Licenciate

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Contents

Abstract

In order to reduce the high dependence on fossil fuels and oil, solar energy is one of the alternatives. There are several very important absorber materials in the thin film photovlotaic technology, such as, the chalcopyrite $CuIn_{1-x}Ga_xSe_2$ (CIGS), Cu_2ZnSnS_2 (CZTS) and $Cu_2ZnSnSe_2$ (CZTSe), the efficiency of CIGS has been reached up to around 20%, so the accurate information for this kind of absorber materials is of great importance in order to design the photovlotaic (PV) materials.

In this licenciate, the parameterization of the band dispersion for the uppermost three valence bands (VBs) and the lowest conduction band (CB) in CIGS with $x = 0, 0.5$, and 1 is explored, which is based on the $k \cdot p$ method, but extended it up to high order. It demonstates that the VBs and CB are quite non-parabolic away from the Γ point, which means that the effecive mass on Γ point is not suitable to discribe the materials properties like band filling and strong excitation effects. At last, the ε spectra of $CuIn_{0.5}Ga_{0.5}Se_2$ is calculated, and compared with the experiment result from $CuIn_{0.7}Ga_{0.3}Se_2$ at 40 K, which demonstates that the overall shape of ε spectra both of calculated and experimented is in good agreement.

The lowest CB and three uppermost VBs of CIGS is parameterized in order to better understand and discribe the anisotropy and non-parabolic of the energy dispersion. In order to illustrate the non-parabolic of the band dispersion, the effective electron and hole mass tensors are abtained in four symmetry directions, to futher illustrate the non-parabolic, the constant energy surface are calculated for the three topmost VBs as well as the lowest CB. Based on the non-parabolic parameterization and compared with parabolic band energy approximation, the density-of-states (DOS), Fermi energy and the carrier concentrations are calculated and analyzed. To summarize, one can better understand and analyze the electrical properties in the CIGS alloys.

The ε spectra of $CuIn_{0.5}Ga_{0.5}Se_2$ is determined by the full-potential linearized augmented plane wave calculations (FPLAPW), which shows a good agreement with the result from Spectroscopic ellipsometry, which illustrates the result of $CuIn_{0.7}Ga_{0.3}Se_2$ at 40 K, furthermore, the probable electronic origins of observed interband critical points (CP) is discussed, and the electronic origins of each CP are examined based on the results from the FPLAPW calculations. At last, the band to band analysis of the contribution to the total ε_2 spectrum is explored.

Chapter 1

Introduction

With the increasing of energy consumption, more and more energy or power is needed. The required energy is mainly satisfied by the fossil fuels and oil, unfortunately, which is very limited energy, one day they will be dispeared if keeping the current pace to use. So it is urgent to explore more sustainable and healthy energy source, solar energy is one of the answer since it is abundant and clean.

So far, the solar cell based on silicon dominate the solar world, however, silicon is an indirect band gap material, moreover, it is very expensive to fabricate the PV device, so more and more thin film solar cells based on some absorber materials also are catching up recently, such as copper indium gallium (di)selenide (CIGS), cadmium telluride (CdTe) and so on. CIGS and CdTe both of them are direct band gap material, especitally, the conversion efficiency of CIGS already reached up to 20.4% by the scientist in the Swiss Federal Laboratories for Materials Science and Technology at the moment, who develop the thin film solar cells on flexible polymer foils.

CIGS material takes the attention from different researchers' group in the world since the higher conversion efficiency, so there are plenty of papers already published to illustrate the different aspects of CIGS, for example,

In this licentiate, the research material is CIGS, the motivation is that CIGS is a very promising thin film absorber material, although the macroscopic properties of CIGS already are farily well understood, there are only little researchs about the details of the electronic energy band dispersion near the uppermost VBs and CB, which is important for analyzing and understanding electrical properties. So the objective of this licentiate is to improve the parabolic band dispersion approximation by parametering the band dispersion using the higher order expasion of the traditional k · p method. In this licenciate, the parameterization of the energy bands for the three uppermost VBs and the lowest CB is presented, and compared with results from the parabolic band approximation and non-parablic band dispersion. And also, since the low temperature SE study of CIGS is rare, so the ε spectra of CIGS is compared and analysed by experment and theoretical calculation.

Chapter 2

Electronic structure calculations

2.1 The quantum many-body problem

The solid is a set which includes a huge amount of atoms (around $10^{23}/cm^3$), and the atom is constructed by nuclei and electrons. According to the quantum mechanics principles, we will know all the properties of solid matter if we can figure out a way to solve the quantum many-body Schrödinger equation exactly. Let us start from the time-independent many-body Schrödinger equation,

$$\hat{H}\Psi(\{\mathbf{R}_I, \mathbf{r}_i\}) = E\Psi(\{\mathbf{R}_I, \mathbf{r}_i\}) \tag{2.1}$$

where $\Psi(\{\mathbf{R}_I, \mathbf{r}_i\})$ is the exact wavefunction for the above Schrödinger equation, $\mathbf{r}_i$ and $\mathbf{R}_I$ stands for electron and nucleus coordinators, respectively, E is the energy of the system, $\hat{H}$ is Hamiltonian which has the following form:

$$
\begin{aligned}
\hat{H} = &-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_{i,I} \frac{Z_I\,e^2}{4\pi\varepsilon_0|\mathbf{r}_i - \mathbf{R}_I|} \\
&+ \frac{1}{2}\sum_{i\neq j} \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J} \frac{Z_IZ_J\,e^2}{4\pi\varepsilon_0|\mathbf{R}_I - \mathbf{R}_J|}
\end{aligned}
\tag{2.2}
$$

where the indices i, j are used for electron and I, J are used for atomic nuclei, Z_I means the charge of the I-th nucleus, here I is a number, and (I)-th means the ordinal number of I, M denotes nuclear mass, m_e is the electron mass, ε_0 is vacuum permittivity.

The equation 2.2 has the following form in atomic units:

$$
\begin{aligned}
\hat{H} = &-\sum_i \frac{\nabla_i^2}{2} - \sum_I \frac{\nabla_I^2}{2M_I} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \\
&+ \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J} \frac{Z_IZ_J}{|\mathbf{R}_I - \mathbf{R}_J|}
\end{aligned}
\tag{2.3}
$$

In equation 2.3, the first and second terms are the kinetic energy operator of the electron and nuclei, respectively, and the other terms in order are Coulomb

interaction between electrons and nuclei, electrons and electrons and nuclei and nuclei.

Since there are so many atoms to calculate in reality, more importantly, we don't know exactly the form of the wavefunction neither, so we can not solve the equation 2.1 exactly at present, but people already figure out some ways to approximate the exact solution. Generally we can divide these approximations into three different levels, the first level is the Born-Oppenheimer approximation and the second level is Hartree, Hartree-Fock (HF), density functional theory (DFT) and kohn-sham (KS) equation, the last level is the approximation for solving the secular equation, which is an equation that is solved to find the eigenvalue of matrix.

