Doctoral Thesis

Theoretical Study of the Quantized Hall Conductivity in Graphene by using Nonperturbative Magnetic-Field-Containing Relativistic Tight-Binding Approximation Method

HIROSHIMA UNIVERSITY

MD. ABDUR RASHID

Main Supervisor：Katsuhiko Higuchi

Graduate School of Advanced Science and Engineering
Hiroshima University

March, 2024

Theoretical Study of the Quantized Hall Conductivity in Graphene by using Nonperturbative Magnetic-Field-Containing Relativistic Tight-Binding Approximation Method

MD. ABDUR RASHID

D213705

A Thesis Submitted to
the Graduate School of Advanced Science and Engineering of
Hiroshima University in Partial Fulfillment of the
Requirement for the Degree of
Doctor of Philosophy in Science

March, 2024

Dedication

This thesis is dedicated to my most respectable and beloved parents and my beloved daughters Atkia Nawal and Atifa Iffat.

Acknowledgements

I feel extremely delighted to express my heart-felt gratitude to those who have assisted me to accomplish my PhD work imparting their valuable time, suggestions and advices. I am really grateful to them.

First of all, the person whom I will ever remember for his selfless as well as relentless help in doing my PhD work and at the same time without whose explicit assistance I could never be able to fulfil my job, is my revered supervisor Professor Katsuhiko Higuchi. His constant patronage and encouragement, constructive suggestions and necessary advices have incited me a lot to reach my goal. I am indebted to him.

Next, I would like to express my sincere gratitude to Professor Masahiko Higuchi, who helped me time to time giving his valuable suggestions in time of my PhD work. I express my gratefulness to him.

I also offer my sincere gratitude to Professor Hiroshi Shimahara, Professor Arata Tanaka, and Professor Yasuhiro Tada for their encouragement.

My gratefulness goes to those students of the Institute of Theoretical Physics too, who helped me with their advices and discussions. I would also render my special thanks to Amit Shrestha, Tomoya Aizawa and Md. Leaket Ali for their advice and assistance.

I would like to appreciate the staffs of AdSM, especially Ms. Terumi Nakadate, Hiroshima University, who were very helpful and always ready to help and provide necessary assistance.

I owe a lot to Hiroshima University of Japan in particular for giving me an opportunity to pursue my PhD study in Japan. I further express my heartfelt gratitude to the same university for assisting me with a scholarship entitled " Next Generation Fellowship "(Grant No. JPMJSP2132) supported by JST.

Last but not the least, I feel very indebted to my parent for his constant love and mental support in all my weal and woe. Finally, I am also grateful to my spouse Mst. Isma Tara and my two beloved daughters, Atkia Nawal and Atifa Iffat for their encouragement, support and takes care of me.

Once again, I thank all of my well-wishers.

Md. Abdur Rashid

March, 2024

Contents

Chapter 1

Introduction

Nowadays, graphene as a two-dimensional (2D) material is becoming a more attractive revolutionary research material in order to be used in devices for the industrial applications. Materials immersed in a uniform magnetic field exhibit many properties such as Landau diamagnetism, curie paramagnetism, Langevin diamagnetism, de Haas-van Alphen (dHvA) effect, Shubnikov-de Haas (SdH) effect, quantum Hall effect (QHE), and so on. The QHE is the most important property in 2D condensed matter physics to make a device. The 2D system at low temperature and strong magnetic field has more potential for the quantum phenomena after discovering the quantization of the quantum Hall effect [1]. The integer quantum Hall effect has been observed in a two-dimensional electron gas (2DEG) system in a semiconductor heterostructures system [1,2]. The energy spectrum in a 2DEG system immersed in a uniform strong magnetic field becomes quantized due to the quantization of the orbital motion according to Onsager`s area quantization rule. This system provides an ideal message for understanding the quantum transport phenomena in a 2D system. For this reason, researchers have tremendous interest in research on 2D materials specifically graphene about the electronic properties in 2D condensed matter systems. The 2D material belonging to honeycomb lattice structure with two atoms per unit cell specifically graphene demonstrates some peculiar properties for its unique electronic energy band structure due to the inequivalent two K points namely Dirac point (K and $\acute{K}$) in the first Brillouin zone (BZ). The conduction and valence band in graphene forms a conically shaped valley by touching each other at the Dirac point in the first BZ which leads to the extraordinary property in graphene. Graphene shows some extraordinarily peculiar properties due to the linear energy dispersion relation in the lower energy region which means near the Dirac point. Therefore, graphene as a 2D material has become a potential material as a promising material in the electronics and spintronics fields for its some extra properties [3-10]. When a uniform magnetic field is applied perpendicular to the graphene sheet, it exhibits some distinctive

properties such as strong orbital diamagnetism [11-24], reduced effective g-factor [25-27], unconventional oscillation of magnetization [28-30], half-integer quantum Hall effect (QHE) [31-44], anomalous QHE in the honeycomb lattice [32-34,36], and quantized Hall conductivity [42,43,45]. The half-integer quantum Hall effect in graphene leads that graphene becoming a promising material for spintronics. In addition, at room temperature, the large energy gap generated by the magnetic field in graphene compared to a standard 2DEG system [43], graphene has been considered as a more practical useable material for the property of the QHE.

It is noted that for the interesting results of graphene in theoretical predictions [31,32], and experimental discoveries [4,33,41-44], many researchers concentrate their minds on the research of the half-integer QHE as an excellent property in 2D materials. Specifically, the half-integer quantized Hall conductivity (σ_{Hall}) in graphene with filling factors (FFs) of 2, 6, 10, 14, etc. was experimentally observed in a low magnetic field of approximately 14 (T) [4] or below 10 (T) [33] due to the corresponding energy level splitting, which is well known as the half-integer QHE. There are many methods are discussed for the reason of the half-integer QHE, more clearly, the effect of the half-integer QHE in graphene was theoretically described based on the tight-binding (TB) approximation method and/or the effective mass Hamiltonian method [32,34-40]. The important notice about the interesting half-integer QHE in graphene is that the quantized σ_{Hall} with FFs of 0 and 4 which are the different sets of FFs compared with the above-mentioned set of FFs was also observed experimentally comparatively in the high magnetic field region of approximately 45 (T) [41]. The quantized σ_{Hall} in graphene with FFs of 0, 4, 8, 12, etc. has also been predicted theoretically, and this set of FFs for the quantized σ_{Hall} attributed to the energy splitting caused by the spin-Zeeman effect [39].

The well-known magnetic field dependence energy spectrum namely the Hofstadter butterfly diagram [46] is obtained theoretically and can be explained clearly as the magnetic energy spectrum of energy levels of electrons in a magnetic field. The most important information about the QHEs is carried in the gap in the Hofstadter butterfly diagram [47-50]. According to the various conventional theoretical methods [32,34-40], the energy diagram for the magnetic energy spectrum is enumerated using magnetic hopping integrals (hopping integrals in the presence of a magnetic field). The magnetic hopping integrals are the product of the hopping integrals (hopping integrals

in the absence of a magnetic field) and the Peierls phase. The hopping integrals can be calculated by the Slater-Koster table which leads the relativistic version of the Slater-Koster table. But the Peierls phase approximation corresponds to a lowest-order perturbation theory [51], the energy diagram is relatively erroneous in the high magnetic field region and lacks accuracy even in the low magnetic field region [51]. For the worst calculation, the Hofstadter butterfly diagram in the low magnetic field region may be affected by spin-orbit interactions [51]. The relativistic effect, magnetic effect, and the effect of the periodic potential should be considered in the calculation of the diagram of the magnetic energy spectrum for more accuracy. For this aim, the nonperturbative effects of the magnetic field and the spin-orbit interaction should be taken for the appropriate magnetic energy spectrum to investigate the QHE in graphene.

Recently, the magnetic-field-containing relativistic tight-binding approximation (MFRTB) [52] and the nonperturbative MFRTB methods [51] have been developed by Higuchi group for a better description of the properties of materials immersed in a uniform magnetic field. The above-mentioned methods enable the calculation of the realistic magnetic energy band structure of materials immersed in a magnetic field by taking the effects of the magnetic field, the effect of the periodic potential, and the relativistic effect. Thus far, the MFRTB method can revisit the Haas-van Alphen oscillations [53,54] and magnetic breakdown [54] and predict the additional oscillation peaks of the magnetization [55-57]. The nonperturbative MFRTB method reveals that nonperturbative effects appear both in high and low magnetic field regions [51] and successfully predicts the second-order phase transition of silicon from a band insulator to a metal [58]. The above-mentioned discussions are based on the magnetic energy band structure calculated using the MFRTB or nonperturbative MFRTB method.

In this thesis, a novel description of the orbital motion of the magnetic Bloch electron is explained to describe the quantum Hall effect using the nonperturbative MFRTB method. The theoretical calculations are performed to investigate the QHE in graphene based on the magnetic energy band structure using the nonperturbative MFRTB method. Because the description of the quantum Hall effect based on the first principles calculations has not been made yet. The Fermi energy dependence of σ_{Hall} is investigated using the nonperturbative MFRTB method [45]. It is evident that the quantized σ_{Hall} with FFs of 2, 6, 10, 14 etc., and with 0, 4, 8, 12 etc., is revisited

successfully using the nonperturbative MFRTB method [45]. The former set of FFs has wide plateaus (WPs) and the latter set of FFs has narrow plateaus (NPs) due to the corresponding energy splitting. It is noted that both plateaus are the Fermi energy and magnetic field dependence. The width of the WPs relatively decreases with increasing Fermi energy due to the negative curvature of the energy band at zero magnetic field. The spin-Zeeman effect and the spin-orbit interaction are the reasons for the NPs in graphene. The width of the NPs belongs to the Fermi energy and magnetic field dependence that are shown later.

This thesis is decorated in the following fashion:

In Chapter 2, the description of the relativistic tight binding (TB) approximation method in the absence of a magnetic field as a building block is decorated to describe the MFRTB approximation method. In this Chapter, the relativistic version of the Slater-Koster (SK) table is also presented for the calculation of the relativistic hopping integrals for the zero magnetic field case. The nonperturbative MFRTB method is presented in Chapter 3 to express the magnetic hopping integrals approximately in terms of both the relativistic hopping integrals for zero magnetic field case and magnetic-field dependent phase factor (Peierls phase factor). In Chapter 4, the derivation of the Streda formula is briefly discussed to calculate the magnetic field dependence Hall conductivity using the nonperturbative MFRTB method. The application of the non-perturbative MFRTB method to a two-dimensional honeycomb lattice, graphene is discussed in Chapter 5. In this Chapter, the magnetic hopping integrals are also presented in tabular form. The calculating results such as magnetic field dependence of energy spectrum, Fermi energy dependence of quantized Hall conductivity, Fermi energy dependence of the width of the WPs with comparing conventional theoretical model and magnetic field dependence of the width of the NPs with comparing spin Zeeman effect are presented in Chapter 6. Finally, in Chapter 7, the conclusion remarks of this thesis are presented.

Chapter 2

Relativistic Tight Binding (TB) approximation method for zero magnetic field

In this Chapter, the Relativistic Tight Binding (TB) approximation method for zero magnetic field is described in the following sequence:

2.1 Matrix elements of the Dirac Hamiltonian

In order to derive the expression of the matrix elements of the Dirac Hamiltonian, let us consider an electron moves only in a periodic potential in the crystal in the absence of a magnetic field. The Hamiltonian of this system is given by [59]

$$H = c\vec{\alpha}.\vec{p} + \beta mc^2 + \sum_{\vec{R}_n}\sum_i V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_i\right) \tag{2.1}$$

In Eq. (2.1), $\vec{p}$ $(= -i\hbar\vec{\nabla})$, m and c are the energy-momentum of the electron, rest mass of the electron, and velocity of light respectively, the quantities, $\vec{\alpha} \equiv (\alpha_x, \alpha_y, \alpha_z)$ and β stand for the usual 4×4 matrices and also denote the Hermitian operators [59], $V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i)$ is the scalar potential that is caused by the nucleus of an atom, a_i; where the atom, a_i is located at the position $\vec{R}_n + \vec{d}_i$, where $\vec{R}_n$ and $\vec{d}_i$ are the lattice translation vector, and the vector specifying position of the an atom, a_i in the crystal respectively.

The electron in the above-mentioned system obeys the Dirac equation. The Dirac equation for this electron in a periodic potential in the absence of a magnetic field is given by [59]

$$H\psi_{\alpha,\vec{k}}(\vec{r}) = E_{\alpha,\vec{k}}\psi_{\alpha,\vec{k}}(\vec{r}) \tag{2.2}$$

In Eq. (2.2), $\psi_{\alpha,\vec{k}}(\vec{r})$ and $E_{\alpha,\vec{k}}$ are the four-component eigenfunction and eigenvalue respectively, the subscripts α, and $\vec{k}$ in $\Psi_{\alpha,\vec{k}}(\vec{r})$ and $E_{\alpha,\vec{k}}$ are the band index and crystal momentum, respectively.

