

Electronic structure and thermoelectric properties of the intermetallic compound Yb_2Ge

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A thesis submitted to the
University of Madras
in partial fulfillment of the requirements
for the award of the degree of

Master of Science
in Physics

MARCH 2019



DEPARTMENT OF PHYSICS
DWARAKA DOSS GOVERDHAN DOSS VAISHNAV COLLEGE

Acknowledgements

The author wishes to thank Dr. R Vidya, for her guidance and valuable inputs given during the entire course of the project, which was pivotal not just in gaining an understanding of the subject of Density Functional Theory, but also in shaping appreciation towards the subject. The Head of the Department of Medical Physics at Anna University is also acknowledged for providing the amenities and environment to carry out the project.

The author wishes to thank Dr. D Syamala, the Head of the Department of Physics (Shift -2) at Dwaraka Doss Goverdhan Vaishnav College for her constant push to achieve higher and loftier in academic pursuits. The author also wishes to thank Prof. M Amudha for promptly monitoring the developments of the project. The faculty of the Department are also acknowledged for their immense support in this endeavour.

The author wishes to thank Mr. T Premkumar and the research scholars of the Department of Medical Physics for helping out with the details of computation using Quantum ESPRESSO and for sustaining an atmosphere conducive for learning and discussion.

Abstract

Thermoelectrics are materials that can generate electricity by application of a temperature gradient or vice versa through thermoelectric effect. Thermoelectrics could play a major role in the global search for sustainable energy. The intermetallic compound Yb_2Ge is identified here as a viable material for the construction of thermoelectric devices. The properties of this material have been studied computationally using density functional theory (DFT). In this regard, the open-source software Quantum ESPRESSO has been used to perform calculations such as self-consistent field (scf), geometrical optimization (opt), density of states (dos), bands structure (bands) and transport properties on Yb_2Ge . The electronic band structure calculations show that Yb_2Ge has a small band gap with a narrow peak in the density of states close to Fermi level. The conduction band minima and the valence band maxima are dispersed, which is desirable for a higher electrical conductivity. This characteristic often indicates a large thermopower, which is a necessary requirement for good thermoelectric performance.

Keywords: Density Functional Theory, Thermoelectrics, Intermetallics, Yb_2Ge , Quantum ESPRESSO, Band Structure, Density of States.

§1 Introduction

The production and conversion of energy into various forms for practical applications are among the most pivotal endeavours of human civilization. In the recent decades there has been a greater awareness about the ills of fossil fuels and recognition of their advancing scarcity. The emission of greenhouse gases and its impact on global climate change poses a major threat to the existence of the planet. Therefore a frantic search for more sustainable energy sources is timely.

In this regard thermoelectric materials have been receiving widespread attention in recent times because they serve a vital role in the sustainable energy crisis. One way of improving the sustainability of electricity is through scavenging of waste heat with suitable thermoelectric devices. Other energy conversion devices such as solar cells and fuel cells are also relevant, but their large scale commercialization is crippled by factors such as their poor efficiency, high cost and poor long term stability. Thermoelectric devices can theoretically convert any form of heat, including solar and waste heat into electricity. An added advantage of thermoelectric generators would be the lack of moving parts and are therefore free of vibration and noise during production. This makes solid state thermoelectric generators to be silent, reliable, and scalable. [1]

Efforts to replace the alternator in cars with a thermoelectric generator mounted on the exhaust stream are already underway, thereby improving fuel efficiency. Further, the advances in thermoelectrics could similarly enable the replacement of compression-based refrigeration with solid-state Peltier coolers. Most of the currently studied thermoelectrics possess a conversion efficiency

of 5-20%. This can further be enhanced experimentally by methods such as doping, alloying and nanostructuring.[2] Finding newer materials which can be used as thermoelectrics is also a prime area of research.

Currently, there are three approaches to find better thermoelectric material.

These are stated below:

- traditional experimental approach
- quantum mechanics based computational approach like Density Functional Theory (DFT), and
- recent machine learning (ML) based data-driven approach.

Amongst these, the traditional experimental approaches are not an efficient way of exploring new unknown structural and thermoelectric properties as they focus mostly on modifying known material compounds by doping and nano-structuring in order to make known thermoelectric materials better.

Although machine learning based approach has shown some success in finding new materials with good structural properties (that are capable of being a thermoelectric), ML is a nascent application area, where, obtaining bountiful data is an expensive process.[3]

Therefore, the Density functional theory based computational approach would produce results that are quite in agreement with experimental results, in addition to being theoretically sound and accurate. The results generated by DFT could potentially be used to make more precise experimentation and would drastically reduce wastage of resources. The massive amounts of data generated by DFT computations could also serve as primer data for training ML, and a trained ML is expected to save time in finding potential material in the vast material search-space.

§1.1 Introduction to thermoelectrics

Thermoelectrics are materials that can generate electricity from the application of a temperature gradient, or vice versa, through the Seebeck-Peltier thermoelectric effect. By exploiting this coupling between thermal and electrical properties, thermoelectric devices can be made that carry heat from a cold to a hot side (refrigeration) or that generate electricity from heat flows.

The fundamental principles governing thermoelectricity have been established over the past 200 years. However, the development of superior thermoelectric materials requires an in-depth understanding of the electron and phonon transport phenomena in such materials.[4] Inorganic materials are classic materials that are prominently used in thermoelectric research.

Some examples include skutterudites, telluride-based materials (e.g., PbTe, Bi₂Te₃, etc.), rare earth chalcogenides (e.g., La_{3-x}Te₄), copper ion liquid-like materials (e.g., Cu₂Se), Si–Ge alloys, half-Heusler (HH) alloys, and clathrates.

Recently, new classes of materials such as carbon nanomaterials, electronically conducting polymers, carbon nanomaterials and polymer nanocomposites have been proposed. The percentage contribution of these materials to thermoelectric technologies is presented in Fig. 1.1

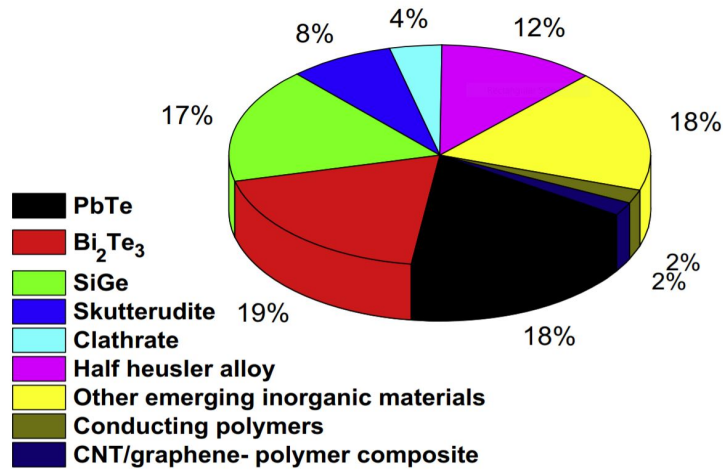


Fig. 1.1 The percentage contribution of different materials to thermoelectric devices.

§1.2 Seebeck and Peltier Effects

The conversion of the temperature difference between two non-similar electrical conductors or semiconductors directly into electric potential is known as Seebeck effect. This is explained by the fact that the electron energy levels in each metal or semiconductor shifted differently and a potential difference between the junctions, which in turn creates an electric current. The reverse case is also applicable where an application of potential difference to the two dissimilar electrical conductors will give rise to a difference in temperature at their junction. This is referred to as Peltier effect.

§1.3 Conflicting properties in thermoelectrics

The efficiency of a thermoelectric device is determined by the dimensionless quantity called ‘figure of merit’, which is defined by :

$$ZT = \frac{\sigma \alpha^2 T}{\kappa}$$

where, α is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity of the material. In order to maximize the thermoelectric figure of merit (ZT) of a material, a large thermopower (absolute value of the Seebeck coefficient), high electrical conductivity, and low thermal conductivity are required.

As these transport characteristics depend on interrelated material properties, a number of parameters need to be optimized to maximize ZT .

To ensure that the Seebeck coefficient is large, there should only be a single type of carrier. Mixed n-type and p-type conduction will lead to both charge carriers moving to the cold end, cancelling out the induced Seebeck voltages. Low carrier concentration insulators and even semiconductors have large Seebeck coefficients. However, low carrier concentration also results in low electrical conductivity. The interrelationship between carrier concentration and Seebeck coefficient can be seen from relatively simple models of electron transport. For metals or degenerate semiconductors the Seebeck coefficient is given by:

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}$$

where n is the carrier concentration and m^* is the effective mass of the carrier. The electrical conductivity (σ) and electrical resistivity (ρ) are related to n through the carrier mobility μ , given by:

$$\frac{1}{\rho} = \sigma = ne\mu$$

The effective mass of the charge carrier provides another conflict as large effective masses produce high thermopower but low electrical conductivity. The m^* in the above equation refers to the density-of-states effective mass, which increases with flat, narrow bands with high density of states at the Fermi surface.

However, as the inertial effective mass is also related to m^* , heavy carriers will move with slower velocities, and therefore small mobilities, which in turn leads to low electrical conductivity. The exact relationship between effective mass and mobility is complex, and depends on electronic structure, scattering mechanisms and anisotropy.

An ideal thermoelectric material must exhibit (a) high electrical conductivity, (b) high Seebeck coefficient, and (c) low thermal conductivity. The high Seebeck coefficient ensures a large potential, the high electrical conductivity is needed to minimize the Joule heating effect, and the low thermal conductivity is needed to create a large temperature gradient. Proper control of these parameters for a single material is a challenging task. By lowering the lattice thermal conductivity and by optimizing the electronic thermal conductivity, low thermal conductivity can be obtained.

§2 Density Functional theory

Consider a situation where the properties of a well-defined collection of atoms are to be described. One of the important things to learn about this system would be the total energy of the system and also the variation of total energy if these atoms were to move around. In order to define the position of an atom, one has to define both the positions of the atomic nucleus and the position of its electrons.