2.2   The Born-Oppenheimer approximation

In order to simplify the equation 2.1, the first attempt is to seperate the wavefunction of electrons and nuclei, i.e., $\Psi(\{\mathbf{R}_I, \mathbf{r}_i\}) = \theta(\mathbf{R})\Psi(\mathbf{r})$, but since there is a couple term between the electron and nucleus in the Schrödinger Hamitonian in equation 2.3, so we can not do that simply. On the other hand, let us look at the equation 2.3 again, and we can find that there is a "small" value $1/M$, which is part of the nucleus kinetic energy operator term, the reason is that the mass of nucleus is much larger than that of electron, so if we treat the mass as infinity, the result is that the electron is seen as interacting under both the "external" potential caused by nuclei that are fixed in some positions and that of other electrons. We can see more vividly description from Figure 1 below.
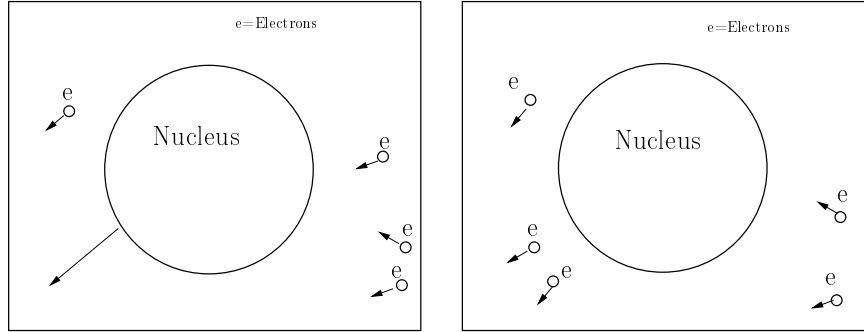

Figure 2.1: Left one: normal interacting system. Right one. The born-Oppenheimer approximation. The arrow denotes the movement of the nucleus or electron

The separation of motion between electrons and nuclei is called the Born-Oppenheimer approximation, since the position of nuclei is fixed, so we can define

$$\Psi(\{\mathbf{R}_I, \mathbf{r}_i\}) \approx \Psi_{bo}(\{\mathbf{r}_i, \mathbf{R}\}) = \theta(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) \tag{2.4}$$

where $\Psi_{bo}(\{\mathbf{r}_i, \mathbf{R}\})$ is the wavefunction of electrons for Born-Oppenheimer approximation, $\mathbf{R}$ is only discrete value belonging to the set of atomic positions, so now, we can recheck the equation 2.3 again, we find out that the term of

nuclei kinetic is gone, the term of interacting between nuclei is simplified as a constant. Now, we can redefine the equation 2.3 as follows:

$$
\begin{aligned}
\hat{H}_{bo} &= -\sum_i \frac{\nabla_i^2}{2} - \sum_i V_{ext}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \\
&= \hat{T} + \hat{V}_{ext} + \hat{V}_{int} + N_{II}
\end{aligned}
\tag{2.5}
$$

where $\hat{H}_{bo}$ is the Hamitonian corresponding the Born-Oppenheimer approximation, the second term is the nuclei potential acting on the electrons,

$$
V_{ext}(\mathbf{r}_i) = \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}
\tag{2.6}
$$

where the subscript "ext" in the second term means "$external$", so this term is about external potentials interaction. The corresponding Schrödinger equation is:

$$
\hat{H}_{bo}\Psi_{bo}(\mathbf{r}_i, \mathbf{R}) = \mathbf{E}_{bo}\Psi_{bo}(\mathbf{r}_i, \mathbf{R})
\tag{2.7}
$$

where E_{bo} is the energy of this electronic system. So far, the discussion above is only considering the Schrödinger equation of electron, i.e., equation 2.7, so how about the Schrödinger equation of nucleus? First, comparing equation 2.3 and 2.5, we can rewrite the total Schrödinger Hamitonian as

$$
\hat{H} = -\sum_I \frac{\nabla_I^2}{2M_I} + \hat{H}_{bo}
\tag{2.8}
$$

so the new Schrödinger equation with equation 2.8 and 2.4 is

$$
(-\sum_I \frac{\nabla_I^2}{2M_I} + \hat{H}_{bo})(\theta(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R})) = E_m(\mathbf{R})(\theta(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R}))
\tag{2.9}
$$

where E_m is the total energy of above system, after some steps of derivation, we can end up with the following equation:

$$
(\hat{H}_{I1} + \hat{H}_{I2} + \hat{H}_{I3} + E_{bo}(\mathbf{R}))\theta(\mathbf{R}) = E_m\theta(\mathbf{R})
\tag{2.10}
$$

where

$$
\begin{aligned}
\hat{H}_{I1} &= -\sum_I \frac{\nabla_I^2}{2M_I} \\
\hat{H}_{I2} &= -\sum_I \frac{1}{M_I}\int \Psi(\mathbf{r}, \mathbf{R})^* \nabla_I \Psi(\mathbf{r}, \mathbf{R})d\mathbf{r}\nabla_I \\
\hat{H}_{I3} &= -\sum_I \frac{1}{M_I}\int \Psi(\mathbf{r}, \mathbf{R})^* \nabla_I^2 \Psi(\mathbf{r}, \mathbf{R})d\mathbf{r}
\end{aligned}
\tag{2.11}
$$

from equation 2.10, we observer that we can get the lattice dynamical properties of certain system within the Born-Oppenheimer approximation, and in this

equation, we also need the gourd state energy $E_{bo}(\mathbf{R})$ of electron system to solve equation 2.10, here $\mathbf{R}$ is the parametrilized value from the atom position. In summary, we derive the Schrödinger equation of electron and nucleus seperatly in this section, and usually, when we refer to calculate the ground state properties, we means to take use of the Schrödinger equation of electron only, e.g., equation 2.7, and we use Schrödinger equation of nucleus for the calculation of lattice dynamics.

So far, we notice that the equation 2.5 is much simpler than equation 2.3, but still not solvable, so we need further more excellent approximations to solve this many-body problem.

2.3 Hartree and Hartree-Fock approximation

Hartree or Hartree-Fock method is straightforward to get the expression we are expecting using the mathematical approaches, and both of them focus on the treatment of wavefunction, however, the wavefunction in Hartree method is not flexible enough, and better but not enough (lacking of correlation term) in Hartree Fock method.

