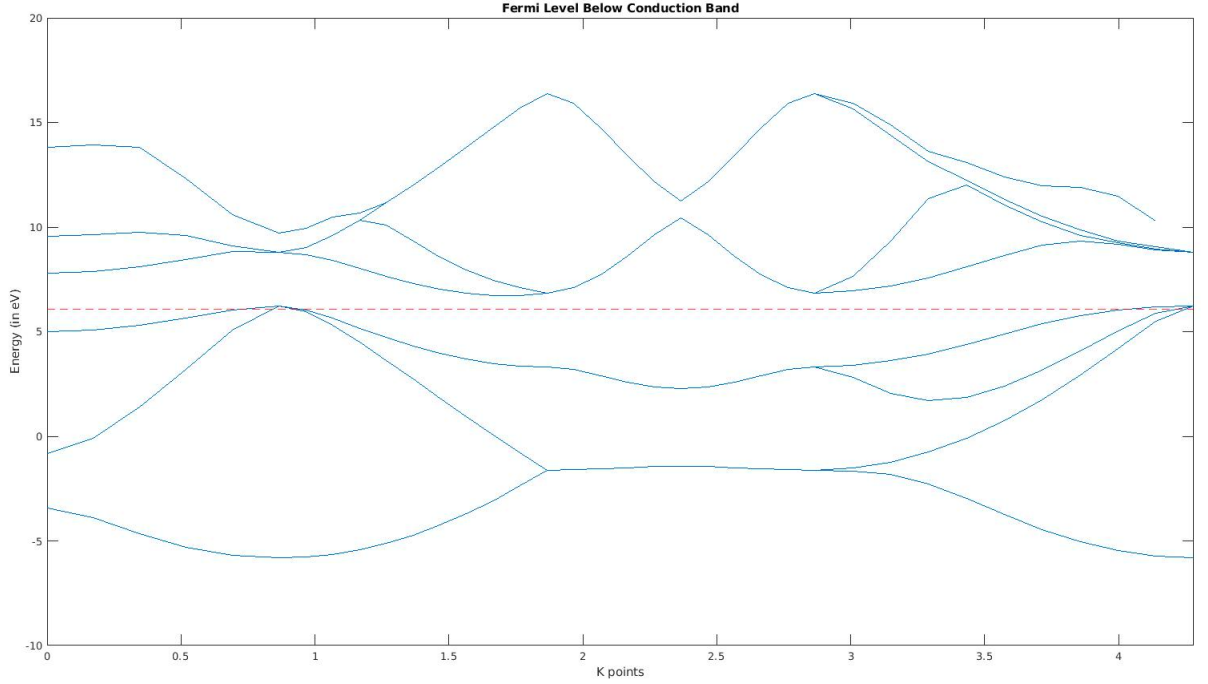bandstructure using MATLAB, we get the following graph

Figure 6: Location of Fermi Energy

Note that, in the previous graph, they have assumed fermi energy at 0. This is not wrong as the absolute values of energies have no sense. In the graph above, they have just used a different value for reference energy. What we want to point out here, is that the fermi energy is below the conduction band, which implies that Silicon is insulating in nature as observed in experiments.