An important observation to be made here is that the atomic nuclei are much heavier than the electrons. This means that the electrons respond much more rapidly to changes in their surroundings than nuclei can respond. Thus the problem is now split into parts. First, one solves, for fixed positions of the atomic nuclei, the equations that describe the electron motion. For a given set of electrons moving in the field of a set of nuclei, one finds the lowest energy configuration, or state, of the electrons. The lowest energy state is known as the ground state of the electrons, and the separation of the nuclei and

electrons into separate mathematical problems is the Born – Oppenheimer approximation.

If the M nuclei are at positions $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M$, then one can express the ground state energy E as a function of the positions of these nuclei, $E(\mathbf{R}_1, \dots, \mathbf{R}_M)$. This function is known as the adiabatic potential energy surface of the atoms.

Once this potential energy is calculated the original problem of finding the change in energy of the material as the atoms are moved around, can be calculated.

§2.1 The Schrödinger Equation

Consider the same collection of atoms with M nuclei and N electrons. The time independent Schrödinger equation corresponding to this system is given by:

$$\left[\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j<i}^N U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi = E\psi$$

Here, m is the mass of the electron. The three terms in brackets in this equation define, in order, the kinetic energy of each electron, the interaction energy between each electron and the collection of atomic nuclei, and the interaction energy between different electrons. For the Hamiltonian, ψ is the electronic wave function, which is a function of each of the spatial coordinates of each of the N electrons, therefore, $\psi = \psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, and E is the ground state energy of the electrons. The ground state energy is independent of time, hence this is the time-independent Schrödinger equation. Although the electron wave function is a function of each of the coordinates of all N electrons, it is possible to approximate ψ as a product of individual electron wave functions $\psi = \psi_1(\mathbf{r}_1) \cdot \psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N)$. This expression for the wave function is known as a Hartree product and serves as a good approximation.

§2.2 Electron Density

One should note that N , the number of electrons, is considerably larger than M , the number of nuclei, simply because each atom has one nucleus and lots of electrons. If one is interested in a single molecule of CO_2 , the full wave function would be a 66-dimensional function (3 dimensions for each of the 22 electrons). If one is interested in a nanocluster of 100 Pt atoms, the full wave function requires more the 23,000 dimensions! These numbers give an insight about why solving the Schrödinger equation for practical materials has occupied many brilliant minds for a good fraction of a century.[5]

The term in the Hamiltonian defining electron-electron interactions is the most critical one from the point of view of solving the equation. The form of this contribution means that the individual electron wave function defined above, $\psi_i(\mathbf{r})$, cannot be found without simultaneously considering the individual electron wave functions associated with all the other electrons. In other words, the Schrödinger equation is a many-body problem.

Although solving the Schrödinger equation can be viewed as the fundamental problem of quantum mechanics, it is worth realizing that the wave function for any particular set of coordinates cannot be directly observed. The quantity that can (in principle) be measured is the probability that the N electrons are at a particular set of coordinates.

This probability is equal to $|\psi_i(\mathbf{r})|^2$. A closely related quantity is the density of the electrons at a particular position in space, $n(\mathbf{r})$. This can be written in terms of the individual electron wave functions as

$$n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

Here, the summation goes over all the individual electron wave functions that are occupied by electrons, so the term inside the summation is the probability that an electron in individual wave function $\psi_i(\mathbf{r})$ is located at position \mathbf{r} .

The factor of 2 appears because electrons have spin and the Pauli exclusion principle states that each individual electron wave function can be occupied by two separate electrons provided they have different spins. The conclusion of this discussion is that the electron density, $n(\mathbf{r})$, which is a function of only three coordinates, contains a great amount of the information that is actually physically observable from the full wave function solution to the Schrödinger equation, which is a function of $3N$ coordinates.

§2.3 Hohenberg - Kohn theorems

The entire field of density functional theory rests on two fundamental mathematical theorems proved by Kohn and Hohenberg and the derivation of a set of equations by Kohn and Sham in the mid-1960s.

The first theorem, proved by Hohenberg and Kohn, states as follows: “ The ground-state energy from Schrödinger equation is a unique functional of the electron density.”

This theorem states that there exists a one-to-one mapping between the ground-state wave function and the ground-state electron density, i.e., a functional. Thus the ground state energy E can be expressed as $E[n(\mathbf{r})]$, where $n(\mathbf{r})$ is the electron density. Hence this gets its due name - density functional theory. Another important observation made from Hohenberg and Kohn’s result is that the ground state electron density uniquely determines all the properties including the energy and wave function of the ground state. This is important because, one can use this to solve the Schrödinger equation by finding a function of three spatial variable, the electron density, rather than $3N$ variables.

Unfortunately, although the first Hohenberg-Kohn theorem rigorously proves that a functional of the electron density exists that can be used to solve the Schrödinger equation, the theorem says nothing about the nature of the functional.

The second Hohenberg –Kohn theorem defines an important property of the functional: The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.

If the “true” functional form were known, then one could vary the electron density until the energy from the functional is minimized, giving us a prescription for finding the relevant electron density. This variational principle is used in practice with approximate forms of the functional.

§2.4 The Kohn - Sham equation

A useful way to write down the functional described by the Hohenberg – Kohn theorem is in terms of the single-electron wave functions, $\psi_i(\mathbf{r})$. These functions collectively define the electron density, $n(\mathbf{r})$. The energy functional can be written as

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{\text{XC}}[\{\psi_i\}]$$

where the first term corresponds to the collection of terms one can write down in an analytical form, and everything else forms the second term. The ‘known’ term includes four contributions:

$$\begin{aligned} E_{\text{known}}[\{\psi_i\}] = & \frac{\hbar^2}{m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3 r + \int V(\mathbf{r}) n(\mathbf{r}) d^3 r \\ & + \frac{e^2}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' + E_{\text{ion}}. \end{aligned}$$

The terms on the right are, in order, the electron kinetic energies, the Coulomb interactions between the electrons and the nuclei, the Coulomb interactions between pairs of electrons, and the Coulomb interactions between pairs of nuclei. The other term in the complete energy functional, $E_{\text{XC}}[\{\psi_i\}]$, is the exchange correlation functional, and it is defined to include all the quantum mechanical effects that are not included in the ‘known’ terms.

Kohn and Sham showed that the task of finding the right electron density can be expressed in a way that involves solving a set of equations in which each equation only involves a single electron. The Kohn –Sham equations have the form

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{XC}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

This equation superficially appears similar to the previous equation; however the key difference is that the Kohn - Sham equation misses the summations that appear inside the full Schrödinger equation. This is because the solution of the Kohn–Sham equations are single-electron wave functions that depend on only three spatial variables, $\psi_i(\mathbf{r})$.

On the left-hand side of the Kohn–Sham equations there are three potentials, V , V_H , and V_{XC} . The first potential V defines the interaction between an electron and the collection of atomic nuclei. The second is called the Hartree potential and is defined by :

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r'.$$

This potential describes the Coulomb repulsion between the electron being considered in one of the Kohn –Sham equations and the total electron density defined by all electrons in the problem. The Hartree potential includes a self-interaction contribution because the electron described in the Kohn – Sham equation is also part of the

total electron density, so part of V_H involves a Coulomb interaction between the electron and itself.

The self interaction is unphysical, and the correction for it is one of several effects that are lumped together into the final potential in the Kohn–Sham equations, V_{XC} , which defines exchange and correlation contributions to the single electron equations. V_{XC} can formally be defined as a functional derivative of the exchange – correlation energy:

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})}.$$

§2.5 Iterative algorithm to solve the Kohn - Sham equation

To solve the Kohn – Sham equations, the Hartree potential must be defined, and to define the Hartree potential one must know the electron density. But in order to find the electron density, one must know the single-electron wave

functions, and to know these wave functions one must solve the Kohn – Sham equations. To break this circle, the problem is usually treated in an iterative way as outlined in the following algorithm:

1. Define an initial, trial electron density, $n(\mathbf{r})$.
2. Solve the Kohn – Sham equations defined using the trial electron density to find the single-particle wave functions, $\psi_i(\mathbf{r})$.
3. Calculate the electron density defined by the Kohn –Sham single particle wave functions from step 2,

$$n_{KS}(\mathbf{r}) = 2 \sum \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}).$$

4. Compare the calculated electron density, $n_{KS}(\mathbf{r})$, with the electron density used in solving the Kohn –Sham equations, $n(\mathbf{r})$. If the two densities are the same, then this is the ground-state electron density, and it can be used to compute the total energy. If the two densities are different, then the trial electron density must be updated in some way. Once this is done, the process begins again from step 2.

This iterative method can lead to a solution of the Kohn – Sham equations that is self-consistent.

§2.6 Exchange correlation functional

To solve the Kohn - Sham equation iteratively using the algorithm described above, one must first perform the difficult task of defining the exchange correlation functional, $E_{\text{XC}}[\{\psi_i\}]$.

In fact, the true form of the exchange –correlation functional whose existence is guaranteed by the Hohenberg –Kohn theorem is simply not known. Fortunately, there is one case where this functional can be derived exactly: the uniform electron gas.

In this situation, the electron density is constant at all points in space; that is, $n(\mathbf{r}) = \text{constant}$. This situation may appear to be of limited value in any real material since it is variations in electron density that define chemical bonds and generally make materials interesting. But the uniform electron gas provides a practical way to actually use the Kohn – Sham equations. To do this, one can set the exchange – correlation potential at each position to be the known exchange – correlation potential from the uniform electron gas at the electron density observed at that position:

$$V_{\text{XC}}(\mathbf{r}) = V_{\text{XC}}^{\text{electron gas}}[n(\mathbf{r})].$$

This approximation uses only the local density to define the approximate exchange – correlation functional. Hence it is called the local density approximation (LDA). The LDA gives us a way to completely define the Kohn– Sham equations, but it is crucial to remember that the results from these equations do not exactly solve the true Schrödinger equation because the true exchange –correlation functional for the system is not being used. The development of functionals that more faithfully represent nature remains one of the most important areas of active research in quantum physics.