2.3.1 Hartree approximation

The simplest approximation of the wavefunction for many-body Schrödinger equation is the form of acting like non-interacting electrons, so the wavefunction with N non-interacting electrons has the following expression:

$$\Psi_h(\{\mathbf{r}_i\}) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N) \tag{2.12}$$

where i goes through all the electrons, and means state of the i-th electron in the position of $\mathbf{r}_i$, from here and following the R is suppressed in the wavefunction since they are position fixed. So the total energy of the system we can write down in the following way :

$$E_h = < \Psi_h(\{\mathbf{r}_i\})|\ \hat{H}_{bo}\ |\Psi_h(\{\mathbf{r}_i\}) > \tag{2.13}$$

So making the substitution using equation 2.5 and 2.12 into equation 2.13, we can get the total energy of system:

$$
\begin{aligned}
E_h = \sum_i &< \phi_i(\mathbf{r})|\ -\frac{\nabla_r^2}{2} + V_{ext}(\mathbf{r})\ |\phi_i(\mathbf{r}) > \\
&+ \frac{1}{2}\sum_{i\neq j} < \phi_i(\mathbf{r})\phi_j(\mathbf{r}')|\ \frac{1}{|\mathbf{r}-\mathbf{r}'|}\ |\phi_i(\mathbf{r})\phi_j(\mathbf{r}') >
\end{aligned}
\tag{2.14}
$$

In order to calculate the stationary state of the system, so the variation of the wavefunction should be zero variation in the energy, so here we can set up the following equation with Lagrange multiplier E_h^i

$$\delta[E_h - \sum_i E_h^i(< \phi_i(\mathbf{r})|\phi_i(\mathbf{r}) > -1)] = 0 \tag{2.15}$$

In order to calculate the term $\delta(E_h)$, we have to know

$$\delta(\sum_i < \phi_i(\mathbf{r})| - \frac{\nabla_\mathbf{r}^2}{2} + V_{ext}(\mathbf{r}) \ |\phi_i(\mathbf{r}) >)$$

$$= \sum_i \{< \delta\phi_i(\mathbf{r})| - \frac{\nabla_\mathbf{r}^2}{2} + V_{ext}(\mathbf{r}) \ |\phi_i(\mathbf{r}) > + < \delta\phi_i(\mathbf{r})| - \frac{\nabla_\mathbf{r}^2}{2} + V_{ext}(\mathbf{r}) \ |\phi_i(\mathbf{r}) >^*\}$$

$$(2.16)$$

and

$$\delta(\frac{1}{2} \sum_{i \neq j} < \phi_i(\mathbf{r})\phi_j(\mathbf{r}')| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_i(\mathbf{r})\phi_j(\mathbf{r}') >)$$

$$= \frac{1}{2} \sum_{i \neq j} \{< \delta\phi_i(\mathbf{r})\phi_j(\mathbf{r}')| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_i(\mathbf{r})\phi_j(\mathbf{r}') > \qquad (2.17)$$

$$+ < \phi_i(\mathbf{r})\delta\phi_j(\mathbf{r}')| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_i(\mathbf{r})\phi_j(\mathbf{r}') > + T_{rem}\}$$

where T_{rem} is the remaining terms, actually these remaining terms will not affect the derivation. Before getting the final result, there is one more identity

$$< \phi_i(\mathbf{r})\delta\phi_j(\mathbf{r}')| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_i(\mathbf{r})\phi_j(\mathbf{r}') >$$

$$= \int d\mathbf{r}d\mathbf{r}' \phi_i^*(\mathbf{r})\delta\phi_j^*(\mathbf{r}')\frac{1}{|\mathbf{r} - \mathbf{r}'|}\phi_i(\mathbf{r})\phi_j(\mathbf{r}')$$

$$= \int d\mathbf{r}'d\mathbf{r} \phi_i^*(\mathbf{r}')\delta\phi_j^*(\mathbf{r})\frac{1}{|\mathbf{r}' - \mathbf{r}|}\phi_i(\mathbf{r}')\phi_j(\mathbf{r}) \qquad (2.18)$$

$$= < \delta\phi_j(\mathbf{r})\phi_i(\mathbf{r}')| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_j(\mathbf{r})\phi_i(\mathbf{r}') >$$

So the equation 2.17 will become

$$\delta(\frac{1}{2} \sum_{i \neq j} < \phi_i(\mathbf{r})\phi_j(\mathbf{r}')| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_i(\mathbf{r})\phi_j(\mathbf{r}') >)$$

$$(2.19)$$

$$= \sum_{i \neq j} \{< \delta\phi_i(\mathbf{r})\phi_j(\mathbf{r}')| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_i(\mathbf{r})\phi_j(\mathbf{r}') > + \frac{T_{rem}}{2}\}$$

Taking use of the above two equation 2.15, 2.16, 2.19 and variation in the term of $\delta\phi_i^*(\mathbf{r})$, finally we end up with

$$(-\frac{\nabla_\mathbf{r}^2}{2} + V_{ext}(\mathbf{r}) + \sum_{j \neq i} < \phi_j(\mathbf{r}') \ |\frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_j(\mathbf{r}') >)\phi_i(\mathbf{r}) = E_h^i \phi_i(\mathbf{r}) \qquad (2.20)$$

where E_h^i also can be treated as the energy corresponding the (i)-th electron in the position of $\mathbf{r}$, the equation 2.20 is a group of dependent single particle equations, and after checking it, we can find out which is an equation that is self-consistent and can be solved using computer by iteratively.

2.3.2 Hartree-Fock approximation

Hartree approximation is the lowest level approximation, and Hartree-Fock approximation is the method which considers the antisymmetry of the wavefunction, which means that if the positions of two electrons (with same spin) are exchanged, the wave function should change the sign, like:

$$\Psi_{hf}(\{\cdots \mathbf{r}_i \cdots \mathbf{r}_j\}) = -\Psi_{hf}(\{\cdots \mathbf{r}_j \cdots \mathbf{r}_i\}) \tag{2.21}$$

Slater introduced an excellent way to construct the wavefunction due to the equation 2.21 based on the Hartree approximation, the wavefunction of many-body Schrödinger equation is written down in a matrix determinant way for the number of N electrons (without spin):

$$\Psi_{hf}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \cdots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \cdots & \phi_1(\mathbf{r}_N) \\ \vdots & \vdots & & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix} \tag{2.22}$$

where i goes through all the electron, and $\phi_i(\mathbf{r}_i)$ means state of the (i)-th electron in the position of $\mathbf{r}_i$, so if we exchange two rows in the equation 2.22, we will find out the result is satisfied with the equation 2.21.

Now repeating all the processes already done through the Hartree approximation , we will know the total energy of Hartree-Fock as follows:

$$\begin{aligned} E_{hf} = &\sum_i < \phi_i(\mathbf{r})| \ -\frac{\nabla_r^2}{2} + V_{ext}(\mathbf{r}) \ |\phi_i(\mathbf{r}) > \\ &+ \frac{1}{2} \sum_{i \neq j} < \phi_i(\mathbf{r})\phi_j(\mathbf{r}')| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_i(\mathbf{r})\phi_j(\mathbf{r}') > \\ &- \frac{1}{2} \sum_{i \neq j} < \phi_i(\mathbf{r}')\phi_j(\mathbf{r})| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_i(\mathbf{r})\phi_j(\mathbf{r}') > \end{aligned} \tag{2.23}$$

In the same mathematical skill but more complicated like in previous section, we can get the dependent singe particle Hartree-Fock equation:

$$\begin{aligned} &\{-\frac{\nabla_i^2}{2} + V_{ext}(\mathbf{r}) + \sum_{j \neq i} < \phi_j(\mathbf{r}') \ |\frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_j(\mathbf{r}') >\}\phi_i(\mathbf{r}) \\ &- \sum_{i \neq j} < \phi_j(\mathbf{r}')| \ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \ |\phi_i(\mathbf{r}') >)\phi_j(\mathbf{r}) = E_{hf}^i \phi_i(\mathbf{r}) \end{aligned} \tag{2.24}$$

Comparing with Hartree equation, there is an extra term in the equation above, which is called exchange term, and at the same time, in order to organize the equation in a nice and clear way, finally we define:

$$\{-\frac{\nabla_i^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\}\phi_i(\mathbf{r}) = E_{hf}^i \phi_i(\mathbf{r}) \tag{2.25}$$

where

$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}') - \rho_i^{HF}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{2.26}$$

and $\rho_i^{HF}(\mathbf{r}, \mathbf{r}') = \sum_j \frac{\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')}{\phi_i(\mathbf{r})\phi_i^*(\mathbf{r})}$; $\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$. And also we find that we can solve it in the same way like Hartree approximation but plus one extra term.

