HIGH EFFICIENT OPTOELECTRONIC MODELING TOOL FOR NOVAL SOLAR PHOTOVOLTAIC MATERIALS

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Abstract

Solar energy is a leading renewable energy source, its long-term availability and remarkable potential has really helped a lot in recovering the growing environmental problems. Recently, solar photovoltaic (PV) materials have drawn great interest of scientific community for implementation of solar cell with direct bandgap and high absorption co-efficient capability. Development of economical solar cell materials helps to bring down the overall installation cost so that a common person can afford it.

The current work contains everything you need to know about solar PV energy, including three generations of solar PV technology, a comprehensive analysis of potential solar PV materials, and a reliable and cost-effective Density functional theory (DFT) methodology, as well as various exchange correlation functions ((i.e. modified Becke and Johnson, (mBJ) potentials, (PBE-sol))) and the WIEN2K software simulation tool, that can be used to investigate a broad variety of semiconducting materials optoelectronic properties (i.e. energy bands, density of states, dielectric tensor components, absorption coefficient, reflectivity, refractivity, dielectric loss with high accuracy) in order to understand whether or not the material is suitably utilize to develop novel solar cells.

Chapter-1

SOLAR PHOTOVOLTAIC CELL AND NOVAL MATERIAL REVIEW

1.1. Introduction

A mechanism to produce direct electricity from sun light is accounted by photovoltaic (PV) effect, where the term light and electricity is related with photo and voltaic term, respectively. The purpose to generate direct electricity from sun light is fulfilled by means of a solar cell which is a semiconductor light sensitive device. Edmund Becquerel was the first French scientist who observed the photovoltaic effect in 1839 [1] but its original flavor come in picture after origin of quantum theory and solid state physics. First crystalline silicon solar cell with 6% efficiency was discovered by Chapin et al. [2] in Bell laboratory in 1954. Later on researchers continuously tried their best effort to invent highly efficient solar PV materials [3-13]. Commercially first solar PV system was introduced in the 1950s by US in to their space program. Presently maximum global market is captured by silicon-based PV cells but there are other semiconductor materials and depending upon their performance and costing these semiconductors are providing reasonable competition to Si based solar cell. In this chapter we will discuss the major types of Si and non-Si based PV materials.

1.2. Solar Photovoltaic (PV) Cell

A voltage generation phenomena (Photovoltaic Effect) takes place when the light is incident on a device, known as solar cell. In order to collect maximum solar energy from solar spectrum and converted it in to usable electrical energy the device used in solar cell fabrication is wide area semiconducting device.

The solar spectrum contains the intensity of radiation that is continuously changes. Relation between energy (E) and wavelength of radiation is (λ) is:

$$E = \frac{hc}{\lambda} \tag{1}$$

Where E is photon energy, h is Planks constant, c is speed of light.

In Figure 1.1 variation of power (kilowatt meter square) with wavelength (micrometres) is shown. From Figure1 it is clear that after attending maximum power decay in power is observed with increase in wavelength.

The total intensity of incoming solar radiation can be calculated from area under the curve [1, 4].

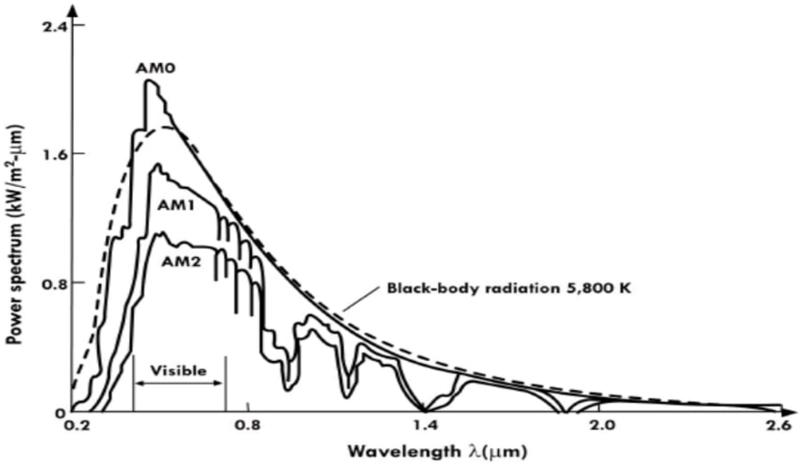

Figure 1.1 Solar spectrum associated with various air mass conditions. The spectrum AM0 related to outside the atmosphere, AM_1 is at the zenith, and AM_2 is at an angle of 60^0. Taken from Physics of semiconductor devices - S.M. Sze.

1.2.1. Photovoltaic energy conversion

As stated earlier electromagnetic energy associated with ultraviolet, visible and infrared wavelengths converted in to direct electrical energy (either current or voltage) by photovoltaic energy conversion technique [5]. The photovoltaic energy conversion takes place in following steps:

1. The first step in which absorption of light leads to the transition inside the material from ground state to excited state.

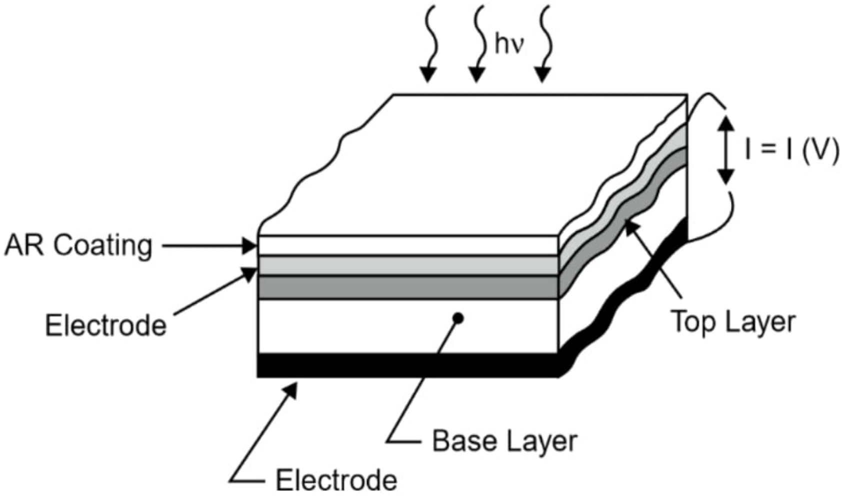

Figure 1.2 Cross-section of a typical solar cell.

2. In next step negative and positive charge carriers are separated out in opposite directions via inbuilt electric field in the depletion region.
3. After this free charge carriers i.e. negative charge and the charge carriers are collected on cathode anode contact.

Above figure 1.2 indicate the cross-sectional view of solar PV system. The anti-reflection (AR) coating is used to eliminate reflectivity losses.

1.2.2. Important Characteristics of Solar Cells

The electronic properties of solar PV cell are explored through their equivalent circuit as shown in Figure 1.3.

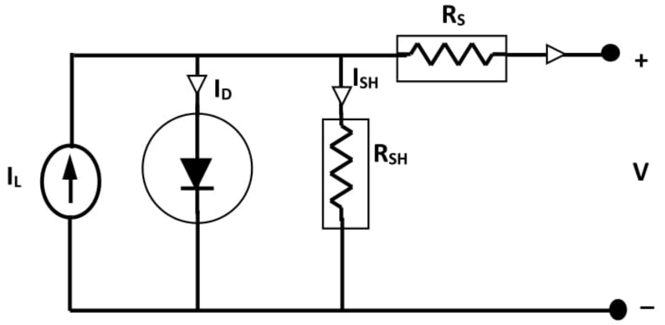

Figure 1.3 Equivalent circuit of solar cell

For an ideal solar cell diode are arranged parallel in to current source. Due to non ideality present in the device shunt (R_{SH}) and series resistance (Rs) are introduced in the equivalent circuit.

Under solar irradiation, total current can be obtained by subtracting photo generated current from diode current. Mathematically,

$$I = I_0(e^{qv/kT} - 1) - I_{ph} \tag{2}$$

To understand solar cell characteristics short circuit current (I_{SC}) and open circuit voltage (V_{OC}) are two important aspects. These two important situations are shown in Figure 1.4 and 1.5. Solar cell I_{SC} is obtained charges are allowed to move freely through the circuit and no any build up potential is present. In this condition no diode current is produced, hence current generated by solar cell is maximum.