The best known class of functional after the LDA uses information about the local electron density and the local gradient in the electron density; this approach defines a generalized gradient approximation (GGA). It is tempting to think that because the GGA includes more physical information than the LDA it must be more accurate. Unfortunately, this is not always correct.

It is because there are many ways in which information from the gradient of the electron density can be included in a GGA functional, there are a large number of distinct GGA functionals. Two of the most widely used functionals in calculations involving solids are the Perdew –Wang functional (PW91) and the Perdew –Burke–Ernzerhof functional (PBE). Each of these functionals are GGA functionals, and dozens of other GGA functionals have been developed and used, particularly for calculations with isolated molecules.

Since different functionals give different results for any particular configuration of atoms, it is necessary to specify the functional used in any particular calculation. The current description of GGA functionals as including information from the electron density and the gradient of this density suggests that more sophisticated functionals can be constructed that use other pieces of physical information.

The use of LDA or GGA leads to significant error in total energy value for transition series elements. This error arises from the self-interaction error in LDA and GGA and can be corrected by adding a Hubbard value (U). This is applied mainly for those atoms containing valence d electrons, and is superfluous in the case of s block and p block elements.

§2.5 Quantum ESPRESSO

In order to carry out DFT based computations, one is in need of a software suite. The list of available softwares include are VASP (Vienna Ab initio Simulation Package), CP2K, Gaussian, TBLMTO

(Tight Binding Linear Muffin Tin Orbital Potential) package etc. However all the calculations presented in this thesis were performed on the open-source package Quantum ESPRESSO.

QUANTUM ESPRESSO is an integrated suite of computer codes for electronic structure calculations and materials modeling, based on density-functional theory, plane waves, and pseudopotentials (norm-conserving, ultrasoft, and projector-augmented wave).[6]

The basic computations/simulations that can be performed include:

- Calculation of the Kohn-Sham (KS) orbitals and energies for isolated or extended/periodic systems, and their ground-state energies;
- Complete structural optimizations, using Hellmann-Feynman forces and stresses
- Ground states for magnetic or spin-polarized system, including spin-orbit coupling and non-collinear magnetism.
- ab initio molecular dynamics (MD)
- density-functional perturbation theory (DFPT) to calculate second and third derivatives of the total energy at any arbitrary wavelength, providing phonon dispersions, electron-phonon and phonon-phonon interactions, and static response functions

§3 Computations on semiconductors, metals and insulators.

Before the DFT computation for a suitable thermoelectric is undertaken, computations are performed for a set of semiconductors, metals and insulators for studying their electronic properties from the respective band structure and density of states. A useful way to distinguish between metals, semiconductors and insulators is to plot the available energies for electrons at different quasi momenta (k points or k vectors) and visualize the obtained band structure. The bands for semiconductors show a very small band gap between the conduction and the valence band. This band gap could either be a direct band gap or an indirect band gap. The minimal-energy state in

the conduction band and the maximal-energy state in the valence band are each characterized by a certain quasi-momentum (k point) in the Brillouin zone. If the band gap is between the conduction band minimum and valence band maximum of the same k point, then the band gap thus formed is called a direct band gap. In such a case, electron in the valence band can jump to the conduction band without any change in k point.

However if the conduction band minimum and valence band maximum are of different k points, then the band gap is referred to as indirect band gap. In this case, the electron cannot jump from the highest energy state to the conduction band without a change in momentum. And such a transition is a phonon-assisted transition.

§3.1 Silicon

Consider two atoms of Silicon in a primitive cell. The known parameters such as the positions of the atoms and the cell parameter are given in the input file. The contents of the self consistent field (scf) calculation is in the input file given below.

§3.1.1 SCF calculation for Si

```
&CONTROL
  calculation = "scf"
  max_seconds = 8.64000e+04
  pseudo_dir = "C:\Users\Rohith\.burai\.pseudopot"
  tprnfor     = .TRUE.
  tstress     = .TRUE.
/
&SYSTEM
  a           = 5.46873e+00
  degauss     = 1.00000e-02
  ecutrho     = 1.00000e+02
  ecutwfc     = 2.50000e+01
  ibrav       = 2
  nat         = 2
  ntyp        = 1
  occupations = "fixed"
  smearing    = "gaussian"
/
&ELECTRONS
  conv_thr    = 1.00000e-06
```

```

        electron_maxstep = 200
        mixing_beta       = 7.00000e-01
        startingpot       = "atomic"
        startingwfc       = "atomic+random"
/

K_POINTS {automatic}
4 4 4 0 0 0

ATOMIC_SPECIES
Si      28.08550  Si.pbe-rrkj.UPF

ATOMIC_POSITIONS {angstrom}
Si      -4.101546   4.101546   4.101546
Si      -2.734364   2.734364   2.734364

```

§3.1.2 Lattice parameter optimization for Si

The trial value for the lattice parameter given is 5.46873 in Bohr units. This corresponds to approx. 10.2 Å. The conversion factor between Bohr units and Angstrom is 1a.u. (Bohr unit) = 0.52917720859 Å.

Once the scf calculation is performed, Quantum ESPRESSO computes the total energy of the system. The default value of energy is given in units of Rydberg (Ry). Here again, the conversion factor is 1Ry = 13.605698066eV. The following code is executed in order to optimize the lattice constant.

```

#!/bin/sh
rm -f si.eos.out si.etot_vs_alat
touch si.etot_vs_alat

for alat in 9.8 9.9 10.0 10.1 10.2 10.3 10.4 10.5 10.6 10.7 ; do

cat > si.eos.in << EOF
&control
    Calculation = 'scf',
    prefix='silicon',
    pseudo_dir='C:\Users\Rohith\.burai\.pseudopot',
    outdir='C:\Users\Rohith\output'
/
&system
    ibrav= 2, celldm(1)=$alat, nat= 2, ntyp= 1,
    ecutwfc = 20.0,
/
&electrons

```

```

/
ATOMIC_SPECIES
Si 28.086 Si.pz-vbc.UPF
ATOMIC_POSITIONS
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
K_POINTS automatic
4 4 4 1 1 1
EOF
pw.x -in si.eos.in > si.eos.out
grep -e 'lattice parameter' -e ! si.eos.out | \
awk '/lattice/{alat=$(NF-1)}/!/{print alat, $(NF-1)'}>> si.etot_vs_alat

done

```

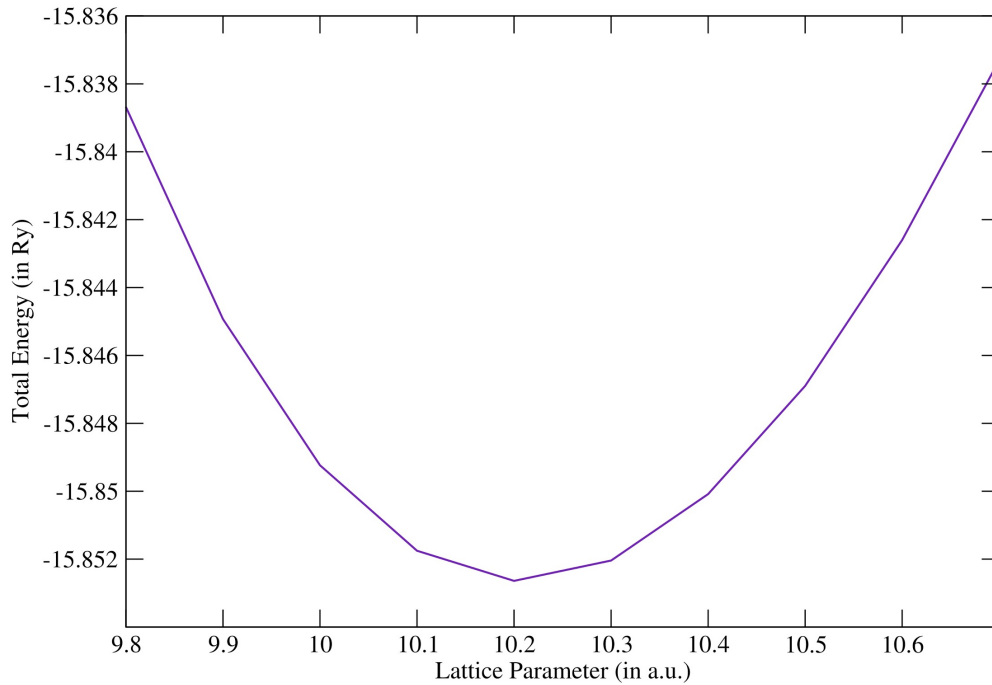


Figure 3.1 - Variation of Total Energy with lattice parameter (in a.u.)

The energy minimum corresponds to 10.2 a.u.

This result gives the total energy (in Ry) as a function of the lattice parameter expressed in a.u. (Bohr units). It can be deduced from Figure 3.1, that the energy is the least for the lattice constant value 10.2 Å. This now taken to be the optimized value for lattice parameter for further calculations.

When the code is executed through multiple iterations, the value of the total energy saturates. This is a necessary test for the convergence of total energy. If convergence is not achieved then the given input file must be modified or optimized so as to achieve convergence. Figure 3.2 shows that convergence of total energy has been achieved below in a few iterations.

