

The electronic structure of a material is the basic information that is further used to obtain its various properties and categorize them for a particular application. Generally, the geometry of a material, its constituent element arrangement, orbital environment, and multiple bonding characteristics are information that decides the electronic structure of a solid. Following quantum mechanics, the Schrodinger equation is used to describe a system's wavefunction and determine electronic structure description. The expression is given by;

$$H\psi = E \psi \quad (3.1)$$

H is the Hamiltonian operator, ψ is the system's wave function, and E is its corresponding energy eigenvalue. The Hamiltonian operator is a composite of potential (V) and kinetic energy terms $\left(-\frac{\hbar^2}{2m} \nabla^2\right)$ as;

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V \quad (3.2)$$

Where $\hbar$ is reduced Planck's constant, and $\nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplace operator.

The Schrodinger equation can only be solved for simple systems, such as hydrogen atoms and, H_2^+ molecular ions due to the complexity of the associated terms. Various numerical methods are presented to be used in conjunction with the Schrodinger equation to derive the electronic structure of more complex systems.

3.1 Many-Body Problem

A microscopic system, having several interactive particles, is the subject of the many-body problem. The ground state properties of such many-body systems with electrons and nuclei are described by the time-independent Schrodinger equation. For example, for a system of N electrons with N' number of nuclei, the Schrodinger equation is given by;

$$H\psi(r_1, r_2, \dots, r_N, R_1, R_2, \dots, R_{N'}) = E\psi(r_1, r_2, \dots, r_N, R_1, R_2, \dots, R_{N'}) \quad (3.3)$$

Where E is the total energy of the system and ψ represents the many-body wave function with spatial coordinates denoted by $\mathbf{r}$. H is Hamiltonian operator which can written in atomic unit as;

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{\alpha=1}^{N'} \frac{\nabla_{\alpha}^2}{M_{\alpha}} + \sum_{i < j=1}^N \frac{1}{|r_i - r_j|} + \sum_{\alpha < \beta=1}^{N'} \frac{Z_{\alpha} Z_{\beta}}{|R_{\alpha} - R_{\beta}|} - \sum_{i=1}^N \sum_{\alpha=1}^{N'} \frac{Z_{\alpha}}{|r_i - R_{\alpha}|} \quad (3.4)$$

M_{α} , R_{α} , and Z_{α} are the mass, coordinates and charge of α^{th} nucleus and r_i denotes the position of the i^{th} electron. The initial two terms are kinetic energies of electrons and nuclei respectively, third term denotes the electron-electron interaction, the fourth term shows the interaction between

nuclei, and the last term corresponds to the interaction between electrons and nuclei. Here solving this equation is almost impossible due to the coupled motion of electron and nuclei and having $3(N+N')$ spatial coordinates in the system. The Born-Oppenheimer approximation is used for the simplification of given equation by decoupling the motion of electrons and nuclei (Born & Oppenheimer, 1927). It assumes that the nuclei are static compare to electrons because electrons move much faster than nuclei at any instant of time. Or it can be said that the system can be considered as frozen nuclei with surrounding electrons moving at ground state. Therefore, the change in nuclear configuration is negligible during one cycle of electronic motion and the second term in the equation 3.4 can be taken as zero and the fourth term can be considered as constant which can be added later and here omitted. As a result the Hamiltonian reduces to electronic Hamiltonian and found as;

$$H_e = \left(-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{\alpha=1}^{N'} \frac{Z_\alpha}{|r_i - R_\alpha|} \right) + \sum_{i < j=1}^N \frac{1}{|r_i - r_j|} \quad (3.5)$$

Here the first term is single electron term while the second one is two-body columbic repulsion term. Therefore, the wavefunction ψ can be decomposed into electronic and nuclear wavefunctions as:

$$\psi(r_1, r_2, \dots, r_N, R_1, R_2, \dots, R_{N'}) = \psi(r_1, r_2, \dots, r_N) \phi_n(R_1, R_2, \dots, R_{N'}) \quad (3.6)$$

Although somewhat simplification is achieved through the Born-Oppenheimer approximation, but still remain difficult to exactly solve equation 3.5 as too many electrons are present in the system. Even for a two-electron system such as He atom, the Schrodinger equation cannot be solved easily. Through Hartree's method the electron's motion are approximated as an independent particle approach. According to this method, electrons are assumed to be independent and they move in an effective potential which takes into consideration the attraction due to nucleus and the average effect of the interactions between electrons as well.

The wavefunction of the system is thus given by;

$$\psi(r_1, r_2, \dots, r_N) = \phi_1(r_1) \phi_2(r_2) \dots \phi_N(r_N) \quad (3.7)$$

Where $\phi_i(r_i)$ is the i^{th} electronic orbital.

And the as per the independent particle approximation (mean field approximation) one particle Schrödinger equations can be written as;

$$\left[-\frac{1}{2} \nabla_i^2 - \sum_{\alpha=1}^N \frac{Z_\alpha}{r_{i\alpha}} + \sum_{i=1}^N \sum_{j=1, j \neq i}^N \int |\phi_j(j)|^2 \frac{1}{r_{ij}} d\tau_j \right] \phi_i(i) = \varepsilon_i \phi_i(i) \quad (3.8)$$

Where $\sum_{i=1}^N \sum_{j=1, j \neq i}^N \int |\phi_j(j)|^2 \frac{1}{r_{ij}} d\tau_j$ is called Hartree's operator which includes electron interaction with surrounding and is actually the coulombic term. This equation can be solved iteratively by initially guessing $\phi_j(j)$ with the self-consistent field way.