3. **Density of States**

To get the density of states, after an scf calculation, we need to perform a non-scf calculation with a more dense k-point grid and higher cutoff values. We use pw.x module for nscf calcuation as well, and in the calculations variable, we set it to nscf. An additional variable verboity is set True and Occupations = Tetrahedra (more on occupations later). Following that, we get the fermi energy from nscf output and prepare the input file for dos.x module which gives us the plotting values for density of states. We get a plot as shown on the next page.
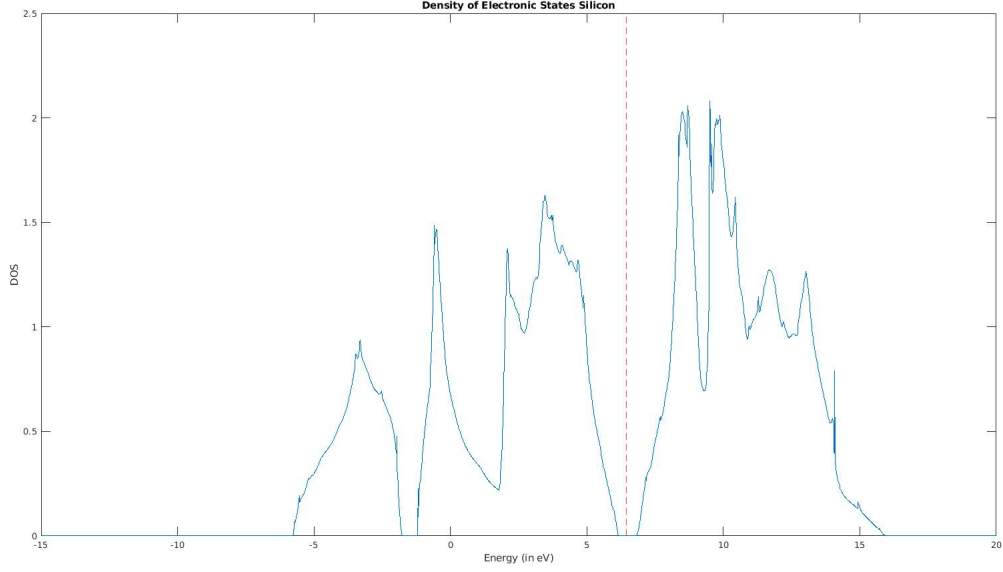
Figure 7: Electronic Density of States Silicon

We can also find the orbital projected density of states, in the sense, we can find contribution of s p d f orbitals to the total density of states. We make use of projwfc.x module to do this. We get the values of s and p contributions of each atom in the unit cell. We plot the projections using MATLAB
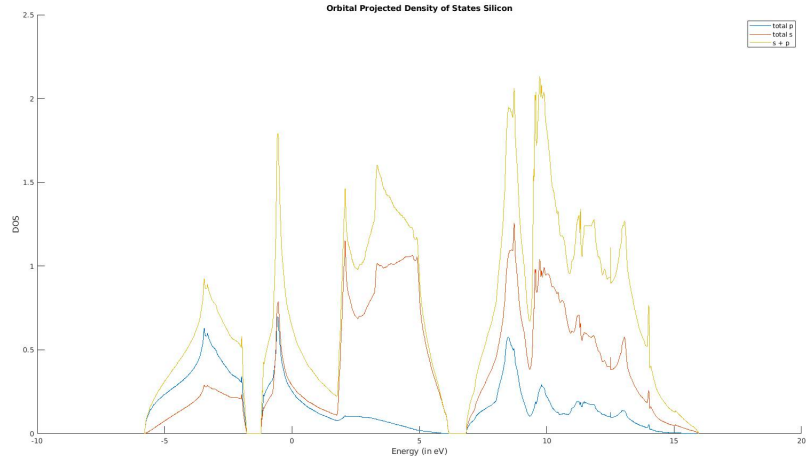

Figure 8: Projected Electronic Density of States

4. Phonon Dispersions

Quantum Espresso has ph.x module to find the phonon dispersion relations. Basically, we have to find the eigenfrequencies at each k point. Once we have the ground state charge density, we use the Hellman-Feynman theorem to get the forces on atoms for small perturbations and then get the phonon frequencies. First, we need to perform SCF calculation followed by a ph.x In the input file for ph.x calculations,

we specify the number of k points. In our case, we kept nq1 = 4, nq2 = 4, nq3 = 4. Figure below shows the input file for a ph,x calculation.

```
 1 Phonons of Si
 2  &inputph
 3    tr2_ph=1.0d-14,
 4    amass(1)=28.0855,
 5    prefix='SIPH',
 6    !outdir='directory where large files are written/'
 7    outdir='./tmp'
 8    fildyn='si.dyn',
 9    ldisp = .true.,
10    nq1 = 4, nq2 = 4, nq3 = 4
11  /
12
```