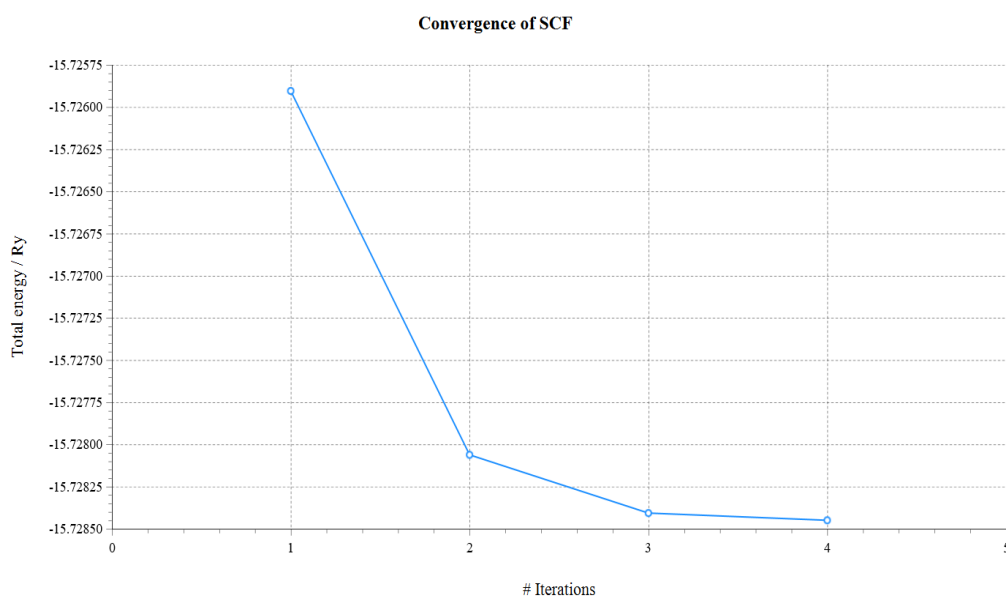


Figure 3.2 - The convergence of total energy has been achieved after 4 iterations.

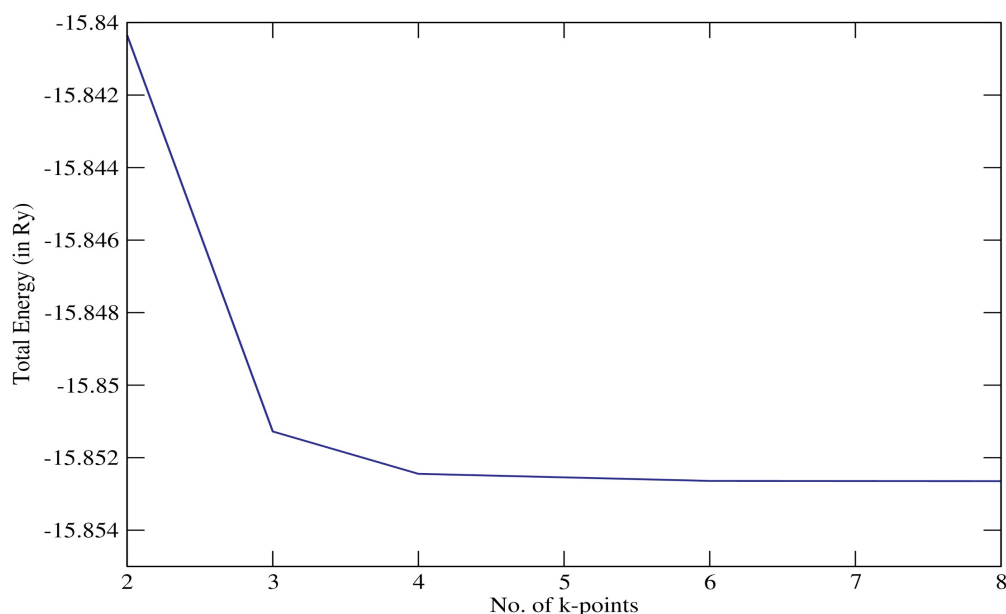


Figure 3.3 - The variation between number of k points and total energy.

The variation between the number of k points and total energy is given in Figure 3.3. The saturation of total energy occurs with a greater number of k points used in the k point grid.

The output of the scf file gives the total energy calculated along with the energy contribution due to one-electron contribution, hartree contribution, exchange correlation contribution and ewald contribution. The one electron contribution is the energy corresponding to the Coulombic attraction between an electron and the nucleus. The Hartree energy is a correction term and arises due to the self interaction between and electron and itself.

The other unknown terms form a part of the exchange correlation energy and is verily dependent on the nature and type of the pseudopotential used in calculation of scf. A change in

pseudopotential will accordingly change the exchange correlation functional, its corresponding exchange correlation energy and consequently the total energy.

```
highest occupied level (ev):    6.0835
```

```
total energy          =   -15.85264031 Ry
Harris-Foulkes estimate =   -15.85264035 Ry
estimated scf accuracy <    0.00000009 Ry
```

The total energy is the sum of the following terms:

```
one-electron contribution =    4.78582276 Ry
hartree contribution      =    1.07820387 Ry
xc contribution           =   -4.81690833 Ry
ewald contribution        =   -16.89975862 Ry
```

```
convergence has been achieved in   5 iterations
```

§3.1.3 Band Structure calculation for Si

In order to calculate the band structure for Si, the k point path through high symmetry points must be specified, along with the required number of grid points. The intermediate grid points are given so as to obtain a smooth curve for band structure.

```
&CONTROL
  calculation = "bands"
  max_seconds = 8.64000e+04
  pseudo_dir  = "C:\Users\Rohith\.burai\.pseudopot"
  tprnfor     = .TRUE.
  tstress     = .TRUE.
/

&SYSTEM
  a          = 5.46873e+00
  degauss    = 1.00000e-02
  ecutrho    = 1.00000e+02
  ecutwfc    = 2.50000e+01
  ibrav      = 2
  nat        = 2
```



```

        nbnd          = 8
        ntyp          = 1
        occupations    = "fixed"
        smearing       = "gaussian"
/

&ELECTRONS
    conv_thr          = 1.00000e-06
    electron_maxstep   = 200
    mixing_beta        = 7.00000e-01
    startingpot        = "atomic"
    startingwfc        = "atomic+random"
/

&BANDS
    lsym              = .FALSE.
    spin_component     = 1
/

K_POINTS {tpiba_b}
12
gG      20
X       20
W       20
K       20
gG      20
L       20
U       20
W       20
L       20
K       0
U       20
X       0

ATOMIC_SPECIES
Si      28.08550  Si.pbe-rrkj.UPF

ATOMIC_POSITIONS {angstrom}
Si      -4.101546  4.101546  4.101546
Si      -2.734364  2.734364  2.734364

```

The term `degauss` indicated in the input file refers to the value of Gaussian spreading (in Ry) for Brillouin zone integration in metals. It is typically zero for non metals. Since Si is a semiconductor, it is assigned a value of 0.01Ry. The parameters `ecutrho` and `ecutwfc` correspond to the optimized values for charge density cutoff and kinetic energy cutoff respectively.

The output for the band structure calculation results in a number of .dat files, which can be appropriately plotted using tools such as XMGrace or GNUplot to obtain the band structure. Along with this, non self-consistent field calculation and the density of states calculation are also performed and plotted in Figure 3.4 and Figure 3.5.

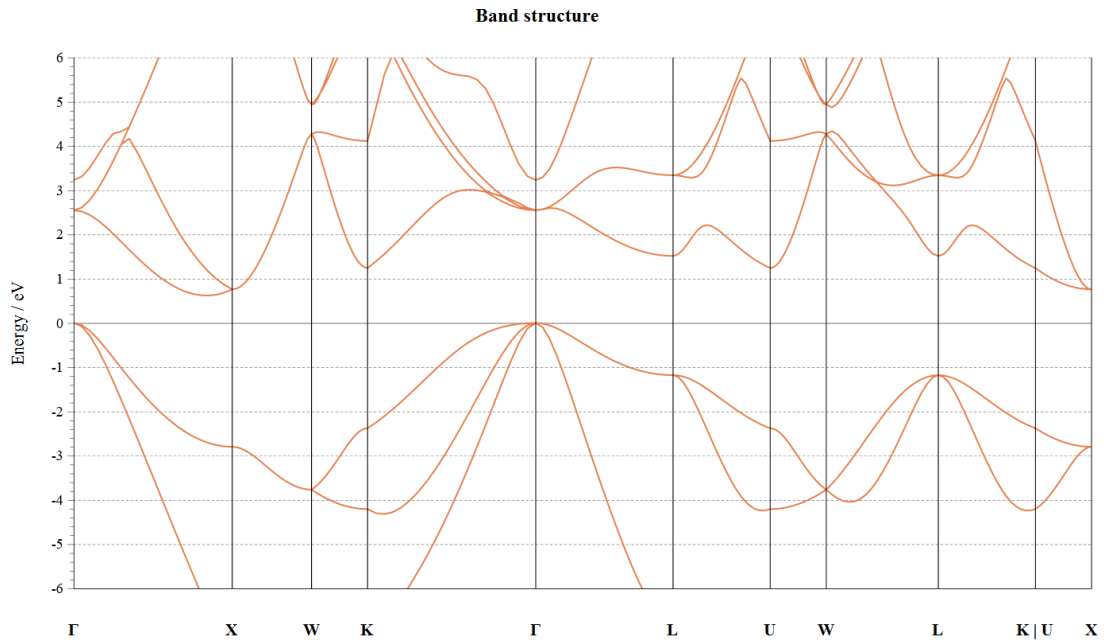


Figure 3.4 - Band Structure for Si showing a small band gap which is characteristic of a semiconductor.