Later in 1930, Slater and Fock noted that as electrons are fermions while Hartree solution neither take spin into account nor follows the wave function anti-symmetry law. Then they proposed a new method called Hartree Fock approach by incorporating the antisymmetric into the electronic wave function ψ to describe it in better way. The anti-symmetrized wave function is given by a Slater determinant as (JOACHAIN, 2017);

$$\psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{1,\alpha}(1) & \Psi_{1,\beta}(1) & \cdots & \Psi_{N,\beta}(1) \\ \Psi_{1,\alpha}(2) & \Psi_{1,\beta}(2) & \cdots & \Psi_{N,\beta}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_{1,\alpha}(N) & \Psi_{1,\beta}(N) & \cdots & \Psi_{N,\beta}(N) \end{vmatrix} \quad (3.9)$$

Where $\phi(q)$ is the single particle orbital, q represents spatial as well as spin coordinates of the electrons, and $\eta = \alpha, \beta, \dots v$ belongs to the states of the electrons. The factor $1/\sqrt{N!}$ appears in the above expression due to the $N!$ possible permutations of electronic coordinates. Finally, the Hartree-Fock equation can be written as;

$$\begin{aligned} \left[-\frac{1}{2} \nabla_i^2 + v_i \right] \phi_i(r) + \sum_{j=1}^N \int |\phi_j(r')|^2 \frac{1}{|r - r'|} \phi_i(r) d\tau_j \\ + \sum_{j=1}^N \int \phi_j^*(r') \phi_i(r') \frac{1}{|r - r'|} \phi_i(r) d\tau_j = \epsilon_i \phi_i(r) \end{aligned} \quad (3.10)$$

The initial term comprises a single electron term that incorporates both potential and kinetic energy. The second term is a Hartree-like term, and the third term is an exchange term derived from the solution of the Slater determinant and the cross-cross term of the determinant expression. This equation can also be solved in the self-iterative method. Hence, incorporating multiple modifications starting from Schrodinger equation Hartree Fock gives us better approximation in wavefunction approach and are found suitable for obtaining solution for atoms and molecules. Currently, this is not our focus due to the significant challenge associated with storing data using the wavefunction approach, particularly for big systems.

3.2 Density Functional Theory (DFT)

In 1960, DFT was developed as an alternative of the Hartree-Fock method with lower computational costs (Eberhard Engel, 2011). Through this method wavefunctions are replaced with the functionals of the spatially dependent electron density in order to get the solution. The main issue with a wavefunction is its dependence on $4N$ variables ($3N$ spatial and N spin coordinates). Therefore, for a practical system a large value of N makes the calculations very tough to handle. While using DFT the $4N$ degree of freedom get reduced to only 3 degrees of freedom because here electron density is used as a fundamental property. The publication of the Hohenberg-Kohn theorems provided a solid theoretical basis for the density functional theory which are discussed in the next section.

In quantum mechanics, the probability of finding electron 1 in dx_1 , electron 2 in dx_2 , ...electron N in dx_N (' x ' includes both spatial and spin coordinates, i.e., $x=\{r,\sigma\}$) is given by:

$$|\psi(r_1\sigma_1, r_2\sigma_2, \dots, r_N\sigma_N)|^2 dr_1 dr_2 \dots dr_N. \quad (3.11)$$

The probability of finding an electron in infinitesimally small volume element dr_1 around a point r_1 is given by the electronic density and defined as:

$$n(r_1) = N \sum_{\sigma_1, \sigma_2, \dots, \sigma_N} \int dr_2 \dots \int |\psi(r_1\sigma_1, r_2\sigma_2, \dots, r_N\sigma_N)|^2 dr_2 \dots dr_N \quad (3.12)$$

Where σ_i is spin corresponding to i^{th} electron.

The operator corresponding to the density observable is

$$n(r_1) = \sum_{i=1}^N \sum_{\sigma_i} \delta(r_1 - r_i) \quad (3.13)$$

3.2.1 The Hohenberg-Kohn Theorems and Kohn-Sham approach

Hohenberg and Walter Kohn (Hohenberg & Kohn, 1964) utilized electronic density $n(r)$ to illustrate the concept of ground state electronic energy in 1964. The H-K theory commences by examining the system of particles that are in interaction within the external potential $V_{ext}(r)$. There are two primary theorems proposed in that article:

Theorem 1: Every observable quantity of a quantum system can be calculated from the density of the system alone. Which means that the basic variable is no more the many-body wavefunction $\psi\{r\}$ but the electron density $n(r)$.

Theorem 2: The variational principle can be used to find the exact electron density in the ground state. The ground state density is the density that minimizes the total energy. Any additional energy corresponding to the system's random density is thus greater than the energy corresponding to the ground state density.

$$E_{GS}[n(r)] \geq E_{GS}[n_{GS}(r)] \quad (3.14)$$

The abbreviation for the ground state is GS.