2.4 Density functional theory

Hartree and Hartree-Fock methods are very classic methods to solve many-body Schrödinger equation. However, HF method only includes the exchange, but badly in the electron correlation, so they are not suitable in the case of electrons in solid. Apart from the two methods mentioned before, there is another modern method to deal with the more complicated calculation of electrons, namely, density functional theory (DFT), which is introduced by Hohenberg and Kohn in 1964, Kohn and Pople was awarded by Chemistry Nobel Prize in 1998.

The idea of this method is to treat the electron density of solid instead of using the many-particle wavefunction, so we can benefit that the degree of freedom reduces from 3N (N is the number of electrons) to 3, which is apparently less complicate than those of Hartree and Hartree-Fock during calculation.

2.4.1 The Density as Basic Variable

There are two questions coming out if we consider the electron density as the role of wavefunction. The first one is whether it is the equivalence relation between the electron density and wavefunction of the system, and the second one is how to solve this problem. In order to know that there are two very basic theorems introduced by Hohenberg and Kohn:

Theorem 1 *The first theorem says that the external potential $V_{ext}(\boldsymbol{r})$ is determined uniquely for any of electon system by the ground state electron density ρ_0.*

The above theorem also indicate that all the ground state properties are decied by the true ground state density ρ_0, for example, the total energy $E=E[\rho_0]$. The above theorem also explains the equivalence relation between the electron density and wavefunction, because Hamiltonian is obtained from external potentials, then one can get the wavefunction, so the corresponding electron density is determined, however, from the theorem, the external potential is unique decided by electron density, so the electron density contains the same information of wavefunction.

The proof of theorem is following:

Now, let us assume that there exsits two external potentials named $V_{ext}^1(\mathbf{r})$ and $V_{ext}^2(\mathbf{r})$ leading to the same ground state electron density ρ_0, but obviously, which will lead to two different Hamiltonians, that is, $\hat{H}_1$ and $\hat{H}_2$, and as well as two different corresponding wavefunctions named Ψ_1 and Ψ_2. Since Ψ_1 are not the ground state wavefunction of $\hat{H}_2$, the same rules to Ψ_2 and $\hat{H}_1$, so two following inequality equations will be satisfied:

$$
\begin{aligned}
E_1 = \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle &< \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle \\
E_2 = \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle &< \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle
\end{aligned}
\tag{2.27}
$$

Taking advangtage of the form of Hamitonian from equation 2.5, one can get:

$$
\begin{aligned}
&\langle \Psi_2 \,|\hat{H}_1|\, \Psi_2 \rangle \\
&= \langle \Psi_2 \,|\hat{H}_2 + \hat{H}_1 - \hat{H}_2|\, \Psi_2 \rangle \\
&= \langle \Psi_2 \,|\hat{H}_2|\Psi_2 \rangle + \langle \Psi_2|\hat{H}_1 - \hat{H}_2|\, \Psi_2 \rangle \\
&= E_2 + \int d\mathbf{r}(V_{ext}^1(\mathbf{r}) - V_{ext}^2(\mathbf{r}))\rho_0
\end{aligned}
\tag{2.28}
$$

So using 2.27 and 2.28, one can get:

$$
E_1 < \ E_2 + \int d\mathbf{r}(V_{ext}^1(\mathbf{r}) - V_{ext}^2(\mathbf{r}))\rho_0
\tag{2.29}
$$

Another similar inequality equation will be gained if one changes the form of equation $\langle \Psi_1 \,|\hat{H}_2|\, \Psi_1 \rangle$ like equation 2.28.

$$
E_2 < \ E_1 + \int d\mathbf{r}(V_{ext}^2(\mathbf{r}) - V_{ext}^1(\mathbf{r}))\rho_0
\tag{2.30}
$$

so plus the left and right sides from equation 2.29 and 2.31, one will gain a contradictory result:

$$
E_1 + E_2 < \ E_2 + E_1
\tag{2.31}
$$

So the external potential $V_{ext}(\mathbf{r})$ is unique.

Theorem 2 *The second theorem says that there is a universal functional for the total energy in the terms of the electron density ρ with any external potential $V_{ext}(\boldsymbol{r})$, and the exact ground state density is gained when the ground state total energy functional reaches its minimal value, that is, E[ρ]>E[ρ_0], where ρ is not the ground state density.*

The proof of theorem is following: Because of the first theorem, so the total energy can be expressed in the following way (ignoring the interaction between nuclei):

$$
\begin{aligned}
E[\rho] \ &= \langle \Psi| \ \hat{T} \ + \ \hat{V}_{int} \ + \ \hat{V}_{ext} \,|\Psi\rangle \\
&= \langle \Psi| \ \hat{T} \ + \ \hat{V}_{int} \,|\Psi\rangle + \langle \Psi| \ \hat{V}_{ext} \,|\Psi\rangle \\
&= \ F[\rho] \ + \ \int \rho(\mathbf{r})V_{ext}
\end{aligned}
\tag{2.32}
$$

In the above equation 2.32, the term of $F[\rho]$ is the universal functional since all the systems of electrons.

Now, let us say ρ_0 is the exact ground state electron density, from first theorem, we know there exists one unique external potential V_{ext}, so the corresponding Hamitonian and wavefunction are $\hat{H}$ and Ψ_0, assuming that a different electron density ρ which is not exact ground state density corresponding to the wavefunction Ψ_0, then we will get:

$$
E[\rho_0] = \langle \Psi_0 \,|\hat{H}|\, \Psi_0 \rangle < \langle \Psi \,|\hat{H}|\, \Psi \rangle \ = E[\rho]
\tag{2.33}
$$

so from above equation, we know the total energy for the case of exact ground state electron density is lower than any other cases, which also means that one can get the exact ground state electron density by minimizing the total energy.

From those two theorems, we definitely know how to solve this problem theoretically, but in practice, we do not know $E[\rho]$, how it looks like, so we still need one more method to deal with it, namely, Kohn-Sham (KS) equation.