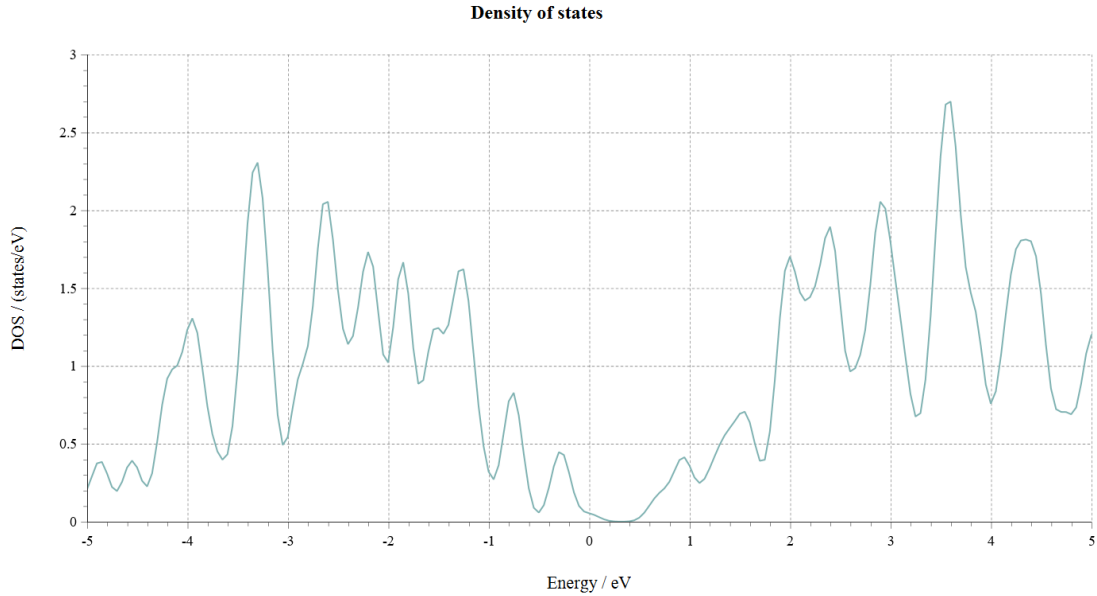


Figure 3.5 - Density of states for Si

§3.1.4 Results and discussion for Si

The following observations about the semiconducting material Si can be made from the band structure and dos.

- The valence bands stay well below the Fermi energy level as is expected from any material.
- A very narrow band gap of about 0.7672 eV is obtained from the data. This is less when compared to the experimental value of 1.14 eV. This is explained by the fact that DFT tends to underestimate the band gap. Physically, this discrepancy arises because the true, exact Kohn-Sham exchange-correlation functional depends on the total electron number and changes as the total electron count passes through each integer; This is generally referred to as the derivative discontinuity.
- The band gap for Si is an indirect band gap. This means that an electron in the valence band of Si jumps to the conduction

band only by a change in quasi momentum (k point). This is referred to as phonon assisted transition.

- The density of states for Si shows a gap, roughly about 0.6 eV near the Fermi energy level. This value is in accordance with the known experimental value.
- The various peaks in the density of states indicate that a majority of electrons have an energy level corresponding to these states.

§3.2 Aluminium

Now the various fore-mentioned calculations are repeated for Aluminium. Aluminium has only one atom per unit cell in an fcc lattice. Since Al is a metal, a significant difference in certain input parameters is expected. Consequently, the results would also be in tune with that for a conductor, such as crossing of bands etc.

§3.2.1 SCF calculation for Al

```
&CONTROL
  calculation = "scf"
  max_seconds = 8.64000e+04
  pseudo_dir = "C:\Users\Rohith\.burai\.pseudopot"
/

&SYSTEM
  a          = 4.03893e+00
  degauss    = 1.00000e-02
  ecutrho     = 1.00000e+02
  ecutwfc    = 2.50000e+01
 ibrav       = 2
  nat        = 1
  ntyp       = 1
  occupations = "smearing"
  smearing    = "marzari-vanderbilt"
/

&ELECTRONS
  conv_thr      = 1.00000e-06
  electron_maxstep = 200
  mixing_beta    = 7.00000e-01
  startingpot     = "atomic"
  startingwfc     = "atomic+random"
/
```

```

K_POINTS {automatic}
  5  5  5  0  0  0

ATOMIC_SPECIES
Al      26.98154  Al.pbe-rrkj.UPF

ATOMIC_POSITIONS {angstrom}
Al      0.000000  0.000000  0.000000

```

It is noteworthy to mention that new parameters such as occupations, smearing and degauss acquire relevance. There are potentially three different values for smearing - gauss (g), marzari-vanderbilt (mv) and methfessel-paxton (mp). Each of these present a different sampling method for Brillouin-zone integration in metals which converges exponentially with the number of sampling points. The scf calculation is performed for each setting with different values for degauss and the results are compared.

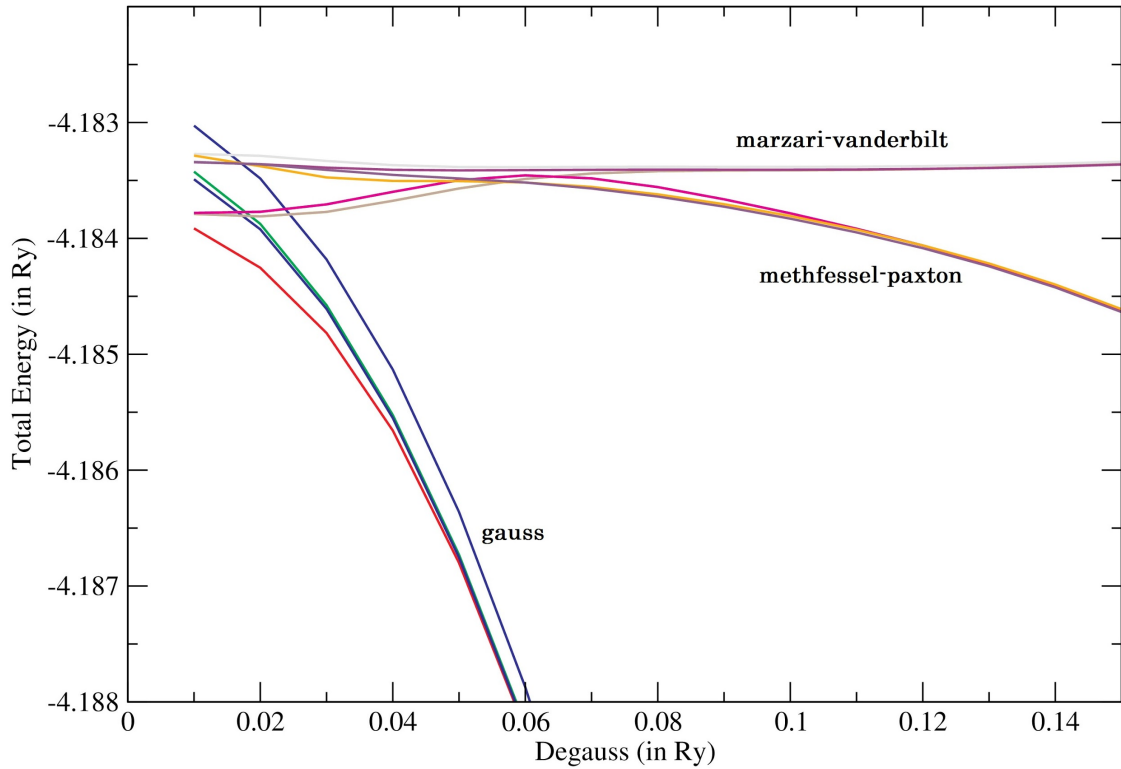


Figure 3.6 - The total energy is expressed as a function of degauss for various values of smearing.

It can be seen from Figure 3.6 that the energy bands are saturated for marzari-vanderbilt value of smearing. This parameter is used for further calculations of bands and dos.

§3.2.2 Band Structure calculation for Al

```
&CONTROL
  calculation = "bands"
  max_seconds = 8.64000e+04
  pseudo_dir = "C:\Users\Rohith\.burai\.pseudopot"
/
&SYSTEM
  a          = 4.03893e+00
  degauss    = 1.00000e-02
  ecutrho    = 1.00000e+02
  ecutwfc    = 2.50000e+01
  ibrav      = 2
  nat        = 1
  nbnd       = 4
  ntyp       = 1
  occupations = "smearing"
  smearing   = "marzari-vanderbilt"
/
&ELECTRONS
  conv_thr    = 1.00000e-06
  electron_maxstep = 200
  mixing_beta = 7.00000e-01
  startingpot = "atomic"
  startingwfc = "atomic+random"
/
&BANDS
  lsym        = .FALSE.
  spin_component = 1
/
K_POINTS {tpiba_b}
12
gG    20
X     20
W     20
K     20
gG    20
L     20
U     20
W     20
L     20
K     0
U     20
X     0

ATOMIC_SPECIES
```

Al 26.98154 Al.pbe-rrkj.UPF

ATOMIC_POSITIONS {angstrom}

Al 0.000000 0.000000 0.000000

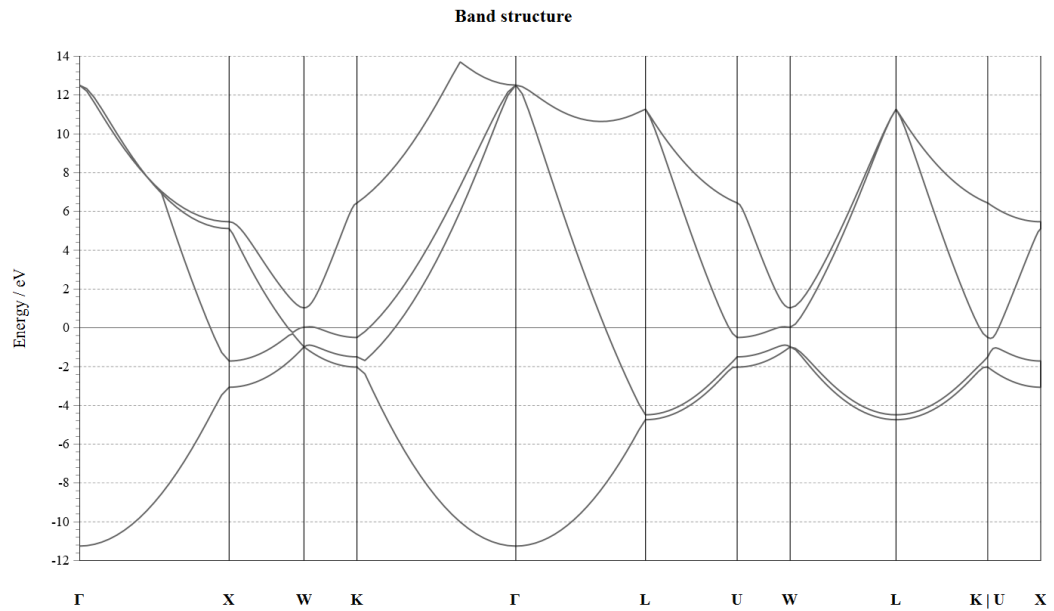


Figure 3.7 - The band structure for Al with overlapping bands characteristic of a metal.