Hohenberg and Kohn Theorems laid the foundation for Density Functional Theory. Kohn and Sham capitalized on the ideas. The Kohn-Sham scheme aims to replace many-electron interaction problems with the non-interacting electron with the same ground state energy equal to the original interacting many-electrons (Eberhard Engel, 2011). Finally, the total energy of a many-electron system subject to an external potential is determined using KS decomposition.

$$E[n] = T_0[n(r)] + \int dr n(r) V_{ext}(r) + E_H[n(r)] + E_{xc}(r) \quad (3.15)$$

And the term used are explained as;

Electron density; $n(r) = \sum_i^{occ} |\Psi_i(r)|^2$

Potential due to nuclei; $V_{ext} = -\sum_n \frac{Z_n}{r-R_I}$

Classical coulomb energy; $E_H[n] = \frac{1}{2} \iint dr dr' \frac{n(r)n(r')}{|r-r'|}$

Exchange & correlation; $E_{xc}[n] = \int dr n(r) \epsilon_{xc}[n(r)]$

Equation 3.15 comprises the following terms: kinetic energy (first term), external potential (second term), classical Coulomb interaction (third term), and exchange and correlation (fourth term). The exchange and correlation term includes all the non-considered term such as correction for kinetic energy for interacting particles, self-energy correction, particle exchange, particle correlation etc. Hence the density-based KS equation can be said as;

$$\left[\frac{1}{2} \nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r) \quad (3.16)$$

Therefore, using the above one particle equation and solving self iteratively like the Hartree-Fock expression, one can solve this even though not knowing the exchange-correlation energy explicitly.

3.3 Self-Consistent Field (SCF) calculation

In the initial stage calculation, guessing the initial electron density and calculating the effective potential, which is the sum of $V_{ext}(r)$, $V_H(r)$ and $V_{xc}(r)$ is followed by solving the Kohn-Sham equation, which results in the single-particle wave functions. Next, a comparison is conducted between the electron densities from before and after utilizing the calculated single-particle wave function to ascertain the updated electron density. When the old and new electron densities are identical, the optimized ground-state electron density is considered. Furthermore, in the event that the two-electron densities differ, the mixed electron density (consisting of X percent of the original electron density and Y percent of the final electron density) is utilized. This process is iterated until the new and old electron densities are compared once more. Repetition of this procedure occurs until convergence is attained. The SCF cycle schematic is illustrated in Figure 3.1.

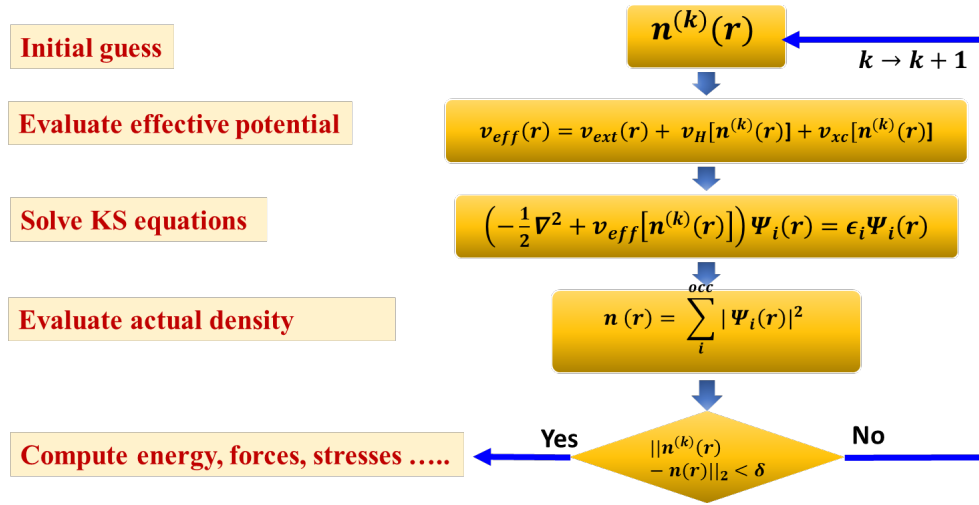


Figure 3.1 The flow chart of self-consistent field calculation.

3.4 Exchange and correlation functionals

Approximating the more precise exchange and correlation energies is crucial. To accomplish this, numerous techniques have been created, including hybrid functionals, local density approximation (LDA), and generalized gradient approximation (GGA). These functionals have different performance level for multiple applications as well as varied computational requirement. Jacob's ladder analogy is popular for analyzing the computational complexity and accuracy level of the well-known exchange and correlation functionals. This ladder connects the ground of Hartree only with no exchange-correlation functional to the heaven of exact functional. There are five steps in the ladder which correspond to the different level of functionals. As steps approached toward the heaven the accuracy becomes higher but the computational requirement increases with each step.

3.4.1 Local Density Approximation (LDA)

This is a most basic form of exchange correlation functionals, where the electrons are modelled as a uniformly distributed electron-gas. It considers that the electron density is localized at a certain point of where E_{xc} is needed. Using LDA, the exchange-correlation energy can be expressed as (Kohn & Sham, 1965);

$$E_{xc}^{LDA}[n] = \int n(r) \epsilon_{xc}[n] dr \quad (3.17)$$

Where $\epsilon_{xc}[n]$ is exchange and correlation energy density at the same point.