2.5   The Kohn-Sham equation

Since I already introduced the Hartree and Hartree Fock method to solve the many-body problem, both of which are based on the idea which is to transform complex many-body problem to single particle problem by using wavefunction, but Density functional theory only consider to take use of information from Hamitonian, but not sovable, so is it possbile to combine these two ideas together? the answer is yes,the DFT is solved by Kohn-Sham equation introduced by Kohn and Sham in 1965, which I recommended a way to construct in the following text (ignoring the interaction between nuclei)

First of all, the total energy can be expressed by the following:

$$
\begin{aligned}
E[\rho] &= T[\rho] + V_{int}[\rho] + V_{ext}[\rho] \\
&= \underbrace{(T[\rho] - T_0[\rho]) + (V_{int}[\rho] - V_{HF}[\rho])}_{} + T_0[\rho] + V_{HF}[\rho] + V_{ext}[\rho] \\
&= T_0[\rho] + V_{HF}[\rho] + V_C[\rho] + V_{ext}[\rho]
\end{aligned}
\tag{2.34}
$$

where $E[\rho]$ is the total energy, ρ is the ground state density;$V_{int}[\rho]$, $T[\rho]$ and $V_{int}[\rho]$ are the energy from external potential, the exact kinetic and the exact electron-electron potential energy; $T_0[\rho]$ is the kinetic energy of a non-interacting electrons, $V_{HF}[\rho]$ is the potential from Hartree-Fock approximation.

From the Hartree-Fock approximation, we can further know that:

$$
V_{HF}[\rho] = V_H[\rho] + V_X[\rho] \tag{2.35}
$$

where $V_H[\rho]$ and $V_X[\rho]$ are the Hartree contribution and exchange contribution, respectively, so the equation (13) can be further defined like the following:

$$
\begin{aligned}
E[\rho] &= T_0[\rho] + V_H[\rho] + V_{ext}[\rho] + \underbrace{V_X[\rho] + V_C[\rho]}_{} \\
&= T_0[\rho] + V_H[\rho] + V_{ext}[\rho] + V_{XC}[\rho]
\end{aligned}
\tag{2.36}
$$

where $V_{XC}[\rho]$ is the exchange-correlation term. From equation 2.34, the explicit expression of $V_{XC}[\rho]$ we do not know. but the first three terms we already know

$$
T_0[\rho] = \ <\Psi_i(\mathbf{r}) \ | -\frac{\nabla_r^2}{2} \ |\Psi_i(\mathbf{r})> \tag{2.37}
$$

$$
V_H[\rho] = \frac{1}{2} \int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{2.38}
$$

$$
V_{ext}[\rho] = \int \mathrm{d}\mathbf{r}\rho(\mathbf{r})V_{ext} \tag{2.39}
$$

In order to derive the ground state of the above system, we can view this problem as the process of minimizing the total energy by varying the wavefunction Ψ^*, since we can construct from wavefunction to electron density (equation 2.42),

just like the derivation in the section of Hartree, we finally can get the Kohn-Sham equation.

$$(-\frac{\nabla_r^2}{2} + V_{KS})\Psi_i(\mathbf{r}) = E_{ks}^i\Psi_i(\mathbf{r}) \tag{2.40}$$

where

$$
\begin{aligned}
V_{KS} &= V_{ext}[\rho] + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{XC}}{\delta\rho(\mathbf{r})} \\
&= V_{ext}[\rho] + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}
\end{aligned} \tag{2.41}
$$

we can think of the Hamiltonian in another point of view, e.g., single particle system with three different potentials. Now the problem turns out to be like the single particle form with the degree of freedom of 3.

So the many-body problem now is transformed to the single electron problem, if the v_{xc} is exact, the exact ground-state density is :

$$\rho(\mathbf{r}) = \sum_i \Psi_i^*(\mathbf{r})\Psi_i(\mathbf{r}) \tag{2.42}$$

There is no total energy equation expression yet, however, if one can change the equation 2.40 as

$$\sum_i \Psi_i^*(\mathbf{r})(-\frac{\nabla_i^2}{2} + V_{KS})\Psi_i(\mathbf{r}) = \sum_i \Psi_i^* E_{ks}^i\Psi_i(\mathbf{r}) \tag{2.43}$$

Based on equation 2.36 and 2.43, we will get the total energy expression:

$$
\begin{aligned}
E &= \sum_i E_{ks}^i - \frac{1}{2}\int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
&+ V_{XC}[\rho] - \int v_{xc}\rho(\mathbf{r})
\end{aligned} \tag{2.44}
$$

So far there are two problems still in the air, one is the exact format of v_{xc}, the other one is how to solve the Kohn-Sham equation.

2.6 The exchange-correlation energy

This part is the most difficult part during the process of solving the Kohn-Sham equation, because it is unknown so far, so there are varies of approximations about it, like the local density approximation (LDA), generalized-gradient approximation (GGA) and so on.

2.6.1 The local density approximation

The local density approximation is the simplest way to approximate the exchange-correlation part, and the idea is that the value of the exchange-correlation energy in the very tiny small volume is equal to the homogeneous electrons with the same density in the volume, the explicit equation is:

$$E_{xc}^{LDA} = \int \rho(\mathbf{r})\varepsilon_{xc}((\rho(\mathbf{r})))\mathrm{d}\mathbf{r} \tag{2.45}$$

where E_{xc}^{LDA} is the exchange-correlation energy functional for the LDA, $\rho(\mathbf{r})$ is the charge density in the position of $\mathbf{r}$, ε_{xc} is homogeneous electrons gas with variable of $\rho(\mathbf{r})$.

The ε_{xc} is an ideal state within a solid, which assumes that the charge is homogeneously all over the space:

$$\rho(\mathbf{r}) = \rho = \frac{N}{V} \tag{2.46}$$

Where N is number of electrons within the solid, and V is the volume of solid, which also means that the ε_{xc} is the function of $\rho(\mathbf{r})$, not functional.

2.6.2   The Generalized gradient approximation

The GGA is the approximation beyond the LDA, which incorporates not only the density within the tiny volume, but also the gradient of the density, the explicit equation is:

$$E_{GGA}^{xc} \;=\; \int \rho(\mathbf{r})\varepsilon_{xc}((\rho(\mathbf{r})), \nabla\rho(\mathbf{r}))\mathrm{d}\mathbf{r} \tag{2.47}$$

where is the exchange-correlation energy functional for the GGA, is the gradient of charge density in the position of r.

Of course, there are more modern methods to approximate the exchange-correlation energy, such as: the optimized effective potential (OEP) method and the hybrid functionals and so on.

2.7   Solving the secular equation

The process for solving Kohn-Sham equation can be solved by iteration as well, but the difference between for solving Kohn-Sham equation and Hartree or Hartree-fock equation is that the wavefunction is replaced by the electron density, so first an initial electron density is defined by some way, and later on the equation is solved iteratively until the reasonable solution is obtained.