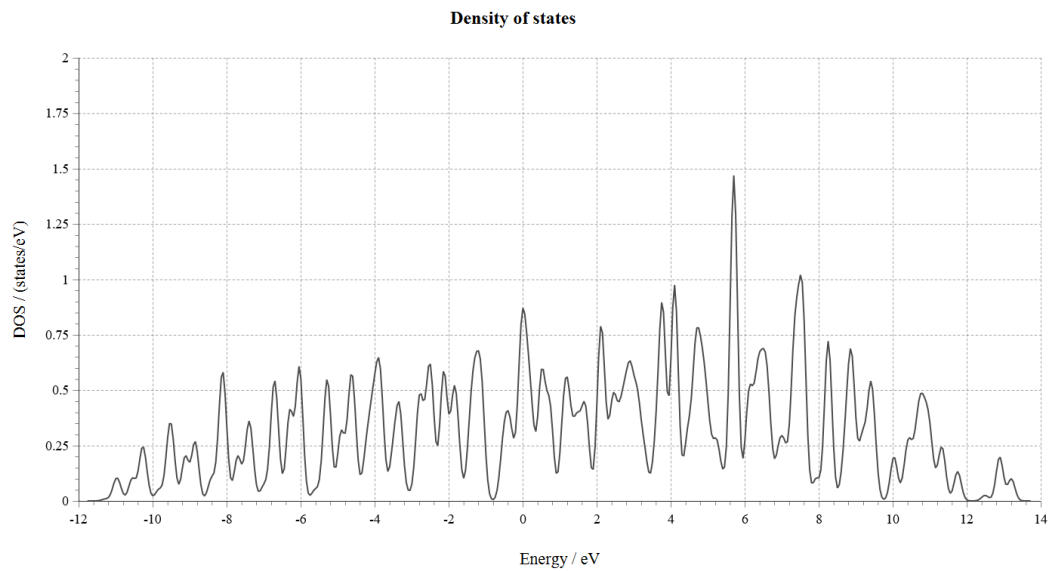


Figure 3.8 - DOS for Al showing a narrow peak at the Fermi level.

§3.2.3 Results and discussion for Al

The following observations about the conducting metal Al can be made from the band structure and dos.

- The valence bands and conduction bands criss cross and overlap, which is a characteristic of any metal.
- This, and further the narrow peaks, imply a very a high electrical conductivity that is expected of metals.
- The peak at the Fermi level in the dos for Al shows the high density of states corresponding to this energy.

§3.3 Sodium Chloride

Now the various fore-mentioned calculations are repeated for NaCl. Since NaCl is an insulator, the results are expected to show properties such as wide band gaps.

§3.3.1 SCF calculation for NaCl

```
&CONTROL
  calculation = "scf"
  max_seconds = 8.64000e+04
  pseudo_dir = "C:\Users\Rohith\.burai\.pseudopot"
  tprnfor     = .TRUE.
  tstress     = .TRUE.
/

&SYSTEM
  a           = 5.69169e+00
  degauss     = 1.00000e-02
  ecutrho     = 2.25000e+02
  ecutwfc     = 2.50000e+01
 ibrav       = 2
  nat         = 2
  ntyp        = 2
  occupations = "fixed"
  smearing    = "gaussian"
/

&ELECTRONS
  conv_thr    = 1.00000e-06
  electron_maxstep = 200
  mixing_beta = 7.00000e-01
  startingpot = "atomic"
  startingwfc = "atomic+random"
/
```



```

K_POINTS {automatic}
  4  4  4  0  0  0

ATOMIC_SPECIES
Na      22.98977  Na.pbe-sp-van_ak.UPF
Cl      35.45270  Cl.pbe-n-van.UPF

ATOMIC_POSITIONS {angstrom}
Na      0.000000  0.000000  0.000000
Cl      -2.845847  2.845847  2.845847

```

§3.3.2 Band Structure calculation for NaCl

The section of code, specific to band structure calculation for NaCl, such as high symmetry points and grid points, is given here.

```

&ELECTRONS
  conv_thr      = 1.00000e-06
  electron_maxstep = 200
  mixing_beta    = 7.00000e-01
  startingpot    = "atomic"
  startingwfc    = "atomic+random"
/
&BANDS
  lsym          = .FALSE.
  spin_component = 1
/
K_POINTS {tpiba_b}
12
gG      20
X       20
W       20
K       20
gG      20
L       20
U       20
W       20
L       20
K       0
U       20
X       0

ATOMIC_SPECIES
Na      22.98977  Na.pbe-sp-van_ak.UPF
Cl      35.45270  Cl.pbe-n-van.UPF

ATOMIC_POSITIONS {angstrom}
Na      0.000000  0.000000  0.000000
Cl      -2.845847  2.845847  2.845847

```

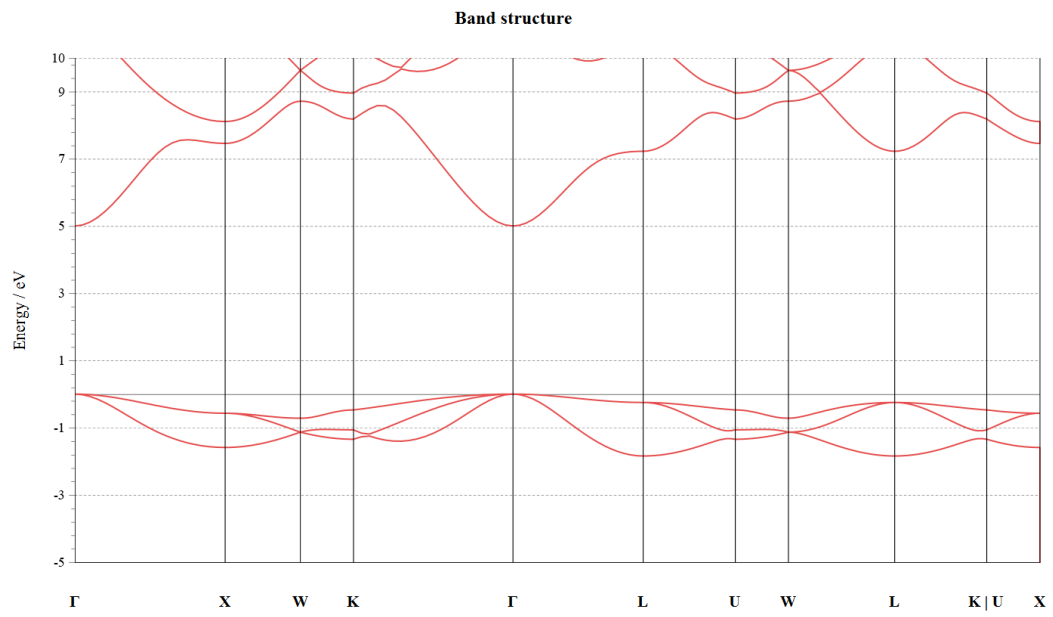


Figure 3.9 - The band structure for NaCl showing wide band gaps.

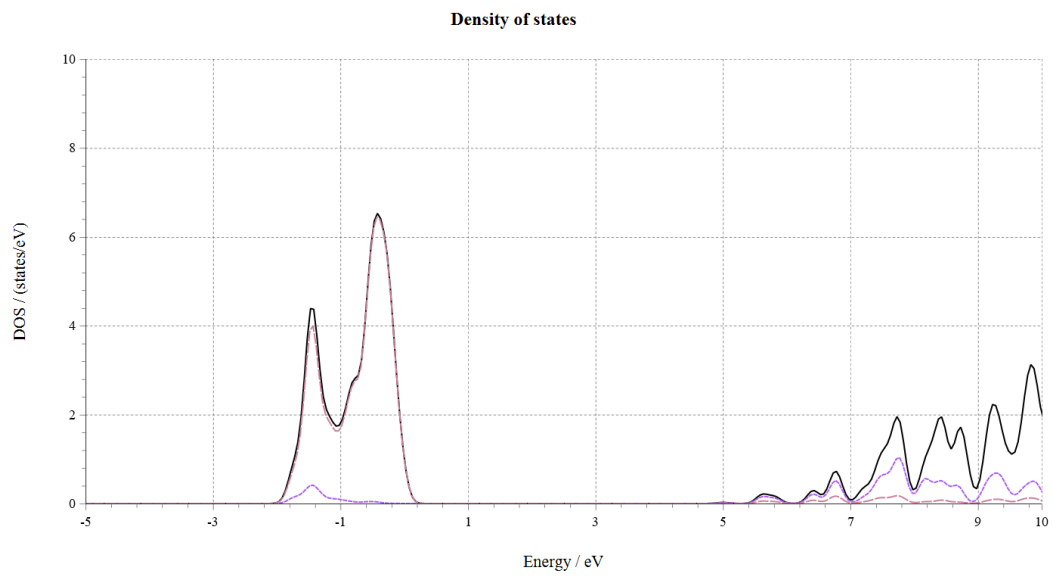


Figure 3.10 - The DOS for NaCl.