3.4.2 Generalized gradient approximation (GGA)

Another approximation, distinct from the local density approximation, is predicated on both the density of the same point and the neighborhood of the considered point. In other words, it is also gradient-dependent and is referred to as a "semi-local functional" as a result (Perdew et al., 1996).

$$E_{xc}[n^\sigma] = \int dr e_{xc}^{GGA}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \quad (3.18)$$

3.4.3 Hybrid Functional

As we know in the Hartree Fock approximation, the exchange energy term is exact; therefore using the Hartree Fock exchange and taking LDA/GGA correlation energy one can think for more accurate functional. But this mixed approach (adding HF exchange with LDA/GGA correlation) does not fit well and give very bad results due to error associated with exchange as well as in correlation energy term in the LDA/GGA which however ($E_x^{LDA/GGA}$ and $E_c^{LDA/GGA}$) lie in opposite direction so that it cancels out or compensate each other therefore LDA/GGA work well on its own. Therefore, the effective way to introduce a mixing parameter such that a fraction of HF exchange is considered and the remaining fraction of correlation energy can be taken from the GGA or LDA. For instance, fraction 'a' is defined such as $0 < a < 1$ and functional form is written as;

$$E_{xc}^{hybrid} = a E_x^{exact} + (1 - a)E_x^{GGA} + E_c^{GGA} \quad (3.19)$$

Here a parameter can be taken by fits to data sets, or based on XC hole arguments. This functional still benefit from error cancellation and also take advantage of nice properties of exact exchange as well. e.g. B3LYP, HSE06 etc.

3.5 Limitations of DFT:

There are various software such as VASP, Quantum Espresso, WIEN2k, SIESTA, ABINIT etc, that solve the Kohn-Sham equations but are based on the electronic ground state of any system. Electronic excitations and non-equilibrium processes were never intended to be described by density functional theory (DFT). The Kohn-Sham formulation of DFT, for example, may precisely predict the equilibrium structures of semiconductors but cannot predict their related optical properties quantitatively. The following are aspects of material properties that can be computed with high precision using DFT:

- Ground state structures;
- vibrational characteristics;
- cohesive and binding energies;
- electron affinity and ionization potential of molecules;
- band structures of metals and semiconductors.

Conversely, certain material properties, such as the following, can not be reliably calculated to via DFT:

- electronic band gaps of insulators and semiconductors;
- excitonic information of a material;
- magnetic properties materials (typically systems containing atomic-like localised d or f electronic states) and strongly correlated systems
- Defect Properties in semiconductors.
- Temperature dependent optoelectronic properties

Hence, we see that the density functional theory (DFT) has a great deal of restrictions and cannot be regarded a "universal" method for finding the properties of materials. In spite of this, the Kohn-

Sham eigenfunctions and eigenvalues prove to be a helpful starting point for more complex (and time-consuming) approaches, even in situations where density functional theory (DFT) fails. For example, in order to estimate band gaps in density functional theory, it is typical to begin with the Kohn-Sham equations and then add 'quasiparticle' corrections (Aryasetiawan & Gunnarsson, 1998). Similarly, for explaining the magnetic characteristics of Mott-Hubbard insulators, the Kohn-Sham eigenstates and eigenvalues can be used as a starting point for more complex computations based on 'dynamical mean-field theory' (Georges et al., 1996).

3.6 Phonon Dynamics

The atomic bonds in solid crystals form a periodic three-dimensional lattice. Internal and external thermal energies cause the atoms in the systems to vibrate like little springs linked together. The result is mechanical waves that propagate across the lattice, dissipating energy as heat and sound. Because a wave packet can move through the crystal with a defined kinetic energy and momentum, it can be considered a particle in quantum mechanics and this quantum of vibrational mechanical energy is called a phonon in condensed matter Physics. The lattice dynamical properties can be obtained by starting with phonon calculations.

3.6.1 Density Functional Perturbation Theory (DFPT)

Predicting the linear response and associated physical properties of periodic systems subjected to external perturbations, such as atomic displacement in the primitive unit cell, and homogeneous external fields, is a common application of the DFPT (Baroni et al., 1987; Gonze, 1995). Generally, the derivative of total energy with respect to atomic displacements and a homogeneous electric field is connected with numerous aspects in solid-state physics. Forces exerted on nuclei, stresses, and dipole moments make up the first derivative, while the linear response coefficients, first-order Hamiltonian, and polarizability tensor are examples of second-order derivatives of total energy.

The "interatomic force constants" are used to characterize the molecular vibrations in the harmonic approximation. When a nucleus is moved out of its equilibrium position in the linear regime, these forces are generated; they are the second derivatives of the total energy of the change in locations of the nuclei. The nonlinear dielectric tensor and anharmonic force constants (phonon-phonon interaction, Grüneisen parameters) are examples of higher-order derivatives encountered in the nonlinear regime. This approach relies on computing the second-order perturbation of the DFT total energy, $\delta^2 E$, within the framework of density functional theory.

Let us consider one perturbation and assume every atom is moved out of its equilibrium position by an amount δu . This causes changes to the external potential V_{ext} , the wave function of the Kohn-Sham equation, and the charge density $n(r)$. A diagonalization of the dynamical matrix yields the atomic frequencies:

$$D_{sas'\beta}(q) = \sqrt{\frac{1}{M_s M_{s'}}} \sum_v \frac{\partial^2 E_{tot}}{\partial u_{\mu s \alpha} \partial u_{v s' \beta}} e^{iq(R_v - R_\mu)} \quad (3.20)$$

Where s and s' iterate over atoms, α and β are cartesian components for each atom while $u_{\mu s \alpha}$ and $u_{v s' \beta}$ are the atomic displacements and R_μ , R_v indicate the Bravais lattice vectors. A grid of q -points is used to compute the energy and wave-function derivatives, which in turn yield the entire dispersion. For more detailed explanations, see (Baroni et al., 2001).