In order to estimate the appropriate form of the relativistic atomic orbitals of an atom similar to the non-relativistic Tight-Binding (TB) approximation method, it is very important to expand the four-component eigenfunction, $\Psi_{\alpha,\vec{k}}(\vec{r})$ by using the Bloch sum of the relativistic atomic orbitals as a basis function. The expanded four-component eigenfunction is given by

$$\psi_{\alpha,\vec{k}}(\vec{r}) = \sum_{nlJM} \sum_i C_{nlJM,i}^{\alpha,\vec{k}} \ \Phi_{nlJM}^{a_i,\vec{k}}(\vec{r}) \tag{2.3}$$

In Eq. (2.3), $C_{nlJM,i}^{\alpha,\vec{k}}$ and $\Phi_{nlJM}^{a_i,\vec{k}}(\vec{r})$ are the expansion coefficient, and the Bloch sum of the relativistic atomic orbitals of an atom. The Bloch sum for the normalized condition is given by

$$\Phi_{nlJM}^{a_i,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_n} e^{i\,\vec{k}.(\vec{R}_n+\vec{d}_i)}\, \varphi_{nlJM}^{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i) \tag{2.4}$$

In Eq. (2.4), $\varphi_{nlJM}^{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i)$ is the relativistic atomic orbitals of an atom, a_i. In Eqs. (2.3) and (2.4), the letters n, l, J and M are the principal, azimuthal, total angular momentum, and magnetic quantum numbers, respectively. It is noted that the number l is related to the parity, which is conserved in the atomic system [59]. In Eq. (2.4), N is the total number of unit cells in the given system. Since the relativistic atomic orbital, $\varphi_{nlJM}^{a_i}(\vec{r})$ of an atom, a_i, obeys the Dirac equation in the given system, the Dirac equation for the relativistic atomic orbital, $\varphi_{nlJM}^{a_i}(\vec{r})$ is given by

$$\left[c\vec{\alpha}.\vec{p} + \beta mc^2 + V_{a_i}(\vec{r})\right]\varphi_{nlJM}^{a_i}(\vec{r}) = \bar{\varepsilon}_{nlJM}^{a_i}\varphi_{nlJM}^{a_i}(\vec{r}) \tag{2.5}$$

In Eq. (2.5), $\bar{\varepsilon}_{nlJM}^{a_i}$ is the atomic spectrum of an atom, a_i for zero magnetic field case. The relativistic atomic orbital, $\varphi_{nlJM}^{a_i}(\vec{r})$ is related to the four-component eigenfunction of $\psi_{\alpha,\vec{k}}(\vec{r})$. The relativistic atomic orbital, $\varphi_{nlJM}^{a_i}(\vec{r})$ is given by [59]

$$\varphi_{nlJM}^{a_i}(\vec{r}) = \frac{1}{r}\begin{bmatrix} F_{nlJ}^{a_i}(\vec{r})\ \mathcal{Y}_{l,J}^{M}(\theta,\phi) \\ iG_{nlJ}^{a_i}(\vec{r})\ \mathcal{Y}_{2J-l,J}^{M}(\theta,\phi) \end{bmatrix} \tag{2.6}$$

In Eq. (2.6), $F_{nlJ}^{a_i}(\vec{r})$ and $G_{nlJ}^{a_i}(\vec{r})$ are the large and small components of the radial part of the relativistic atomic orbitals, $\varphi_{nlJM}^{a_i}(\vec{r})$ respectively, and $\mathcal{Y}_{l,J}^{M}(\theta,\phi)$ is the spinors spherical

harmonics of order l and also the function of the total angular momentum [59]. Here, the parity is given by $(-)^l$, where l takes two values $l \equiv J + \frac{1}{2}\varpi$ and $l \equiv J - \frac{1}{2}\varpi$ and ϖ is a quantum number which is defined by $\varpi = +1$ for the states of parity $(-)^{J+\frac{1}{2}}$ and $\varpi = -1$ for the states of parity $(-)^{J-\frac{1}{2}}$ [59].

Using Eqs. (2.2) and (2.3), we have

$$H \sum_{nlJM} \sum_i C^{\alpha,\vec{k}}_{nlJM,i}\, \Phi^{a_i,\vec{k}}_{nlJM}(\vec{r}) = E_{\alpha,\vec{k}} \sum_{nlJM} \sum_i C^{\alpha,\vec{k}}_{nlJM,i}\, \Phi^{a_i,\vec{k}}_{nlJM}(\vec{r}) \tag{2.7}$$

Using Eqs. (2.4) and (2.7), we have

$$H \sum_{nlJM} \sum_i \sum_{\vec{R}_n} C^{\alpha,\vec{k}}_{nlJM,i}\, e^{i\,\vec{k}.(\vec{R}_n+\vec{d}_i)}\, \varphi^{a_i}_{nlJM}\left(\vec{r} - \vec{R}_n - \vec{d}_i\right) = E_{\alpha,\vec{k}} \sum_{nlJM} \sum_i \sum_{\vec{R}_n} C^{\alpha,\vec{k}}_{nlJM,i}\, e^{i\,\vec{k}.(\vec{R}_n+\vec{d}_i)}\, \varphi^{a_i}_{nlJM}\left(\vec{r} - \vec{R}_n - \vec{d}_i\right) \tag{2.8}$$

Multiplying by $\varphi^{a_j}_{\acute{n}\acute{l}\acute{J}\acute{M}}(\vec{r} - \vec{d}_j)^{\dagger}$ from left on both sides in Eq. (2.8) and integrating, then Eq. (2.8) becomes

$$\sum_{nlJM} \sum_i \sum_{\vec{R}_n} C^{\alpha,\vec{k}}_{nlJM,i}\, e^{i\,\vec{k}.\left(\vec{R}_n+\vec{d}_i\right)} \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{J}\acute{M}}(\vec{r} - \vec{d}_j)^{\dagger} H \varphi^{a_i}_{nlJM}\left(\vec{r} - \vec{R}_n - \vec{d}_i\right) d^3r = E_{\alpha,\vec{k}} \sum_{nlJM} \sum_i \sum_{\vec{R}_n} C^{\alpha,\vec{k}}_{nlJM,i}\, e^{i\,\vec{k}.(\vec{R}_n+\vec{d}_i)} \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{J}\acute{M}}(\vec{r} - \vec{d}_j)^{\dagger} \varphi^{a_i}_{nlJM}\left(\vec{r} - \vec{R}_n - \vec{d}_i\right) d^3r \tag{2.9}$$

The relativistic hopping integral between two atoms, a_i and a_j from Eq. (2.9) is given by

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right) = \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{J}\acute{M}}\left(\vec{r} - \vec{d}_j\right)^{\dagger} H \varphi^{a_i}_{nlJM}\left(\vec{r} - \vec{R}_n - \vec{d}_i\right)\, d^3r \tag{2.10}$$

If the relativistic atomic orbitals, $\varphi_{nlJM}^{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i\right)$ are highly localized around $(\vec{R}_n+\vec{d}_i)$, the overlap integral from Eq. (2.9) is given by

$$\int \varphi_{nlJM}^{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i)^{\dagger}\varphi_{\acute{n}\acute{l}\acute{j}\acute{M}}^{a_j}\left(\vec{r}-\vec{R}_m-\vec{d}_j\right)d^3r=\delta_{\vec{R}_n+\vec{d}_i,\vec{R}_m+\vec{d}_j}\delta_{nlJM,\acute{n}\acute{l}\acute{j}\acute{M}} \tag{2.11}$$

Using Eqs. (2.10) and (2.11), then Eq. (2.9), becomes

$$\begin{aligned}&\sum_{nlJM}\sum_i\sum_{\vec{R}_n}e^{i\,\vec{k}.(\vec{R}_n+\vec{d}_i)}t_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}^{a_ja_i}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)C_{nlJM,i}^{\alpha,\vec{k}}\\&\qquad=E_{\alpha,\vec{k}}\sum_{nlJM}\sum_i\sum_{\vec{R}_n}e^{i\,\vec{k}.(\vec{R}_n+\vec{d}_i)}\delta_{\vec{R}_n+\vec{d}_i,\vec{R}_m+\vec{d}_j}\delta_{nlJM,\acute{n}\acute{l}\acute{j}\acute{M}}\,C_{nlJM,i}^{\alpha,\vec{k}}\end{aligned} \tag{2.12}$$

After simplifying, Eq. (2.12) becomes

$$\begin{aligned}&\sum_{nlJM}\sum_i\sum_{\vec{R}_n}e^{i\,\vec{k}.(\vec{R}_n+\vec{d}_i-\vec{d}_j)}t_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}^{a_ja_i}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)C_{nlJM,i}^{\alpha,\vec{k}}\\&\qquad=E_{\alpha,\vec{k}}\delta_{i,j}\,\delta_{nlJM,\acute{n}\acute{l}\acute{j}\acute{M}}\,C_{nlJM,i}^{\alpha,\vec{k}}\end{aligned} \tag{2.13}$$

The matrix element of the Dirac Hamiltonian from Eq. (2.13) is given by

$$H_{(\acute{n}\acute{l}\acute{j}\acute{M})\,j\,,\,(nlJM)i}\left(\vec{k}\right)=\sum_{\vec{R}_n}e^{i\,\vec{k}.(\vec{R}_n+\vec{d}_i-\vec{d}_j)}t_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}^{a_ja_i}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right) \tag{2.14}$$

Using Eq. (2.14) into Eq. (2.13), then we have

$$\sum_{nlJM}\sum_i H_{(\acute{n}\acute{l}\acute{j}\acute{M})j\,,\,(nlJM)i}(\vec{k})\,C_{nlJM,i}^{\alpha,\vec{k}}=E_{\alpha,\vec{k}}\delta_{i,j}\delta_{nlJM,\,\acute{n}\acute{l}\acute{j}\acute{M}}\,C_{nlJM,i}^{\alpha,\vec{k}} \tag{2.15}$$

Since the matrix element in Eq. (2.14) is Hermite, it is possible to calculate the eigenvalues, $E_{\vec{k}}$ in a fixed band for each k point and the four-component eigenfunctions, $\Psi_{\alpha,\vec{k}}(\vec{r})$ for each $\vec{k}$ point by solving Eq. (2.15). For this aim, firstly, it is urgent to calculate the relativistic hopping integrals, $t_{n'\ell'J'M',n\ell JM}^{a_ja_i}(\vec{R}_n+\vec{d}_i-\vec{d}_j)$ which are expressed in Eq. (2.10).

2.2 Relativistic hopping integrals for the cases: $\vec{R}_n = 0, \vec{d}_i = \vec{d}_j$ and $\vec{R}_n \neq 0, \vec{d}_i \neq \vec{d}_j$

2.2.1 In case of $\vec{R}_n = 0$ and $\vec{d}_i = \vec{d}_j$

Using Eq. (2.1) into Eq. (2.10), the relativistic hopping integrals become

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}(\vec{R}_n + \vec{d}_i - \vec{d}_j)$$
$$= \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r} - \vec{d}_j)^\dagger \left[c\vec{\alpha}.\vec{p} + \beta mc^2 + \textstyle\sum_{\vec{R}_n}\sum_j V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_j\right)\right] \varphi^{a_i}_{nlJM}(\vec{r} - \vec{d}_i)\ d^3r$$
$$= \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r} - \vec{d}_j)^\dagger \left[c\vec{\alpha}.\vec{p} + \beta mc^2 + V_{a_i}(\vec{r} - \vec{d}_i)\right] \varphi^{a_i}_{nlJM}(\vec{r} - \vec{d}_i)\, d^3r$$
$$+ \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r} - \vec{d}_j)^\dagger \textstyle\sum_{\vec{R}_n \neq 0}\sum_{\acute{\imath}\neq i} V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_{\acute{\imath}}\right)\varphi^{a_i}_{nlJM}(\vec{r} - \vec{d}_i)\, d^3r \qquad (2.16)$$

Using Eq. (2.5) into Eq. (2.16), the first term becomes

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}(\vec{R}_n + \vec{d}_i - \vec{d}_j) = \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r} - \vec{d}_j)^\dagger \bar{\varepsilon}^{a_i}_{nlJM}\varphi^{a_i}_{nlJM}(\vec{r} - \vec{d}_i)\, d^3r$$
$$+ \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r} - \vec{d}_j)^\dagger \textstyle\sum_{\vec{R}_n \neq 0}\sum_{\acute{\imath}\neq i} V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_{\acute{\imath}}\right)\varphi^{a_i}_{nlJM}(\vec{r} - \vec{d}_i)\, d^3r \qquad (2.17)$$

Using Eq. (2.11) into Eq. (2.17), the first term becomes

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}(\vec{R}_n + \vec{d}_i - \vec{d}_j) = \bar{\varepsilon}^{a_i}_{nlJM}\delta_{nlJM,\acute{n}\acute{l}\acute{j}\acute{M}}\,\delta_{j,i}$$
$$+ \int \varphi^{a_i}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r} - \vec{d}_i)^\dagger \textstyle\sum_{\vec{R}_n}\sum_{\vec{k}} V_{a_k}\left(\vec{r} - \vec{R}_n - \vec{d}_{\acute{k}}\right)\ \varphi^{a_i}_{nlJM}(\vec{r} - \vec{d}_i)\, d^3r \qquad (2.18)$$
$$\vec{R}_n + \vec{d}_{\acute{k}} \neq \vec{d}_i$$

In Eq. (2.18), the second term is the energy of the crystal field. In Eq. (2.18), the scalar potential, $V_{a_k}(\vec{r} - \vec{R}_n - \vec{d}_{\acute{k}})$ is constant for the symmetrical behavior at position $\vec{r} = \vec{d}_i$ due to the relativistic

atomic orbitals, $\varphi^{a_i}_{n'\ell'J'M'}(\vec{r}-\vec{d}_i)$ and $\varphi^{a_i}_{n\ell JM}(\vec{r}-\vec{d}_i)$ are sufficiently localized around $\vec{r}=\vec{d}_i$. The integral part in Eq. (2.18) would be vanished for the orthogonality condition of relativistic atomic orbitals, $\varphi^{a_i}_{n'\ell'J'M'}(\vec{r}-\vec{d}_i)$ and $\varphi^{a_i}_{n\ell JM}(\vec{r}-\vec{d}_i)$ in the condition of $n'\neq n$, $l'\neq l, J'\neq J$ and $M'\neq M$. For this reason, the energy of the crystal field can be approximated in the following form:

$$\int \varphi^{a_i}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_i)^{\dagger}\Big\{\sum_{\vec{R}_n}\sum_{\vec{k}} V_{a_k}\left(\vec{r}-\vec{R}_n-\vec{d}_k\right)\Big\}\varphi^{a_i}_{nljM}(\vec{r}-\vec{d}_i)\,d^3r \qquad \vec{R}_n+\vec{d}_k\neq\vec{d}_i$$
$$=\Delta\bar{\varepsilon}^{a_i}_{nljM}\delta_{\acute{n}\acute{l}\acute{j}\acute{M},nljM} \tag{2.19}$$

Using Eqs. (2.18) and (2.19), the relativistic hopping integrals become

$$t^{a_ja_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nljM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)=\bar{\varepsilon}^{a_i}_{nljM}\delta_{nljM\acute{n}\acute{l}\acute{j}\acute{M}}\,\delta_{j,i}+\Delta\bar{\varepsilon}^{a_i}_{nljM}\delta_{\acute{n}\acute{l}\acute{j}\acute{M},nljM}$$
$$=(\bar{\varepsilon}^{a_i}_{nljM}+\Delta\bar{\varepsilon}^{a_i}_{nljM})\delta_{nljM,\acute{n}\acute{l}\acute{j}\acute{M}}\,\delta_{j,i} \tag{2.20}$$