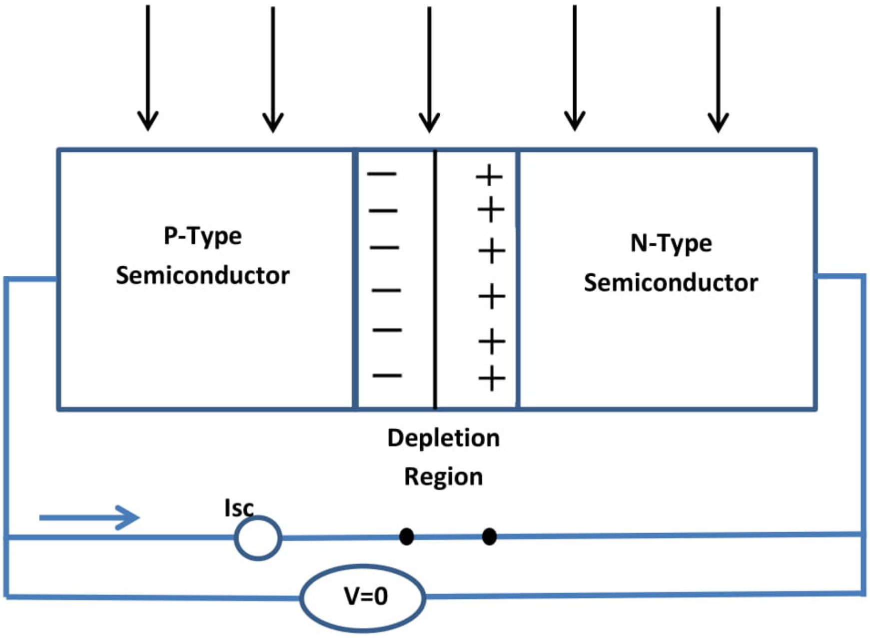

Figure 1.4 Short circuits current

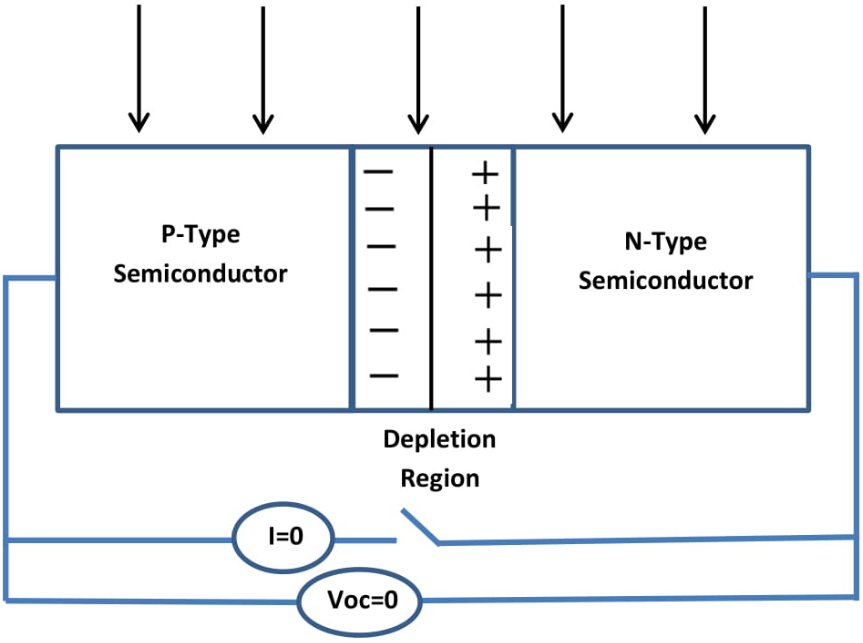

Figure 1.5 Open circuit voltage

In case of V_{OC} charge builds up on each sides cause diode current to flow. The solar cell goes under equilibrium condition when the diode current and photo generated current (I_{Ph}) become equal. Typically for silicon solar cell current is around 1mA and voltage is around 0.5V. In Figure 1.6 we have shown IV-characteristics of solar cell: The output power of solar cell is obtained by by multiplying current and voltage. To check the quality of solar cell, we use the term fill factor (ff) which is defined as the ratio of maximum power (P_{max}=Im*Vm) to the product of the open circuit voltage (Voc) and the short circuit current (Isc).

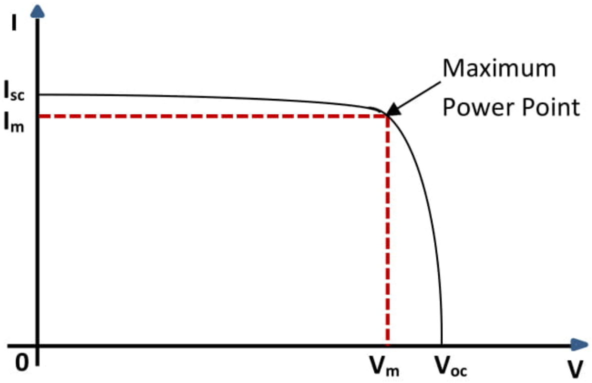

Figure 1.6 IV-characteristics of solar cell

$$ff = \frac{I_m V_m}{I_{sc} V_{oc}} \tag{3}$$

For a perfect rectangular shaped IV curve, fill factor value is 1, but generally it ranges between 0.75-0.85. Further efficiency of solar cell is calculated as ratio of output and input power:

$$\eta = \frac{P_{out}}{P_{in}} \tag{4}$$

1.2.3. Solar Cells, Module and Arrays

Solar PV cells are connected in series and parallel combination to form solar module. For obtaining high power level individual cells are connected in series and /or parallel. For PV system these modules act as fundamental building blocks. When number of solar PV modules is connected in series and parallel combination they form solar PV array. Solar PV array is act as a complete power generating station. The complete structure of PV cells, PV modules and PV array are shown in Figure 1.7 (a, b, c) [6, 7].

1.2.4. Application of Solar PV Systems:

Solar PV system is applicable in both space and terrestrial energy generation. Today we can find out various use of solar cell in residential, space, solar grids, solar thermal etc.

Figure 1.7 (a) Solar PV Cell

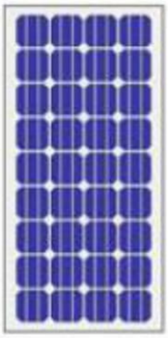

Figure 1.7 (b) Solar PV Module

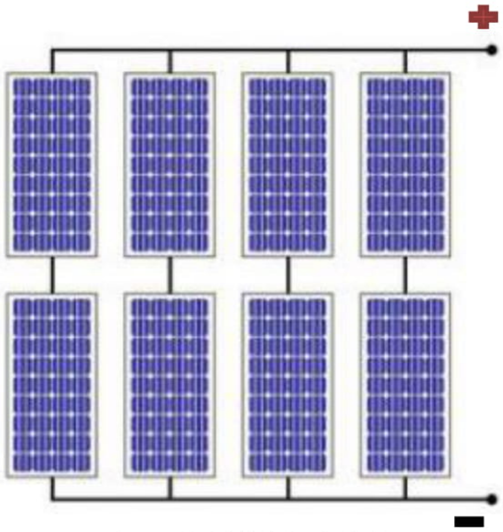

Figure 1.7 (c) Solar PV Array

1.3. Types of Solar Cells

The solar cell materials can be classified in to different category depending on their electromagnetic radiation absorption capability, energy conversion efficiency and the manufacturing cost.

In the present section we are going to discuss three generation of solar cell materials [8]:

1. First Generation
2. Second Generation
3. Third Generation

1.3.1. First-Generation: Crystalline Silicon

Silicon (Si) is the basic semiconductor material with energy band gap 1.1 eV. It is used in first generation (1G) of solar cells materials that is categorised in terms of either single crystalline or multi-crystalline. The working principle of 1G solar cells are based on simple p-n junction diode whereas light incident on the cell surface an electron hole pair generated. Due to inbuilt electric field in the depletion region, electron hole pair is separated. At last metal electrodes are used to collect usable electrical energy. The production of 1G solar cell PV modules was started in 1963 and currently about 85% of global market is captured by this solar PV technology. As far as efficiency is concern 1G solar cell PV modules have efficiency 14% to 17% [9-11]. These solar cells are highly stable and less expensive but there is wastage of slicing wafer in these types of cells.

1.3.1.1. Mono-Crystalline silicon

Fabrication of mono – crystalline silicon cells are done using single crystal of silicon. These types of cells pose highest degree of efficiency up to 20% in 1G solar cell technologies [12].

1.3.1.2. Poly-Crystalline silicon

As compare to mono crystalline solar cell poly-crystalline cells have easy and economical manufacturing process. Efficiency of these cells is 16%. At lab level one can achieve efficiency between18% to 23%. [12]. These polycrystalline cells are preferred because these are less expensive, more stable and well tested technology [13].

1.3.1.3. Amorphous silicon solar cells

Amorphous silicon solar cells have unordered atomic structure so that their proper crystal structure is not possible. The efficiency of these cells lies between 4% to 8%. The reason behind low efficiency of this cell is due to utilization of low cost and large area substrate hence output power declines with time [14, 15].

1.3.2. Second-Generation: Thin-Film

In this generation wafer depositing substrates having low cost such as glass, polymers and metals used to fabricate solar cells [16]. In 2G PV cells technologies manufacturing part of concern it uses 1-10-micron thin absorber layer. 2G technology can be divided in to three categories:

1.3.2.1. Cadmium Telluride and Concept of Multi-junction

CdTe solar cell is cheaper than silicon materials with 16% power conversion efficiency. The major problem associated with this material is the toxicity of Cd and less availability of Te which limit its uses [12].

1.3.2.2. Copper-Indium-Selenide (CIS) and Copper-Indium Gallium-Diselenide (CIGS)

These types of cells are mostly preferred by industries. As compare to all thin film technology the (CIGS) PV cells have highest power conversion efficiency. The efficiency of CIS PV cells are between7% to 16% but in laboratory 20% efficiency is obtained which is comparable to C-Si cells [17]. CIGS solar cells have inbuilt ability to capture direct as well as indirect solar radiations.