Figure 9: Input file for ph.x

From the output of ph.x, we get .dyn files which are the force constants in the reciprocal space. We use q2r.x module to convert these to real space. Once we have done that, we use matdyn.x module to get the phonon density of states. Figure below shows the input of matdyn.x

```
&input
 asr = 'simple'
 dos = .true.
 amass(1) = 28.0855
 flfrc = 'si.k444.fc'
 fldos = 'si.phdos'
 nk1=50, nk2=50, nk3=50
 /
```

Figure 10: Matdyn.x input file

After running it, we get the si.phdos file using which, we plot the phonon density of states as shown on the next page.
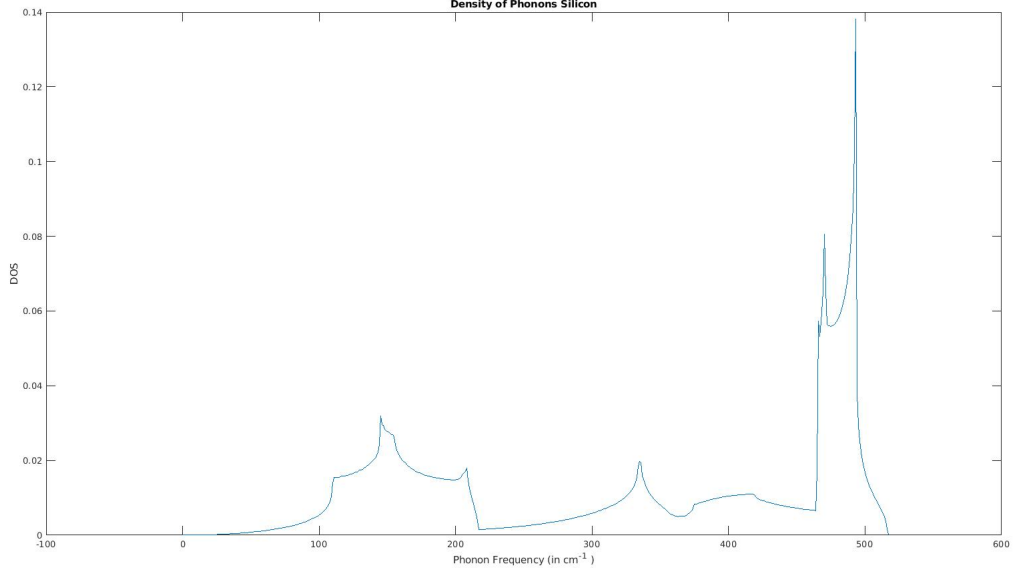
Figure 11: Silicon Phonon Density of States

To get the phonon dispersions, we follow the same steps and make a small change in matdyn.x input file. $flfrq =' si.dos.freq', q\_in\_band\_form = .true., q\_in\_cryst\_coord = .true.$. We also provide the K points over which we have to calculate the dispersion relation. We choose Γ - X - K - Γ - L k path. The dispersion relation is shown below.
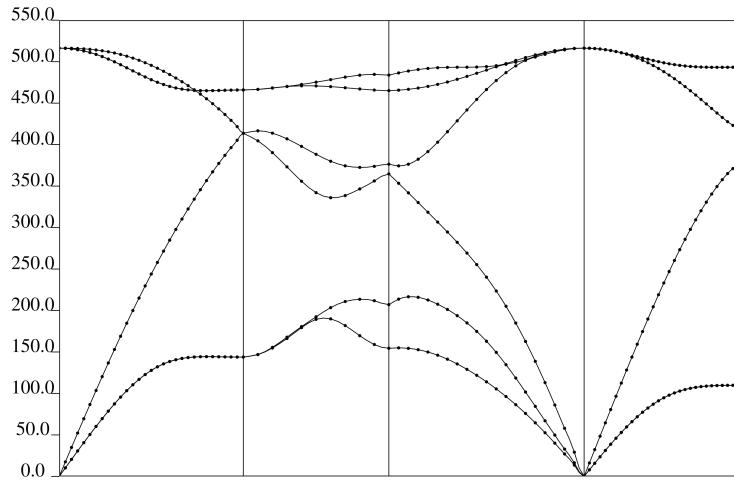

Figure 12: Dispersion Relation of Silicon

With this, we conclude the simulation results for Silicon.