2.2.2 In case of $\vec{R}_n\neq 0$ and $\vec{d}_i\neq\vec{d}_j$

Using Eq. (2.1) into Eq. (2.10), the relativistic hopping integrals become

$$t^{a_ja_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nljM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)$$
$$=\int\varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\left[c\vec{\alpha}.\vec{p}+\beta mc^2+\sum_{\vec{R}_n}\sum_j V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_j\right)\right]\varphi^{a_i}_{nljM}(\vec{r}-\vec{d}_i)\;d^3r$$
$$=\int\varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\left[\left\{c\vec{\alpha}.\vec{p}+\beta mc^2+\frac{V_{a_j}(\vec{r}-\vec{d}_j)+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i)}{2}\right\}\right.$$
$$\left.+\frac{V_{a_j}(\vec{r}-\vec{d}_j)+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_j)}{2}+\sum_{\vec{R}_{\acute{n}}}\sum_{\acute{i},i}V_{a_i}(\vec{r}-\vec{R}_{\acute{n}}-\vec{d}_{\acute{i}})\right]\varphi^{a_i}_{nljM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r \qquad \vec{R}_{\acute{n}}\neq 0\ ,\acute{i}\neq 0,\ \vec{R}_n\neq R_{\acute{n}}\ ,i\neq\acute{i}$$
$$=\frac{1}{2}\int\varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\{c\vec{\alpha}.\vec{p}+\beta mc^2+V_{a_j}(\vec{r}-\vec{d}_j)\varphi^{a_i}_{nljM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r$$

$$+\frac{1}{2}\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\{c\,\vec{\alpha}.\vec{p}+\beta mc^2+V_{a_i}(\vec{r}-\vec{R}_{\boldsymbol{n}}-\vec{d}_{\boldsymbol{i}})\varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r$$

$$+\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\left\{\frac{V_{a_j}(\vec{r}-\vec{d}_j)+V_{a_i}(\vec{r}-\vec{R}_{\boldsymbol{n}}-\vec{d}_{\boldsymbol{j}})}{\mathbf{2}}\right\}\varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r$$

$$+\sum_{\vec{R}_{\acute{n}}}\sum_{i,\,\acute{\imath}}\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}V_{a_i}(\vec{r}-\vec{R}_{\acute{n}}-\vec{d}_{\acute{\imath}})\varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r \qquad (2.21)$$

$\vec{R}_{\acute{n}}\neq 0\ \acute{\imath}\neq 0$

$\vec{R}_n\neq R_{\acute{n}}\ i\neq \acute{\imath}$

For the simplicity Eq. (2.21) can be taken by parts in the following way:

The 1st part of RHS in Eq. (2.21), we have

$$\begin{aligned}\frac{1}{2}\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\{c\vec{\alpha}.\vec{p}+\beta mc^2+V_{a_j}(\vec{r}-\vec{d}_j)\}\varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r\\ =\frac{\mathbf{1}}{\mathbf{2}}\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\bar{\varepsilon}^{a_i}_{nlJM}\ \varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r\\ =\frac{\mathbf{1}}{\mathbf{2}}\bar{\varepsilon}^{a_i}_{nlJM}\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\ \varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r\\ =\frac{1}{2}\bar{\varepsilon}^{a_i}_{nlJM}\times 0\\ =0\end{aligned} \qquad (2.22)$$

The 2nd part of RHS in Eq. (2.21), we have

$$\begin{aligned}&\frac{\mathbf{1}}{\mathbf{2}}\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\{c\vec{\alpha}.\vec{p}+\beta mc^2+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i)\}\varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r\\ =&\frac{\mathbf{1}}{\mathbf{2}}\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\bar{\varepsilon}^{a_i}_{nlJM}\ \varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r\\ =&\frac{\mathbf{1}}{\mathbf{2}}\bar{\varepsilon}^{a_i}_{nlJM}\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r}-\vec{d}_j)^{\dagger}\ \varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r\\ =&\frac{\mathbf{1}}{\mathbf{2}}\bar{\varepsilon}^{a_i}_{nlJM}\times 0\\ =&\,0\end{aligned} \qquad (2.23)$$

From the 4th part of RHS in Eq. (2.21), it is noticeable that it has three central integral parts. Three central integral parts provide a very small numerical value compared to the other integral parts. For this reason, the numerical value of the 4th part can be neglected. From the discussion in Eqs.

(2.22), (2.23), and the 4th part, these three parts are zero. As a result, only the 3rd part remains for the two centrals integrals. Finally, the relativistic hopping integrals in Eq. (2.21) become

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right) = \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}\left(\vec{r}-\vec{d}_j\right)^{\dagger}\left\{\frac{V_{a_j}(\vec{r}-\vec{d}_j)+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_j)}{2}\right\}\varphi^{a_i}_{nlJM}\left(\vec{r}-\vec{R}_n-\vec{d}_i\right)d^3r \quad (2.24)$$

For simplicity, let us consider a new variable $\vec{r}-\vec{d}_j=\vec{r}$ in Eq. (2.24), then

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right) = \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}\left(\vec{r}\right)^{\dagger}\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\varphi^{a_i}_{nlJM}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)d^3r \quad (2.25)$$

Using Eqs. (2.19) and (2.25) into Eq. (2.13) then we can get the Dirac Hamiltonian

$$H_{(\acute{n}\acute{l}\acute{j}\acute{M})j,(nlJM)i}(\vec{k}) = (\bar{\varepsilon}^{a_i}_{nlJM}+\Delta\bar{\varepsilon}^{a_i,\vec{d}_i}_{nlJM})\,\delta_{nlJM,\acute{n}\acute{j}\acute{M}}\,\delta_{j,i}+\sum_{\vec{R}_n}(\,1-\delta_{R_n,0}\,\delta_{j,i})e^{i\,\vec{k}.(\vec{R}_n+\vec{d}_i-\vec{d}_j)} \times t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right) \quad (2.26)$$

2.3 TB parameters for the relativistic hopping integrals

The relativistic hopping integrals, $t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)$ can be expressed in terms of several relativistic TB parameters that are the same of the non-relativistic hopping integrals [60]. By using relativistic hopping integrals in the case of non-relativistic [60,61], the relativistic TB parameter can be defined as the relativistic hopping integral between two sites that are placed on the *z*-axis. For this aim, the atom, a_j is placed at the origin and the atom, a_i is placed in a position where the position is away from the origin by the distance, $\left|\vec{R}_n+\vec{d}_i-\vec{d}_j\right|$. More clearly, the

distance, $\left|\vec{R}_n + \vec{d}_i - \vec{d}_j\right|$ is the distance between the position of the atoms, a_i and origin. Then the relativistic TB parameter can be defined as, $t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\left|\vec{R}_n + \vec{d}_i - \vec{d}_j\right|\hat{e}_z\right)$ where $\hat{e}_z$ denotes the unit vector in the direction of the z-axis. The relativistic TB parameters can be defined using the condition $n, \acute{n}, l, \acute{l}, J, \acute{J}$ and $|M|$.

$$K_d^{a_j a_i}(\acute{n}\acute{l}\acute{J},\, nlJ)_{|M|} = t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\left|\vec{R}_n + \vec{d}_i - \vec{d}_j\right|\hat{e}_z\right)$$
$$= \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{J}\,|\acute{M}|}\left(\vec{\acute{r}}\right)^{\dagger}\left\{\frac{V_{a_j}\left(\vec{\acute{r}}\right)+V_{a_i}\left(\vec{\boldsymbol{r}}-\left|\vec{R}_n-\vec{d}_i+\vec{d}_j\right|\hat{e}_z\right)}{2}\right\}\varphi^{a_i}_{nlJM}\left(\vec{\boldsymbol{r}} - \left|\vec{R}_n - \vec{d}_i + \vec{d}_j\right|\hat{e}_z\right)d^3r \tag{2.27}$$

In Eq. (2.27), the subscript, d in $K_d^{a_j a_i}(\acute{n}\acute{l}\acute{J},\, nlJ)_{|M|}$ represents the dependence of the relativistic TB parameter on the distance, $\left|\vec{R}_n - \vec{d}_i + \vec{d}_j\right|$. Therefore, the distance, $\left|\vec{R}_n - \vec{d}_i + \vec{d}_j\right|$ is equal to the distance between the first nearest neighboring atoms, second nearest neighboring atoms, and so on, then d denotes the number of 1, 2... respectively. For the s and p orbitals of carbon atom in case of $l = 0$ and $l = 1$, ten kinds of relativistic TB parameters are in the following:

$K_d^{a_j a_i}(\acute{n}\,0\frac{1}{2},\, n\,0\;\frac{1}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\,0\frac{1}{2},\, n\,1\;\frac{1}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\,0\frac{1}{2},\, n\,1\;\frac{3}{2})_{\frac{1}{2}}$

$K_d^{a_j a_i}(\acute{n}\,1\frac{1}{2},\, n\,0\;\frac{1}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\,1\frac{1}{2},\, n\,1\;\frac{1}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\,1\frac{1}{2},\, n\,1\;\frac{3}{2})_{\frac{1}{2}}$

$K_d^{a_j a_i}(\acute{n}\,1\frac{3}{2},\, n\,0\;\frac{1}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\,1\frac{3}{2},\, n\,1\;\frac{1}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\,1\frac{3}{2},\, n\,1\;\frac{3}{2})_{\frac{1}{2}}$

$K_d^{a_j a_i}(\acute{n}\,1\frac{3}{2},\, n\,1\;\frac{3}{2})_{\frac{3}{2}}$

If we consider the relativistic TB parameters, $K_d^{a_j a_i}(\acute{n}\acute{l}\acute{J},\, nlJ)_{|M|}$ are independent of atoms a_j and a_i, then, the relativistic TB parameters can be defined by $K_d(\acute{n}\acute{l}\acute{J},\, nlJ)_{|M|}$. Therefore, we have seven kinds of relativistic TB parameters instead of ten kinds of relativistic TB parameters in the following:

$K_d^{a_j a_i}(\acute{n}\, 0\frac{1}{2},\, n\, 0\ \frac{1}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\, 0\frac{1}{2},\, n\, 1\ \frac{1}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\, 0\frac{1}{2},\, n\, 1\ \frac{3}{2})_{\frac{1}{2}}$

$K_d^{a_j a_i}(\acute{n}\, 1\frac{1}{2},\, n\, 1\ \frac{1}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\, 1\frac{1}{2},\, n\, 1\ \frac{3}{2})_{\frac{1}{2}}$ $K_d^{a_j a_i}(\acute{n}\, 1\frac{3}{2},\, n\, 1\ \frac{3}{2})_{\frac{1}{2}}$

$K_d^{a_j a_i}(\acute{n}\, 1\frac{3}{2},\, n\, 1\ \frac{3}{2})_{\frac{3}{2}}$

By using the large and small components of the relativistic atomic orbitals which are expressed in Eq. (2.6), then the relativistic TB parameters, $K_d\ (\acute{n}\acute{l}\acute{J},\ nlJ)_{|M|}$ can be perfectly approximated.

In the following subsequent section, firstly, I would like to express the expressions of the relativistic hopping integrals for the four cases:

(i) $\acute{J} = \acute{l} + \frac{1}{2}$ and $\mathrm{J} = l + \frac{1}{2}$

(ii) $\acute{J} = \acute{l} + \frac{1}{2}$ and $\mathrm{J} = l - \frac{1}{2}$

(iii) $\acute{J} = \acute{l} - \frac{1}{2}$ and $\mathrm{J} = l + \frac{1}{2}$

(iv) $\acute{J} = \acute{l} - \frac{1}{2}$ and $\mathrm{J} = l - \frac{1}{2}$

2.4 Expressions of the relativistic hopping integral for the relativistic version of the Slater -Koster table

The relativistic hopping integrals, $t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right)$ in terms of several relativistic TB parameters, $K_d^{a_j a_i}(\acute{n}\acute{l}\acute{J},\ nlJ)_{|M|}$ by using Slater-Koster table for the non- relativistic hopping integrals [60] that are expressed in terms of the linear combination of some TB parameters. In order to calculate the relativistic hopping integrals for the relativistic version of the Slater-Koster table in terms of several relativistic TB parameters, we consider the spinor spherical harmonics, $\mathcal{Y}^M_{lJ}(\theta, \phi)$ in the following

$$\mathcal{Y}_{lj}^{M}(\theta,\phi)=\begin{bmatrix}\sqrt{\frac{J+M}{2}}Y_{l,M-\frac{1}{2}}(\theta,\phi)\\ \sqrt{\frac{J-M}{2}}Y_{l,M+\frac{1}{2}}(\theta,\phi)\\ -\sqrt{\frac{J-M+1}{2(J+1)}}Y_{l,M-\frac{1}{2}}(\theta,\phi)\\ \sqrt{\frac{J+M+1}{2(J+1)}}Y_{l,M+\frac{1}{2}}(\theta,\phi)\end{bmatrix}\quad\begin{matrix}\text{for } J=l+\frac{1}{2}\\ \\ \\ \text{for } J=l-\frac{1}{2}\end{matrix} \tag{2.28}$$

In Eq. (2.28), the symbols, $Y_{l,M-\frac{1}{2}}(\theta,\phi)$ and $Y_{l,M+\frac{1}{2}}(\theta,\phi)$ are the spherical harmonics. Using Eqs. (2.6) and (2.28), we can write the four-component of relativistic eigenfunction in the following for $J=l+\frac{1}{2}$ in Eq. (2.29) and for $J=l-\frac{1}{2}$ in Eq. (2.30) respectively.

$$\varphi_{nljM}^{a_i}(\vec{r})=\frac{1}{r}\begin{bmatrix}F_{nlJ}^{a_i}\sqrt{\frac{J+M}{2}}Y_{l,M-\frac{1}{2}}(\theta,\phi)\\ F_{nlJ}^{a_i}\sqrt{\frac{J-M}{2}}Y_{l,M+\frac{1}{2}}(\theta,\phi)\\ -iG_{nlJ}^{a_i}\sqrt{\frac{J-M+1}{2(J+1)}}Y_{2J-l,M-\frac{1}{2}}(\theta,\phi)\\ iG_{nlJ}^{a_i}\sqrt{\frac{J+M+1}{2(J+1)}}Y_{2J-l,M+\frac{1}{2}}(\theta,\phi)\end{bmatrix} \tag{2.29}$$

and

$$\varphi_{nljM}^{a_i}(\vec{r})=\frac{1}{r}\begin{bmatrix}-F_{nlJ}^{a_i}\sqrt{\frac{J-M+1}{2(J+1)}}Y_{l,M-\frac{1}{2}}(\theta,\phi)\\ F_{nlJ}^{a_i}\sqrt{\frac{J+M+1}{2(J+1)}}Y_{l,M+\frac{1}{2}}(\theta,\phi)\\ iG_{nlJ}^{a_i}\sqrt{\frac{J+M}{2J}}Y_{l-1,M-\frac{1}{2}}(\theta,\phi)\\ iG_{nlJ}^{a_i}\sqrt{\frac{J-M}{2J}}Y_{l-1,M+\frac{1}{2}}(\theta,\phi)\end{bmatrix} \tag{2.30}$$

Using Eqs. (2.29) and (2.30) into Eq. (2.25), we can express the relativistic hopping integrals in term of several TB parameters for the four cases step by step.