1.3.3. Third-Generation PV technology

These are the emerging technology which is attracting the researchers. These 3G PV technologies includes nanostructured, organic-inorganic, hybrid solar cell etc. The working concept of these cells is same as p-n junction PV cell. Efficiency of these types of cells is high potential and it can overcome the Shockely-Queisser limit of 1G & 2G solar PV system, thus 31-41% power efficiency can be obtained for single bandgap occupied solar PV materials.

1.3.3.1. Dye sensitized solar cells (DSSC)

Michael Gratzel was the first to that demonstrate DSSC using TiO_2 and ruthenium metal to achieve 11% efficiency. The overall processing cost of DSSC is very less as compare to conventional PV cells and it is also possible to use flexible substrate to fabricate these kind of solar cell. The major drawback with these cells is that it can degrade under the influence of UV radiations [19].

1.3.3.2. Organic photovoltaic (OPV) solar cells

Organic or polymer materials are used in order to fabricate these types of solar cells. These types of cell are low in cost; light in weight and fabrication of these is also easy [18].

1.3.3.3. Nanostructured solar cells

Nanostructured solar cells are one of the emerging and advanced future solar PV techniques with same working principle as of DSSC, PV technology [20]. Advantage of adopting these techniques is:

(i) It is possible to eliminate Shockely-Queisser barrier in order to achieve 31%–41% power conversion efficiency.

(ii) The manufacturing cost is decline due to adaption of low cost chemical deposition techniques.

1.4. Review

This section deals with the work done on the ternary and quaternary chalcopyrite compounds.

1996 – 2000

Gonzalez et al. 1996 [21] have studies the temperature dependence optical properties of $CuGaS_2$ compound. Choi et al. 1996 [22] have used Bridman technique to synthesized the bulk crystal of $CuGaS_2$. Rigid ion model technique has been implemented by Azuhata et al. 1996 [23] to perform lattice dynamical analysis of $CuAl(S_2, Se_2)$ and $CuAlSe_2$ compounds. Syrbu et al. 1996 [24] have studied WDR spectra for investigating band gap of $CuInS_2$ compound. Using the FP-LAPW muffin tin orbital method Ahuja et al. 1997 [25] have studied the electronic structure of $CuGaS_2$ material. Excitonic as well as wavelength derivative reflectivity spectra of $CuGaSe_2$ compound has been reported by Syrbu et al. 1997 [26]. Krauss et al.1997 [27] have investigated the optical behaviour of $CdAl_2S_4$ single crystal. Chalapathy et al. 1998 [28] have studied the optoelectronic, crystallographic and stoichiometry properties of $CuGaSe_2$ compound. Chichibu et al. 1998 [29] have reported photo-reflectance and optical absorption spectra. To find out band gap and excitonic resonance energies of $CuInSe_2$ and $CuGaSe_2$ compounds Kawashima et al. 1998 [30] have measured dielectric constants, refractivity, reflectivity, and absorption coefficient of $CuGaSe_2$ and $CuInSe_2$ semiconducting compounds. Mudryi et al. 1998 [31] have prepared PL measurements for $CuInSe_2$ and $CuGaSe_2$ compounds to study their excitonic emission. Park et al. 1998 [32] have used the chemical transport reaction method to prepare single crystal of $CdA1_2Se_4$ and $CdA1_2Se_4$:Co_2^+ compounds. Abedin et al. 1998 [33] have studied frequency development in $AgGaSe_2$ semiconductor to analyse the infrared radiation phenomena within 18 mm range. The (Photoluminescence) PL measurements of the chalcopyrite crystals $CuGaSe_2$ and $CuInS_2$ have been reported by Krustok et al.1999 [34] to investigate the changes in shape and intensity of the emission bands within the variation in temperature. Lazewski et al. 1999 [35] have performed Ab-initio calculations for structure and lattice dynamics of $CuInSe_2$. Wang et al. 2000 [36] have grown the crystals of $CuInSe_2$ using horizontal Bridgman method and have also characterized their structural properties. Gallardo et al. 2000 [37] have reported the optical nature of $CuInS_2$ at high temperature. Gupta et al. 2000 [38] have studied the presence of phonons in the $CdAl_2Se_4$ compound using short-range force constant and a modified rigid ion model. Close spaced vapor transport technique has been implemented by Torres et al. 2000 [39] in order to obtain the $CdIn_2Te_4$ thin films.

2001 – 2005

Alonso et al. 2001 [40] have performed the SE measurements on ternary $CuXZ_2$ (X=In, Ga; Z=S, Se) compounds to study their dielectric tensor. Matsushita et al. 2001 [41] have analyzed the lattice defects in $CuInS_2$ single crystals prepared by the horizontal Bridgman method. The defect chemistry, PL, efficiency and admittance spectroscopy measurements on $CuInS_2$-based solar cells have been carried out by Siemer et al. 2001 [42]. Piezoelectric photo-acoustic spectra of $CuInS_2$ have been studied by Wakita et al. 2001 [43]. Optical properties measurements on $CuMX_2$ (M=In, Ga; X=S, Se) compounds have been performed by Alonso et al. 2001 [44] using SE technique. Lavrentiev et al. 2001 [45] have reported the linear relation between anion displacement and band gap. Structural and electronic behavior of $ZnGeAs_2$ and $CuInS_2$ compounds have been reported by Janotti et al. 2001 [46] and Lazewski et al. 2002 [47] respectively. Chemical transport reaction mechanism has been adopted by Sato et al. 2003 [48] to develop single crystals of $CuGaSe_2$. Eryigit et al. 2003 [49] have performed first-principles calculation for $CuInS_2$ to determine their structural, dielectric and dynamical behavior. Using vertical temperature gradient technique Choi et al. 2003 [50] have fabricated Mn-doped $ZnGeAs_2$ and $ZnSnAs_2$ single crystals. Scheer et al. 2004 [51] have synthesized $CuInS_2$ based thin solar film after Cu/In bilayers sulphurization. Meyer et al. 2004 [52] have investigated the degradation phenomena for $CuInSe_2$ compound. FP-LAPW technique have been implemented by Belhadj et al. 2004 [53] to find out structural and optoelectronic behavior of MNZ_2 (M=Cu; N=In, Ga: Z Se) compounds. Using Bridgman method, Hong et al. 2004 [54, 55] have grown single crystal of $CdIn_2Te_4$. Using first-principle calculations Lambrecht et al. 2004 [56] have investigated the band gap of $CdSiAs_2$ and $CdSiP_2$ compounds. Laksari et al. 2005 [57] have studied the electronic and optical calculations for chalcopyrite crystals. The electronic behaviour of $CuInS_2$ has been studied by Nanu et al. 2005 [58] by using DLTS technique. Treating plane wave as a basis set for DFT calculation, Raulot et al. 2005 [59] have analyzed opto-electronic behavior of $Cu(In,Ga)(S,Se)_2$ semiconductor compounds. Klaer et al. 2005 [60] have performed damp heat stress test to judge the stability of $CuInS_2$ and $Cu(In, Ga)Se_2$ compounds. Optical properties investigations of $CuInSe_2$ has been carried out by Kozlov et al. 2005 [61] to check its feasibility in PV devices. Deshmukh et al. 2005 [62] have implemented time-domain approach for solar cell AC parameter calculations for $CuInSe_2$ compounds. A review on $CuInSe_2$ wide band gap solar cells material have been presented by Sharma et al. 2005 [63]. Absorption and photoluminescence property of $CdGa_2Te_4$ have been studied by Ozaki et al.2005 [64]. Sabayleh et al. 2005 [65] have investigated optical prperties of $CdIn_2Te_4$ compound with change in percentage doping of Mn.

