Chapter 2

Methodology
2. Introduction

The understanding and exploitation of the properties of systems of interacting electrons and atomic nuclei is primarily related to condensed matter physics and materials science. The information on structural, mechanical, electrical, vibrational, thermal and optical properties can be resulting all the way through the knowledge of the electronic properties. Hence, it is necessary to understand its electronic structure to recognize the function of a material. EMD [1] is linked with the electronic structure of a material which yields the amount of electrons with momentum \( p \) as \( n(p)d^3p \). EMD can be measured experimentally by number of methods like x-ray Compton scattering [2-3], (e,2e) spectroscopy (EES)[4] and positron annihilation spectroscopy (PAS)[5].

The thesis employs Compton scattering technique. The materials composed of electrons and nuclei comprise strongly interacting many body systems that makes the straight solution of the Schrödinger's equation an impractical proposition. Elaboration of sufficiently accurate and approximate techniques tells us the progress as said by Dirac in the far 1929 [6]. The first principle calculations which are based on DFT have been receiving a great consideration because of its high precision. This simulation is very useful for basic understanding of the structure with the electronic properties. The detailed description of the experimental technique and theoretical study is given below. This chapter basically includes two main parts: 2.1 Experimental details, 2.2 Computational details.

2.1 Experimental Technique

In 1922, Arthur H. Compton (1892-1962) [7] was the first to measure photon-electron scattering while performing research on X-rays scattering by light elements. He observed the scattering of X-rays from electrons in a carbon target and observed scattered X-rays with a longer wavelength than that incident upon the target. The main focus of the experiment is Compton scattering, although it is more important to know the interactions of high energy electromagnetic photon radiation with materials. Gamma rays are the high energy photons which release from the radioactive sources. When these high energy radiations interact with matter, their energy can be absorbed by materials mainly in three
ways; photoelectric effect, Compton scattering and pair production. Further, several lesser ways are also present such as bremsstrahlung and X-ray production. Usually, photon is an energetic radiation such as an X-ray photon or gamma ray photon and the charged particle is an electron well thought-out to be at rest.

Compton scattering is the scattering of photons by charged particles where photon transfers some energy and momentum to the charged particle while it moves with a reduced energy and a change in momentum. To develop the theory of Compton scattering, laws of conservation of energy and momentum are used with the relativistic values of these parameters. Figure 1 shows the scattering of an incident photon having energy \( E = h \nu \) and momentum \( p = \frac{h \nu}{c} = \frac{h}{\lambda} \) (symbol \( h \), \( \nu \) and \( \lambda \) stands for Plank’s constant, the photon’s frequency and wavelength) moving in the positive x direction and interacting with an electron which is at rest with energy equal to its rest energy, \( E_0 = m_0 c^2 \) (\( m_0 \) is the rest mass of the electron) and momentum \( p_e = 0 \). Now, using the conservation laws of energy and momentum an equation for wavelength shift is given as

\[
\Delta \lambda = \frac{h}{m_e c} \left( 1 - \cos \theta \right) 
\]

Here, \( \lambda_i \) and \( \lambda_f \) are the wavelength of incident and the scattered photon whereas \( \theta \) is the scattering angle.

Eq. (2.1) depends only upon the scattering angle. Eq. (2.1) can be written in the energy form as

\[
E' = \frac{E}{1 + \frac{m_0 c^2}{E} (1 - \cos \theta)}
\]

where, \( E \) and \( E' \) are the energies of the photon before and after the scattering whereas \( \theta \) is the scattering angle.
Compton clarified and observed the data by assuming the particle (photon) nature of light and applying conservation of energy and momentum. Energy of the scattered photon is lowered and therefore it has a longer wavelength. Scattering comprises of elastic (coherent) scattering and inelastic (incoherent) scattering. The elastic scattering of photon rely strongly on the atomic numbers (Z) of scatterers whereas Compton scattering depends weakly on Z. When part of photon energy is transferred to an effectively free electron, the photon scatters with lower energy than the incident one and hence Compton scattering occurs. Practically this signifies that the incident photon must have larger energy as compare to the electron binding energy. This is found to be in dissimilarity to the photoelectric effect, that depends very strongly on Z and it becomes most probable when the incident photon energy is equal to or slightly greater than the electron binding energy. The photoelectric effect decreases rapidly as the photon energy increases beyond the electron binding energy and Compton Effect becomes most dominating.
2.1.1 Principle of Compton scattering