2.4.1 In case of $\acute{j} = \acute{l} + \frac{1}{2}$ and $j = l + \frac{1}{2}$

In this case, using Eqs. (2.29) and (2.30) into Eq. (2.25), the relativistic hopping integrals become

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nljM}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right) = \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}\left(\vec{\acute{r}}\right)^{\dagger} \left\{\frac{V_{a_j}(\acute{r}) + V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_i\right)}{2}\right\} \varphi^{a_i}_{nljM}\left(\vec{r} - \vec{R}_n - \vec{d}_i\right) d^3r$$

$$= \int \sqrt{\frac{\acute{j}+\acute{M}}{2\acute{j}}}\ \frac{1}{r\, r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\,\acute{M}-\frac{1}{2}}(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j\right)}{2}\right\} \sqrt{\frac{j+M}{2j}}\ \ F^{a_i}_{nlj}\left(\vec{r}_{ijn}\right) Y_{l,\,M-\frac{1}{2}}(\theta_{ijn},\, \phi_{ijn}) d^3r$$

$$+ \int \sqrt{\frac{\acute{j}-\acute{M}}{2\acute{j}}}\ \frac{1}{r\, r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\,\acute{M}+\frac{1}{2}}(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j\right)}{2}\right\} \sqrt{\frac{j-M}{2j}}\ \ F^{a_i}_{nlj}\left(\vec{r}_{ijn}\right) Y_{l,\,M+\frac{1}{2}}(\theta_{ijn},\, \phi_{ijn}) d^3r$$

$$+ \int -\sqrt{\frac{\acute{j}-\acute{M}+1}{2(\acute{j}+1)}}\ \frac{1}{r\, r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})\}^*\ Y^*_{\acute{l}+1\,\acute{M}-\frac{1}{2}}(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j\right)}{2}\right\} \{-\sqrt{\frac{J-M+1}{2(J+1)}}\ \ iG^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\}$$

$$\times Y_{l+1,\,M-\frac{1}{2}}(\theta_{ijn},\, \phi_{ijn}) d^3r$$

$$+ \int \sqrt{\frac{\acute{j}+\acute{M}+1}{2(\acute{j}+1)}}\ \frac{1}{r\, r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})\}^*\ Y^*_{\acute{l}+1\,\acute{M}+\frac{1}{2}}(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j\right)}{2}\right\} \{\sqrt{\frac{J+M+1}{2(J+1)}}\ \ iG^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\}$$

$$\times Y_{l+1,\,M+\frac{1}{2}}\left(\theta_{ijn},\, \phi_{ijn}\right) d^3r \qquad (2.31)$$

2.4.2 In case of $\acute{j} = \acute{l} + \frac{1}{2}$ and $j = l - \frac{1}{2}$

In this case, using Eqs. (2.29) and (2.30) into Eq. (2.25), the relativistic hopping integrals become

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nljM}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right) = \int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}\left(\vec{\acute{r}}\right)^{\dagger} \left\{\frac{V_{a_j}(\acute{r}) + V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_j\right)}{2}\right\} \varphi^{a_i}_{nljM}\left(\vec{r} - \vec{R}_n - \vec{d}_i\right) d^3r$$

$$= -\int \sqrt{\frac{\acute{j}+\acute{M}}{2\acute{j}}}\ \frac{1}{r\, r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\,\acute{M}-\frac{1}{2}}(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}\left(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j\right)}{2}\right\} \sqrt{\frac{J-M+1}{2(J+1)}}\ \ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)$$

$$\times Y_{l,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$+\int\sqrt{\frac{\acute{\jmath}-\acute{M}}{2\acute{\jmath}}}\;\frac{1}{r\,r_{ijn}}\;F^{a_j}_{\acute{n}\acute{l}\acute{\jmath}}(\vec{r})^*\;Y^*_{\acute{l},\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\sqrt{\frac{J+M+1}{2(J+1)}}\;\;F^{a_i}_{nlJ}(\vec{r}_{ijn})$$

$$\times Y_{l,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$+\int-\sqrt{\frac{\acute{\jmath}-\acute{M}+1}{2(\acute{\jmath}+1)}}\;\frac{1}{r\,r_{ijn}}\;\{iG^{a_j}_{\acute{n}\acute{l}\acute{\jmath}}(\vec{r})\}^*\;Y^*_{\acute{l},+1\;\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\{\sqrt{\frac{J+M}{2J}}\;\;iG^{a_i}_{nlJ}(\vec{r}_{ijn})\}$$

$$\times Y_{l-1,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$+\int\sqrt{\frac{\acute{\jmath}+\acute{M}+1}{2(\acute{\jmath}+1)}}\;\frac{1}{r\,r_{ijn}}\;\{iG^{a_j}_{\acute{n}\acute{l}\acute{\jmath}}(\vec{r})\}^*\;Y^*_{\acute{l},+1\;\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\{\sqrt{\frac{J-M}{2J}}\;\;iG^{a_i}_{nlJ}(\vec{r}_{ijn})\}$$

$$\times Y_{l-1,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.32)$$

2.4.3 In case of $\acute{J}=\acute{l}-\frac{1}{2}$ and $J=l+\frac{1}{2}$

In this case, using Eqs. (2.29) and (2.30) into Eq. (2.25), the relativistic hopping integrals become

$$t^{a_ja_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)=\int\varphi^{a_j}_{\acute{n}\acute{l}\acute{J}\acute{M}}\left(\vec{\acute{r}}\right)^\dagger\left\{\frac{V_{a_j}\left(\vec{\acute{r}}\right)+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_j)}{2}\right\}\varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_n-\vec{d}_i)d^3r$$

$$=-\int\sqrt{\frac{\acute{\jmath}-\acute{M}+1}{2(\acute{\jmath}+1)}}\;\frac{1}{r\,r_{ijn}}\;F^{a_j}_{\acute{n}\acute{l}\acute{\jmath}}(\vec{r})^*\;Y^*_{\acute{l},\,\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\sqrt{\frac{J+M}{2J}}\;\;F^{a_i}_{nlJ}(\vec{r}_{ijn})$$

$$\times Y_{l,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$+\int\sqrt{\frac{\acute{\jmath}+\acute{M}+1}{2(\acute{\jmath}+1)}}\;\frac{1}{r\,r_{ijn}}\;F^{a_j}_{\acute{n}\acute{l}\acute{\jmath}}(\vec{r})^*\;Y^*_{\acute{l},\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\sqrt{\frac{J-M}{2J}}\;\;F^{a_i}_{nlJ}(\vec{r}_{ijn})$$

$$\times Y_{l,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$+\int-\sqrt{\frac{\acute{\jmath}+\acute{M}}{2\acute{\jmath}}}\;\frac{1}{r\,r_{ijn}}\;\{iG^{a_j}_{\acute{n}\acute{l}\acute{\jmath}}(\vec{r})\}^*\;Y^*_{\acute{l}-1\;\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\{\sqrt{\frac{J-M+1}{2(J+1)}}\;\;iG^{a_i}_{nlJ}(\vec{r}_{ijn})\}$$

$$\times Y_{l,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$+\int \sqrt{\frac{\acute{J}-\acute{M}}{2\acute{J}}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})\}^*\ Y^*_{\acute{l}-1\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\{\sqrt{\frac{J+M+1}{2(J+1)}}\ \ iG^{a_i}_{nlJ}(\vec{r}_{ijn})\}$$

$$\times Y_{l,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.33)$$

2.4.4 In case of $\acute{J}=\acute{l}-\frac{1}{2}$ and $J=l-\frac{1}{2}$

In this case, using Eqs. (2.29) and (2.30) into Eq. (2.25), the relativistic hopping integrals become

$$t^{a_ja_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)=\int\varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}\left(\vec{\acute{r}}\right)^\dagger\left\{\frac{V_{a_j}\left(\vec{\acute{r}}\right)+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_j)}{2}\right\}\varphi^{a_i}_{nlJM}\left(\vec{r}-\vec{R}_n-\vec{d}_i\right)d^3r$$

$$=\int\sqrt{\frac{\acute{J}-\acute{M}+1}{2(\acute{J}+1)}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\,\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\sqrt{\frac{J-M+1}{2(J+1)}}\ \ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)$$

$$\times Y_{l,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$+\int\sqrt{\frac{\acute{J}+\acute{M}+1}{2(\acute{J}+1)}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\sqrt{\frac{J+M+1}{2(J+1)}}\ \ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)$$

$$\times Y_{l,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$+\int\sqrt{\frac{\acute{J}+\acute{M}}{2\acute{J}}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})\}^*\ Y^*_{\acute{l}-1\,\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\{\sqrt{\frac{J+M}{2J}}\ \ iG^{a_i}_{nlJ}(\vec{r}_{ijn})\}$$

$$\times Y_{l-1,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$+\int\sqrt{\frac{\acute{J}-\acute{M}}{2\acute{J}}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})\}^*\ Y^*_{\acute{l}-1\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\{\sqrt{\frac{J-M}{2J}}\ \ iG^{a_i}_{nlJ}(\vec{r}_{ijn})\}$$

$$\times Y_{l-1,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.34)$$

In Eqs. (2.31), (2.32), (2.33) and (2.34), the arguments $(\vec{r}_{ijn},\theta_{ijn},\,\phi_{ijn})$ stand for the polar coordinates of the vector, $(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)$. The relativistic hopping integrals, $t^{a_ja_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)$ can be calculated in terms of $K^{a_ja_i}_d(\acute{n}\acute{l}\acute{J},\,nlJ)_{|M|}$ by using Eqs. (2.31), (2.32), (2.33) and

(2.34) for the combinations of $(\acute{n}\acute{l}\acute{J}\acute{M})$ and $(nlJM)$ atomic orbitals. Now I explain how to calculate the relativistic hopping integrals for the combination of atomic orbitals in the following two cases:

(i) $(\acute{n}\ 0\frac{1}{2}\frac{1}{2})$ and $(\mathrm{n}\ 0\frac{1}{2}\frac{1}{2})$

(ii) $(\acute{n}\ 0\frac{1}{2}\frac{1}{2})$ and $(\mathrm{n}\ 1\frac{1}{2}\frac{1}{2})$

(i) Relativistic hopping integrals for the combination of $(\acute{n}\ 0\frac{1}{2}\frac{1}{2})$ and $(\mathrm{n}\ 0\frac{1}{2}\frac{1}{2})$ atomic orbitals:

From Eq. (2.31), we can write the expression of $t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)$ for $(\acute{n}\acute{l}\acute{J}\acute{M})$ and $(nlJM)$ atomic orbitals

$$
\begin{aligned}
& t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right) \\
&= \int \sqrt{\frac{\acute{J}+\acute{M}}{2\acute{J}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{J}}(\vec{r})^*\ Y^*_{\acute{l},\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J+M}{2J}}\ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right) \\
&\qquad\qquad \times Y_{l,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \\
&+ \int \sqrt{\frac{\acute{J}-\acute{M}}{2\acute{J}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{J}}(\vec{r})^*\ Y^*_{\acute{l},\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J-M}{2J}}\ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right) \\
&\qquad\qquad \times Y_{l,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \\
&+ \int -\sqrt{\frac{\acute{J}-\acute{M}+1}{2(\acute{J}+1)}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{J}}(\vec{r})\}^*\ Y^*_{\acute{l}+1\,\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\{-\sqrt{\frac{J-M+1}{2(J+1)}}\ \{iG^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\} \\
&\qquad\qquad \times Y_{l+1,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \\
&+ \int \sqrt{\frac{\acute{J}+\acute{M}+1}{2(\acute{J}+1)}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{J}}(\vec{r})\}^*\ Y^*_{\acute{l}+1\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J+M+1}{2(J+1)}}\ \{iG^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\} \\
&\qquad\qquad \times Y_{l+1,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r
\end{aligned}
\tag{2.35}
$$

The 1st term of RHS in Eq. (2.35), we have

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{\text{1st term}}$$

$$=\int\sqrt{\frac{\acute{j}+\acute{M}}{2\acute{j}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J+M}{2J}}\ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)$$

$$\times Y_{l,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.36)$$

Using of $(\acute{n}\ 0\,\frac{1}{2}\frac{1}{2})$ and $(\mathrm{n}\ 0\,\frac{1}{2}\frac{1}{2})$ atomic orbitals, Eq. (2.36) becomes

$$t^{a_j a_i}_{\acute{n}\,0\frac{1}{2}\frac{1}{2},\ n\,0\,\frac{1}{2}\frac{1}{2}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{\text{1st term}}$$

$$=\int\sqrt{\frac{\frac{1}{2}+\frac{1}{2}}{2\frac{1}{2}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\,0\,\frac{1}{2}}(\vec{r})^*\ Y^*_{0,\,\frac{1}{2}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{\frac{1}{2}+\frac{1}{2}}{2\frac{1}{2}}}\ F^{a_i}_{n\,0\,\frac{1}{2}}\left(\vec{r}_{ijn}\right)$$

$$\times Y_{0,\,\frac{1}{2}-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$=\int\frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})^*\ Y^*_{0,\,0}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\ F^{a_i}_{n\,0\,\frac{1}{2}}\left(\vec{r}_{ijn}\right)Y_{0,\,0}\,(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.37)$$

The 2nd term of RHS in Eq. (2.35), we have

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{\text{2nd term}}$$

$$=+\int\sqrt{\frac{\acute{j}-\acute{M}}{2\acute{j}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J-M}{2J}}\ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)$$

$$\times Y_{l,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.38)$$

Using of $(\acute{n}\ 0\,\frac{1}{2}\frac{1}{2})$ and $(\mathrm{n}\ 0\,\frac{1}{2}\frac{1}{2})$ atomic orbitals, Eq. (2.38) becomes

$$t^{a_j a_i}_{\acute{n}\,0\frac{1}{2}\frac{1}{2},\ n\,0\,\frac{1}{2}\frac{1}{2}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{\text{2nd term}}$$

$$= +\int \sqrt{\frac{\frac{1}{2}-\frac{1}{2}}{2\frac{1}{2}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\,0\,\frac{1}{2}}(\vec{r})^*\ Y^*_{0,\frac{1}{2}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{\frac{1}{2}-\frac{1}{2}}{2\frac{1}{2}}}\ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)$$

$$\times\, Y_{0,\frac{1}{2}+\frac{1}{2}}\,(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$= +\ 0 \qquad (2.39)$$

The 3rd term of RHS in Eq. (2.35), we have

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{\text{3rd term}} =$$

$$+\int \sqrt{\frac{\acute{J}-\acute{M}+1}{2(\acute{J}+1)}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{J}}(\vec{r})\}^*\ Y^*_{\acute{l},+1,\,\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J-M+1}{2(J+1)}}\ \{iG^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\}$$

$$\times\, Y_{l+1,\,M-\frac{1}{2}}\,(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.40)$$