2006 – 2010

$CuGaS_2$ thin film were prepared by Gullen et al. 2006 [66] using elemental evaporation technique. The electronic structure calculations for $CuGaS_2$ have been performed by Palacios et al. 2006 [67] using VASP code. An ab-initio investigation have been undertaken by Gurel et al. 2006 [68] for evaluating elastic and lattice dynamical nature of $CuAlSe_2$ using DFT method. In order to check the $Cu(In,Ga)(S,Se)_2$ compounds PV devices, Halverson et al. 2006 [69] have investigated the electronic and optical properties. Electronic structure calculations for $CuInSe_2$ and $Cu(ln,Ga)Se_2$ have been performed by Medvedeva et al. 2006 [70] using FP-LMTO method. Laksari et al. 2006 [71] have studied optoelectronic behavior of $XGaS_2$ (X=Cu, Ag) compounds using FP-LAPW method. High-quality of $ZnSnAs_2$ semiconductor compound has been prepared by Marenken et al. 2006 [72]. Resistivity and Hall coefficient dependencies over hydrostatic pressure for $CdSnAs_2$ and InAs compounds have been studied by Mollaev et al. 2006 [73]. Hot-press technique have been implemented by Kinoshita et al. 2006 [74] to synthesized $AgGaSe_2$ crystal. Using chemical vapor transport method, Levenko et al. 2007 [75] have prepared $CuGaS_2$ compound. A study on polarized spectra for $CuGaS_2$ crystal has been performed by Sobolov et al. 2007 [76]. Structural and electronic properties of $XGaZ_2$(X=Ag,Cu; Z=S,SSe) have been reported by Chen et al. 2007 [77]. Palacios et al. 2007 [78] have studied the optical properties of $CuGaS_2$ compound using DFT method. Investigation of dielectric tensor of $CuGaS_2$ and $CuInS_2$ has been reported by Levcenko et al. 2007 [79]. Novel salinization/sulphurization growth process technique has been used by Tivanov et al. 2007 [80] to study the optical nature of Cu (ln, Ga)(S,Se_2) compound. Total energy evolution for AgGa(S_2, Se_2); CuGa(S_2, Se_2) have been investigated by Chen et al. 2007 [81] using DFT. Spectroscopic-ellipsometry and thermoreflectance spectra for $CdIn_2Te_4$ have been reported by Take et al.2007 [82]. Optical properties of $CuGaS_2$ semiconductor has been studied by Aguilera et al. 2008

[83] within frame work of DFT. X-ray emission and absorption spectra for $CuGaSe_2$ and $ZnGeAs_2$ compounds have been reported by Drahokoupil et al. 2008 [84]. Levchenko et al. 2008 [85] have performed both spectroscopy and PL measurements for $CuGaSe_2$. Reshak et al. 2008 [86] have reported electronic and optical properties of $CuInX_2$ (X = S, Se, Te) using FPLAPW method. Tight-binding method has been implemented by Huitle et al. 2008 [87] to perform electronic band structure calculations of CulnM(S, Se, Te) compounds electronic band structure calculations. Using spray-ILGAR method Camus et al. 2008 [88] have synthesized $CulnS_2$ films. Bedi et al. 2008 [89] have prepared $AgInSe_2$ films from thermal evaporation process. Yoshino et al. 2008 [90] have studied hot-press technique in order to prepare the crystal of $AgInSe_2$ compound. Deposition and characterization of $CuZnS_2$ has been reported by Uhuegbu et al.2008 [91]. Boyd et al. 2009 [92] have used wedge technique methods to study the linear and nonlinear properties of $CuGaS_2$. A first-principles study on the electronic and optical properties for ($CuXS_2$, X = Al, Ga, in, and $AgGaS_2$) have been reported by Brik et al. 2009 [93] using CASTEP code. Thin films of nanocrystalline $CuGaS_2$ has been prepared by material has been prepared by Prabukanthan et al. 2009 [94] using chemical vapor transport method. A first principle study has been carried out by Brik et al. 2009 [95] to determine optoelectronic properties of $CuMS_2$ (M = Al, Ga, In) and $AgGaS_2$ compounds. Asubar et al. 2009 [96] have used an ultra-high vacuum chamber to fabricate $ZnSnAs_2$ epitaxial films. In order to detect native defects in II–IV–V_2 compounds, magnetic resonance technique has been implemented by Gehlhoff et al. 2009 [97]. Xu et al. 2009 [98, 99] have used FPLAPW+lo techniques to evaluate the structural and optoelectronic properties of $ZnSiAs_2$ and $CuGaS_2$. Aguilera et al. 2010 [100] have reported the optoelectronic structure calculations for $CuGaS_2$ using DFT approach. Soni et al. 2010 [101] have investigated the electronic and optical properties of $CuGaS_2$ and $CuInS_2$ compounds using FP-LAPW and LCAO computational method to highlight the utility of these compounds in solar cells. Screened-exchange LDA technique have been used by Maeda et al. 2010 [102] to examine the electronic properties of $CuXSe_2$(X=In, Ga, Al), compounds. Heidemann et al. 2010 [103] have studied Planck's generalized rule for $CuInS_2$ compound to determine its correlation effect among quasi-Fermi level splitting and local defect absorbance. The optoelectronic behaviour of $CulnS_2$ compound has been measured by Oku et al. 2010 [104]. Vidal et al. 2010 [105] have studied the electronic structure of $Culn(S, Se)_2$ using GW and hybrid functional. Low-temperature molecular beam epitaxy methodology to deposit the $ZnSnAs_2$ film has been implemented by

Agastuma et al. 2010 [106]. Optical absorption, spectroscopic-ellipsometry and photo reflectance spectroscopy of $AgInSe_2$ has been reported by Koitabashi et al. 2010 [107]. Using Hot-wall process Pathak et al. 2010 [108] have grown $AgInSe_2$ thin films. Stoichiometric melt technique has been implemented by Zawilski et al. 2010 [109] to prepare $CdSiP_2$. Using spectrophotometry technique Uhuegbu et al. 2010 [110] have prepared $CuZnS_2$ semiconducting thin film.