Aluminum

We follow a similar procedure to that of Silicon. Some points which are to be observed. Metals have a slow convergence and may require a lot more dense k point grid, very high cut off values to achieve convergence. Another parameters called Occupations is mentioned in SCF calculations. We digress here to briefly state its meaning and usage.

1. **Brief Note on Occupations**
When finding the density by summing up the kohn sham energy eigen wavefunctions, discrete k points are used in the Brillouin zone. For each state, the occupancy of that state binary (0 or 1). However, for metals the bands crossing the Fermi level are only partially occupied, and a discontinuity exists at the Fermi surface, where the occupancies suddenly jump from 1 to 0. In this case, one will often need a prohibitively large amount of k-points in order to make calculations converge. To avoid using a large number of K points, we choose a distribution function that varies smoothly over 0 to 1 close to the Fermi Energy for the occupancy. (Eg : Fermi Dirac distribution) Available options in occupations are :
• smearing (as explained in previous slide, using a smooth distribution function)
• tetrahedra (well suited for DOS calculations, not for force/optimization/dynamics calculations)
• tetrahedra_lin
• tetrahedra_opt
• fixed (for insulators with a band gap)
• from_input
Types of Smearing :
• gaussian or gauss
• methfessel-Paxton
• marzari-Vanderbilt
• fermi-dirac

2. **Convergence Results**
We did similar convergence test for aluminum. It takes more iterations in case of Aluminium to obtain convergence. We present the results for convergence w.r.t. K points, ecutwfc, lattice parameter (we also perform a vc-relax calculation to get exact equilibrium lattice parameter)
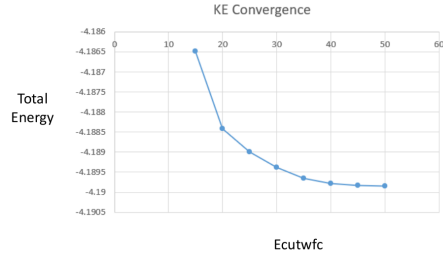
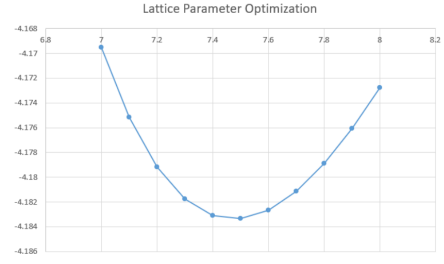Figure 13: Convergence w.r.t cut-off energy
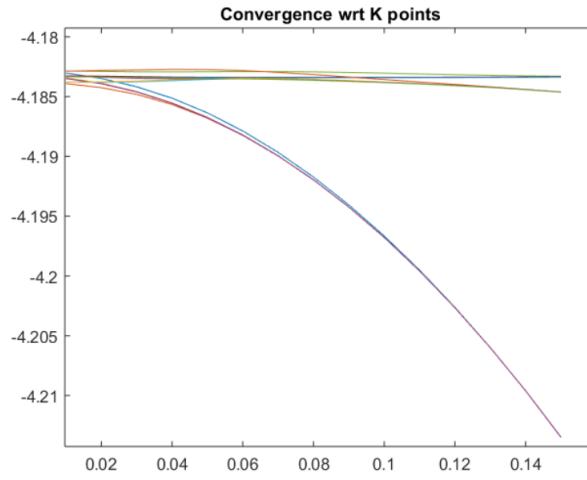

Figure 14: Lattice Paramter vs total energy

Figure 15: Convergece wrt K points for three different types of Smearing

From the figure, we can see that by varying K points, not much change was seen.