Using of $(\acute{n}\ 0\frac{1}{2}\frac{1}{2})$ and $(\mathrm{n}\ 0\frac{1}{2}\frac{1}{2})$ atomic orbitals, Eq. (2.40) becomes

$$t^{a_j a_i}_{(\acute{n}\ 0\frac{11}{22},\ \mathrm{n}\ 0\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{\text{3rd term}}$$

$$= +\int \sqrt{\frac{\frac{1}{2}-\frac{1}{2}+1}{2(\frac{1}{2}+1)}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{0+1,\frac{1}{2}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}$$

$$\times\sqrt{\frac{\frac{1}{2}-\frac{1}{2}+1}{2\left(\frac{1}{2}+1\right)}}\ \{iG^{a_i}_{n\,0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}Y_{0+1,\frac{1}{2}-\frac{1}{2}}\,(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$= +\int \sqrt{\frac{1}{3}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{1,0}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}$$

$$\times\sqrt{\frac{1}{3}}\ \{iG^{a_i}_{n\,0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}Y_{1,0}\ (\theta_{ijn},\,\phi_{ijn})d^3r$$

$$= +\frac{1}{3}\int \frac{1}{r\,r_{ijn}}\ iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{1,0}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}iG^{a_i}_{n\,0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}$$

$$\times Y_{1,0}\ (\theta_{ijn},\ \phi_{ijn}) d^3\mathrm{r} \tag{2.41}$$

The 4th term of RHS in Eq. (2.35), we have

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{\text{4th term}}$$

$$= +\int \sqrt{\frac{\acute{J}+\acute{M}+1}{2(\acute{J}+1)}}\ \frac{1}{r\, r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{J}}(\vec{r})\}^*\ Y^*_{\acute{l}+1,\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}$$

$$\times \sqrt{\frac{J+M+1}{2(J+1)}}\ \{iG^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\} \times Y_{l+1,\,M+\frac{1}{2}}\ (\theta_{ijn},\ \phi_{ijn}) d^3r \tag{2.42}$$

Using of ($\acute{n}\ 0\ \frac{1}{2}\ \frac{1}{2}$) and (n $0\ \frac{1}{2}\ \frac{1}{2}$) atomic orbitals, Eq. (2.42) becomes

$$t^{a_j a_i}_{\acute{n}\ 0\frac{11}{22},\ \ n\ 0\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{\text{4th term}}$$

$$= +\int \sqrt{\frac{\frac{1}{2}+\frac{1}{2}+1}{2(\frac{1}{2}+1)}}\ \frac{1}{r\, r_{ijn}}\ \{iG^{a_j}_{\acute{n}\ 0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{0+1,\frac{1}{2}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}$$

$$\times \sqrt{\frac{\frac{1}{2}+\frac{1}{2}+1}{2\left(\frac{1}{2}+1\right)}}\ \{iG^{a_i}_{n0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\} Y_{0+1,\frac{1}{2}+\frac{1}{2}}\ (\theta_{ijn},\ \phi_{ijn}) d^3r$$

$$= +\int \sqrt{\frac{2}{3}}\ \frac{1}{r\, r_{ijn}}\ \{iG^{a_j}_{\acute{n}\ 0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{1,1}\ (\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}$$

$$\times \sqrt{\frac{2}{3}}\ \{iG^{a_i}_{n0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\} Y_{1,1}\ (\theta_{ijn},\ \phi_{ijn}) d^3r$$

$$= +\frac{2}{3}\int \frac{1}{r\, r_{ijn}}\ \{iG^{a_j}_{\acute{n}\ 0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{1,1}\ (\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}$$

$$\times \{\mathrm{iG}^{a_i}_{n0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\} Y_{1,1}\ (\theta_{ijn},\ \phi_{ijn}) \mathrm{d}^3\mathrm{r} \tag{2.43}$$

Using Eqs. (2.37), (2.39), (2.41) and (2.43), then Eq. (2.35) becomes

$$t^{a_j a_i}_{\acute{n}\,0\frac{11}{22''}\;\;n\,0\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)$$

$$=\int\frac{1}{r\,r_{ijn}}\;F^{a_j}_{\acute{n}\,0\,\frac{1}{2}}(\vec{r})^*\;Y^*_{0,\,0}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\;F^{a_i}_{n\,0\,\frac{1}{2}}\left(\vec{r}_{ijn}\right)Y_{0,\,0}\left(\theta_{ijn},\,\phi_{ijn}\right)d^3r$$

$$+\frac{1}{3}\int\frac{1}{r\,r_{ijn}}\;\{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\;Y^*_{1,0}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\{iG^{a_i}_{n\,0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}Y_{1,0}\;\left(\theta_{ijn},\,\phi_{ijn}\right)d^3r$$

$$+\frac{2}{3}\int\frac{1}{r\,r_{ijn}}\;\{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\;Y^*_{1,1}\left(\theta,\phi\right)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\;\{iG^{a_i}_{n0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}Y_{1,1}\;\left(\theta_{ijn},\,\phi_{ijn}\right)d^3r$$

(2.44)

If the atoms, a_j and a_i are placed along z axis, using the relation in Eq. (2.27), the relativistic hopping integrals, $t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M}\,,nlJM}\left(\left|\vec{R}_n+\vec{d}_i-\vec{d}_j\right|\hat{e}_z\right)$ is equal to the relativistic TB parameter, $K_d^{a_j a_i}(\acute{n}\acute{l}\acute{J}\,,\;nlJ)_{\frac{1}{2}}$. The above statement leads this condition, $t^{a_j a_i}_{\acute{n}\,0\frac{11}{22''}\;\;n\,0\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)=K_d^{a_j a_i}(\acute{n}\;0\;\frac{1}{2},\;n\;0\;\frac{1}{2})_{\frac{1}{2}}$. Then, Eq. (2.44) becomes

$$K_d^{a_j a_i}(\acute{n}\;0\;\frac{1}{2},\;n\;0\;\frac{1}{2})_{\frac{1}{2}}$$

$$=\int\frac{1}{r\,r_{ijn}}\;F^{a_j}_{\acute{n}\,0\,\frac{1}{2}}(\vec{r})^*\;Y^*_{0,\,0}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\left|\vec{R}_n-\vec{d}_i+\vec{d}_j\right|\hat{e}_z\right)}{2}\right\}\;F^{a_i}_{n\,0\,\frac{1}{2}}\left(\vec{r}_{ijn}\right)Y_{0,\,0}\left(\theta_{ijn},\,\phi_{ijn}\right)d^3r$$

$$+\frac{1}{3}\int\frac{1}{r\,r_{ijn}}\;\{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\;Y^*_{1,0}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left|\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right|\hat{e}_z}{2}\right\}\{iG^{a_i}_{n\,0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}Y_{1,0}\;\left(\theta_{ijn},\,\phi_{ijn}\right)d^3r$$

$$+\frac{2}{3}\int\frac{1}{r\,r_{ijn}}\;\{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\;Y^*_{1,1}\left(\theta,\phi\right)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\left|\vec{R}_n-\vec{d}_i+\vec{d}_j\right|\hat{e}_z\right)}{2}\right\}\;\{iG^{a_i}_{n0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}Y_{1,1}\;\left(\theta_{ijn},\,\phi_{ijn}\right)d^3r$$

(2.45)

Let, [Appendix A]

$$(ss\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\frac{1}{2},n\,0\frac{1}{2}\right)}=$$

$$\int\frac{1}{r\,r_{ijn}}\;F^{a_j}_{\acute{n}\,0\,\frac{1}{2}}(\vec{r})^*\;Y^*_{0,\,0}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\left|\vec{R}_n-\vec{d}_i+\vec{d}_j\right|\hat{e}_z\right)}{2}\right\}F^{a_i}_{n\,0\,\frac{1}{2}}\left(\vec{r}_{ijn}\right)Y_{0,\,0}\left(\theta_{ijn},\,\phi_{ijn}\right)d^3r$$

(2.46)

$$(pp\sigma)^{S\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},\,n\,0\,\frac{1}{2}\right)} =$$

$$\int \frac{1}{r\,r_{ijn}} \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\, Y^*_{1,0}(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r})+V_{a_i}|\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j|\hat{e}_z}{2}\right\} \{iG^{a_i}_{n\,0\frac{1}{2}}(\vec{r}_{ijn})\} Y_{1,0}\ (\theta_{ijn},\ \phi_{ijn}) d^3r$$

(2.47)

$$(pp\pi)^{S\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},\,n\,0\,\frac{1}{2}\right)} =$$

$$\int \frac{1}{r\,r_{ijn}} \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\, Y^*_{1,1}\,(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-|\vec{R}_n-\vec{d}_i+\vec{d}_j|\hat{e}_z)}{2}\right\} \{iG^{a_i}_{n0\frac{1}{2}}(\vec{r}_{ijn})\} Y_{1,1}\ (\theta_{ijn},\ \phi_{ijn}) d^3r$$

(2.48)

It is noted that in Eqs. (2.46), (2.47) and (2.48), the letters, L and S indicate the large and small components of the relativistic atomic orbitals respectively. The label by letters $l\ or\ \acute{l}$ takes the value of $0,1,2,\ldots\ldots$ for the atomic orbitals namely $s, p, d,\ \ldots.$ respectively and the label M is expressed as $\sigma, \pi,\ \delta, \ldots.$ in place of $0, \pm1, \pm2, \ldots\ldots$ respectively.

Using Eqs. (2.46), (2.47) and (2.48) into Eq. (2.45), then Eq. (2.45) becomes

$$K_d^{a_j a_i}(\acute{n}\ 0\ \tfrac{1}{2},\ n\ 0\ \tfrac{1}{2})_{\frac{1}{2}} = (ss\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},\,n\,0\,\frac{1}{2}\right)} + \frac{1}{3}(pp\sigma)^{S\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},\,n\,0\,\frac{1}{2}\right)} + \frac{2}{3}(pp\pi)^{S\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},\,n\,0\,\frac{1}{2}\right)}$$

(2.49)

It is confirmed from Eq. (2.49), the relativistic TB parameters, $K_d^{a_j a_i}(\acute{n}\ 0\ \frac{1}{2},\ n\ 0\ \frac{1}{2})_{\frac{1}{2}}$ is the resultant or the linear combination of the atomic orbitals for the large and small components of the relativistic atomic orbitals. We can write the relativistic hopping integrals, $t^{a_j a_i}_{\acute{n}0\frac{11}{22},\ \ n0\frac{11}{22}}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right)$ by using cubic harmonics or real harmonics [61] that are given in the following Eqs. (2.50), (2.51) and (2.52) [Appendix B] instead of the spherical harmonics that are inserted in Eq. (2.44).

$$Y_{0,0}(\theta,\phi) = C_s(\theta,\phi) \tag{2.50}$$

$$Y_{1,0}(\theta,\phi) = C_z(\theta,\phi) \tag{2.51}$$

$$Y_{1,1}(\theta,\phi) = -\frac{1}{\sqrt{2}}[(C_x(\theta,\phi) + iC_y(\theta,\phi)] \tag{2.52}$$

The relativistic hopping integrals from Eq. (2,44) becomes

$$t^{a_j a_i}_{\acute{n}0\frac{11}{22},\ n0\frac{11}{22}}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right)$$

$$= \int \frac{1}{r\, r_{ijn}}\, F^{a_j}_{\acute{n}\,0\,\frac{1}{2}}(\vec{r})^*\, C_s^*(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j)}{2}\right\} F^{a_i}_{n\,0\,\frac{1}{2}}\left(\vec{r}_{ijn}\right) C_s\left(\theta_{ijn},\, \phi_{ijn}\right) d^3r$$

$$+ \frac{1}{3}\int \frac{1}{r\, r_{ijn}}\, \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\, C_z^*(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j)}{2}\right\}$$

$$\times \{iG^{a_i}_{n\,0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\} C_z\left(\theta_{ijn},\, \phi_{ijn}\right) d^3r$$

$$+ \frac{2}{3}\int \frac{1}{r\, r_{ijn}}\, \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\, \{-\frac{1}{\sqrt{2}}[(C_x(\theta,\phi) + iC_y(\theta,\phi)]^*\} \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j \boldsymbol{d}_j)}{2}\right\}$$

$$\times \left\{iG^{a_i}_{n0\frac{1}{2}}(\vec{r})\right\} \{-\frac{1}{\sqrt{2}}[\left(C_x\left(\theta_{ijn},\, \phi_{ijn}\right) + iC_y\left(\theta_{ijn},\, \phi_{ijn}\right)\right]\} d^3r \tag{2.53}$$

In Eq. (2.53), the symbols, $C_s(\theta,\phi)$, $C_x(\theta,\phi)$, $C_y(\theta,\phi)$ and $C_z(\theta,\phi)$ are the cubic harmonics [Appendix B]. After simplifying, Eq. (2.53) becomes

$$t^{a_j a_i}_{\acute{n}0\frac{11}{22},\ n0\frac{11}{22}}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right)$$

$$= \int \frac{1}{r\, r_{ijn}}\, F^{a_j}_{\acute{n}\,0\,\frac{1}{2}}(\vec{r})^*\, C_s^*(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j)}{2}\right\} F^{a_i}_{n\,0\,\frac{1}{2}}\left(\vec{r}_{ijn}\right) C_s\left(\theta_{ijn},\, \phi_{ijn}\right) d^3r$$

$$+ \frac{1}{3}\int \frac{1}{r\, r_{ijn}}\, \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\, C_z^*(\theta,\phi) \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j)}{2}\right\} \{iG^{a_i}_{n\,0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\} C_z\left(\theta_{ijn},\, \phi_{ijn}\right) d^3r$$

$$+ \frac{1}{3}\int \frac{1}{r\, r_{ijn}}\, \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\, [C_x(\theta,\phi)]^*\} \left\{\frac{V_{a_j}(\vec{r}) + V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i + \vec{d}_j)}{2}\right\} \left\{iG^{a_i}_{n0\frac{1}{2}}\left(\vec{r}_{ijn}\right)\right\} C_x\left(\theta_{ijn},\, \phi_{ijn}\right) d^3r$$

$$+\frac{1}{3}\int \frac{1}{r\, r_{ijn}} \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^* \ [C_x(\theta,\phi)]^*\}\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\left\{iG^{a_i}_{n0\frac{1}{2}}(\vec{r}_{ijn})\right\} iC_y(\theta_{ijn},\ \phi_{ijn})\, d^3r$$

$$+\frac{1}{3}\int \frac{1}{r\, r_{ijn}} \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^* \ [iC_y(\theta,\phi)]^*\}\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\left\{iG^{a_i}_{n0\frac{1}{2}}(\vec{r}_{ijn})\right\} C_x(\theta_{ijn},\ \phi_{ijn})\, d^3r$$

$$+\frac{1}{3}\int \frac{1}{r\, r_{ijn}} \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^* \ [iC_y(\theta,\phi)]^*\}\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j)}{2}\right\}\left\{iG^{a_i}_{n0\frac{1}{2}}(\vec{r}_{ijn})\right\} iC_y(\theta_{ijn},\ \phi_{ijn})\, d^3r \tag{2.54}$$