2011 – 2015

Liborio et al. 2011 [111] have reported the band gap of $CuGaSe_2$ using DFT. First principle approach has been implemented by Aguilera et al. 2011 [112] to study the optical absorption and dielectric behavior of Ti- and Cr-substituted $CuGaS_2$ compounds. FP-LAPW method has been implemented by Soni et al. 2011 [113] to evaluate the optical characteristics of $CuGaSe_2$ and $CuInSe_2$ compounds. Using hybrid DFT technique Liborio et al.2011 [114, 115] have computed the band gap and intrinsic defect for $CuAlS_2$. Electronic structure of $CuInS_2$ and $CuAlS_2$ compounds has been measured by Ho et al. 2011 [116] using Thermos reflectance (TR) technique. A DFT method has been implemented by Verma et al. 2011 [117] to study the optoelectronic and thermal behaviour of $ZnAl_2Se_4$. Rapid thermal processing method for Cu(ln, Ga)S_2 compound have been reported by Riedel et al. 2011. [118]. Energy band gap calculations for $CuInSe_2$ have been performed by Xiao et al. 2011 [119] by using B3PW hybrid functional. Brik et al. 2011 [120] have performed DFT based ab initio study four $CuAlS_2$, $CuGaS_2$, $CuInS_2$ and $AgGaS_2$ ternary compounds. PL measurements for $AgInS_2$ compound has been studied by Hamanaka et al. 2011 [121]. Polarization-dependent absorption measurements for $Cu_2ZnSi(S_4, Se_4)$ compounds have been carried out by Levcenco et al. 2011 [122]. Using FPAPW+lo technique, Boukabrine et al. 2011 [123] have studied self-consistency in $ZnSiAs_2$ and $CdSiAs_2$ compounds. Bhosale et al. 2012 [124] have investigated the phonon dispersion relations and DOS spectra for $CuGaS_2$, $AgGaS_2$ compounds using ab initio approach. Vahidshad et al. 2012 [125] have used facile method to synthesize $CuAlS_2$ nanocrystal. Oda et al.2012 [126] have studied the optical behaviour of $CuInS_2$ and $CuInS_2/ZnS$ core-shell nanocrystals. Levcenco et al.2012 [127] have performed PL and Raman scattering measurement for $Cu_2ZnSiQ_4(Q = S, Se)$ semiconductors. Scanlon et al. 2012 [128] have studied the property of $ZnSnP_2$ and forced that at high temperature it switches from an ordered chalcopyrite to a disordered sphalerite structure. Using pulsed laser grow technique, Peshek et al. 2012 [129] have synthesized $ZnGeAs_2$ compound. Lattice dynamical investigation for $ZnGeP_2$ and $ZnSnP_2$ compounds have been studied by Basak et al.2012 [130]. Using thermos reflectance spectroscopy techniques Ho et al.2012 [131] have studied optical properties of $AgAlS_2$ compound. Electronic structure study for $CuGaS_2$ using mBJ exchange correlation potential has been reported by Zhang et al. 2013 [132]. Liu et al. 2013 [133] have reported the synthesisis mechanism for $CuGaS_2$ nanoplates of by one-pot thermolysis of a mixture solution of CuCl, $GaCl_3$, and 1-dodecanethiol in no coordinating solvent 1-octadecene. Pohl et al. 2013 [134] have measured the electronic as well as thermodynamic properties of $CuInSe_2$ and $CuGaSe_2$ compounds using hybrid DFT technique. Quantum dots of $CuInSe_2$ have been synthesized by Panthani et al. 2013 [135]. Guc et al. 2013 [136] have performed the Polarized Raman scattering for Cu_2ZnSi (S_4, Se_4) compounds to study their vibrational behaviour. The structural and electronic behavior of $CdAl_2Se_4$ compounds has been studied by Singh et al. 2013 [137] using numerous exchange correlation functional. Rowley et al. 2013 [138] have performed optical rectification analysis for $ZnGeP_2$ compound in near infrared region $ZnGeP_2$ compound. To investigate the structural and optoelectronic nature of $ZnGeAs_2$ compound Tripathy et al. 2013 [139] have undertaken the plane wave pseudo-potential calculation. GGA and EV-GGA exchange correlation potentials embodied in wien2K code have been implemented by Ali et al. 2014 [140] to study the YZ_2 (Y=Al, Ga, In; Z=S, Se) compounds. Ghosh et al. 2014 [141] have reported optoelectronic properties of ternary $CuXY_2$ (X = In, Ga, Al; Y = S, Se, Te) compounds using Becke-Johnson exchange potential method. LPAW wave method have been used by Kumar et al. 2014 [142] to compute the optoelectronic properties of $CuXS_2$ (X=Al, Ga) compounds. Sajid et al. 2014 [143] have studied the optoelectronic structure of $CuYZ_2$ (Y=Al, Ga, In; Z=S, Se) compounds. Zhang et al. 2014 [144] have used mBJ approach to to study electronic structure of $CuGaS_2$. Singh et al. 2014 [145] have investigated the optoelectronic properties of $CuGaS_2$ using DFT calculations. Using ultrasound assisted chemical reduction method Lee et al. 2014 [146] have prepared the thin films of $CuGaS_2$. Chemical vapour transport (CVT) technique has been used to grow the single crystal of (Cu, Ag)AlS_2 compound [147, 148]. Moreh et al. 2014 [149] have used vacuum thermal evaporation technique to deposit the $CuAlS_2$ thin films. Optoelectronic behavior of $CuZS_2$ (Z=Al, Ga, In) compounds have been investigated by Kumar et al. 2014 [150] FP-LAPW method. Amiri et al. 2014 [151] have used facile sonochemical method for fabricate $CuInS_2$ nanostructure. One-step process has been utilized to synthesize the $CuInSe_2$ thin film and $AgInS_2$ nanoparticles [152,153]. Ranjbar et al. 2014 [154] have performed facile one-step process to synthesized $AgInS_2$ nanoparticles. Experimental measurement on reflectivity spectra for $Cu_2ZnSiSe_4$ compound has been performed by Guc et al.2014 [155]. Using modified Bridgman method Levcenko et al. 2014 [156] have prepared $Cu_2ZnSiTe_4$ bulk crystal. Using molecular beam epitaxy technique, Oomae et al. 2014 [157] have prepared Mn doped $ZnSnAs_2$ thin films. Equilibrium condition of $XGeAs_2$ (Zn, Cd) has been reported by Fedorchenko et al.2014 [158] using X-ray, DTA, microstructures and EXDRF investigations. PP plane wave technique has been used by Tripathy et al. 2014 [159] to investigate structural, optoelectronic and elastic behaviour of $ZnGeAs_2$ compound. Single crystals of $CuAlS_2$ and $AgAlS_2$ compounds have been developed by Ho et al.2014 [160] using vapor transport technique. Using Plane wave PP method Kumar et al.2014 [161] have investigate the structural and optoelectronic nature of $ZnSiP_2$. Liu et al. 2015 [162] have used spray pyrolysis technique to prepare $CuGaS_2$ thin films. Time-dependent DFT technique has been used by Mokkath et al. 2015 [163] have studied time-dependent DFT technique for structural and optical investigation of $CunGanSe_2$ and $CunInnSe_2$ nanoclusters ($n = 2, 4, 6$, and 8). Hou et al. 2015 [164] have performed first-principles calculations to study both structural and elastic properties of $CuGaSe_2$ compound. Investigation of electronic and thermoelectric property of $CuAlX_2$ (X=S, Se and Te) has been reported by Gudelli et al. 2015 [165] using DFT calculations. Modelling of thermal photovoltaic collector of $CuInSe_2$ have been performed by Haloui et al.2015 [166]. Suzuki et al. 2015 [167] have prepared thin film of CuInSe compound using spin-coating method. Wei et al. 2015 [168] have used first principles method to calculate thermal conductivity of $CdSiP_2$ and $AgGaS_2$ compounds. Facile one-pot hydrothermal process have been implemented by Zhou et al. 2015 [169] for fabrication of $AgGaS_2$ nanoplates. Nanocrystals of $AgInS_2$ have been synthesized by Yin et al. 2015 [170] using simple wet chemical method. Gurieva et al. 2015 [171] have studied X-ray technique to measure structural behaviour of $Cu_2ZnSiSe_4$ compound. Electronic structure of Mn doped $ZnSnAs_2$ have been studied by Benziane et al. 2015 [172] using GGA approximation. $ZnSnAs_2$ semiconducting compound host matrix is used by Fedorchenko et al. 2015 [173] to synthesize nanogranular semiconductor ferromagnet. Electronic and magnetic properties of $ZnSnAs_2$ have been reported using first principle method [174, 175]. Using chemical vapor deposition technique a nanowires of $ZnSnP_2$ has been prepared by Lee et al. 2015 [176]. Using modified vertical Bridgman technique, Denghui et al. 2015 [177] have prepared $ZnGeP_2$ single crystal. Nakatsuka et al. 2015 [178] have investigated phase of $ZnSnP_2$ compound using flux method. Karunagaran et al. 2015 [179] have performed Bridgman technique for preparing single crystal of $AgInSe_2$ compound. Using one-pot colloidal chemistry route technique Luo et al. 2015 [180] have prepared Au-$CuZnSe_2$ nano sheets. Using flux growth technique, Martinez et al. 2015 [181] have prepared single crystals of $ZnSiP_2$ compound.

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Using DFT method Kumar et al. 2016 [182] have evaluated optoelectronic behaviour of ternary $CuGaS_2$ compound. Modelling of $CuGaS_2$ based thin film solar cell using ZnTe buffer layer has been reported by Singh et al. 2016 [183]. One-step electrodeposition technique has been used by Manfredy et al. 2016 [184] for thin film preparation of $CuGaSe_2$. Thin film of $CuInSe_2$ was prepared by Werner et al. 2016 [185] using metal-organic vapor phase epitaxy method. Various properties of $AgInS_2$ semiconducting material such as, structural, dynamical, mechanical and electronic have been investigated by Nguimdo et al. 2016 [186] using DFT method. Zhang et al. 2016 [187] have studied optoelectronic properties of Cu_2ZnSiS_4 and $Cu_2ZnSiSe_4$ compounds. Chemical vapor transport technique have studied by Litvinchuk et al. 2016 [188] to prepare $Cu_2ZnSiSe_4$ crystal. Uchitomi et al. 2016 [189] have studied molecular beam epitaxy technique to fabricate $ZnSnAs_2$: Mn films. Using flux method Nakatsuka et al. 2016 [190] have prepared $ZnSnP_2$ semiconductor crystals. Vertical gradient freeze method has been used by Yue et al. 2016 [191] to grow $ZnGeP_2$ crystal. The structural optimization and phonon evaluation has been carried out by Sreeparvathy et al. 2016 [192]. Using thermal vacuum evaporation technique Khudayer et al. 2016 [193] have grown $AgAlSe_2$ crystal. Using thermal evaporation method Khudayer et al. 2016 [194] have prepared $AgAlSe_2$ alloy thin films. Sreeparvathy et. al. 2016 [195] have reported the detailed DFT calculations of $ZnXY_2$ (X=Si, Ge, and Sn; Y_2= P and As) and $ZnSiSb_2$ to understand the electronic and transport properties. Nayebi et al. 2017 [196] have studied the pseudo-potential technique to study $CuGaS_2$ nanowires. Grevtsev et al. 2017 [197] have used microwave assisted polyol technique to fabricate $CuGaSe_2$ nanocrystals. Ezike et al. 2017 [198] have used chemical bath deposition technique to synthesized $CuAlSe_2$ thin film. Aydin et al. 2017 [199] come up with non-vacuum spray pyrolysis technique to fabricate fabrication of $CuInS_2$ flexible solar cell. To monitor pre-and post-nucleation stages of $CuInS_2$ nanocrystals, Gromova et al. 2017 [200] have used X-ray diffraction technique using synchrotron radiation. Z-scan technique has been implemented by Li et al.2017 [201] to measure correct refractive index of $ZnGeP_2$ and $AgGaS_2$ compounds. High quality of $AgInS_2$ quantum dots have been synthesized by Cai et al. 2017 [202]. Sonochemical method has been implemented by Panda et al.2017 [203] to prepare $AgInS_2$ quantum dots. Nanoplate and nanoparticles of $AgInS_2$ has been synthesized by Wang et al.2017 [204] using pyridine and 1-dodecanethiol as a solvent. $AgInS_2$ based thin film have been prepared by Zawawi et al. 2017 [205] using inert gas condensation technique. First-principles method has been used by Zamulko et al. 2017 [206] to investigate the structural and optoelectronic behaviour of Cu_2ZnSn_{1-x}(Si/Ge)x$(S/Se)_4$ alloys. Using first-principles technique Yu et al. 2017 [217] has studied structural, dielectric, and lattice dynamical behaviour of $ZnSnP_2$ compound. Bridgman technique has been implemented by Yang et al. 2017 [208] to prepare $ZnGeP_2$ crystal. Lattice, elastic and bulk modulus of $AgAlS_2$ compound have been studied by Hou et al. 2017 [209] using DFT. The birefringence and absorption spectra for $CdSiP_2$ have been reported by Carnio et al. 2017 [210]. Andrade Jr. et al. 2018 [211] have performed solvothermal approach to synthesized Bi-doped $CuGaS_2$ chalcopyrite nanocrystals. Ghosh et al. 2018 [212] have used solution-based thermal decomposition technique to grow $CuGaS_2$ compound in wurtzite and tetragonal Phases. Li et al. 2018 [213] have syntheszed $CuInS_2$/ZnS ternary quantum dots for the application in light-emitting diodes. Using flux method Akari et al. 2018 [214] have been prepared $ZnSnP_2$. Juneja el. al. 2018 [215] have been reported first-principles calculations to study the topological phase transitions in $CdGeSb_2$ and $CdSnSb_2$ compounds.