Where ρ^i and $\rho^{i+1}$are the charge density of the *(i)*th and *(i+1)*th iteration solving Kohn-Sham equation respectively.
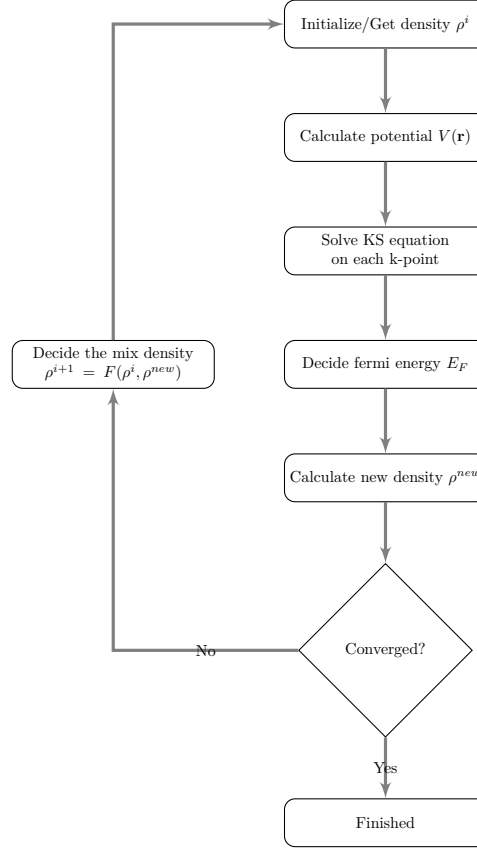
Figure 2.2: Flow chart of the *(i+1)*th iterations for solving Kohn-Sham equation

2.8   Eigenvalue problem

In order to solve the equation 2.40, The Kohn-Sham equation will be transformed into the general eigenvalue problem, first the wavefunction is defined as follows:

$$\Psi(r) = \sum_{j}^{N} C_j \Phi_j(r) \tag{2.48}$$

Where C_j is a complex number, and $\Phi_j(r)$ is the basis of wavefunction.
Now if the Kohn-Sham equation is defined in the following form:

$$\hat{H}\Psi(r) = E\Psi(r) \tag{2.49}$$

So if the equation 2.48 is plugged into the equation 2.49, and then left mupltiply

Φ_j in order, finally it will end up with a set of equations:

$$\begin{bmatrix} \Phi_1\hat{H}\Phi_1 & \Phi_1\hat{H}\Phi_2 & \cdots & \Phi_1\hat{H}\Phi_N \\ \Phi_2\hat{H}\Phi_1 & \Phi_2\hat{H}\Phi_2 & \cdots & \Phi_2\hat{H}\Phi_N \\ \vdots & \vdots & & \vdots \\ \Phi_N\hat{H}\Phi_1 & \Phi_N\hat{H}\Phi_2 & \cdots & \Phi_N\hat{H}\Phi_N \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_N \end{bmatrix}$$
$$= E \begin{bmatrix} \Phi_1\Phi_1 & \Phi_1\Phi_2 & \cdots & \Phi_1\Phi_N \\ \Phi_2\Phi_1 & \Phi_2\Phi_2 & \cdots & \Phi_2\Phi_N \\ \vdots & \vdots & & \vdots \\ \Phi_N\Phi_1 & \Phi_N\Phi_2 & \cdots & \Phi_N\Phi_N \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_N \end{bmatrix} \quad (2.50)$$

if we define $H_{ij} = \Phi_i\hat{H}\Phi_j$ and $S_{ij} = \Phi_i\Phi_j$, then the equation 2.50 becomes:

$$\begin{bmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_N \end{bmatrix}$$
$$= E \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1N} \\ S_{21} & S_{22} & \cdots & S_{2N} \\ \vdots & \vdots & & \vdots \\ S_{N1} & S_{N2} & \cdots & S_{NN} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_N \end{bmatrix} \quad (2.51)$$

and after some maniplulations,

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots & H_{1N}-ES_{1N} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \cdots & H_{2N}-ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1}-ES_{N1} & H_{N2}-ES_{N2} & \cdots & H_{NN}-ES_{NN} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_N \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$
$$(2.52)$$

Apparently, the equation 2.52 is an eigenvale problem, in order to get the C_{ij}, we have to let:

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots & H_{1N}-ES_{1N} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \cdots & H_{2N}-ES_{2N} \\ \vdots & \vdots & & \vdots \\ H_{N1}-ES_{N1} & H_{N2}-ES_{N2} & \cdots & H_{NN}-ES_{NN} \end{vmatrix} = 0 \quad (2.53)$$

Chapter 3

Crystal Structure

3.1 Primitive cell, unit cell and Brillouin zone

Generally the smallest periodical crystal structure is the primitive cell, and some times, several primitive cells are defined together in order to reflect the symmetry of the crystal, and this is called as unit cell.

The copper indium gallium selenium (CIGS) material is taken as an example, which is a tetrahedral bonded semiconductor with the chalcopyrite crystal structure. The following 3.1 is the primitive cell of CIGS.
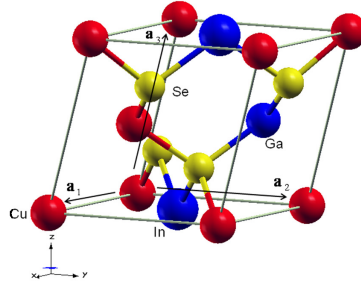

Figure 3.1: The primitive cell of CIGS Red = Cu, yellow = Se, blue = In/Ga

where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the primitive basic vectors, and the integer linear combination of which will runs through all the Bravais lattice point.

Unit: 5.69000 Ångstrom (scale)		
$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$
(1,0,0)	(0,1,0)	(0.5,0.5,0.9923)

Table 3.1: Coordinate of primitive basic vectors for CIGS

3.2 Reciprocal space and Brillouin zone

Assuming that there are three primitive basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$, and if we define that the reciprocal lattice basis vectors like $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$, now we can get:

$$\begin{aligned}
\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)} \\
\mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)} \\
\mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)}
\end{aligned} \tag{3.1}$$

and all the linear combination of reciprocal lattice basis vectors will run over all the reciprocal space.
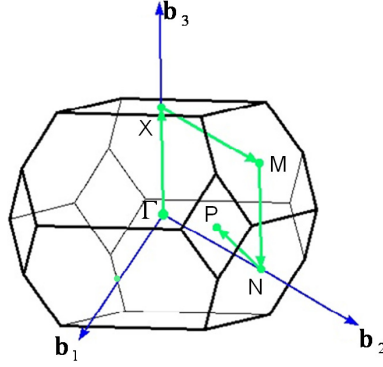

Figure 3.2: The first Brillouin zone of CIGS

The first Brillouin Zone (BZ) is the Wigner-Seitz primitive cell in reciprocal space, for example, the figure 3.2 is the first BZ of CIGS, where $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ are reciprocal lattice basis vectors. The following is the table about high symmetry points of the first BZ.