3. **Bandstructure**

Initially, we do a vc-relax calculation to get the exact lattice paramters. The figure below shows the vc-relax input file. We have used MP smearing with a degauss of 0.01 and ecutwfc of 50 Ry (as obtained from convergence) From the output, we get the equilibrium lattice parameter of 7.487559216 a.u. We show the input file for vc-relax calculation on the next page.

```
 1 | &control
 2     prefix='al'
 3         calculation='vc-relax',
 4     outdir='./tmp',
 5     pseudo_dir='./',
 6         etot_conv_thr = 1e-6 ,
 7     forc_conv_thr = 1e-5
 8
 9 /
10 &system
11     ibrav=  2, celldm(1) =7.6, nat=  1, ntyp= 1,
12     ecutwfc =50.0,
13     occupations='smearing', smearing='methfessel-paxton', degauss=0.01
14 /
15 &electrons
16     conv_thr=1e-8
17 /
18 &ions
19
20 /
21 &cell
22     cell_dofree='ibrav'
23 /
24 ATOMIC_SPECIES
25  Al   26.98 Al.pz-vbc.UPF
26
27 ATOMIC_POSITIONS (alat)
28  Al 0.00 0.00 0.00
29
30 K_POINTS (automatic)
31    12 12 12 0 0 0
```

Figure 16: vc-relax input file

We then proceed with the SCF and bands.x modules as we did for Silicon. We increase K points to 15 x 15 x 15 monkhorst pack grid for SCF calculation. We use the following K path : Γ - X - U-K - Γ - L - W - X We get the bandstructure shown
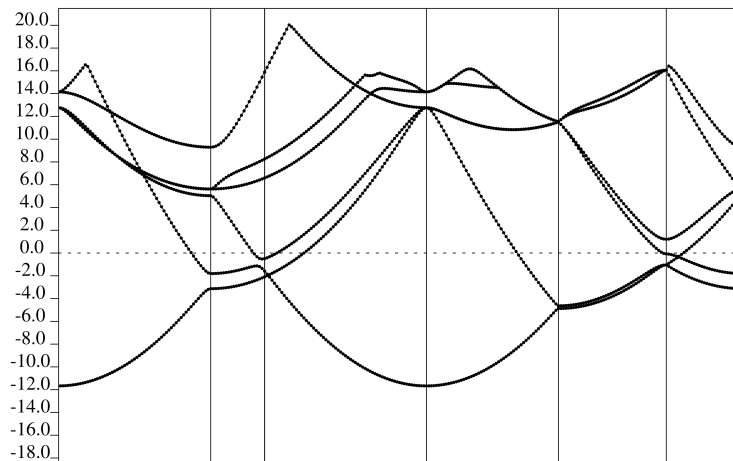

Figure 17: Aluminum Bandstructure

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We can see that the conduction and valence bands intersect and the zero energy (fermi energy used as reference) crosses the conduction band which proves that Aluminum is conducting in nature. In the matlab plot below, we show this fact by plotting the fermi energy which we get from scf calculations.
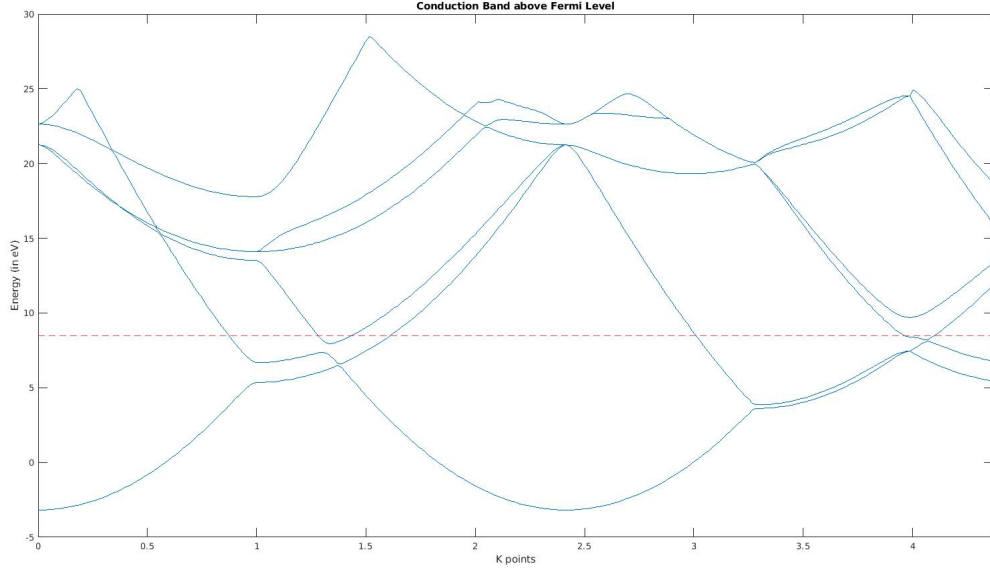