3.7 Transport Phenomena in solids

Heat, electricity, and matter are transported through a material under the effect of a temperature gradient, an electric field potential, or an atomic concentration gradient are part of

transport phenomena in solids. To analyze transport phenomena, we require conservation laws expressed as continuity equations and equations that describe how a specific quantity responds to a disturbance using transport coefficients.

In today's world, comprehending transport phenomena is crucial for the advancement of high-performance materials and devices used in fields as diverse as thermoelectrics, nanoelectronics, and energy conversion. By treating electrons as particles, we have gained insight into thermal and electrical processes.

By including the electrical conductivity σ in the macroscopic form, the current density can be calculated as follows:

$$\vec{J} = \sigma \vec{E} \quad (3.21)$$

Where, with the definition of effective mass (m):

$$\sigma = \frac{ne^2\tau}{m} \quad (3.22)$$

A difference in temperature, ΔT , is created by thermal conduction, and similar to electrical conduction, it may be possible to find a link between the particle velocity and the amount of energy due to thermal flow. The heat current is given by:

$$U = \frac{1}{3} C v^2 \tau \Delta T \quad (3.23)$$

Where the thermal conduction (introducing the mean free path Λ) is:

$$\kappa = \frac{1}{3} C v \Lambda \quad (3.24)$$

A coupling phenomenon can be observed between the electrical current and the thermal current in certain metals and semiconductors. An indication of this link can be found in the fact that electrons carrying thermal current also generate electric fields by conveying charge. Because of this interaction between heat and charge transfer gives rise to thermoelectric phenomena.

3.7.1 Boltzmann Transport Equation (BTE)

The BTE equations have been traditionally employed to simulate the thermoelectric properties of the materials. From first principles, the BTE approximates the Seebeck Coefficient (S), Electrical conductivity (σ) and the electronic thermal conductivity (κ_e) with precision. It is a statistical approach that computes nanoscale properties in close proximity to equilibrium conditions. The non-equilibrium system can be investigated further from the properties of the equilibrium system. Charge transport is approximated by the utilization of group velocities of charge carriers in conjunction with occupational probability and shifting chemical potential. Assuming a system with non-uniform particle density and temperature, the equilibrium distribution function, which also varies from location to location, determines the particle distributions within local regions. The global non-equilibrium distribution is represented by local equilibrium distributions in a non-equilibrium Boltzmann transport equation.

In the context of a system of randomly moving electrons, let us examine the distribution function $f(\vec{r}, \vec{k}, t)$, which quantifies the probability of locating an electron at position $\vec{r}$ with a

crystal momentum $\vec{k}$ at time t . Varying values of the distribution function result from three processes (M. S. Dresselhaus, 2001):

- (a) **Particle diffusion:** Particle diffusion refers to the process by which electrons migrate from regions of high concentration to those of low concentration.
- (b) **Collisions between particles:** The formation of heat and loss of kinetic energy are potential consequences of Collisions between particles, which are time dependent.
- (c) **Impact of external fields:** Illustrative instances of external fields include temperature gradients and external currents that are introduced into the system.

Therefore, the general equation can write as:

$$\frac{df(\vec{r}, \vec{k}, t)}{dt} = \left. \frac{df(\vec{r}, \vec{k}, t)}{dt} \right|_{diffusion} + \left. \frac{df(\vec{r}, \vec{k}, t)}{dt} \right|_{collision} + \left. \frac{df(\vec{r}, \vec{k}, t)}{dt} \right|_{fields} \quad (3.25)$$

After solving, the BTE equation can be rewritten as:

$$\frac{df(\vec{r}, \vec{k}, t)}{dt} + \vec{v}(\vec{k}) \frac{df(\vec{r}, \vec{k}, t)}{d\vec{r}} + \frac{d\vec{k}}{dt} \frac{df(\vec{r}, \vec{k}, t)}{d\vec{k}} = \left. \frac{df(\vec{r}, \vec{k}, t)}{dt} \right|_{collision} \quad (3.26)$$

3.7.1.1 Relaxation Time Approximation (RTA)

In order to simplify the equation above, the collision contribution is frequently calculated using the constant RTA technique, which assumes that the relaxation time is unaffected by the position and velocity of the electrons. The relaxation time refers to the duration required for an electron to go from a non-equilibrium state to equilibrium once the external field is deactivated.

$$\frac{df(\vec{r}, \vec{k})}{dt} = -\frac{f(\vec{r}, \vec{k}) - f_0(\vec{r}, \vec{k})}{\tau} \quad (3.27)$$

With this approximation, the BTE equation solved to obtain current density $\vec{j}(\vec{r}, t)$:

$$\vec{j}(\vec{r}, t) = \frac{e}{4\pi^3} \int \vec{v}(\vec{k}) \cdot f(\vec{r}, \vec{k}, t) d^3\vec{k} \quad (3.28)$$

Where $d^3\vec{k}$ is the element of 3D wave vector space.

Further, from the BTE the electronic parameter used in thermoelectricity can be derived.