Using the non-relativistic Slater Koster table [60], then Eq. (2.54) becomes

$$t^{a_j a_i}_{\acute{n}0\frac{11}{22},\ \ n0\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)$$

$$=(ss\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}z^2(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}(1-z^2)(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}$$

$$+\frac{1}{3}x^2(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}(1-x^2)(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}$$

$$+\frac{i}{3}xy\,[(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}-(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}]$$

$$-\frac{i}{3}xy\,[(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}-(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}]$$

$$+\frac{1}{3}y^2(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}(1-y^2)(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}$$

$$=(ss\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}z^2(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}(1-z^2)(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}$$

$$+\frac{1}{3}x^2(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}(1-x^2)(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{i}{3}xy\,[(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}-(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}]$$

$$-\frac{i}{3}xy\,[(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}-pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}]+\frac{1}{3}y^2(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}(1-y^2)(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}$$

$$=(ss\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}\,(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}$$

$$=(ss\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{1}{3}\,(pp\sigma)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)}+\frac{2}{3}(pp\pi)^{s\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,0\,\frac{1}{2}\right)} \tag{2.55}$$

Using Eqs. (2.49) and (2.55). we have the relation between the relativistic hopping integrals and relativistic TB parameter in the following

$$K_d^{a_j a_i}(\acute{n}\ 0\ \tfrac{1}{2},\ n\ 0\ \tfrac{1}{2})_{\frac{1}{2}} = t^{a_j a_i}_{\acute{n}0\frac{11}{22},\ \ n0\frac{11}{22}}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right) \tag{2.56}$$

(ii) Relativistic hopping integrals for the combination of $(\acute{n}\ 0\frac{1}{2}\frac{1}{2})$ and $(\mathrm{n}\ 1\frac{1}{2}\frac{1}{2})$ atomic orbitals

Form Eq. (2.32), we can write the expression of the relativistic hopping integrals, $t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right)$ for $(\acute{n}\acute{l}\acute{J}\acute{M})$ and $(nlJM)$ atomic orbitals.

$$\begin{aligned}
&t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right) = \\
&-\int \sqrt{\frac{\acute{j}+\acute{M}}{2\acute{j}}}\ \frac{1}{r\, r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\,\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J-M+1}{2(J+1)}}\ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\times \\
&\qquad\qquad Y_{l,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \\
&+\int \sqrt{\frac{\acute{j}-\acute{M}}{2\acute{j}}}\ \frac{1}{r\, r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J+M+1}{2(J+1)}}\ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\times \\
&\qquad\qquad Y_{l,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \\
&+\int -\sqrt{\frac{\acute{j}-\acute{M}+1}{2(\acute{j}+1)}}\ \frac{1}{r\, r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})\}^*\ Y^*_{\acute{l}+1,\,\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J+M}{2J}}\ \{iG^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\} \\
&\qquad\qquad \times Y_{l-1,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \\
&+\int \sqrt{\frac{\acute{j}+\acute{M}+1}{2(\acute{j}+1)}}\ \frac{1}{r\, r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})\}^*\ Y^*_{\acute{l}+1,\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\{\sqrt{\frac{J-M}{2J}}\ \{iG^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\} \\
&\qquad\qquad \times Y_{l-1,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r
\end{aligned} \tag{2.57}$$

The 1st term of RHS in Eq. (2.57), we have

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{1st\ term}$$

$$=-\int\sqrt{\frac{\acute{j}+\acute{M}}{2\acute{j}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J-M+1}{2(J+1)}}\ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)$$

$$\times\ Y_{l,\,M-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.58)$$

Using of $(\acute{n}\ 0\ \frac{1}{2}\frac{1}{2})$ and $(\mathrm{n}\ 1\ \frac{1}{2}\frac{1}{2})$ atomic orbitals, Eq. (2.58) becomes

$$t^{a_j a_i}_{\acute{n}\ 0\frac{11}{22},\ \mathrm{n}\ 1\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{1st\ term}$$

$$=-\int\sqrt{\frac{\frac{1}{2}+\frac{1}{2}}{2\frac{1}{2}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\ 0\frac{1}{2}}(\vec{r})^*\ Y^*_{0,\frac{1}{2}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{\frac{1}{2}-\frac{1}{2}+1}{2(\frac{1}{2}+1)}}\ F^{a_i}_{n\ 1\frac{1}{2}}\left(\vec{r}_{ijn}\right)$$

$$\times\ Y_{1,\frac{1}{2}-\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r$$

$$=-\sqrt{\frac{1}{3}}\int\frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\ 0\frac{1}{2}}(\vec{r})^*\ Y^*_{0,0}\ (\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\ F^{a_i}_{n\ 1\frac{1}{2}}\left(\vec{r}_{ijn}\right)$$

$$\times\ Y_{1,0}\ (\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.59)$$

The 2nd term of RHS in Eq. (2.57), we have

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{2nd\ term}=$$

$$+\int\sqrt{\frac{\acute{J}-\acute{M}}{2\acute{J}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})^*\ Y^*_{\acute{l},\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J+M+1}{2(J+1)}}\ F^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)$$

$$\times\ Y_{l,\,M+\frac{1}{2}}(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.60)$$

Using of ($\acute{n}\ 0\ \frac{1}{2}\frac{1}{2}$) and (n $1\ \frac{1}{2}\frac{1}{2}$) atomic orbitals, Eq. (2.60) becomes

$$t^{a_j a_i}_{\acute{n}\,0\frac{11}{22},\ n\,1\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{2nd\ term}$$

$$= +\int \sqrt{\frac{\frac{1}{2}-\frac{1}{2}}{2\frac{1}{2}}}\ \frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})^*\ Y^*_{0,\frac{1}{2}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{\frac{1}{2}+\frac{1}{2}+1}{2(\frac{1}{2}+1)}}\ F^{a_i}_{n1\frac{1}{2}}\left(\vec{r}_{ijn}\right)$$

$$\times Y_{0,\frac{1}{2}+\frac{1}{2}}(\theta_{ijn},\ \phi_{ijn})d^3r$$

$$= +0 \tag{2.61}$$

The 3rd term of RHS in Eq. (2.57), we have

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{3rd\ term} =$$

$$+\int -\sqrt{\frac{\acute{J}-\acute{M}+1}{2(\acute{J}+1)}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})\}^*\ Y^*_{\acute{l}+1,\acute{M}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{J+M}{2J}}\ \{iG^{a_i}_{nlJ}\left(\vec{r}_{ijn}\right)\}$$

$$\times Y_{l-1,\,M-\frac{1}{2}}(\theta_{ijn},\ \phi_{ijn})d^3r \tag{2.62}$$

Using of ($\acute{n}\ 0\ \frac{1}{2}\frac{1}{2}$) and (n $1\ \frac{1}{2}\frac{1}{2}$) atomic orbitals, Eq. (2.62) becomes

$$t^{a_j a_i}_{\acute{n}\,0\frac{11}{22},\ n\,1\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{3rd\ term} =$$

$$+\int -\sqrt{\frac{\frac{1}{2}-\frac{1}{2}+1}{2(\frac{1}{2}+1)}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{0+1,\frac{1}{2}-\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\sqrt{\frac{\frac{1}{2}+\frac{1}{2}}{2\frac{1}{2}}}\ \{iG^{a_i}_{n\,1\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}$$

$$\times Y_{1-1,\frac{1}{2}-\frac{1}{2}}(\theta_{ijn},\ \phi_{ijn})d^3r$$

$$= -\sqrt{\frac{1}{3}}\int \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{1,0}\ (\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\{iG^{a_i}_{n\,1\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}$$

$$\times Y_{0,0}\ (\theta_{ijn},\ \phi_{ijn})d^3r \tag{2.63}$$

The 4th term of RHS in Eq. (2.57), we have

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{4th\ term}=$$
$$+\int\sqrt{\frac{\acute{j}+\acute{M}+1}{2(\acute{j}+1)}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\acute{l}\acute{j}}(\vec{r})\}^*\ Y^*_{\acute{l}+1,\,\acute{M}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\{\sqrt{\frac{J-M}{2J}}\ \{iG^{a_i}_{nlJ}(\vec{r}_{ijn})\}$$
$$\times\ Y_{l-1,\,M+\frac{1}{2}}\,(\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.64)$$

Using of $(\acute{n}\ 0\ \frac{1}{2}\frac{1}{2})$ and $(n\ 1\ \frac{1}{2}\frac{1}{2})$ atomic orbitals, Eq. (2.64) becomes

$$t^{a_j a_i}_{\acute{n}\ 0\frac{11}{22},\ n\ 1\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)_{4th\ term}=$$
$$+\int\sqrt{\frac{\frac{1}{2}+\frac{1}{2}+1}{2(\frac{1}{2}+1)}}\ \frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\ 0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{0+1,\frac{1}{2}+\frac{1}{2}}(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\{\sqrt{\frac{\frac{1}{2}-\frac{1}{2}}{2\frac{1}{2}}}\ \{iG^{a_i}_{n1\frac{1}{2}}(\vec{r}_{ijn})\}$$
$$\times\ Y_{1-1,\frac{1}{2}+\frac{1}{2}}\,(\theta_{ijn},\,\phi_{ijn})d^3r$$
$$=0 \qquad (2.65)$$

Using Eqs. (2.59), (2.61), (2.63) and (2.65) into Eq. (2.57) then Eq. (2.57) becomes

$$t^{a_j a_i}_{\acute{n}\ 0\frac{11}{22},\ n\ 1\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)=$$
$$-\sqrt{\frac{1}{3}}\int\frac{1}{r\,r_{ijn}}\ F^{a_j}_{\acute{n}\ 0\frac{1}{2}}(\vec{r})^*\ Y^*_{0,0}\,(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}F^{a_i}_{n\,1\frac{1}{2}}\left(\vec{r}_{ijn}\right)$$
$$\times\ \ Y_{1,0}\ (\theta_{ijn},\,\phi_{ijn})d^3r$$
$$-\sqrt{\frac{1}{3}}\int\frac{1}{r\,r_{ijn}}\ \{iG^{a_j}_{\acute{n}\ 0\frac{1}{2}}(\vec{r})\}^*\ Y^*_{1,0}\,(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\{iG^{a_i}_{n\,1\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}$$
$$\times\ Y_{0,0}\ (\theta_{ijn},\,\phi_{ijn})d^3r \qquad (2.66)$$

Similarly to (i), if the atoms, a_j and a_i are placed along the z axis, using the relation in Eq. (2.66), the relativistic hopping integrals, $t^{a_j a_i}_{\acute{n}\acute{l}\acute{J}\acute{M},nlJM}\left(\left|\vec{R}_n+\vec{d}_i-\vec{d}_j\right|e_z\right)$ is equal to the relativistic TB parameter, $K_d^{a_j a_i}(\acute{n}\acute{l}\acute{J},\ nlJ)_{\frac{1}{2}}$ and this statement leads the condition, $t^{a_j a_i}_{\acute{n}\,0\frac{11}{22},n\,1\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)=K_d^{a_j a_i}(\acute{n}\ 0\ \frac{1}{2},\ n\ 1\ \frac{1}{2})_{\frac{1}{2}}$. Then, Eq. (2.66) becomes

$$K_d^{a_j a_i}(\acute{n}\ 0\ \tfrac{1}{2},\ n\ 1\ \tfrac{1}{2})_{\frac{1}{2}}=$$

$$-\sqrt{\frac{1}{3}}\int\frac{1}{r\,r_{ijn}}\,F^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})^*\,Y^*_{0,0}\,(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\left|\vec{R}_n+\vec{d}_i-\vec{d}_j\right|e_z\right)}{2}\right\}F^{a_i}_{n\,1\frac{1}{2}}\left(\vec{r}_{ijn}\right)$$
$$\times Y_{1,0}\ (\theta_{ijn},\ \phi_{ijn})d^3r$$
$$-\sqrt{\frac{1}{3}}\int\frac{1}{r\,r_{ijn}}\,\{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\,Y^*_{1,0}\,(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\left|\vec{R}_n+\vec{d}_i-\vec{d}_j\right|e_z\right)}{2}\right\}\{iG^{a_i}_{n\,1\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}$$
$$\times Y_{0,0}\ (\theta_{ijn},\ \phi_{ijn})d^3r \qquad (2.67)$$

Let,

$$(sp\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\frac{1}{2},n\,0\frac{1}{2}\right)}=\int\frac{1}{r\,r_{ijn}}\,F^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})^*\,Y^*_{0,0}\,(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\left|\vec{R}_n+\vec{d}_i-\vec{d}_j\right|e_z\right)}{2}\right\}$$
$$\times F^{a_i}_{n\,1\frac{1}{2}}\left(\vec{r}_{ijn}\right)Y_{1,0}\ (\theta_{ijn},\ \phi_{ijn})d^3r \qquad (2.68)$$

$$(ps\sigma)^{S\,d\,a_j a_i}_{\left(\acute{n}\,0\frac{1}{2},n\,0\frac{1}{2}\right)}=\int\frac{1}{r\,r_{ijn}}\,\{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\,Y^*_{1,0}\,(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\left|\vec{R}_n+\vec{d}_i-\vec{d}_j\right|e_z\right)}{2}\right\}$$
$$\times\{iG^{a_i}_{n\,1\frac{1}{2}}\left(\vec{r}_{ijn}\right)\}Y_{0,0}\ (\theta_{ijn},\ \phi_{ijn})d^3r \qquad (2.69)$$

If we consider the above Eqs. (2.68) and (2.69), then eq. (2.67) becomes

$$K_d^{a_j a_i}(\acute{n}\ 0\ \tfrac{1}{2},\ n\ 1\ \tfrac{1}{2})_{\frac{1}{2}}=-\sqrt{\frac{1}{3}}(sp\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\frac{1}{2},n\,1\frac{1}{2}\right)}-\sqrt{\frac{1}{3}}(ps\sigma)^{S\,d\,a_j a_i}_{\left(\acute{n}\,0\frac{1}{2},n\,1\frac{1}{2}\right)} \qquad (2.70)$$

Similarly to (i), we can write the relativistic hopping integrals, $t^{a_j a_i}_{\acute{n}0\frac{11}{22},\ n1\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)$ by using cubic harmonics [61] [Appendix A] instead of the spherical harmonics that are inserted in Eq. (2.44). The relativistic hopping integrals from Eq. (2.44) becomes

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{m},nljm}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)=$$
$$-\sqrt{\frac{1}{3}}\int\frac{1}{r\,r_{ijn}}\,F^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})^*\,C^*_s(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}F^{a_i}_{n\,1\frac{1}{2}}(r_{ijn})C_z\,(\theta_{ijn},\,\phi_{ijn})d^3r$$
$$-\sqrt{\frac{1}{3}}\int\frac{1}{r\,r_{ijn}}\,\{iG^{a_j}_{\acute{n}\,0\frac{1}{2}}(\vec{r})\}^*\,C^*_z(\theta,\phi)\left\{\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i+\vec{d}_j\right)}{2}\right\}\{iG^{a_i}_{n\,1\frac{1}{2}}\left(r_{ijn}\right)\}C_s\,(\theta_{ijn},\,\phi_{ijn})d^3r \tag{2.71}$$