§3.3.3 Results and discussion for NaCl

The following observations about the insulating material NaCl can be made from the band structure and dos.

- The valence bands and conduction bands have a wide band gap in between them which is a characteristic of an insulator
- This implies a very low electrical conductivity that is expected of insulators.
- There are no peaks at Fermi energy level which is in good agreement with experimental results.

§4 Computations on Yb₂Ge

The binary compounds with general formula M₂X (M = Ca, Sr, Ba, Eu, Yb) (X = Si, Ge, Sn, Pb) have been extensively studied in the literature. Except Yb₂Sn, which crystallizes with the Ni₂In structure, and Yb₂Si, whose existence is still doubtful, all the other known compounds belong to the Pb₂Cl type, including the intermetallic compound of choice, Yb₂Ge.

Yb₂Ge crystallizes in the orthorhombic lattice in space group number 62, much alike Pb₂Cl, with lattice parameters:

$$\begin{aligned} a &= 4.818 \text{ \AA} \\ b &= 7.461 \text{ \AA} \\ c &= 8.954 \text{ \AA} \\ \alpha &= \beta = \gamma = 90^\circ \end{aligned}$$

§4.1 SCF calculation

```
&CONTROL
  calculation = "scf"
  max_seconds = 8.64000e+04
  pseudo_dir = "C:\Users\Rohith\.burai\.pseudopot"
/

&SYSTEM
  a = 4.81773e+00
  b = 7.46135e+00
  c = 8.95411e+00
```

```

degauss          = 1.00000e-02
ecutrho          = 3.54905e+02
ecutwfc          = 3.94339e+01
ibrav            = 8
nat              = 12
nspin            = 2
ntyp             = 2
occupations      = "smearing"
smearing         = "gaussian"
starting_magnetization(1) = 2.00000e-01
starting_magnetization(2) = 0.00000e+00
/

```

```

&ELECTRONS
  conv_thr        = 1.00000e-06
  electron_maxstep = 200
  mixing_beta     = 4.00000e-01
  startingpot     = "atomic"
  startingwfc     = "atomic+random"
/

```

```

K_POINTS {automatic}
8 4 2 0 0 0

```

```

ATOMIC_SPECIES
Yb 173.04000 Yb.pbe-spn-rrkjus_psl.1.0.0.UPF
Ge 72.61000 Ge.pbe-n-rrkjus_psl.1.0.0.UPF

```

```

ATOMIC_POSITIONS {angstrom}
Yb 3.613297 6.293768 0.680539
Yb 1.204432 1.167582 8.273569
Yb 3.613297 2.563093 3.796515
Yb 1.204432 4.898257 5.157593
Yb 1.204432 3.875224 1.620129
Yb 3.613297 3.586126 7.333979
Yb 1.204432 0.144549 2.856925
Yb 3.613297 7.316801 6.097184
Ge 1.204432 5.606369 8.029122
Ge 3.613297 1.854981 0.924986
Ge 1.204432 1.875694 5.402040
Ge 3.613297 5.585656 3.552068

```

The output file for scf shows the total energy of the given set of 12 atoms, 8 of Yb and 4 of Ge (thus making 4 formula units of Yb₂Ge).

```

the Fermi energy is 7.8740 ev
total energy          = -958.58898970 Ry
Harris-Foulkes estimate = -958.58897673 Ry
estimated scf accuracy < 0.00000090 Ry

```

The total energy is the sum of the following terms:

```

one-electron contribution = -164.36564411 Ry
hartree contribution      = 107.21792866 Ry
xc contribution           = -482.10797422 Ry

```

```

ewald contribution      =    -419.33043802 Ry
smearing contrib. (-TS) =     -0.00286201 Ry

total magnetization     =      0.03 Bohr mag/cell
absolute magnetization  =      0.08 Bohr mag/cell

```

convergence has been achieved in 8 iterations

§4.2 Band Structure Calculation

```

&CONTROL
  calculation = "bands"
  max_seconds = 8.64000e+04
  pseudo_dir = "C:\Users\Rohith\.burai\.pseudopot"
/

```

```

&SYSTEM
  a              = 4.81773e+00
  b              = 7.46135e+00
  c              = 8.95411e+00
  degauss        = 1.00000e-02
  ecutrho        = 3.54905e+02
  ecutwfc        = 3.94339e+01
  ibrav          = 8
  nat            = 12
  nbnd           = 144
  nspin          = 2
  ntyp           = 2
  occupations    = "smearing"
  smearing       = "gaussian"
  starting_magnetization(1) = 2.00000e-01
  starting_magnetization(2) = 0.00000e+00
/

```

```

&BANDS
  lsym           = .FALSE.
  spin_component = 1
/

```

```

K_POINTS {tpiba_b}
16
gG      20
X       20
S       20
Y       20
gG      20
Z       20
U       20
R       20
T       20
Z       0
Y       20
T       0
U       20
X       0
S       20
R       0

```

It is to be noted here that 16 high symmetry points are used in the k point path selection. This results in a total of 181 k points for the band structure calculation. Note also that the band structure calculation is performed using both GGA and GGA+U techniques.