Points Coordinates($\mathbf{b}_1$,$\mathbf{b}_2$,$\mathbf{b}_3$)			
Γ	0	0	0
X	0	0	1/2
M	0	1/2	1/2
N	0	1/2	0
P	1/2	1/2	1/2

Table 3.2: *High Symmetry Points of BZ for CIGS*

3.3 Band structure and density of state

In solid, there are huge amount of atoms which interact each other, so the discrete of energy split into the huge number of state with small difference, those are defined as energy band, it is very important if we want to know more about electrons or optical properties. So the band structure of CIGS is given as follows:
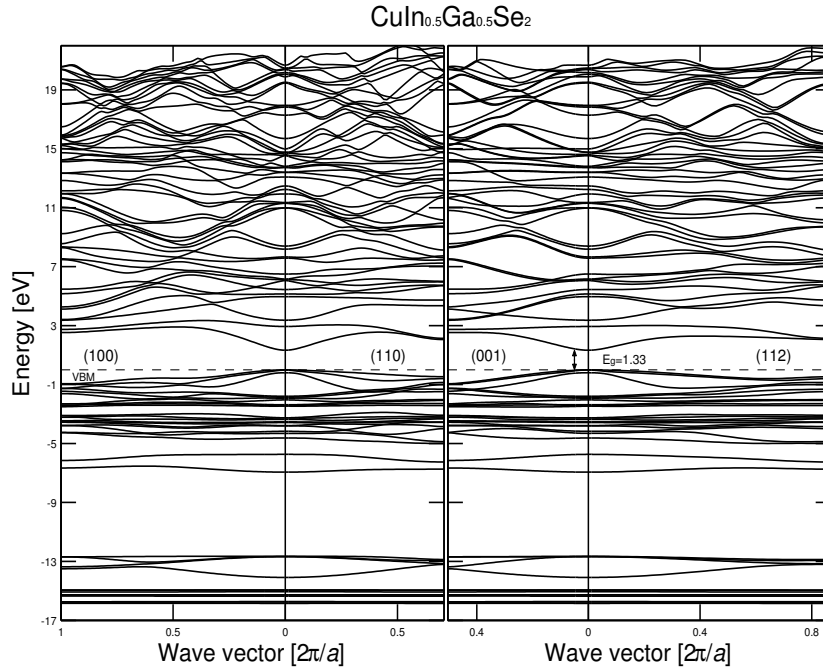

Figure 3.3: The band structure of CIGS

The density of states (DOS) of a system is the number of states which could be occupied per interval of energy. And the DOS of CIGS is:

?????????????????? add DOS figure ???????????????????????

Chapter 4

FP-LAPW method

4.1 Introduction

So far, We already know how to solve the Kohn-Sham equation, however, there are still two more questions in the air, what is the exact form of wavefunction and potential in the realistical calculation ?

One maybe naturally choose the a set of plane waves as wavefunction because of bloch theory, but there is a drawback about the plane wave when discribing the nearby the atomic core region, because the wavefunction change dramatically, so one needs to choose more plane waves to define it, which means it will take more time to calculate.

Slater re-consider the way to discribe the wavefunction, he splits the unit cell into two regions, one is the sphere region which is defined by the center of atom, but non-overlap each sphere, called muffin tin (MT) region, the remaining region is called interstitial (I) region. And an atomic like function is defined as the wavefunction in MT region, this is reason why the method is called augmented plane wave (APW), and in the interstitial region wavefunction is discribed as plane wave, which is reasonable, because the wave function approaching atomic core is somehow like inside atom, but far away the atomic core, the electron behaves like free electrons, so plane wave is suitable. However, the drawback of APW method is the wavefunction is dependent with the energy, which leads to the nonlinear eigenvalue problem, so in order to get the exact energy, the method have to decide repeatlly, which is really time-consumming. In order to find a way out, is it possible to let the wavefunction energy-independent?, Andesen and Koelling and Arbman?? proposes a way to discribe that, he notices that the taylor expansion of radial function, and make use of it to linearize the APW method, so the method is called Linearized Augmented Plane Wave (LAPW) method. However, the drawback is that this method does not discribe the core state well, so the method is corrected by method of LAPW+LO and LAPW+lo, which is proposed by ?? and ?? respectively.

?????????????????? need to understant more about LAPW+LO and +lo ?????????????????????????

4.2   Augmented Plane Wave method

Slater defines the wavefunction like the following equation:

$$\phi_{\mathbf{k+G}}^{APW}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k+G})\mathbf{r}} & \text{if } \mathbf{r} \in I, \\ \sum\limits_{\alpha} \sum\limits_{\ell m} f_{\ell m}(r_\alpha, \mathbf{k+G}, E) Y_{\ell m}(\hat{\mathbf{r}}_\alpha) & \text{if } \mathbf{r} \in S_\alpha, \end{cases}$$

where $f_{\ell m}(r_\alpha, \mathbf{k+G}, E) = A_{\ell m}^\alpha(\mathbf{k+G})\mathbf{u}_\ell^\alpha(\mathbf{r}_\alpha, \mathbf{E})$ and $A_{\ell m}^\alpha(\mathbf{k+G})$is the expasion coefficients, and $u_\ell^\alpha(r_\alpha, E)$ is the radial function, which is dependent with energy E, and the radial function could be decided by the following:

$$(-\frac{1}{2}\frac{d^2}{dr_\alpha^2} + \frac{\ell(\ell+1)}{2r_\alpha^2} + V(r_\alpha) - E)r_\alpha u_\ell(r_\alpha) = 0 \tag{4.1}$$

where $V(r_\alpha)$ is the spherical potential. The following is the figure about this basis function
Because wavefunction has dual representations, one has to make sure the continousiny on the sphere, which is solved by matching each ℓm of the dual representation.

???????????????????? add the representations figure of basis function ???????????????????????????
from the above figure, $\mathbf{r} = \mathbf{R}^\alpha + \mathbf{r}_\alpha$ is guaranteed. so taking use of the Rayleigh expansion formula:

$$e^{i(\mathbf{k+G})\mathbf{r}} = e^{i(k+G)\mathbf{R}^\alpha} 4\pi \sum_{\ell m} i^\ell j_\ell(|\mathbf{k}+\mathbf{G}|r_\alpha) Y_{\ell m}(\hat{\mathbf{r}}_\alpha) Y_{\ell m}^*(\mathbf{k}\hat{+}\mathbf{G}) \tag{4.2}$$

after matching those two representations, the following equation is satisfied:

$$A_{\ell m}^\alpha(\mathbf{k+G}) = \frac{\mathbf{e^{i(k+G)R^\alpha}} 4\pi \sum\limits_{\ell m} \mathbf{i^\ell j_\ell}(|\mathbf{k+G}|\mathbf{r}_\alpha) \mathbf{Y_{\ell m}^*(k\hat{+}G)}}{\sqrt{\mathbf{\Omega}}\mathbf{u}_\ell^\alpha(\mathbf{r}_\alpha, \mathbf{E})} \tag{4.3}$$

There are two main drawbacks about the APW method: The first one is that the wavefuntion is energy dependent, which means that the code will search for the energy in order to calculate the exact energy, so it is really time consumming.The second one the less harmful, but also sometimes it will cause problem when $u_\ell^\alpha(r_\alpha, E) = 0$ during matching.