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Chapter-2

OPTOELECTRONIC MODELING TOOL

2.1. Introduction

This chapter deals with the detailed methodology implemented to study the electronic and optical properties of proposed materials. Quantum mechanics provides a logically consistent theory of matter on the microscopic level which uses Schrodinger equation based quantum mechanics which is the basic theory that involve in the investigation of solid state physics, nuclear physics, chemistry etc. The solution of Schrodinger equation for many particle systems is done by approximation methods. It is well known that a system includes many electrons and many nuclei to describe this system, we need a many body wave function (ψ), which can takes account of state of each atoms and ions.

The many body Schrodinger equation is written as: -

$$\left[-\sum_{\mathrm{i}}\frac{\hbar^2}{2\mathrm{m_e}}\nabla_i^2-\sum_I\frac{\hbar^2}{2\mathrm{M_I}}\nabla_i^2-\frac{1}{2}\sum_{i\neq j}\frac{\mathrm{e}^2}{4\pi\in_0}\frac{1}{|r_i-r_j|}-\frac{1}{2}\sum_{I\neq j}\frac{\mathrm{e}^2}{4\pi\in_0}\frac{Z_IZ_J}{|R_I-R_J|}-\frac{1}{2}\sum_{i,I}\frac{\mathrm{e}^2}{4\pi\in_0}\frac{Z_I}{|r_i-R_I|}\right]\Psi=E_{Tot}\Psi \qquad (2.1)$$

Here the eigenvalue, E_{tot}, is actually the overall energy of the system & ψ represents the many body wave functions. In equation (2.1) the first and second terms correspond to kinetic energy (K.E) of N-electrons and nuclei, the third and fourth term represent the columbic repulsion between the electron and nuclei. The columbic attraction between electrons and nuclei is taken care in last term.

In equation (2.1) $\hbar = 1.054 \times 10^{-34}$ Js, is the reduced plank constant, $m_e = 9.109 \times 10^{-31}$ Kg. is the mass of electron, $m_p = 1.67 \times 10^{-27}$ Kg, is the mass of proton, $e = 1.602 \times 10^{-19}$ C, is electron charge and $\in_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum.

In Hartree unit equation (2.1) can be expressed as:

$$\left[-\sum_{\mathrm{i}}\frac{\nabla_i^2}{2}-\sum_I\frac{\nabla_I^2}{2\mathrm{M_I}}-\sum_{i,I}\frac{Z_I}{|r_i-R_I|}+\frac{1}{2}\sum_{i\neq j}\frac{1}{}\frac{1}{|r_i-r_j|}-\frac{1}{2}\sum_{I\neq j}\frac{Z_IZ_J}{|R_I-R_J|}\right]\Psi=E_{Tot}\Psi \qquad (2.2)$$

The exact solution of equation (2.2) is impossible because it involves many electrons as well as many nuclei. Hence to solve equation (2.2) we need to consider appropriate approximations. Some of approximations are considered here are:

2.1.1 Born-oppenheimer approximation

In Born-oppenheimer approximation the motion of electron and nuclei are considered separately because of higher weight of nuclei (approximately 1800 times to e^-).The K.E of nuclei is assumed to be minimal due to their less mobility's and the columbic repulsion between positively charged nuclei is assumed to be a constant.

Now, the equation (2.1) can be rewritten as follows:

$$\left[-\sum_{\mathrm{i}}\frac{\nabla_i^{\,2}}{2}-\sum_{i,I}\frac{Z_I}{|r_i-R_I|}+\frac{1}{2}\sum_{i\neq j}\frac{1}{\,}\frac{1}{|r_i-r_j|}\right]\Psi=E_{Tot}\Psi \tag{2.3}$$

The nuclei position R_I is treated as an external entity where as ψ is now the function of only electron positions, i.e. $\psi=\psi\,(r_1, r_2 \ldots.. r_n)$. The columbic potential experienced by e^- given as:

$$V_n(r)=\sum_I\frac{Z_I}{r-R_I} \tag{2.4}$$

Now the equation (2.3) converted in to:

$$\left[-\sum_{\mathrm{i}}\frac{\nabla_i^{\,2}}{2}-\sum_i V_n(r_i)+\frac{1}{2}\sum_{i\neq j}\frac{1}{|r_i-r_j|}\right]\Psi=E_{Tot}\Psi \tag{2.5}$$

Equation (2.5) is the fundamental equation for investigation of structure of electron. equation (2.5) includes electrons and their columbic repulsion.

Suppose,

$$H(r_1,r_2\ldots\ldots r_N)=\left[-\sum_{\mathrm{i}}\frac{\nabla_i^{\,2}}{2}-\sum_i V_n(r_i)+\frac{1}{2}\sum_{i\neq j}\frac{1}{|r_i-r_j|}\right]\Psi=E_{Tot}\Psi \tag{2.6}$$

where H ($r_1, r_2 \ldots.. r_n$) stands for many body Hamiltonian which is the combination of K.E and P.E.

Further equation (2.5) can be rewritten as:

$$H\Psi=E\Psi \tag{2.7}$$

We can also define single electron Hamiltonian: -

$$H_0(r) = -\frac{1}{2}\nabla^2 + V_n(r) \tag{2.8}$$

So, many body Hamiltonian can be written as:

$$H(r_1, r_2 \ldots\ldots r_N) = \sum_i H_o(r_i) + \frac{1}{2}\sum_{i \neq j} \frac{1}{|r_i - r_j|} \tag{2.9}$$

2.2. Independent electrons approximation:

The equation (2.5) is still complicated and difficult to solve, as it consists of interactions of many electrons. Exact solution of this equation is not possible, hence approximation method were invented by number of researchers since the late 1920s (Thomas 1927, Fermi 1928, Pauling 1928, Hartree 1928[1], Slater 1929) to solve it. Independent electron approximation assumes that electrons would not see each other. So, the form of Schrodinger equation is as follows:

$$\sum_i H_0(r_i)\Psi = E\Psi \tag{2.10}$$

equation (2.10) can be rewritten as:

$$\Psi(r_1, r_2 \ldots\ldots r_N) = \phi_1(r_1) \ldots\ldots\ldots \phi_N(r_N) \tag{2.11}$$

According to above approximation electrons are now independently treated and probability of finding electron N at r_N obtained by product of individual probability of finding the ith electron at position r_i.. If ϕ_i is the single electronic wave function than:

$$H_0(r)\phi_i(r) = \varepsilon_i \phi_i(r) \tag{2.12}$$

Where ε_i is the eigen value & ε_1 be the smallest eigen value.

Above approximation can’t obey Pauli’s exclusion principle. So we have to solve these problems next approximation.

2.3. Mean field approximation

In above mean field approximation electronic columbic repulsion has been ignored from many body Schrodinger equation.

In the mean field approximation the single particle description and the coulomb repulsion effects both are considered. From the Poisson's equation:

$$\nabla^2 \varphi(r) = 4\pi nr \tag{2.13}$$

In above equation potential energy V_H (r) = – $\varphi(r)$, stands for Hartree potential.

Using this term in equation (2.13), it becomes

$$\nabla^2 V_H(r) = -4\pi nr \tag{2.14}$$

and

$$V_H(r) = \int dr' \frac{n(r')}{r - r'} \tag{2.15}$$

equation (2.13) shows that each element of volume dr' has a charge dQ = – n(r'). Further dr' is responsible for generating columbic potential at point r given by dQ/(r – r')

This approaches fails at atomic scale level and fore, all the electrons under influence of Hartree potential, the equation (2.12) can be improved by taking account of Hartree potential term.

$$\left[-\frac{\nabla^2}{2} + V_n(r) + V_H(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r) \tag{2.16}$$

$$n(r) = \sum_i \left| \phi_i(r) \right|^2 \tag{2.17}$$

$$\nabla^2 V_H(r) = -4\pi n(r) \tag{2.18}$$

This Hartree potential (V_H) is the average potential which is experienced by all electrons and this is called mean field approach.

2.4. Kohn-Sham Equations

Hohenberg-Kohn in 1964 addresses that total energy of a many-body system is a functional of electron density. Using this concept, Kohn-Sham in 1965 [2, 6] gave an equation to describe the many body system. The Kohn-Sham equation is written as follows:

$$\left[-\frac{\nabla^2}{2}+V_n(r)+V_H(r)+V_{XC}(r)\right]\phi_i(r)=\varepsilon_i\phi_i(r) \tag{2.19}$$

Here the term V_{xc} (r) is called exchange and correlation potential and is expressed as:

$$V_{XC}(r)=\frac{\delta E_{XC}[n]}{\delta n} \tag{2.20}$$

V_{xc} (r) is defined as functional derivative of exchange co-relation energy with respect to electron density, ε is the energy of Kohn-Sham orbital and ϕ are the Kohn-Sham orbitals. The exchange correlation term obey Pauli exclusion Principle. Exchange terms tells that if two electrons have same spin, these electrons are not allowed to stay at same place at the same time, whereas the correlation term inform about the electronic correlated motion between two anti-parallel electrons due to columbic repulsion.