The categorization of the scattering process can be done accordingly in two parts that is single particle system and collective system on the basis of the momentum transfer. The interference effects are absent in single particle system and the properties of the system become conclusive. In collective system the interference between the scattering amplitude is crucial and the scattering taken place from many particles. Following equations shows the conservation of energy in the interaction process and conservation laws for momentum.

\[
\hbar \omega_1 + \frac{p_1^2}{2m_0} = \hbar \omega_2 + \frac{p_2^2}{2m_0}, \quad \hbar \mathbf{k}_1 + \mathbf{p}_1 = \hbar \mathbf{k}_2 + \mathbf{p}_2
\]

or \[\hbar \mathbf{k} + \mathbf{p}_1 = \mathbf{p}_2\] (2.3)

Where \(\omega_1\) and \(\omega_2\) are the angular frequencies of incident and scattered photon and \(\mathbf{k} = \mathbf{k}_1 - \mathbf{k}_2\) is the conventional scattering vector or momentum transferred to the electron, respectively.

The transfer of energy can be written as

\[
\hbar \omega = \hbar \omega_1 - \hbar \omega_2
\]

\[
= \frac{p_2^2}{2m_0} - \frac{p_1^2}{2m_0} = \frac{(p_1 + \hbar k)^2}{2m_0} - \frac{p_1^2}{2m_0}
\]

\[
= \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar k}{m_0} p_z
\] (2.4)

The first term on the right side in the above equation is known to be recoil term which depends on the scattering vector \(k\) and also decides the Compton peak position. It is independent of the initial momentum of the electron. The second term suggests that the component of the electron momentum on to the scattering vector contributes to the energy shift known as Doppler term. Doppler broadening line shape is known as Compton profile, which depends on impulse approximation. If the electron is at rest this
term is supposed to be absent. So from equation (2.4), it is clear that at a fixed scattering angle, the energy shift or recoil energy varies over a range which is characteristic of momentum distribution of the target electron.

### 2.1.2 Inspiration behind Compton scattering

During the experimental process, the direction of the incident photons is fixed and the energy distribution of the photon scattered at a fixed angle $\theta$ is measured, which is made as close to $180^\circ$ as possible in order to increase the magnitude of the scattering vector. The hypothetical relation of Compton profile to the scattering cross section is

$$
\frac{d^2\sigma}{d\Omega dE} = C(E_1, E_2, \theta, p_z) J(p_z)
$$

(2.5)

where $p_z = \frac{k_p k_1}{|k|}$

The calculation of function $C$ is done for the relativistic energies by Eisenberger and Reed [8] for scattering angle of $180^\circ$ and by Ribberfors [9] for all scattering angles. Whereas Compton profile $J(p_z)$ can be determined by the component of momentum $p_z$

$$
J(p_z) = \int_{p_x} \int_{p_y} n(p_x, p_y, p_z) dp_x dp_y
$$

(2.6)

Where the momentum density function for the electrons in the sample is defined as

$$
n(p) = \sum_{i} |\chi_i(p)|^2
$$

and

$$
\chi_i(p) = \frac{1}{(2\pi\hbar)^{3/2}} \int \Psi_i(r) \exp(-ip.r) d^3r
$$

(2.7)

where $\psi_i(r)$ is the position space wave function for the electron in the $i^{th}$ state. The summation is done over all occupied state. So we can conclude that the Compton profile provides a manner to examine the various band structure models used to generate solid-state wave function.

Moving on, Compton profile $J(p_z)$ has the property that
\[ \int_{-\infty}^{\infty} J(p_z) \, dp_z = N \] (2.8)

Where \( N \) represents the number of electrons implicated in the scattering process.