Figure 18: Location of Fermi Energy

4. Density of States

With a similar procedure as given in silicon, but using denser set of k point grid for nscf calcuation, we get the DOS as well as orbital projected DOS using projwfc.x
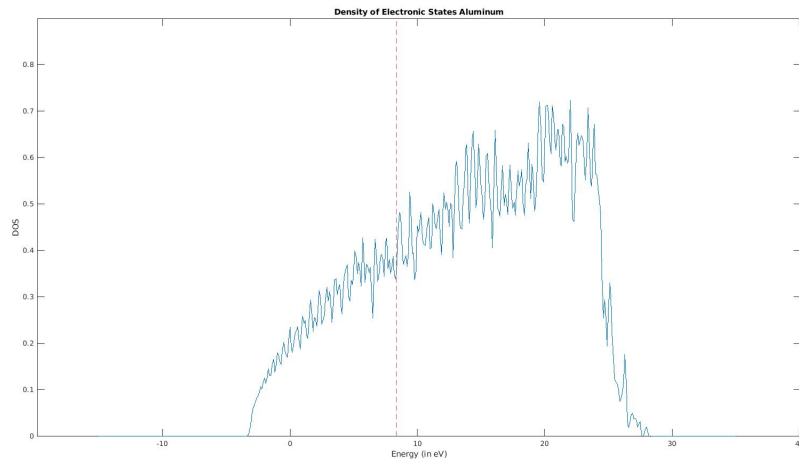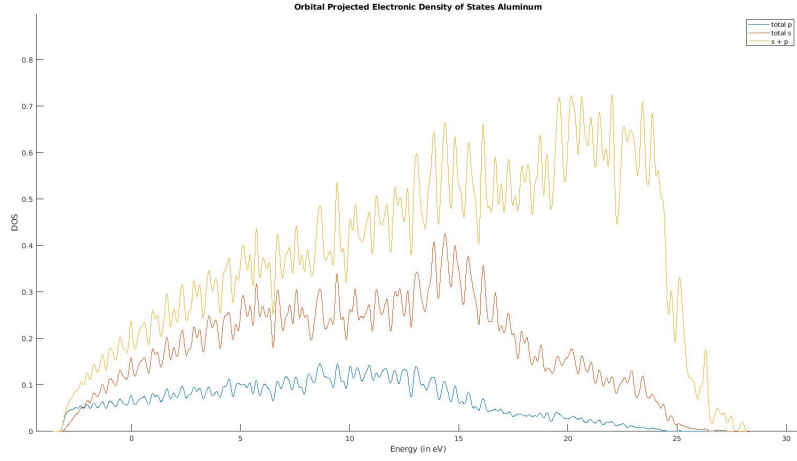

Figure 19: Electronic DOS of Al

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Figure 20: Orbital projected DOS