3.7.1.2 The electronic parameters derived from the BTE:

(i) Electrical Conductivity and Electronic thermal conductivity

By using Equation 3.19 & 3.26 electrical conductivity is given by:

$$\vec{\sigma} = \frac{e}{4\pi^3} \int \tau \vec{v}(\vec{k}) \cdot \vec{v}(\vec{k}) \cdot \frac{\partial f_0(E)}{\partial E} d^3\vec{k} \quad (3.29)$$

The lattice heat is carried out by the electrons as well as the vibrating atoms. Hence, the thermal conductivity of any material is the sum of the electronic and lattice contribution.

$$\kappa_{tot} = \kappa_e + \kappa_l \quad (3.30)$$

From the BTE we can calculate the electronic contribution part, which is given by:

$$\kappa_e = \frac{1}{4\pi^3 T} \cdot \int \tau \vec{v} \cdot \vec{v} (E - E_F)^2 \cdot \frac{\partial f_0(E)}{\partial E} d^3 \vec{k} \quad (3.31)$$

To simplify the above equations. Some approximations are introduced:

(a) In the case in which $E - E_F \ll k_B T$, the distribution function is replaced with Maxwell-Boltzmann distribution:

$$f_0(E) = e^{\frac{E - E_F}{k_B T}} \quad (3.32)$$

(b) Electronic bands are assumed as parabolic

$$E = \frac{\hbar^2 k^2}{2m^*} \quad (3.33)$$

(c) It is assumed that relaxation time remains constant.

Consequently, the ultimate formulation for the variables $\vec{\sigma}$ and κ_e is

$$\sigma = \frac{2e^2 \tau}{m^*} \left(\frac{m^* k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} e^{\frac{-E_F}{k_B T}} \quad (3.34)$$

$$\kappa_e \propto m^{*\frac{5}{2}} T^{\frac{5}{2}} \tau e^{\frac{-E_F}{k_B T}} \quad (3.35)$$

To conduct a quantitative comparison with experiments, the often-used assumption of constant relaxation time (CRT) is sometimes insufficient. The next section explains a straightforward model that goes beyond the constant relaxation time approximation and depends on energy and temperature.

(iii) Seebeck coefficient

The characteristic coefficient that regulates the Seebeck effect is denoted by S . This effect occurs when a material subjected to a temperature gradient T displays an open circuit voltage $V = -S\Delta T$ in the absence of current flow. The Seebeck coefficient is:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}} \quad (3.36)$$

3.7.2 Scattering mechanism for electrons

Electronic transport properties in semiconductors are decided carrier scattering within the material. Electron can collide through variety of mechanism, including electron-phonon or lattice scattering, electron-electron scattering, electron-impurity, and electron-defect collisions (Ashcroft, 1976). Majorly the lattice scattering and impurity scattering are considered in our study to compute the electron transport properties using material parameters obtained from first-principles. The Fermi golden rule used to calculate the scattering rates for elastic and inelastic scatterings from an initial nk state, where n is a band index, and k is a wave vector, to a final $mk + q$ state can be written as the equations 3.37 and 3.38 respectively:

$$\tau_{nk \rightarrow mk+q}^{-1} = \frac{2\pi}{\hbar} |g_{nm}(k, q)|^2 \delta(\varepsilon_{nk} - \varepsilon_{mk+q}) \quad (3.37)$$

$$\tau_{nk \rightarrow mk+q}^{-1} = \frac{2\pi}{\hbar} |g_{nm}(k, q)|^2 \times [(n_q + 1 - f_{mk+q}^0) \delta(\Delta \varepsilon_{k,q}^{nm} - \hbar \omega_q) + (n_q + f_{mk+q}^0) \delta(\Delta \varepsilon_{k,q}^{nm} + \hbar \omega_q)] \quad (3.38)$$

where $\hbar$, δ , n and f are the Planck's constant, Dirac delta function, Bose-Einstein distribution, and Fermi-Dirac distribution. The ϵ_{nk} corresponds to the energy of the $|nk\rangle$ state and $g_{nm}(k, q)$ is the coupling matrix element of the considered scattering mechanism. The $-\hbar\omega_q$ and $+\hbar\omega_q$ correspond to the photon emission and absorption.

3.7.2.1 Polar-optical Scattering

The primary electron scattering mechanism that significantly impacts crystalline semiconductors is electron-phonon scattering. This occurs as a result of electrons being scattered by the thermal motion of the lattice. Optical scattering is only significant when the charge distribution on neighboring ion sites has opposite signs in polar semiconductors. Furthermore, variations in optical phonon modes result in the creation of dipoles that scatter charge carriers. This process is found crucial in compound semiconductors III-V and II-VI (Ridley, 1996). The polar optical phonon scattering matrix element is given by;

$$g^{POP}(k, q) = \left[\frac{\hbar\omega_{PO}}{2} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_s} \right) \right]^{\frac{1}{2}} \frac{\langle mk + q | nk \rangle}{|q|} \quad (3.39)$$

Where k_B , ϵ_s , ϵ_{∞} , ω_{PO} and q is the Boltzmann constant, static dielectric constant, high-frequency dielectric constant, polar optical phonon frequency, and phonon wave vector. The polar-optical scattering is explicitly dependent on phonons energy. We will see in Chapter 6, the parameters determined from phonon calculations used to calculate the scattering rate play a critical role in determining transport coefficients.

3.7.2.2 Acoustic phonon scattering

Energy shifts in energy band extrema, which occur as a result of crystal compression and expansion during acoustic mode vibrations, are linked to acoustic phonons. Acoustic phonon scattering is analyzed in terms of the elastic deformation potential, and the rate of scattering is defined as:

$$g^{ADP}(k, q) = \left[\frac{k_B T \epsilon_d^2}{B} \right]^{\frac{1}{2}} \langle mk + q | nk \rangle \quad (3.40)$$

Where B , ϵ_d and T Bulk modulus, volume deformation potential, and temperature respectively.