Similarly (i), using the non-relativistic Slater-Koster table [60], Eq. (2.71) becomes

$$t^{a_j a_i}_{\acute{n}\acute{0}\frac{11}{22},\ n1\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)$$
$$=-\sqrt{\frac{1}{3}}g_z(sp\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,1\,\frac{1}{2}\right)}-\sqrt{\frac{1}{3}}g_z(ps\sigma)^{L\,d\,a_j a_i}_{\left(\acute{n}\,0\,\frac{1}{2},n\,1\,\frac{1}{2}\right)} \tag{2.72}$$

Using Eqs. (2.70) and (2.72). we have the relation between the relativistic hopping integrals and relativistic TB parameter in the following

$$K_d^{a_j a_i}(\acute{n}\,0\,\tfrac{1}{2},\,n\,1\,\tfrac{1}{2})_{\frac{1}{2}}=g_z(t^{a_j a_i}_{\acute{n}\acute{0}\frac{11}{22},\ n1\frac{11}{22}}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)) \tag{2.73}$$

Similarly to (i) and (ii), it is possible to calculate all relations between relativistic TB parameters, $K_d^{a_j a_i}(\acute{n}\acute{l}\acute{j},\,nlJ)_{\frac{1}{2}}$ and relativistic hopping integrals, $t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{m},nljm}\left(\vec{R}_n+\vec{d}_i-\vec{d}_j\right)$ of the eight atomic orbitals, ($\acute{n}0\frac{1}{2}\pm\frac{1}{2}$), ($\acute{n}1\frac{1}{2}\pm\frac{1}{2}$), ($\acute{n}1\frac{3}{2}\pm\frac{3}{2}$) and ($\acute{n}1\frac{3}{2}\pm\frac{1}{2}$). After calculations of the all relations that are tabulated in **Table-1** in order to upgrade the Slater-Koster table. This table (**Table -1)** is called the relativistic version of the Slater-Koster table.

2.5 Relativistic version of Slater Koster table

Table-1: It is noted that g_x, g_y and g_z are the direction cosines of the vector, $\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right)$.

$(\acute{n}\acute{l}\acute{j}\acute{m})$	$(nljm)$	Hopping integrals, $t^{a_j a_i}_{(\acute{n}\acute{l}\acute{j}\acute{m}),(nljm)}\left(\vec{R}_n + \vec{d}_i - \vec{d}_j\right)$
$(\acute{n}0\frac{1}{2}\frac{1}{2})$	$(n0\frac{1}{2}\frac{1}{2})$	$K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}\frac{1}{2})$	$(n0\frac{1}{2}-\frac{1}{2})$	0
$(\acute{n}0\frac{1}{2}\frac{1}{2})$	$(n1\frac{1}{2}\frac{1}{2})$	$g_z\ K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}\frac{1}{2})$	$(n1\frac{1}{2}-\frac{1}{2})$	$\left(g_x - ig_y\right)K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}\frac{1}{2})$	$(n1\frac{3}{2}\frac{3}{2})$	$-\frac{\sqrt{3}}{2}\left(g_x + ig_y\right)K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}\frac{1}{2})$	$(n1\frac{3}{2}-\frac{3}{2})$	0
$(\acute{n}0\frac{1}{2}\frac{1}{2})$	$(n1\frac{3}{2}\frac{1}{2})$	$g_z\ K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}\frac{1}{2})$	$(n1\frac{3}{2}-\frac{1}{2})$	$\frac{1}{2}\left(g_x - ig_y\right)K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}-\frac{1}{2})$	$(n0\frac{1}{2}\frac{1}{2})$	0
$(\acute{n}0\frac{1}{2}-\frac{1}{2})$	$(n0\frac{1}{2}-\frac{1}{2})$	$K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}-\frac{1}{2})$	$(n1\frac{1}{2}\frac{1}{2})$	$\left(g_x + ig_y\right)K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}-\frac{1}{2})$	$(n1\frac{1}{2}-\frac{1}{2})$	$-g_z K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}-\frac{1}{2})$	$(n1\frac{3}{2}\frac{3}{2})$	0
$(\acute{n}0\frac{1}{2}-\frac{1}{2})$	$(n1\frac{3}{2}-\frac{3}{2})$	$\frac{\sqrt{3}}{2}\left(g_x - ig_y\right)K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}-\frac{1}{2})$	$(n1\frac{3}{2}\frac{1}{2})$	$-\frac{1}{2}\left(g_x + ig_y\right)K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}0\frac{1}{2}-\frac{1}{2})$	$(n1\frac{3}{2}-\frac{1}{2})$	$g_z K_d^{a_j a_i}(2\ 0\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}\frac{1}{2})$	$(n0\frac{1}{2}\frac{1}{2})$	$g_z K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}\frac{1}{2})$	$(n0\frac{1}{2}-\frac{1}{2})$	$\left(g_x - ig_y\right)K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$

$(\acute{n}1\frac{1}{2}\frac{1}{2})$	$(n1\frac{1}{2}\frac{1}{2})$	$K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}\frac{1}{2})$	$(n1\frac{1}{2}-\frac{1}{2})$	0
$(\acute{n}1\frac{1}{2}\frac{1}{2})$	$(n1\frac{3}{2}\frac{3}{2})$	$-\frac{\sqrt{3}}{2}g_z(g_x+ig_y)K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}\frac{1}{2})$	$(n1\frac{3}{2}-\frac{3}{2})$	$\frac{\sqrt{3}}{2}g_z(g_x-ig_y)^2K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}\frac{1}{2})$	$(n1\frac{3}{2}\frac{1}{2})$	$\frac{1}{2}(3g_z^2-1)K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}\frac{1}{2})$	$(n1\frac{3}{2}-\frac{1}{2})$	$\frac{3}{2}g_z(g_x-ig_y)K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}-\frac{1}{2})$	$(n0\frac{1}{2}\frac{1}{2})$	$(g_x+ig_y)K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}-\frac{1}{2})$	$(n0\frac{1}{2}-\frac{1}{2})$	$-g_zK_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}-\frac{1}{2})$	$(n1\frac{1}{2}\frac{1}{2})$	0
$(\acute{n}1\frac{1}{2}-\frac{1}{2})$	$(n1\frac{1}{2}-\frac{1}{2})$	$K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}-\frac{1}{2})$	$(n1\frac{3}{2}\frac{3}{2})$	$-\frac{\sqrt{3}}{2}(g_x+ig_y)^2K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}-\frac{1}{2})$	$(n1\frac{3}{2}-\frac{3}{2})$	$-\frac{\sqrt{3}}{2}g_z(g_x-ig_y)K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}-\frac{1}{2})$	$(n1\frac{3}{2}\frac{1}{2})$	$\frac{3}{2}g_z(g_x+ig_y)K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{1}{2}-\frac{1}{2})$	$(n1\frac{3}{2}-\frac{1}{2})$	$\frac{1}{2}(1-2g_z^2)K_d^{a_j a_i}(2\ 1\ \frac{1}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{3}{2})$	$(n0\frac{1}{2}\frac{1}{2})$	$-\frac{\sqrt{3}}{2}(g_x-ig_y)K_d^{a_j a_i}(2\ 1\ \frac{3}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{3}{2})$	$(n0\frac{1}{2}-\frac{1}{2})$	0
$(\acute{n}1\frac{3}{2}\frac{3}{2})$	$(n1\frac{1}{2}\frac{1}{2})$	$-\frac{\sqrt{3}}{2}g_z(g_x-ig_y)K_d^{a_j a_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{3}{2})$	$(n1\frac{1}{2}-\frac{1}{2})$	$-\frac{\sqrt{3}}{2}(g_x-ig_y)^2K_d^{a_j a_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{3}{2})$	$(n1\frac{3}{2}\frac{3}{2})$	$-\frac{\sqrt{3}}{2}(1-g_z^2)K_d^{a_j a_i}\left(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2}\right)_{\frac{1}{2}}+$ $\frac{1}{4}(1+3g_z^2)K_d^{a_j a_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{3}{2})$	$(n1\frac{3}{2}-\frac{3}{2})$	0
$(\acute{n}1\frac{3}{2}\frac{3}{2})$	$(n1\frac{3}{2}\frac{1}{2})$	$\frac{\sqrt{3}}{2}g_z\left(g_x-ig_y\right)K_d^{a_j a_i}\left(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2}\right)_{\frac{1}{2}}$

		$-\frac{\sqrt{3}}{2}g_z(g_x-ig_y)K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{3}{2})$	$(n1\frac{3}{2}-\frac{1}{2})$	$\frac{\sqrt{3}}{4}(g_x-ig_y)^2K_d^{a_ja_i}\left(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2}\right)_{\frac{1}{2}}$ $-\frac{\sqrt{3}}{4}(g_x-ig_y)^2K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2})_{\frac{3}{2}}$
$(\acute{n}1\frac{3}{2}\frac{1}{2})$	$(n0\frac{1}{2}\frac{1}{2})$	$g_zK_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{1}{2})$	$(n0\frac{1}{2}-\frac{1}{2})$	$-\frac{1}{2}(g_x-ig_y)K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{1}{2})$	$(n1\frac{1}{2}\frac{1}{2})$	$\frac{1}{2}(3g_z^2-1)K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{1}{2})$	$(n1\frac{1}{2}-\frac{1}{2})$	$\frac{3}{2}g_z(g_x-ig_y)K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{1}{2})$	$(n1\frac{3}{2}\frac{3}{2})$	$\frac{\sqrt{3}}{2}g_z(g_x+ig_y)K_d^{a_ja_i}\left(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2}\right)_{\frac{3}{2}}$ $-\frac{\sqrt{3}}{2}g_z(g_x+ig_yK_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{1}{2})$	$(n1\frac{3}{2}-\frac{3}{2})$	$\frac{\sqrt{3}}{4}(\ g_x-ig_y)^2K_d^{a_ja_i}\left(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2}\right)_{\frac{3}{2}}$ $-\frac{\sqrt{3}}{4}(\ g_x-ig_y)^2K_d^{a_ja_i}\left(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2}\right)_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}\frac{1}{2})$	$(n1\frac{3}{2}\frac{1}{2})$	$\frac{1}{4}(3g_z^2+1)K_d^{a_ja_i}\left(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2}\right)_{\frac{1}{2}}$ $+\frac{3}{4}(1-g_z^2)K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2})_{\frac{3}{2}}$
$(\acute{n}1\frac{3}{2}\frac{1}{2})$	$(n1\frac{3}{2}-\frac{1}{2})$	0
$(\acute{n}1\frac{3}{2}-\frac{1}{2})$	$(n0\frac{1}{2}\frac{1}{2})$	$\frac{1}{2}(g_x+ig_y)K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{1}{2})$	$(n0\frac{1}{2}-\frac{1}{2})$	$g_zK_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 0\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{1}{2})$	$(n1\frac{1}{2}\frac{1}{2})$	$\frac{3}{2}g_z(g_x+ig_y)K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{1}{2})$	$(n1\frac{1}{2}-\frac{1}{2})$	$\frac{1}{2}(1-3g_z^2)K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{1}{2})$	$(n1\frac{3}{2}\frac{3}{2})$	$\frac{\sqrt{3}}{4}(g_x+ig_y)^2K_d^{a_ja_i}\left(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2}\right)_{\frac{1}{2}}$ $-\frac{\sqrt{3}}{4}(g_x+ig_y)^2K_d^{a_ja_i}(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2})_{\frac{3}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{1}{2})$	$(n1\frac{3}{2}-\frac{3}{2})$	$\frac{\sqrt{3}}{2}g_z(\ g_x-ig_y)K_d^{a_ja_i}\left(2\ 1\ \frac{3}{2},\ 2\ 1\ \frac{3}{2}\right)_{\frac{1}{2}}$

		$-\frac{\sqrt{3}}{2}g_z(\,g_x-ig_y)K_d^{a_ja_i}\left(2\;1\;\frac{3}{2},\;2\;1\;\frac{3}{2}\right)_{\frac{3}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{1}{2})$	$(n1\frac{3}{2}\frac{1}{2})$	0
$(\acute{n}1\frac{3}{2}-\frac{1}{2})$	$(n1\frac{3}{2}-\frac{1}{2})$	$\frac{1}{4}(1+3g_z^2)K_d^{a_ja_i}\left(2\;1\;\frac{3}{2},\;2\;1\;\frac{3}{2}\right)_{\frac{1}{2}}$ $+\frac{3}{4}(1-g_z^2)K_d^{a_ja_i}(2\;1\;\frac{3}{2},\;2\;1\;\frac{3}{2})_{\frac{3}{2}}$
$\left(\acute{n}1\frac{3}{2}-\frac{3}{2}\right)$	$(n0\frac{1}{2}\frac{1}{2})$	0
$(\acute{n}1\frac{3}{2}-\frac{3}{2})$	$(n0\frac{1}{2}-\frac{1}{2})$	$\frac{\sqrt{3}}{2}(g_x+ig_y)K_d^{a_ja_i}(2\;1\;\frac{3}{2},\;2\;0\;\frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{3}{2})$	$(n1\frac{1}{2}\frac{1}{2})$	$\frac{\sqrt{3}}{2}(g_x+ig_y)^2K_d^{a_ja_i}(2\;1\;\frac{3}{2},\;2\;1\;\frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{3}{2})$	$(n1\frac{1}{2}-\frac{1}{2})$	$-\frac{\sqrt{3}}{2}g_z(g_x+ig_y)K_d^{a_ja_i}(2\;1\;\frac{3}{2},\;2\;1\;\frac{1}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{3}{2})$	$(n1\frac{3}{2}\frac{3}{2})$	0
$(\acute{n}1\frac{3}{2}-\frac{3}{2})$	$(n1\frac{3}{2}-\frac{3}{2})$	$\frac{3}{4}(1-g_z^2)K_d^{a_ja_i}\left(2\;1\;\frac{3}{2},\;2\;1\;\frac{3}{2}\right)_{\frac{1}{2}}$ $+\frac{1}{4}(1+3g_z^2)K_d^{a_ja_i}(2\;1\;\frac{3}{2},\;2\;1\;\frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{3}{2})$	$(n1\frac{3}{2}\frac{1}{2})$	$\frac{\sqrt{3}}{4}\left(g_x+ig_y\right)^2K_d^{a_ja_i}\left(2\;1\;\frac{3}{2},\;2\;1\;\frac{3}{2}\right)_{\frac{1}{2}}$ $-\frac{\sqrt{3}}{4}\left(g_x+ig_y\right)^2K_d^{a_ja_i}(2\;1\;\frac{3}{2},\;2\;1\;\frac{3}{2})_{\frac{1}{2}}$
$(\acute{n}1\frac{3}{2}-\frac{3}{2})$	$(n1\frac{3}{2}-\frac{1}{2})$	$\frac{\sqrt{3}}{2}g_z(g_x+ig_y)K_d^{a_ja_i}\left(2\;1\;\frac{3}{2},\;2\;1\;\frac{3}{2}\right)_{\frac{1}{2}}$ $-\frac{\sqrt{3}}{2}g_z(g_x+ig_y)K_d^{a_ja_i}(2\;1\;\frac{3}{2},\;2\;1\;\frac{3}{2})_{\frac{3}{2}}$