For polycrystalline sample, the spherical average of momentum density is the quantity measured. The isotropic Compton profile is calculated as

\[ J(p_z) = 2\pi \int_{-\infty}^{\infty} p \langle n(p) \rangle \, dp \] (2.9)

Where, \( \langle n(p) \rangle \) is the spherical averaged momentum density. The radial momentum distribution being \( I(p) = 4\pi p^2 \langle n(p) \rangle \), we can rewrite the isotropic Compton profile as

\[ J(p_z) = \frac{1}{2} \int_{-\infty}^{\infty} \frac{I(p)}{p} \, dp \] (2.10)

Fundamentally, the measurement of Compton profile is known to be directional property. It provides a possibility to measure the Compton profiles of a single crystal with scattering vector along various crystallographic directions. The resulting difference between such directional Compton profiles gives anisotropy in momentum density. Ultimately, all the isotropic corrections like background, multiple scattering etc. automatically gets cancelled.

Moreover, the valence electrons are more delocalized in real space than core states, and can interact with more than one ion. This situation has two important outcomes for Compton scattering. The Compton profiles are comparatively narrower, and can be highly anisotropic. This dependency on crystal orientation according to the scattering vector (z-axis) reveals that the full three dimensional momentum densities can only be defined after measuring Compton profile along a large number of independent directions.

One of the most significant applications of Compton scattering and momentum density calculations is providing a test ground for the band-structure models. These calculations are basically concerned with the energy and population of the continuum of Bloch states in a crystal as a function of wave vector. The electron wave vector is minutely related to its momentum, and in case of absence of any interaction with the lattice, the two are identical to within a constant factor (the Planck’s constant). In general, the electron
energy and momentum are amended by lattice interaction. With partly filled conduction band, interactions with the crystal lattice become weak, and the electrons behave like a Fermi gas. Actually, many metals exhibit parabolic Compton profile components, which are features of almost free electrons, and the Fermi momentum, can be extracted experimentally from the cut-off in the parabola.

Directional Compton profiles can yield very sensitive tests of electronic structure calculations. Since the measured profiles are usually influenced by very broad core electron densities, these contributions have to be removed before comparing with band theory results. Core level profiles are comparatively straightforward to model using atomic calculations, and one can simply subtract the calculated core contributions from experimental data to divulge the valence profiles. Alternatively, the directional dependence of the valence momentum density can be scrutinized by subtracting pairs of independent directional profiles, to produce what are known as directional differences profiles or anisotropies in the Compton profiles. This simple but highly successful technique automatically removes all isotropic components, such as core state, along with a number of potential systematic errors like multiple scattering, failure of impulse approximation etc.

Frequently used units for the momentum density are atomic units (a.u.). In this system $e = m = h = 1$ and $c = 137.036$ then the unit of length is equal to Bohr radius. The SI equivalent of 1 a.u. of momentum is $1.99 \times 10^{-24}$ Kg m s$^{-1}$, 1 a.u. of energy is equal to 27.212 eV and 1 a.u. length is equal to $0.52918 \times 10^{-10}$ m (First Bohr orbit radius).

### 2.1.3 Process of measurement

Since the scattering cross section is exceedingly low (~1 barn), the calculation of Compton profiles is a tedious task. Based upon the nature of incident radiation, there are two types of Compton scattering in use i.e. photon Compton scattering and electron Compton scattering. For the present study, photon Compton scattering is used.
Photon Compton Scattering

Compton profile measurement is performed using Am$^{241}$ radioisotope. The energy associated with incident gamma rays of the present isotope is equivalent to 59.54 keV. The scattered radiation is measured by HPGe-detector. The use of 59.54 keV gamma-ray from the Am$^{241}$ radioisotope was first demonstrated successfully by Felsteiner et al. [10] for the Compton profile measurement. The effective counting rate in gamma-ray Compton spectrometer is much higher because it uses the semiconductor detector for the analysis as well as detection of the scattered gamma-rays. But the intrinsic flux of a typical gamma-ray source is three to four times lower than that of X-ray source. When the detector is coupled to a MCA, it provides an energy dispersive spectrometer having very high counting rate due to synchronized data acquisition for different energies. The momentum resolution is determined by the energy resolution of the semiconductor detector which is only about 0.4 to 0.6 a.u.. Am$^{241}$ radioisotope incident gamma-rays on the sample and the gamma-rays get scattered by the sample at a preset angle of 150$^\circ$-175$^\circ$. The raw data is then corrected for background, sample absorption, detector efficiency, detector response function, Compton scattering cross-section, multiple scattering etc. to extract the Compton profile.