3.7.2.3 Impurities scattering

At lower temperatures, the significance of phonon scattering diminishes. Conversely, the prevalence of ionized impurity scattering and other defect scattering processes increases. Ionized impurity matrix element is given by;

$$g^{IMP}(k, q) = \left[\frac{Ze n_{ii}^{1/2}}{\epsilon_s} \right] \frac{\langle mk + q | nk \rangle}{|q|^2 + \beta^2} \quad (3.41)$$

n_{ii} , β , and q is the concentration of ionized impurities, inverse scattering length, and phonon wave vector. The concentration of ionized impurities is; $n_{ii} = C \left(\frac{n_0 - p_0}{Z} \right)$, where n_0 and p_0 are electron and hole concentration respectively, Z is the charge state of the impurity centre, and C is the compensation factor.

The determination of the total relaxation time involves computing the inverse of the total rate, as the scattering probabilities are cumulative for numerous scattering processes.

In this thesis work the electronic scattering rates, lifetime, and mobility are evaluated using the ab initio scattering and transport (AMSET) code (Ganose et al., 2021), which solves the linearized electronic Boltzmann transport equation. AMSET has been shown to perform well in estimating transport qualities when compared to both experimental observation and other highly accurate theoretical methods using the EPW code (Ponce et al., 2016). Specifically, scattering mechanism dependent transport properties are examined under the consideration of scattering from acoustic deformation potential (ADP), ionized impurities (IMP), and polar optical phonons (POP).

3.7.3. Lattice thermal conductivity

The total thermal conductivity, as denoted in equation 3.28, is obtained by adding the electronic and lattice conductivities. The expression for the calculation of κ_l in kinetic theory is as follows:

$$\kappa_l = \frac{C v_q \Lambda_{ph}}{3} \quad (3.42)$$

The heat capacity and average phonon velocity, denoted as, C , and v_q respectively, can be determined by the phonon dispersion. The phonon mean free path, denoted as, Λ_{ph} , the primary factor contributing to this heat conductivity is in semiconductors. The value of the κ_l does not exhibit a direct dependence on the thermoelectric parameters. Achieving a low value of κ_l is advantageous in order to enhance the figure of merit ZT, and this can be accomplished through phonon scattering.

3.7.4. The Unified theory of Thermal Transport (Particle and Wave-like nature)

In 1929, Peierls devised the phonon Boltzmann transport equation (BTE) to describe heat conduction in crystalline materials; Microscopic heat carriers in crystals are phonon wave packets that diffuse and scatter as if they were gas particles (Peierls, 1929). This theory has been employed once after developing suitable algorithms so that its linearized form (LBTE) can be solved using exact diagonalization techniques or approximately through single-mode approximation (SMA) (Garg et al., 2011). However, this theory is characterized align well for system where inter branch spacing of phonons branches are much larger than the linewidths, which are generally called simple crystals. In 1963, Hardy (Hardy, 1963) demonstrated that thermal conductivity can be represented using the phonon velocity operator, whose diagonal elements are the phonon group velocities entering Peierls' BTE, and that the missing off-diagonal terms are negligible in simple crystals. Allen and Feldman noted in 1989 that these off-diagonal elements are not negligible for the disorder system or glasses (P. B. Allen & Feldman, 1989). As a result, Peierls' picture is inadequate for accurately defining phonons and group velocity. Thereby, a harmonic model of thermal transport in glasses was presented, in which coupled vibrational modes from the velocity operator's off-diagonal elements promote heat transfer while disorder inhibits it. These issues are underscored by the LBTE's failure to characterize materials with ultralow thermal conductivity, necessitating the development of new models that anticipate both glass and crystal transport process. In contrast, Allen and Feldman's harmonic theory may be insufficient to illustrate the anharmonic and disordered systems, and crystal-like propagation methods were proposed without a formal justification to explain the outcomes of the experiment.

The PBTE approach is well-defined for crystalline materials, however it was found insufficient to explain the experimentally observed ultralow lattice thermal conductivity. Simoncelli et al. have developed a thermal transport equation based on the phonon velocity operator in response to the limitations of PBTE in explaining lattice thermal transport in substantially anharmonic crystalline materials (Simoncelli et al., 2019). The suggested velocity operator has diagonal and off-diagonal parts that explain particle-like propagation of phonons and wavelike interbranch tunnelling of coherence (diffusons and locons), respectively.

Using unified treatment of phonon transport including contribution of particle-like propagation ($k_p^{\alpha\beta}$) and wave-like tunnelling and loss of coherence between different vibrational modes ($k_c^{\alpha\beta}$), where α and β are indexing the Cartesian directions, the total lattice thermal conductivity ($k_l^{\alpha\beta} = k_p^{\alpha\beta} + k_c^{\alpha\beta}$) is computed using Wigner formalism. Consider the phonon mode indexed by wave vector q and branch s . The particle-like contribution resulting from the diagonal ($s = s'$) terms of the Wigner heat-flux operator, is written as (Simoncelli et al., 2019);

$$k_p^{\alpha\beta} = \frac{1}{VN_q} \sum_{qs} C_q^s v_{q,\alpha}^s v_{q,\beta}^s \tau_q^s \quad (3.43)$$