Now we can define electron density as $n=\sum_1^N|\phi_i|^2$. Exchange correlation potential converted in to $V_{XC}(r)=\frac{\delta E_{XC}[n]}{\delta n(r)}$.

The total energy of the system can be written as:

$$E=\sum_i^N\in_i-\frac{1}{2}\iint\frac{n(r_1)-n(r_2)}{|r_1-r_2|}dr_1.dr_2+E_{XC}[n]-\int V_{XC}(r)n(r)dr \tag{2.21}$$

2.5. Exchange correlation functional:

To solve Kohn-Sham equation exact form of exchange co relation functional is required.

Local density approximation (LDA) is the simplest one used in DFT. LDA involves homogeneous electron gas model in which electron density is assumed to be same at each point. LDA exchange correlation function depends upon local density only. The energy in LDA is given by:

$$E_x^{LDA}[n] = -c_x \int n^{\frac{4}{3}}(r).dr \tag{2.22}$$

Where $c_x = -\frac{3}{2}(\frac{3}{8\pi})^{\frac{1}{3}}$.

Another functional is generalized gradient (GGA) approximation. In GGA the exchange correlation energy not only depends upon local density but also depend on the gradient of density.

When distance between the two elections r is very large, the exact exchange used in GGA is expressed as:

$$E_x^{GGA}[n, \nabla n] = \int f(n, \nabla n)dr \tag{2.23}$$

LDA & GGA approach fail with strong correlated system. To overcome this problem, another functional known as Hybrid functional were introduced.

We can express Hybrid functional in terms of LDA & GGA as follows:

Further it is observed that LDA & GGA underestimate the band-gap of semiconductor and insulators. Tran-and Blaha [3] has introduced modified Becke – Johnson potential (m-BJ), to get improved band-gap result which is a semi-local potential. Mathematically,

$$V_x^{mBJ}(r) = CV^{BR}(r) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t(r)}{n(r)}} \tag{2.24}$$

where n(r) is electron density, $t = (\frac{1}{2})\sum_{i=1}^{N} \nabla\Psi_i * \nabla\Psi_i$ is K.E density and

$V_x^{BR} = \frac{-1}{b(r)}(1 - e^{-x(r)} - \frac{1}{2}X(r)e^{-X(r)})$ is Backe Roussel potential which was introduced to deal with columbic potential arises due to exchange hole.

We can obtain ‘X’ from and equation that involve n, ∇n, ∇^2n and b is obtain by

$$b = [\frac{X^3 e^{-X}}{8\pi n}]^{\frac{1}{3}} \tag{2.25}$$

In equation (2.24) C was chosen such that it depends on square root linearly as $\frac{|\nabla n|}{n}$.

Here C can be expressed as:

$$c = \alpha + \beta(\frac{1}{V_{cell}} \frac{|\nabla n(r')|}{n(r')} d^3 r')^{\frac{1}{2}} \tag{2.26}$$

here α & β are two independent parameter, where x = 0.012 and B = 1.023 and V_{cell} is unit cell volume.

2.6. Self-Consistent Calculations

DFT based Kohn-Sham equation are suitably implemented for solving the electron density n(r) as well as entire energy of the system in its ground state.

Solution of Kohn-Sham equation can be obtained self-consistently. In this mode of calculation, we start with specifying the nuclear positions, so that nuclear potential (Vn) can be calculated. Vn is used to investigate total potential approximately as:

$$V_{tot}(r) = V_n(r) + V_H(r) + V_{XC}(r) \tag{2.27}$$

It is more convenient to take a good guess of n(r) that can be obtained by adding the density of individual atoms of a material. By keeping n(r) in to account V_H(r) and V_{XC}(r) are calculated, which is required to evaluate effective Kohn-Sham potential (V_{tot}). Using this V_{tot} we obtain the solution of Kohn-Sham equation and by solving this equation we get new wave function ϕ_i which is further used to construct more accurate density n, and then more accurate $V_{tot.}$ This process is repeated unless and until the old and new density is not in a required tolerance self-consistency is achieved. The flow chart for self-consistent is shown in figure 2.1.

2.7. Optical Properties

To examine the response of material after its interaction with light, a complex dielectric function $\varepsilon(\omega)$ is used and mathematically:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega) \tag{2.28}$$

where

$$\varepsilon_1(\omega) = n^2 - k^2 \tag{2.29}$$

and

$$\varepsilon_2(\omega) = 2nk = \frac{\sigma}{2\pi\varepsilon_0 f} \tag{2.30}$$

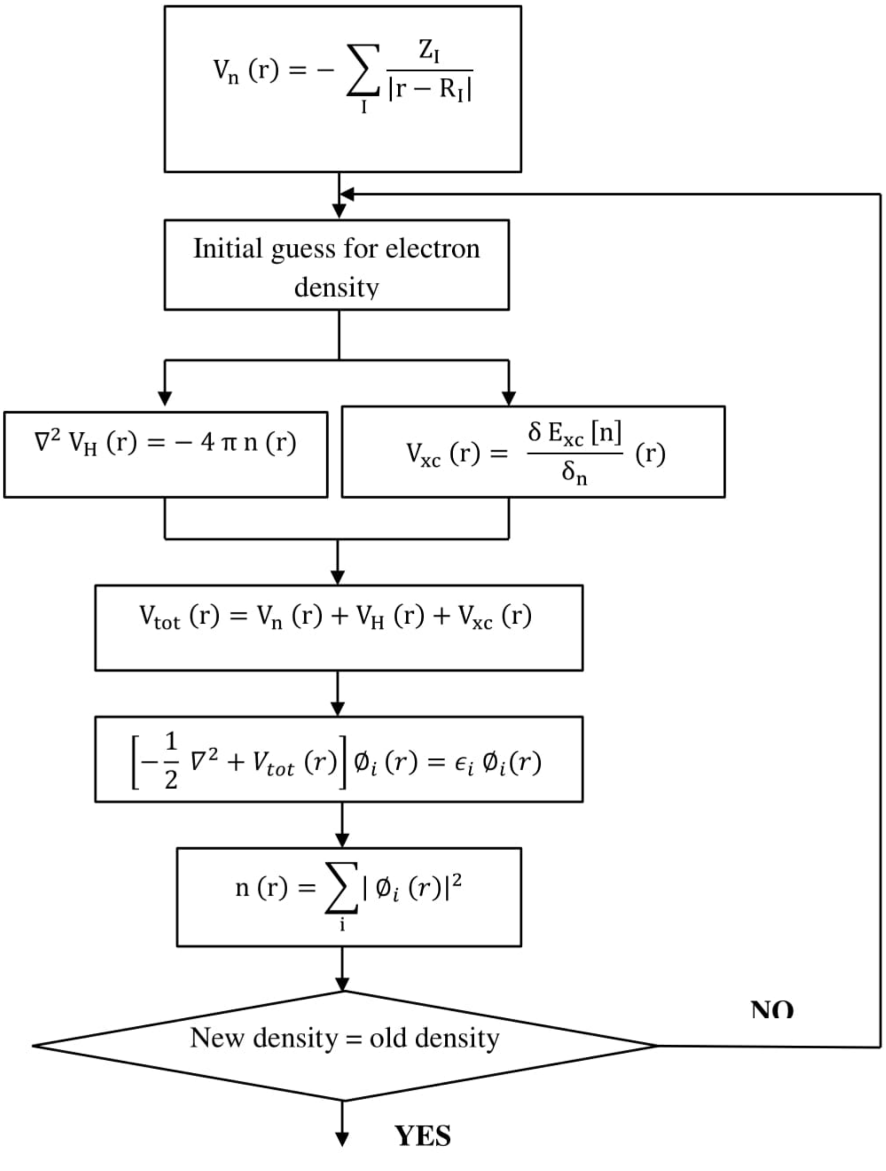

Figure 2.1 Schematic flow Chart for finding self-consistent-solutions of Kohn-Sham equation

The terms n represents the real part of refractive index, k is extinction coefficient, σ is the conductivity of the material and ε_0 is the free space permittivity of the medium.

Both the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ part of the dielectric constant explains the strength of a material when interact with an electric field. $\varepsilon_1(\omega)$ shows dispersive nature with incident photons whereas $\varepsilon_2(\omega)$ completely absorb the energy coming from a time varying electric field. Hence it is mandatory to make high $\varepsilon_2(\omega)$ so that maximum energy is absorbed from time varying electric field.