The advantages of Gamma-ray method over X-ray method are given below:

i. Gamma radiations are highly monochromatic.

ii. The width of the Compton profile is typically ~5% in the range of 100keV while the resolution of detector in this range is 1%.

iii. One can choose a wide range of incident energy radiations by a suitable choice of radioisotope.

Am$^{241}$ and Au$^{198}$ are the most commonly used gamma-ray sources even though Te$^{123}$, Cs$^{137}$, Cr$^{51}$ have also been used. Am$^{241}$ source has been the most popular among all because it has a long half-life of nearly 458 years, which means the strength of the source remains virtually constant. The efficiency of the planar Ge detector used in Compton profile measurements is almost 100% at the main energy 59.54keV at which the scattered radiation has energy in the range of 45-55keV. The self-absorption is very high and only ~30% of the radiation are of 59.54keV which is the major disadvantage of
this method. Photoelectric to Compton cross-section ratio increases with increases in Z at 60keV. Thus, we require a large measuring time for elements with \( Z > 30 \). The other gamma-ray sources mentioned above are not preferred according to certain limitations such as rare availability, high initial cost, very short half-life and lesser detector efficiency at the energies involved. Moreover, there is the problem of bremsstrahlung emitted by the recoil electron and the ejected photoelectrons. Alexandropoulos et al. [11] was the first one to mention this. Mittal et al. [12] group had found that the contribution of bremsstrahlung in Ta spectrum is about 0.3% in the Compton rule for Am\(^{241}\) source. Thus, in high energy Compton spectrometers the contribution of bremsstrahlung is higher as the energy transferred to the recoil electron is more and accordingly the radiations emitted by the electrons will be huge.

2.2 Theoretical details

Many areas of science and technology which includes particle physics, nuclear physics, solid state physics, molecular biology, laser devices and atomic physics considered quantum mechanics as the basic theory. Schrödinger equation is the initial point to start any discussion for Quantum mechanics [13]. It is a differential equation used to describe, how the wave function \( \psi \) represents the motion of a quantum particle under the influence of an external potential \( V( r ) \). Due to the nuclei of the atoms this external potential might be the coulomb electrostatic potential. For a quantum particle which is moving within a three dimensional potential energy field \( V( r ) \), the time independent Schrodinger equation can be represented as

\[
i \hbar \frac{\partial \psi(r)}{\partial t} = H \psi(r)
\]

(2.11)

Here, \( H \) gives the Hamiltonian operator which is the sum of kinetic energy operator and the potential energy operator of the system. Hamiltonian for a single particle having mass \( m \) which is moving through space is given by

\[
H = \frac{-\hbar^2}{2m} \nabla^2 + V( r )
\]

(2.12)
here $\hbar$ is the reduced plank constant. A set of interacting point electrons which are moving quantum mechanically gives a leading theoretical picture of molecular or solid state systems within the potential field of a set of atomic nuclei. These are considered as static according to the Born-Oppenheimer approximation [14]. This approximation method presumes that the nuclei motion is so much sluggish than the motion of the electrons. So they can be regarded as to be stationary. The kinetic energy term of the nuclei can be neglected in the Hamiltonian according to this method. This can be understand by supposing many body system having $N$ electrons and several nuclei in general then the full Hamiltonian can be given as

$$H = \frac{-\hbar^2}{2m_e} \sum_l \nabla^2_l \sum_{l_i} \frac{Z_l e^2}{r_{li}} + \frac{1}{2} \sum_{l \neq j} \frac{e^2}{r_{lj}} - \frac{-\hbar^2}{2M_i} \sum_l \nabla^2_l + \sum_{l,j} \frac{Z_l Z_j e^2}{R_{lj}} \quad (2.13)$$

This equation defines mainly five terms sequentially which are as follows:

i) The kinetic energy of each and every one of the electrons with mass ($m_e$).
ii) The interaction potential energy between all electrons and the atomic nuclei.
iii) The interaction energy between different electrons.
iv) The kinetic energy of all nuclei with mass ($M_i$).
v) The interaction between the nuclei.