5. **Phonons**

Again, we use a similar procedure. For ph.x, we use a 4 x 4 x k point grid. And for matdyn.x, we use a 50 x 50 x 50 k point grid for phonon dos. We get the following phonon density of states
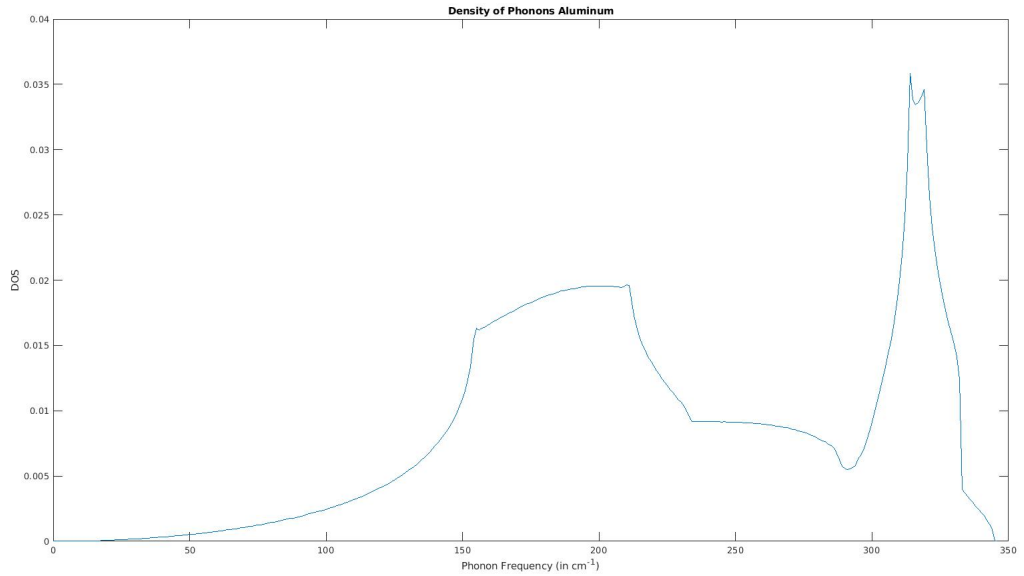

Figure 21: Phonon Density of States Aluminum

For phonons, we use the following K path : Γ - X - U-K - Γ - L - W - X. We the phonon dispersion as shown on the next page.
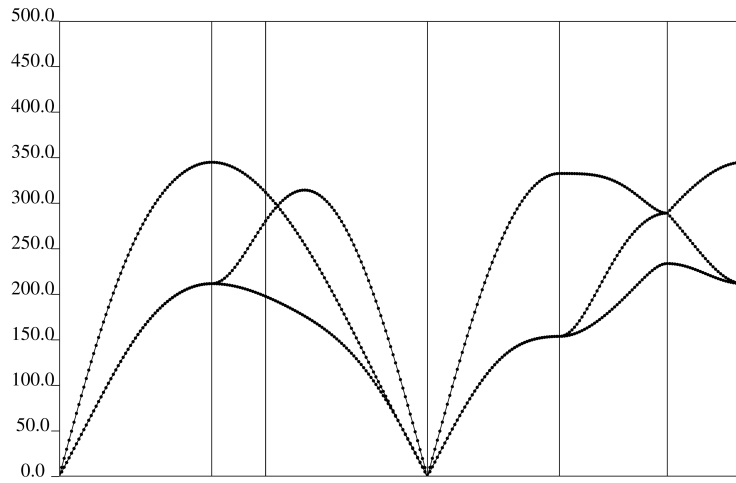
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Figure 22: Dispersion Relation for Aluminum

Note that we do not get any optical mode phonons as there is just a single atom present in the unit cell.

With this, we conclude the simulation results for Aluminum.

Acknowledgements

This summer project provided an opportunity to try out handson state of the art software for materials simulation. Many of the concepts viz. Density Functional Theory, Density of States and various other concepts in Solid State Physics were studied from scratch. I am extremely privileged to be guided by Prof. Dipanshu Bansal in this project. I respect and thank him for providing me this opportunity to do the project work which has opened new opportunities for me.

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