4.3   Linearized Augmented Plane Wave method

In order to decouple the energy and wavefunction, Andersson finds out a way to seperate them, he notices that the taylor expansion of the radail function on certain energy, which can be expressed as follows:

$$u_\ell^\alpha(r_\alpha, E) = u_\ell^\alpha(r_\alpha, E_\ell) + (E - E_\ell)\dot{u}_\ell^\alpha(r_\alpha, E_\ell) \tag{4.4}$$

So he re-defines the wavefuntion in the following way:

$$\phi_{\mathbf{k+G}}^{LAPW}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k+G})\mathbf{r}} & \text{if } \mathbf{r} \in I, \\ \sum\limits_{\alpha} \sum\limits_{\ell m} f_{\ell m}(r_\alpha, \mathbf{k+G}, E_\ell) Y_{\ell m}(\hat{\mathbf{r}}_\alpha) & \text{if } \mathbf{r} \in S_\alpha, \end{cases}$$

where $f_{\ell m}(r_\alpha, \mathbf{k+G}, E_\ell) = A_{\ell m}^\alpha(\mathbf{k+G})\mathbf{u}_\ell^\alpha(r_\alpha, \mathbf{E}_\ell) + \mathbf{B}_{\ell \mathbf{m}}^\alpha(\mathbf{k+G})\dot{\mathbf{u}}_\ell^\alpha(r_\alpha, \mathbf{E}_\ell)$ $A_{\ell m}^\alpha(\mathbf{k+G})$ and $B_{\ell m}^\alpha(\mathbf{k+G})$ is the expansion coefficients, and $\dot{u}_\ell^\alpha(r_\alpha, E_\ell)$ is the derivate of the radial function.

Here energy E_ℓ is considered as pre-calculated parameter, actually, it is chosen by the middle of each l-character band.

Apparently, LAPW method is more suitable in reality, because the wavefunction is decoupled with energy, but it has to match for two parameters, fortunaly, even though, it still use less time comparing with APW method. However, there is one drawbacks, what if energy difference is big in the same ℓ charater, which the E_ℓ is correct, so this situation will cause big error, these states are called as semi-core state, for example, the alkali metal, the actinides and the rare earths and so on.

4.4 Linearized Augmented Plane Wave method + LO

Comparing with LAPW method, LAPW+LO method extend the basis set, and add smaller number of basis set, which has the following format:

$$\phi_{\mathbf{k+G}}^{LO}(\mathbf{r}) = \begin{cases} 0 & \text{if } \mathbf{r} \in I, \\ (A_{\ell m}^\alpha u_\ell^\alpha(r_\alpha, E_\ell) + B_{\ell m}^\alpha \dot{u}_\ell^\alpha(r_\alpha, E_\ell) + C_{\ell m}^\alpha u_\ell^\alpha(r_\alpha, E_\ell'))Y_{\ell m}(\hat{\mathbf{r}}_\alpha) & \text{if } \mathbf{r} \in S_\alpha, \end{cases}$$

where $A_{\ell m}^\alpha$ and $B_{\ell m}^\alpha$ is matching value and derivate on the sphere boundary to zero, but not plane wave, like LAPW did before, and E_ℓ' is the chosen energy from semi-core state.

4.5 Augmented Plane Wave method plus local orbitals

Actually, there is one more method which will deal with the energy-denpendent case, which is called as Augmented Plane Wave method plus local orbitals (APW+lo), the basis function has two kinds, one is similar with equation 4.4, but only without the derivative terms, e.g., $f_{\ell m}(r_\alpha, \mathbf{k+G}, E_\ell) = A_{\ell m}^\alpha(\mathbf{k+G})\mathbf{u}_\ell^\alpha(r_\alpha, \mathbf{E}_\ell)$. And another basis function is:

$$\phi_{\mathbf{k+G}}^{lo}(\mathbf{r}) = \begin{cases} 0 & \text{if } \mathbf{r} \in I, \\ (A_{\ell m,lo}^\alpha u_\ell^\alpha(r_\alpha, E_\ell) + B_{\ell m,lo}^\alpha \dot{u}_\ell^\alpha(r_\alpha, E_\ell))Y_{\ell m}(\hat{\mathbf{r}}_\alpha) & \text{if } \mathbf{r} \in S_\alpha, \end{cases}$$

And the value of $A_{\ell m,lo}^\alpha$ and $B_{\ell m,lo}^\alpha$ are obtained by normalization and local orbital has zero value at the muffin tin boundary.

Chapter 5

K · P method

The band dispersion can be obtained by using the kp method, the basic idea will be explained in the following text. First, The Bloch Theory shows:

$$\Psi_{n,k}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{n,k}(\mathbf{r}) \tag{5.1}$$

where $\Psi_{n,k}(\mathbf{r})$ is the wave function on k point for the nth band, and $e^{i\mathbf{k}\mathbf{r}}$ is plane wave, $u_{n,k}(\mathbf{r})$ is a function which has the same a periodicity as the potential.

Now let us suppose the wavefunction and energy are obtained by some procedures on k_0 point, $\Psi_{n,k_0}(\mathbf{r})$ is the wavefunction and E_{n,k_0} is the energy. And another function is defined as follows:

$$\chi_{n,k}(\mathbf{r}) = e^{i(\mathbf{k}-\mathbf{k_0})\mathbf{r}} \Psi_{n,k_0}(\mathbf{r}) \tag{5.2}$$

The above function $\chi_{n,k}(\mathbf{r})$ is expanded as wave function on k point, and then the wave function on the k point is calculated by:

$$\Psi_{n,k}(\mathbf{r}) = \sum_j C_{n,j}^k \chi_{n,k}(\mathbf{r}) \tag{5.3}$$

From above equation, the wave function is known if the coefficient $C_{n,j}^k$ is obtained, let us substitute the equation 5.3 into Kohn-Sham equation.

$$\left\{ \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \right\} \Psi_{n,k}(\mathbf{r}) = E_{n,k} \Psi_{n,k}(\mathbf{r}) \tag{5.4}$$

then we will finally get the following equation.

$$\sum_j C_{n,j}^k \left\{ \left[E_{j,k_0} - E_{n,k} + \frac{\hbar^2}{2m}(\mathbf{k^2} - \mathbf{k_0^2}) \right] \delta_{j',j} + \frac{\hbar}{m}(\mathbf{k} - \mathbf{k_0})\mathbf{p_{j',j}} \right\} = 0 \tag{5.5}$$

where $\mathbf{p_{j',j}} = \langle u_{j',k_0}(\mathbf{r})|\mathbf{p}|u_{j,k_0}(\mathbf{r})\rangle$.
We also can simpify the above equation in the following format:

$$\sum_j C_{n,j}^k \left\{ H_{j',j} - E_{n,k}\delta_{j',j} \right\} = 0 \tag{5.6}$$

where

$$H_{j',j} = \left[E_{j,k_0} + \frac{\hbar^2}{2m}(\mathbf{k^2} - \mathbf{k_0^2}) \right] \delta_{j',j} + \frac{\hbar}{m}(\mathbf{k} - \mathbf{k_0})\mathbf{p_{j',j}} \qquad (5.7)$$

From the above equation, we can calculate the coefficient $C_{n,j}^k$.

Chapter 6

CIGS material

Chapter 7

Summary