According to Born Oppenheimer equation (2.13) can be written as:

$$H = \frac{-\hbar^2}{2m_e} \sum_l \nabla^2_l - \sum_{l,j} \frac{Z_l e^2}{r_{lj}} + \frac{1}{2} \sum_{l \neq j} \frac{e^2}{r_{lj}} + \sum_{l,j} \frac{Z_l Z_j e^2}{R_{lj}} \quad (2.14)$$

Here, last term represents the interaction between nucleus-nucleus. But the Schrödinger equation is still too complex to be solved because of the electron-electron interaction term. These kinds of models can get the solution using approximation schemes like the independent electron approximation, the Hartree theory and the Hartree- Fock theory. However, one more approach has been very much famous over the last 40 years known to be DFT [15-19].
This method is capable to treat many problems with a sufficient computation which means it is much simpler than the Hartree scheme. The gigantic developments in computer technology have made computational material science to emerge as a manifold branch of science and technology. For the study of complex solid state systems, the computer implementations of DFT have accomplished great importance as a highly production tool. The better understanding of material and process using this technique made it successful. The new possibilities to design devices and novel materials have been offered by this technique by giving precise quantitative physical predictions.

2.2.1 Density functional theory

In 1990 (DFT) became a research tool when results were added to the theory. In beginning it was a guide line in compressed state or phase, it can handle structures having thousands of atoms with high accuracy in energy, electronic structure investigation and force. According to DFT theory, total energy relies on the distribution of electrons density.

The Hohenberg-Kohn Theorem

The Hohenberg-Kohn Theorem is the starting point of discussion about DFT [20]. The intact filed of DFT respites upon the two fundamental theorems in 1964[19] established by Hohenberg and Kohn. The first theorem states that the external potential $V_{\text{ext}}(r)$ can be determined uniquely and fully in an external potential for any system of interacting particles by the ground state electron density, $n(r)$. Further, the external potential and the electron density are related to each other. As per the theorem, the total energy functional $E[n(r)]$ is expressed as,

$$E[n(r)] = \int V_{\text{ext}}(r)n(r)dr + F_{\text{HK}}[n(r)]$$  \hspace{1cm} (2.15)

Where the external potential is represented by $V_{\text{ext}}$. $F_{\text{HK}}[n(r)]$ is called as a universal functional as it is independent on the external potential. The additions of the contribution from inter electronic interaction and the kinetic energy of electrons gives $F_{\text{HK}}[n(r)]$. It is represented as
The second Hohenberg-Kohn theorem states that when \( n(r) \) is standardized to the number of particles in the system, then the systems total energy \( E[n(r)] \) becomes a minimum if \( n(r) \) is the exact ground density.

**The Kohn-Sham Equation**

The Hohenberg-Kohn theorem shows that all ground state observables can be uniquely determined by ground state density and the ground state energy functional \( E[n(r)] \) determines the ground state density. This theorem does not provide us any clue concerning the solution of full Schrödinger equation. In 1965, Kohn and Sham addressed these problems. According to Kohn-Sham scheme, set of equations that only includes a system of non-interacting electrons can represent the ground state electron density [15]. The density \( n(r) \) of the non-interacting system is same as the original system. For this system the energy functional can be provided by

\[
E[n(r)] = T_s[n(r)] + \int V_{eff}(r)n(r)d^3r
\]  

(2.17)

The Kohn-Sham Eigen values can be given by the solution to the Schrödinger equation.

**The exchange-correlation functional**

The accurate form of the exchange-correlation functional is unknown so it is the major problem while solving the Kohn-Sham equation. To approximate the exchange-correlation functional, two main approximation methods have been used are LDA and GGA approximations.