The heat carried through the coupling of vibrational modes, described by off-diagonal ($s \neq s'$) terms, is;

$$k_c^{\alpha\beta} = \frac{\hbar^2}{k_B T^2 V N_q} \sum_{qs} \sum_{s \neq s'} \frac{\omega_q^s + \omega_q^{s'}}{2} v_{q,\alpha}^{s,s'} v_{q,\beta}^{s,s'} \times \frac{\omega_q^s n_q^s (n_q^s + 1) + \omega_q^{s'} n_q^{s'} (n_q^{s'} + 1)}{4(\omega_q^s - \omega_q^{s'})^2 + (\Gamma_q^s + \Gamma_q^{s'})^2} \times (\Gamma_q^s + \Gamma_q^{s'}) \quad (3.44)$$

Where α and β are indexing the cartesian direction. Here, k_B is the Boltzmann constant, V is the unit cell volume, and N_q is the number of phonon wave vectors sampled in the Brillouin zone. C_q^s , v_q^s , τ_q^s , ω_q^s , $v_q^{s,s'}$ and Γ_q^s ($\tau_q^s = \frac{1}{\Gamma_q^s}$) are the heat capacity, group velocity, lifetime, phonon frequency, velocity operator, and scattering rate of a phonon mode, respectively. $n_q^s = [\exp(\frac{\hbar\omega_q^s}{k_B T}) - 1]^{-1}$, is the equilibrium Bose-Einstein distribution. The underlying wave mechanism described by the “coherences” term κ_c is phonon interband tunnelling between any low propagating modes s and s' with the same q . When the frequencies of the two modes ω_q^s and $\omega_q^{s'}$ are closer, the wave coherence ($\sim v/(\omega_q^s - \omega_q^{s'})$, where v is the speed of sound) increases resulting in stronger tunnelling.

ShengBTE and Phono3py code are generally used to compute the lattice thermal conductivity of the material using the above-mentioned theory.

3.7.5. Scattering process in phonons

Similarities exist between the function of phonon scattering in thermal transport and electron scattering in electrical transport properties. In the subsequent sections, we shall provide a concise overview of phonon-phonon scattering, isotope scattering, and phonon-phonon scattering, specifically Umklapp collisions.

3.7.5.1 Phonon-Phonon scattering

Phonons are scattered by other phonons as a result of the potential's anharmonic terms. Two distinct alternatives are:

- (a) Splitting process: a phonon mode qj decays in two modes $q'j'$ and $q''j''$.
- (b) Combination: a phonon mode qj scatters by absorbing another mode $q'j'$ to generate a third phonon mode $q''j''$.

Energy conservation and wavevector preservation differ for normal and Umklapp phonons in anharmonic processes:

❖ N-Process	$qj + q'j' = q''j''$
❖ U-Process	$qj + q'j' = q''j'' + Q$

Q denotes the phonon wave vector, which is analogous to the vectors of reciprocal lattices. Zero value for Q indicates N-process. In the presence of umklapp processes, the scattered phonon wavevector could align in the opposite direction of the energy flow. At high T , for low defect crystals, Umklapp processes, which have a $1/T$ dependence, predominate in the thermal conductivity; hence, they are an essential element to account for when computing the lattice contribution to thermal conductivity.

3.7.5.2 Phonon Boundary scattering

The phenomenon wherein a phonon reflects off the surface from a certain state (qj) is characterized by the boundary scattering process. Phonon-boundary scattering is a notable phenomenon, especially in low-dimensional nanostructures and under conditions of low temperature and phonon density, where the duration of the scattering is not dependent on T . Thus, the relationship between the thermal conductivity and the phonon density in this range proportional to T^3 .

3.7.5.3 Isotope Scattering

Isotope phonon scattering is caused by the presence of distinct isotopes among the elements of the host. The mass disorder in question may have an impact on the lattice thermal conductivity calculation.

3.8 SCAPS Simulator

SCAPS is the one-dimensional solar cell capacitance simulator developed at the university of Gent Belgium (Marc Burgelman et al., 2018). This is a public domain software, used for predicting the photovoltaic performance of the homo/hetero structure solar cells. It solves the one-dimensional coupled semiconductor equations with certain boundary conditions:

$$\frac{\partial}{\partial x} \left(\epsilon_0 \epsilon_r \frac{\partial \varphi}{\partial x} \right) = -q \left(p - n + N_D^+ - N_A + \frac{\rho_{def}}{q} \right) \quad (3.45)$$

$$-\frac{\partial J_n}{\partial x} - U_n + G_n = \frac{\partial n}{\partial t} \quad (3.46)$$

$$-\frac{\partial J_p}{\partial x} - U_p + G_p = \frac{\partial p}{\partial t} \quad (3.47)$$

$$J_n = q\mu_n nE + qD_n \frac{\partial n}{\partial x} \quad (3.48)$$

$$J_p = q\mu_p pE - qD_p \frac{\partial p}{\partial x} \quad (3.49)$$

Here ϵ_0 and ϵ_r are the permittivity values in vacuum and materials, respectively; φ is the electrostatic potential, q is the electronic charge, p and n are hole and electron concentrations, respectively, N_D^+ and N_A^- are the ionized donor and acceptor density, ρ_{def} is the charge defect density, J_n and J_p are the current density due to electron and hole respectively, μ_n and μ_p are the mobility of electron and hole respectively; U_n and U_p are the recombination rate of electron and hole respectively; G_n and G_p are the generation rate of electron and hole respectively; $\partial n/\partial t$ and $\partial p/\partial t$ rate of change of electron and hole concentration respectively; E electric field; D_n and D_p electron and hole diffusion coefficient, respectively.