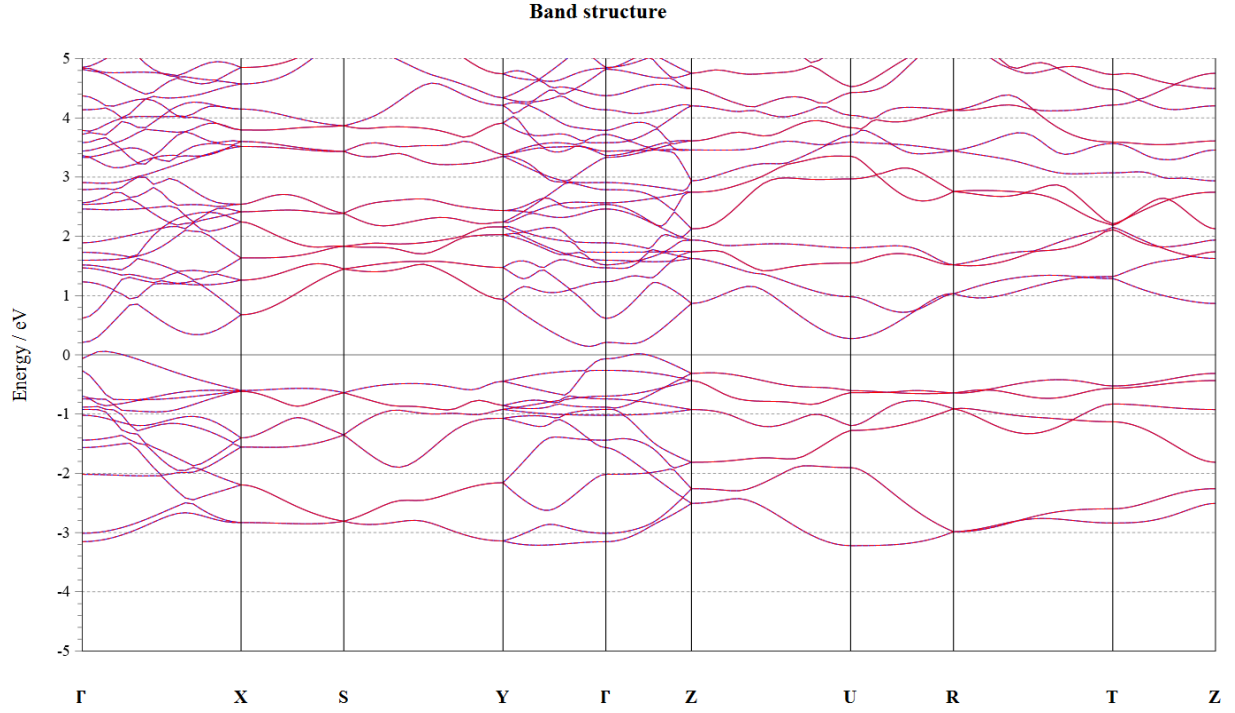


Figure 4.1 - Band structure for Yb₂Ge

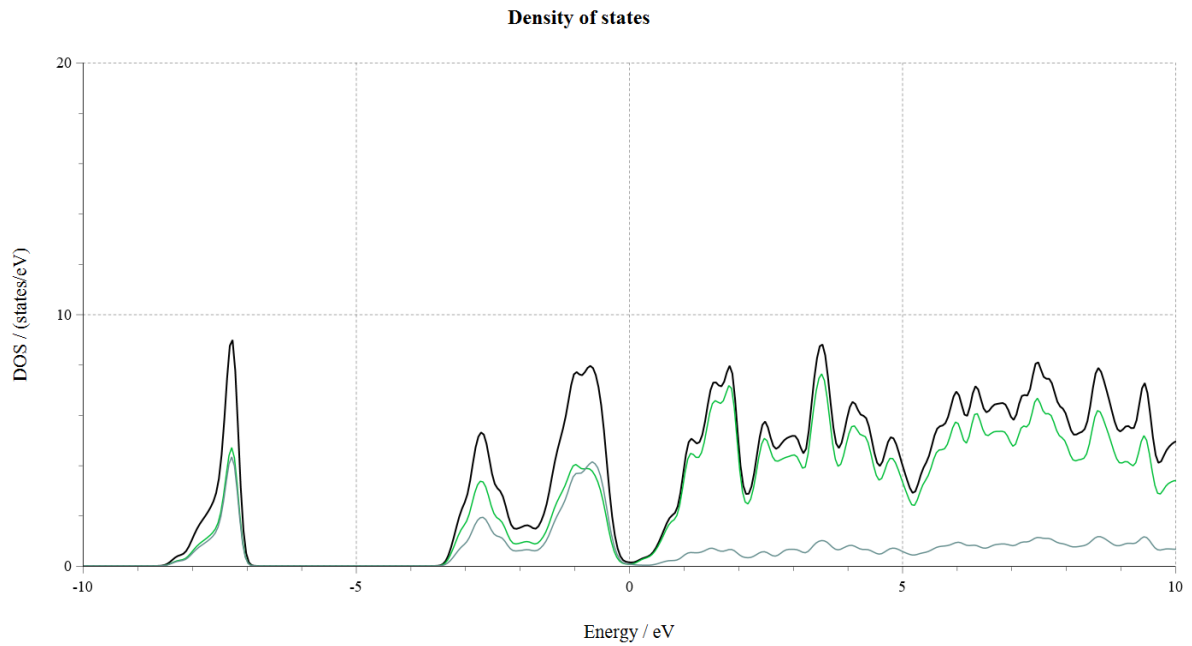


Figure 4.3 - Density of states for Yb₂Ge

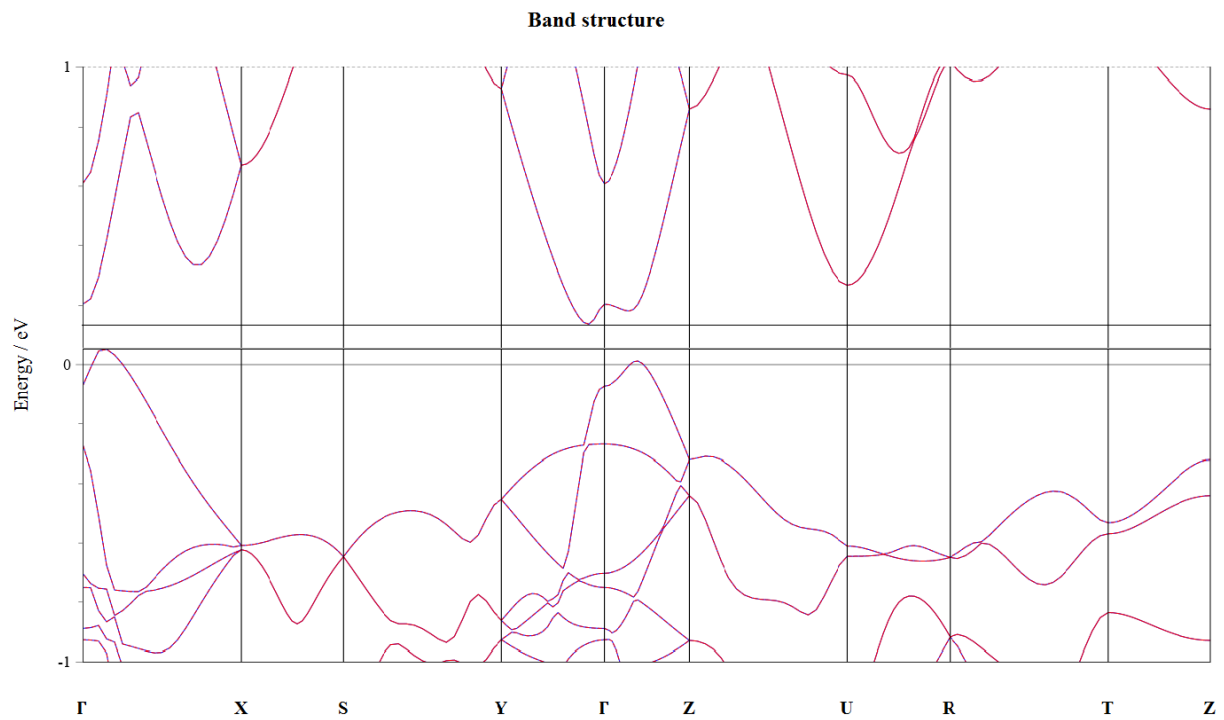


Figure 4.3 - The band gap computed using the exchange correlation functional GGA is about 0.1eV

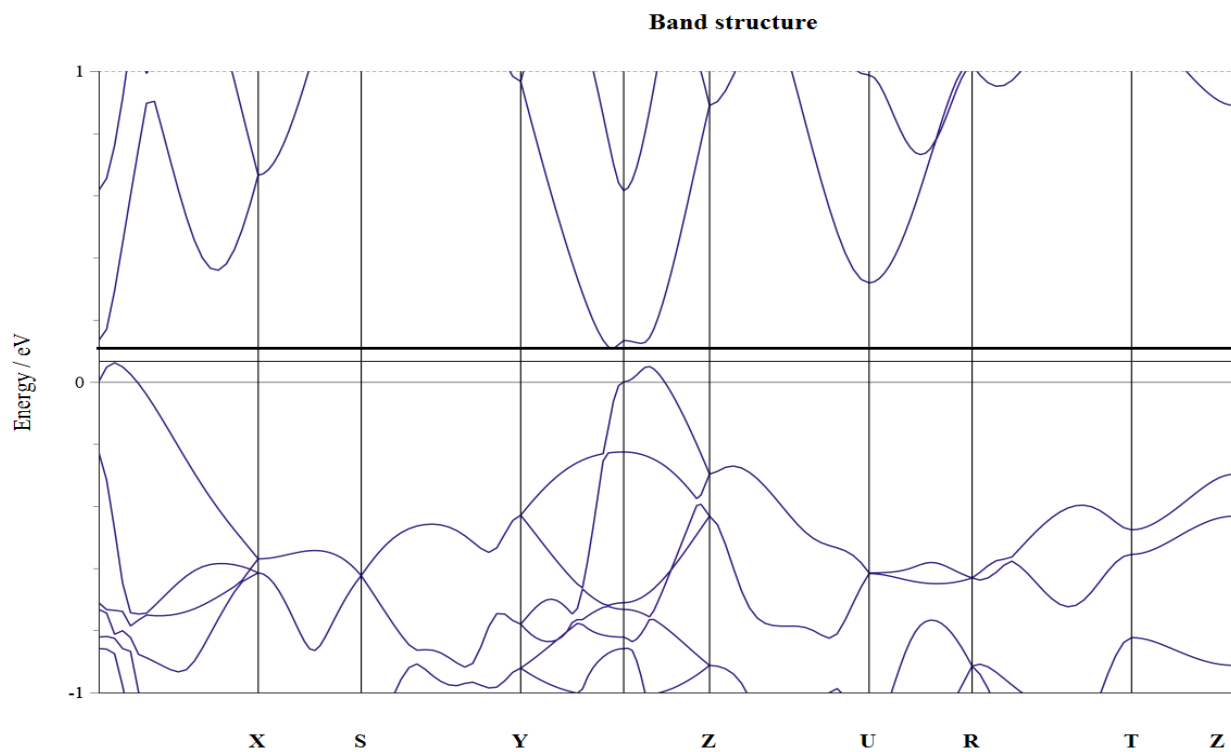


Figure 4.4 - The band gap is improved to 0.045eV using GGA+U

§4.3 Results and discussion

The following observations are made with respect to the molecule Yb_2Ge based on the data computed above.

- The valence bands and conduction bands do not overlap. They possess a small band gap of the order of 0.1eV. The band gap formed is direct.
- The band-gap calculation is complicated by the self-interaction error which arises in the occupied states in standard DFT. If one considers the "true" band structure, then semi-local DFT (using GGA or LDA) has a spurious self-interaction in the occupied states, which over-delocalizes them and forces them to take a higher energy, thus reducing the band-gap.
- A method to correct the self-interaction in DFT for localised atomic-like states (e.g. for d and f-block elements) is to introduce a modest Hubbard U term and do a DFT+U calculation. The Hubbard U introduces a potential which favours localising the states to which it is applied, thus re-localising them (compared to standard Kohn-Sham DFT) and lowering their energy. [7]
- Thus the computation was performed once in GGA yielding a band gap of 0.1eV. Further the computation was performed again in GGA+U, which yielded a more accurate band gap of 0.045eV.
- Since the band gap is low and since the conduction band minimum is dispersed, Yb_2Ge has a relatively high electrical conductivity, which makes it suitable for use as a thermoelectric.

§5 Conclusions

The basic tenets of applying DFT computations to different materials was studied. This leads to an understanding of the types of band structures that materials such as semiconductors, metals and insulators could have, and further the physical properties that could be inferred from them.

The material chosen as the subject, Yb_2Ge , is shown to possess a narrow band gap and good electrical conductivity. The d electrons in Yb lead to an underestimation in band gap values. This is however reduced by using GGA+U. Furthermore, DFT based phonon computation shows that Yb_2Ge possesses very low thermal conductivity. This would imply that the thermoelectric figure of merit would be very high for Yb_2Ge , thus making it a good contender for use in a thermoelectric device.

References

- [1] Snyder and Toberer, Complex thermoelectric materials, Nature materials, Vol 7, February 2008
- [2] Gayner and Kar, Recent advances in thermoelectric materials, Progress in Materials Science, July 2016
- [3] Tabib, Lovvik et al, Discovering thermoelectric materials using machine learning: insights and challenges, Springer Nature, August 2018
- [4] Chen, Dresselhaus et al, Recent developments in thermoelectric materials, International Materials Reviews, August 2003
- [5] Sholl, Density Functional Theory: A Practical Introduction, Wiley Publications, March 2009
- [6] Giannozzi, Baroni et al, Quantum ESPRESSO: a modular and open source software project for quantum simulations of materials, July 2009
- [7] Premkumar, Vidya, Crystal and electronic structure studies on transparent conducting nitrides, IOP Publishing, February 2019

Computational Software

- [1] Quantum ESPRESSO - <https://www.quantum-espresso.org/>
- [2] BURAI 1.3 - <https://nisihara.wixsite.com/burai>
- [3] Xcrysden - <http://www.xcrysden.org/>
- [4] XMGrace - <http://plasma-gate.weizmann.ac.il/Grace/>
- [5] Vesta - <http://jp-minerals.org/vesta/en/>