An important milestone in condensed matter physics is portrayed by the presentation of the tractability and accuracy of LDA and the development of DFT. The most frequently used theoretical tools in materials science has been derived from the first principles quantum mechanical calculations based on the LDA. Before the late 1970’s when several works have illustrated the accuracy of the approach in analyzing the properties of solids [21-24], the immense contribution of the LDA calculations remained limited. It will be

\[
F_{HK}[n(r)] = T[n(r)] + \frac{1}{2}\sum V_h[n(r)]n(r)dr
\]  

(2.16)
quite interesting to identify the fact that why the LDA be supposed to or not be supposed to adequate for calculating properties of materials, but we cannot deny the fact that the most promising arguments are resulted from the direct comparison of calculations with experiments.

\[ V_{XC}^{LDA}(r) = V_{XC}^{\text{electron gas}}[n(r)] \]  \hspace{1cm} (2.18)

The LDA in spite of being very simple known to be very successful in explaining material properties over the most recent decades. Still, we can also see some circumstances where the above approach will not result in sufficiently accurate results. This scenario can come up when the differences in the total energy have to be estimated very truthfully, which are frequently applicable in calculating structural properties and binding. This is quite understood that small inaccuracies can have dramatic effects here. To conclude, LDA is subjected to more or less familiar collapse and hence during the last decade there have been several attempts, by counting effects depending on the variation of the electron density to go beyond this local approximation. Enhanced theoretical schemes and the fast growth in computing facilities have let many types of systems and properties to be studied flourishingly with density functional methods. In GGA, local gradient and local electron density is included within the exchange and correlation energies in the electron density [15].

\[ V_{XC}^{GGA}(r) = V_{XC}^{\text{electron gas}}[n(r)] \]  \hspace{1cm} (2.19)

The information about the density gradient along with the information about the density n(r) at a particular point r is use for the non-homogeneity of the true electron density beyond LDA. GGA proved to be an improvement above LDA for slowly varying charge density systems. The results were very good for molecular geometries and ground state energies using GGA.
Resolving the Kohn-Sham Equation

The Kohn-Sham equation can be solved when the exchange-correlation energy has been approximated. The Kohn-Sham equations have frequentative solution; they should be solved self-consistently. We need to define Hartree potential and the exchange-correlation potential for solving the Kohn-Sham equation for a many body system and for defining the exchange-correlation potential and Hartree potential; we should have knowledge about electron density n(r). We need to know the single electron wave functions to find the electron density. Until we solve the Kohn-Sham equation, we do not have knowledge about these wave functions.

Starting with an initial trial electron density is the well known method to solve the Kohn-Sham equation as illustrated in figure 2.2. Then using the trial electron density, solve these equation. We will have a set of single electron wave function after solving the Kohn-Sham equation. The new electron density can be calculated by using these wave functions. As an input for the next cycle, the new electron density is used. Finally, the difference among the calculated consecutive densities for consecutive iteration is compared. The solution of the Kohn-Sham equation is said to be self consistent. If the difference in electron density among consecutive iterations is lower, then approximately chosen convergence criterion is done. Now the calculated electron density is regarded as the ground state electron density that can be used to calculate the total energy of system.
Figure 2.2. For solving the Kohn-sham equations with the help of self-consistent field (SCF) procedure where cc is an appropriately chosen convergence criterion.
2.2.2 Basis set

To execute the first principles computation, electron waves are represented generally in the way of molecular orbitals Basis set is recognized as the set of functional to produce the orbitals[25-31]. In first principles calculation, plane wave basis sets are generally used, particularly in solid state or system having the periodic boundary conditions.

Localized orbital basis set

Algebraic orbitals are used as the basis functions in localized orbital basis set. Each function is equivalent to a specific atomic orbital. More details about orbital distributions are disclosed or unfolded by the help of these functions. Particularly into solid state systems unlike the analytical functions in plane wave basis, localized orbital basis functions provide numerical values as an atomic-centered spherical polar mesh because of which the calculations become easier with less simulation time. Due to the use of basis functions from atomic orbitals, monomer or molecular calculation can directly be performed without the use of straining cell in localized basis set.