The absorption coefficients $\alpha(\omega)$ indicates penetration of light of appropriate wavelength (λ) into a material before it is absorbed.

$$\alpha(\omega) = \frac{4nk}{\lambda} \tag{2.31}$$

In order to analyze the fractional reflection of light from the surface, we have to investigate reflectivity $R(\omega)$ spectra. Mathematically

$$R(\omega) = \frac{(n(\omega)-1)^2 + k^2}{(n(\omega)-1)^2 + k^2} \tag{2.32}$$

where, $n(\omega)$ and $k(\omega)$ represent the real and imaginary part of complex refractive index respectively. The $n(\omega)$ shows the variation in the velocity of light in two medium. It can be expressed as

$$n(\omega) = \frac{c}{v} \tag{2.33}$$

In the above equation the terms c and v respectively represents the velocity of light in vacuum and medium, respectively.

Energy loss due to high electronic acceleration in the material is expressed as energy loss function $L(\omega)$.

$$L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + i\,\varepsilon_2^2(\omega)} \tag{2.34}$$

2.8. Full Potential Augmented Plane Wave (FP-LAPW) Method

Linearized augmented plane wave (LAPW) method is similar to other energy band method.

In LAPW we especially adopt a basis set for solving the Kohn-Sham equation for ground state electron density [3].

The problem arises due to the rapid variation of wave function, potential and density closer to nuclei can be solved accurately by partitioning a unit cell in to two regions of non-overlapping atomic spheres. Region A, centered towards atomic sites also known as Muffin Tin sphere (MT-spheres) and interstitial region 'B' between the MT spheres. The wave function inside MT – spheres is investigated by spherical harmonics Y_{im} and a radial part. This radial part of wave function is obtain by u_l (r, E_l) and there energy derivative part $\frac{\partial u_i(r,E_l)}{\partial E_l}$. Plane wave is used as a basis set in the interstitial region. We set maximum plane wave as high as possible.

The radial part of wave function is obtained by u_i and their energy derivative:

$$\phi_{Kn} = \sum_{lm}\left[A_{lm}u_l(r,E_l) + B_{lm}\frac{\partial u_l(r,E_l)}{\partial E_l}\right]Y_{lm}(r), \forall_r \in A \tag{2.35}$$

$$\phi_{Kn} = \frac{1}{\sqrt{\omega}}e^{-iK_n r}, \forall_r \in S \tag{2.36}$$

Here kn = k + Kn, k is the wave vector in first brillouin zone, and kn is the reciprocal lattice vector. After the numerical integration of radial Schrodinger equation on a radial mesh inside the spheres, the co-efficient Aim & Bim are obtain which is the function of *kn*, u_l and $\frac{\partial u_l(r,E_l)}{\partial E_l}$.

2.9. WIEN2K

Wein 2k program a code of Viena group is entirely different from others, as it consists of numerous independent F-90 programs to study crystal property and it is connected

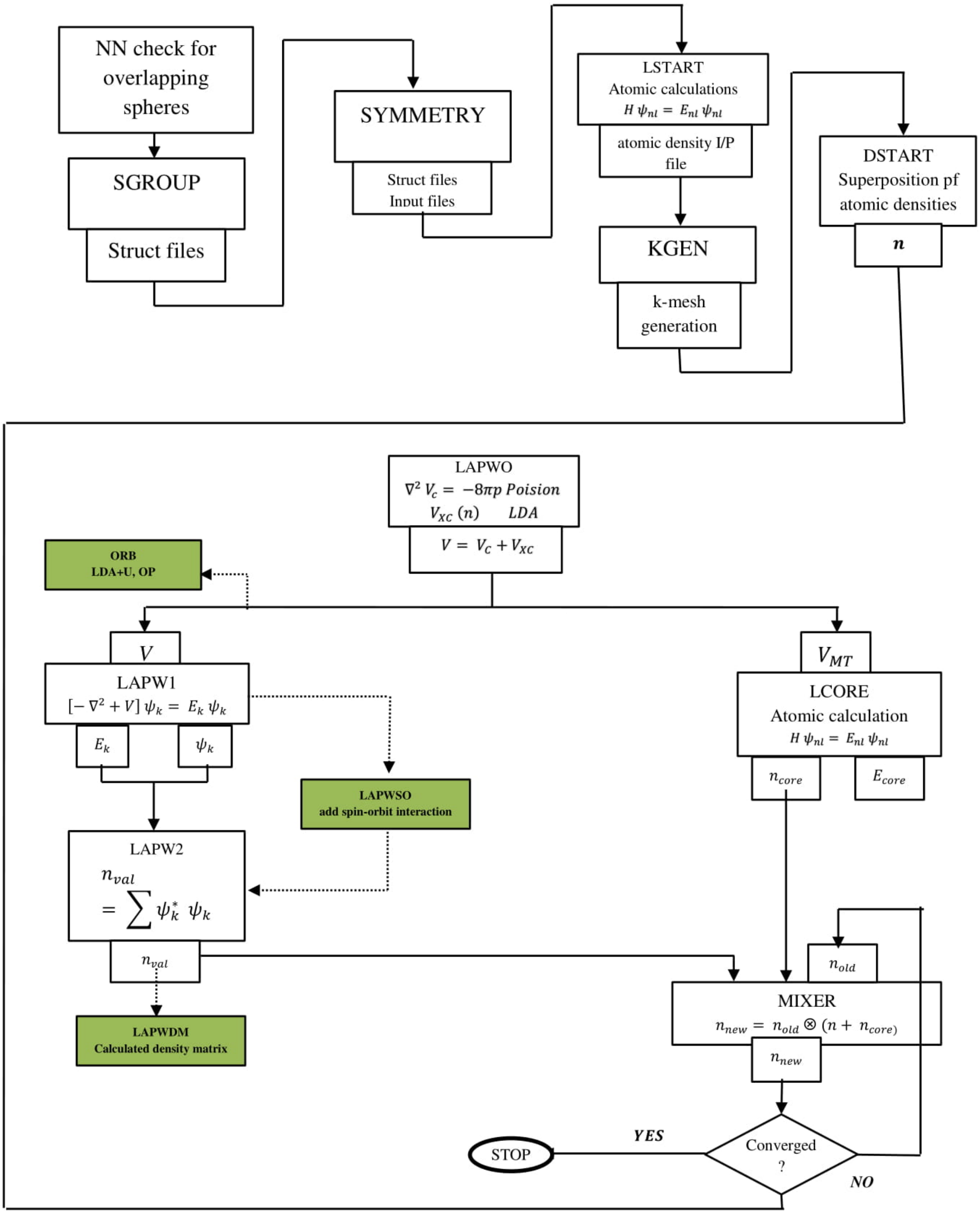

Figure 2.2 Wien2k Flow Chart

together via C-cell scripts that are one of the most powerful scripts among all. Wien2k make use of LAPW basis set within framework of DFT to deal with Kohn Sham equation. The accuracy of wien2k depends upon balanced basis set APW+ Lo, basis set are implemented inside wein2k, for chemically important orbitals [4, 5]. The flow chart of wien2k as shown is figure 2.2 below is divided in to two parts. The top part in the figure 2.2 is reserve for processing input files whereas rest part is for self-consistent investigations. The computation starts with structure files where it contains the information's regarding atomic configuration of the matter, like atomic parameters, Wyckoff positions, muffin tin radial space group etc.

The symmetry calculation inside the unit cell takes place using struct file, subroutines MM, SGROUP and SYMMETRY investigation regarding the overlap between various attired muffin-tin orbitals. The atomic densities for all atoms inside the unit cell are achieved from the next LSTART step. K-mesh files are obtained by initializing KGEN as well as input files. Super position of atomic densities is helpful for constructing initial electron density n(ω), by initializing DSTART. We fix all the required parameters like LDA, GGA, LSDA and energy parameters that separate core states from valence states. In wien2k, to achieve high accuracy together with optional computation time must have good choice. Self-consistent cycle initialized after the generation of starting density. For calculating columbic and exchange correlation potential, we start with LAPWO calculation. The eigen values, eigen functions of valence states and diagonalization of Kohn-Sham equation are required for obtaining LAPW to solve all K-values in K-mesh, the highest occupied energy state of the system, known as Fermi energy is obtain by LAP2 subroutine. If we have the Fermi energy, the valence density is constructed by eigen functions as resulted by LAPW1 and can be expressed as follows:

$$n_{val}(r) = \sum_{\in_{k,i,CE_F}} \phi_k^{*},_i (r) \phi_k,_i (r) \tag{2.37}$$

LCORE subroutine are used to calculate the core electronic energy, that further results in a total core density n_{core}, so total density is expressed as follows:

$$n_{tot} = n_{core} + n_{val} \tag{2.38}$$

The present obtained density is totally altered from the old density n_{old} and a MIXER is used to mix the density to achieve divergence:

$$n_{tot} = n_{old} \otimes (n_{core} + n_{val}) \tag{2.39}$$

During the end of cycle wien2k investigate for convergence between old & new density. If difference occurs then a new iteration is again started where the input is the new density. The process is repeated unless or until both old are new density are not matched so that self-consistency are achieved. After the end of self-consistent cycle, a new density n_{new} is obtained. Also one go for deft analysis of the present calculation, additional packages are also available.

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