Plane wave basis set

Commonly a plane wave is a steady frequency wave of which wave fronts are infinite parallel planes of permanent peak to peak amplitude normal to the velocity vector phase. For ions organized in a periodic way in perfect crystal at 0K, wave functions shall be unlimited in the basis set and it should be calculated for each of the unlimited number of electrons that fill the entire space. This situation can be handled with the help of Bloch’s theorem. According to Bloch’s theorem, periodic condition can be utilize to lower the countless number of wave functions from one electron to number of electrons in unit cell of the crystal. In this case, as a product from the cell periodicity part and wavelike park wave function

$$\varphi_i(r) = e^{ikr}f_i(r) \quad (2.20)$$

It is important to enforce a cut off on the kinetic energy in order to reduce the number of plane waves as kinetic energy of an electron with wave vector k. By raising the kinetic energy cutoffs or the number of plane waves, the corrections of plane wave calculation
can be enhanced systematically. In calculations including periodic boundary conditions like crystal plane wave basis set is widely used.

The theoretical study can be carried out using varieties of software such as WIEN2K, VASP [32-35], CRYSTAL [36], QUANTUM EXPRESSO and lot more. But in this thesis the ab-initio energy calculations are performed using CRYSTAL and VASP code. CRYSTAL is based on Gaussian type functions and pseudo-potentials while VASP depends upon plane waves. The detailed information of both the packages is as follows.

**CRYSTAL Code**

Gaussian type basis sets are the basis of the CRYSTAL [36], *an-initio* simulation package. All electron and valence only basis sets having effective core pseudo-potentials are permitted. Density functional or hybrid approximations, electronic wave functions and properties of periodic systems with Hartree-Fock can be calculated with the help of CRYSTAL. This program uses the spatial symmetry to emit the duplication of atoms which can be explained by symmetry elements. It is compatible with all periodic systems. It supports the 0D molecules with the 32 point groups, for 1D polymer having the symmetry of 75 rod groups and helical symmetry, for 2D films and surfaces having 80 layered groups and the 3D periodic systems having 230 space groups. There is a possibility to execute automated geometry decreases like going from higher dimension to lower e.g 2D to 1D (a slab parallel to a given plane). There are also possibilities for geometry manipulation for e.g displacements, reduction of the symmetry, addition or deletion of an atom.

Both the kohn-sham and hartree-fock equations with local and hybrid functional can be solved with the help CRYSTAL program. Unrestricted calculations, restricted closed shell, restricted open shell can be handled easily with Hartree-Fock method. Further, DFT can deal with various correlation functional (PZ, LYP, VWN) and exchange correlation functional (LDA, BECKE, PWGGA, PBE and a lot more). It is useful for hybrid HF-DFT functional like user defined hybrid functional, B3LYP and B3PW.

Various types of calculations are possible with the help of CRYSTAL code. Major are geometry optimization which includes full optimization (cell parameters and atom
coordinates), single point energy calculation, freezing atoms during the optimization at constant volume or pressure and transition state search. Reflectance spectra harmonic frequencies at gamma point, IR intensities phonon dispersion with an appropriate super cell can be calculated. The calculations of the elastic tensor of crystalline systems, equation states and harmonic frequencies for X-H bonds are also possible with the newest version. It is also possible to calculate numerous physical properties like density of states, band structure, mulliken population analysis, structure factors, dielectric properties, atomic multi-poles and many more.

**VASP Code**

The Vienna Ab-initio Simulation Package (VASP) [32-35] used either projected augmented wave method, Vanderbilt pseudo-potentials or a plane wave basis set for performing ab-initio quantum mechanical molecular dynamics (MD). DFT is the basic methodology for this code, but the code also allocates the use of post-DFT corrections like many-body perturbation theory (GW method), hybrid functional mixing DFT and HF exchange and electronic corrections within the random phase approximation. The approach can be implemented using VASP which is based on the GGA and LDA as variational quantity with the free energy and an accurate evaluation of the immediate electronic ground state at each MD time step.

Some highlights of VASP [37] are given below:

i) To calculate the electronic ground state properties it uses some old techniques for the self consistency cycle. Further, these techniques are very efficient vigorous and consist of a fast scheme for evaluating the self consistent solution of the Kohn-Sham functional.

ii) The symmetry of arbitrary configurations is determined automatically.

iii) The Monkhorst Pack special points are set up using the symmetry code for a resourceful computation of bulk materials.
References