Chapter 3

Nonperturbative Magnetic Field Containing Relativistic Tight Binding (MFRTB) Approximation Method

In this Chapter, the nonperturbative MFRTB approximation method for a uniform magnetic field is described in the following sequence:

3.1 Matrix elements of the Dirac Hamiltonian

3.1.1 In case of $\vec{R}_m + \vec{d}_j = \vec{R}_n + \vec{d}_i$ and

3.1.2 In case of $\vec{R}_m + \vec{d}_j \neq \vec{R}_n + \vec{d}_i$

3.2 Approximation of eigenvalues, $(\varepsilon_\xi^{a_i,0} + \Delta\varepsilon_\xi^{a_i,\vec{d}_i})$ and eigenfunctions, $\psi_\xi^{a_i 0}(\vec{r})$

3.3 Approximation of magnetic hopping integrals, $T_{\eta\xi}^{a_j a_i}(\vec{R}_n - \vec{R}_m + \vec{d}_i - \vec{d}_j)$

3.1 Matrix elements of the Dirac Hamiltonian

In this subsection, the description of the derivation of matrix elements of the Dirac Hamiltonian (H) in case of material immersed in a uniform magnetic field is explained. Now let us consider an electron moves both in a uniform magnetic field and periodic potential. If the electron moves in this system, the electron is affected by the vector potential and periodic potential in the system. The Dirac equation for this dynamic electron is given by [59]

$$H\Phi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\Phi_{\vec{k}}(\vec{r}) \tag{3.1}$$

With

$$H = c\vec{\alpha}.\{\vec{p} + e\vec{A}(\vec{r})\} + \beta mc^2 + \sum_{\vec{R}_n}\sum_i V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i) \tag{3.2}$$

In Eq. (3.1), $\Phi_{\vec{k}}(\vec{r})$ and $E_{\vec{k}}$ are the four-component eigenfunction and eigenvalue respectively, the subscript $\vec{k}$ in $\Psi_{\vec{k}}(\vec{r})$ and $E_{\vec{k}}$ is the crystal momentum. In Eq. (3.2), m, e and c are the rest mass of the electron, the elementary charge of the electron and velocity of light respectively, the quantities, $\vec{\alpha} \equiv (\alpha_x, \alpha_y, \alpha_z)$, and β stand for the usual 4×4 matrices [59]. In Eq. (3.2), the symbols, $\vec{A}(\vec{r})$ and $V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i)$ are the vector potential caused by the uniform magnetic field, $\vec{B}$ which is applied perpendicular to the electric field, and the scalar potential caused by the nucleus of an atom a_i, where the atom is located at the position $\vec{R}_n + \vec{d}_i$, where $\vec{R}_n$ is the lattice translation vector and $\vec{d}_i$ determine specific position of an atom respectively.

If we consider, the uniform magnetic field $\vec{B}$ is applied along the z-axis, then $\vec{B} = B\hat{e}_z$ where $\hat{e}_z$ is the unit vector along the z-axis. According to the Landau gauge transformation, the vector potential $\vec{A}(\vec{r})$ becomes

$$\vec{A}(\vec{r}) = (0, xB, 0) \tag{3.3}$$

It is noted that B is the magnitude of the applied magnetic field which is defined later in Eq. (5.1) in Chapter 5. In order to calculate the appropriate form of the relativistic atomic orbitals of an atom in the presence of a magnetic field similar to the relativistic atomic orbitals of an atom in the absence of a magnetic field, it is urgent to expand the four-component eigenfunction, $\Psi_{\vec{k}}(\vec{r})$ by using the Bloch sum of the relativistic atomic orbitals as a basis function for the development of the non-perturbative MFRTB method.

The expanded four-component eigen function, $\Phi_{\vec{k}}(\vec{r})$ is given by

$$\Phi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}_n} \sum_i \sum_\xi C_{\vec{k}}^{\xi}(\vec{R}_n + \vec{d}_i)\ \psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r}) \tag{3.4}$$

In Eq. (3.4), $C_{\vec{k}}^{\xi}(\vec{R}_n + \vec{d}_i)$ and $\psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})$ are the expansion coefficient and relativistic atomic orbitals respectively. The subscript, ξ in $\psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})$ and superscript, ξ in $C_{\vec{k}}^{\xi}(\vec{R}_n + \vec{d}_i)$ is the quantum number in the atomic system.

The relativistic atomic orbital for an electron in an atom immersed in the uniform magnetic field also obeys the Dirac equation. The Dirac equation in the above system is given by

$$[c\vec{\alpha}.\{\vec{p} + e\vec{A}(\vec{r})\} + \beta mc^2 + V_{a_i}(\vec{r} - \vec{R}_n - \vec{d}_i)]\ \psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r}) = \varepsilon_\xi^{a_i,\vec{R}_n+\vec{d}_i}\ \psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r}) \tag{3.5}$$

In Eq. (3.5), the eigenvalue, $\varepsilon_\xi^{a_i,\vec{R}_n+\vec{d}_i}$ is the atomic spectrum of an atom, a_i in the uniform magnetic field. Using Eqs. (3.4) and (3.1), the Dirac equation becomes

$$H \sum_{\vec{R}_n} \sum_i \sum_\xi C_{\vec{k}}^{\xi}(\vec{R}_n + \vec{d}_i)\ \psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r}) = E_{\vec{k}} \sum_{\vec{R}_n} \sum_i \sum_\xi C_{\vec{k}}^{\xi}(\vec{R}_n + \vec{d}_i)\ \psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r}) \tag{3.6}$$

Multiplying by $\psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}$ from left on both sides in Eq. (3.6) and after integrating, Eq. (3.6) becomes

$$\sum_{\vec{R}_n}\sum_i\sum_{\xi} C_{\vec{k}}^{\xi}(\vec{R}_n+\vec{d}_i)\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger} H\, \psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r = E_{\vec{k}}\sum_{\vec{R}_n}\sum_i\sum_{\xi} C_{\vec{k}}^{\xi}(\vec{R}_n+\vec{d}_i)\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}\ \psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \tag{3.7}$$

Similar to the relativistic TB approximation method (Chapter 2) and conventional MFRTB method [61], the following two equations can be defined from Eq. (3.7) for the matrix element and overlap integral respectively [51],

$$H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} = \int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger} H\, \psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \tag{3.8}$$

$$\delta_{\vec{R}_m,\vec{R}_n}\,\delta_{\eta,\xi}\,\delta_{i,j} = \int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}\, \psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \tag{3.9}$$

Using Eqs. (3.8) and (3.9) into Eq. (3.7) then Eq. (3.7) becomes

$$\sum_{\vec{R}_n}\sum_i\sum_{\xi} C_{\vec{k}}^{\xi}(\vec{R}_n+\vec{d}_i)\, H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} = E_{\vec{k}}\sum_{\vec{R}_n}\sum_i\sum_{\xi} C_{\vec{k}}^{\xi}(\vec{R}_n+\vec{d}_i)\,\delta_{\vec{R}_m,\vec{R}_n}\,\delta_{\eta,\xi}\ \delta_{i,j} \tag{3.10}$$

It is noted that the overlap integrals can be negligible for the different centered of atoms. The Dirac Hamiltonian in a uniform magnetic field can be defined using Eq. (3.2) as:

$$\begin{aligned} \mathrm{H} = \frac{1}{2}[\mathrm{c}\vec{\alpha}.\{\vec{p}+e\vec{A}(\vec{r})\} + \beta mc^2 + V_{a_j}(\vec{r}-\vec{R}_m-\vec{d}_j) \\ + \sum_{l\neq j} V_{a_l}(\vec{r}-\vec{R}_m-\vec{d}_l) + \sum_{k\neq m}\sum_l V_{a_l}(\vec{r}-\vec{R}_k-\vec{d}_l) \\ + \mathrm{c}\vec{\alpha}.\{\vec{p}+e\vec{A}(\vec{r})\} + \beta mc^2 + V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i) \\ + \sum_{l\neq i} V_{a_l}(\vec{r}-\vec{R}_n-\vec{d}_l) + \sum_{k\neq n}\sum_l V_{a_l}(\vec{r}-\vec{R}_k-\vec{d}_l)] \end{aligned} \tag{3.11}$$

In Eq. (3.11), the 2nd term, $V_{a_j}\left(\vec{r}-\vec{R}_m-\vec{d}_j\right)$ is the scalar potential which is caused by nucleus of a_j atom with respect to $\vec{R}_m$, the 3rd term, $\sum_{l\neq j} V_{a_l}\left(\vec{r}-\vec{R}_m-\vec{d}_l\right)$ is the scalar potential which is caused by nucleus of all a_l atoms but not including a_j atom with respect to $\vec{R}_m$, the 4th term, $\sum_{k\neq m}\sum_l V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)$ is scalar potential which is caused by nucleus of all a_l atoms including a_j atom with respect to $\vec{R}_k$ but not including $\vec{R}_m$, the 6th term, $V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i\right)$ is the scalar potential which is caused by nucleus of a_i atom with respect to $\vec{R}_n$, the 7th term, $\sum_{l\neq i} V_{a_l}\left(\vec{r}-\vec{R}_n-\vec{d}_l\right)$ is the scalar potential which is caused by nucleus of all a_l atoms but not including a_i atom with respect to $\vec{R}_n$ and the 8th term, $\sum_{k\neq n}\sum_l V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)$ is the scalar potential caused by nucleus of all a_l atoms including a_i atom with respect to $\vec{R}_k$ but not including $\vec{R}_n$.

Substituting Eq. (3.11) into Eq. (3.8) and then using Eq. (3.5), then the Dirac Hamiltonian becomes

$$
\begin{aligned}
H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} = \tfrac{1}{2}\big[\,\varepsilon_{\xi}^{a_j,\vec{R}_n+\vec{d}_j}\,\delta_{\vec{R}_m,\vec{R}_n}\,\delta_{j,i}\,\delta_{\eta,\xi} + \varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}\,\delta_{\vec{R}_m,\vec{R}_n}\,\delta_{j,i}\,\delta_{\eta,\xi}\big] \\
+\tfrac{1}{2}\textstyle\sum_{l\neq j}\int\ \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger} V_{a_l}\left(\vec{r}-\vec{R}_m-\vec{d}_l\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \\
+\tfrac{1}{2}\textstyle\sum_{l\neq i}\int\ \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger} V_{a_l}\left(\vec{r}-\vec{R}_n-\vec{d}_l\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \\
+\tfrac{1}{2}\textstyle\sum_{k\neq m}\sum_l\int\ \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger} V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \\
+\tfrac{1}{2}\textstyle\sum_{k\neq n}\sum_l\int\int\ \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger} V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r
\end{aligned}
\tag{3.12}
$$

The matrix elements of the Dirac Hamiltonian can be estimated by using Eq. (3.12), for the following two cases:

(i) $\vec{R}_m+\vec{d}_j=\vec{R}_n+\vec{d}_i$ and

(ii) $\vec{R}_m+\vec{d}_j\neq\vec{R}_n+\vec{d}_i$

3.1.1 In case of $\vec{R}_m + \vec{d}_j = \vec{R}_n + \vec{d}_i$

If we consider, $\vec{R}_m + \vec{d}_j = \vec{R}_n + \vec{d}_i$ then $a_j = a_i$ and $\vec{R}_m = \vec{R}_n$, then Eq. (3.12) becomes

$$\begin{aligned} H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} = {} & \varepsilon_{\xi}^{a_j,\vec{R}_n+\vec{d}_j}\,\delta_{\eta,\xi} \\ & + \textstyle\sum_{l\neq j}\int \psi_{\eta}^{a_j,\vec{R}_n+\vec{d}_j}(\vec{r})^{\dagger} V_{a_l}\left(\vec{r}-\vec{R}_n-\vec{d}_l\right)\psi_{\xi}^{a_j,\vec{R}_n+\vec{d}_j}(\vec{r})\,d^3r \\ & + \textstyle\sum_{k\neq n}\sum_{l}\int \psi_{\eta}^{a_j,\vec{R}_n+\vec{d}_j}(\vec{r})^{\dagger} V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_{\xi}^{a_j,\vec{R}_n+\vec{d}_j}(\vec{r})\,d^3r \end{aligned} \tag{3.13}$$

In Eq. (3.13) of RHS, the 2nd and 3rd terms are called the energy of the crystal field. If we consider, relativistic atomic orbitals, $\psi_{\eta}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})$ and $\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})$ are localized at $\vec{R}_n+\vec{d}_i$ but not localized at $\vec{R}_k+\vec{d}_i$. Under this treatment the scalar potential, $V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)$ can be approximated by the $V_{a_l}\left(\vec{R}_n+\vec{d}_i-\vec{R}_k-\vec{d}_l\right)$. So, the 3rd term in Eq. (3.13) becomes

$$\begin{aligned} & \textstyle\sum_{k\neq n}\sum_{l}\int \psi_{\eta}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})^{\dagger} V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})\,d^3r \\ & = \int \psi_{\eta}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})^{\dagger}\left\{\textstyle\sum_{\vec{R}_n}\sum_{l} V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\right\}\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})\,d^3r \\ & \qquad\qquad \vec{R}_k+\vec{d}_l \neq \vec{R}_n+\vec{d}_i \\ & = \int \psi_{\eta}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})^{\dagger}\left\{\textstyle\sum_{\vec{R}_n}\sum_{l} V_{a_l}\left(\vec{R}_n+\vec{d}_i-\vec{R}_k-\vec{d}_l\right)\right\}\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})\,d^3r \\ & \qquad\qquad \vec{R}_k+\vec{d}_l \neq \vec{R}_n+\vec{d}_i \\ & = \Delta\varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}\,\delta_{\eta,\xi} \end{aligned} \tag{3.14}$$

Using Eqs. (3.13) and (3.14), then the matrix elements approximated by

$$H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} \approx \left(\varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i} + \Delta\varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}\right)\delta_{\eta,\xi} \tag{3.15}$$

In Eq. (3.15), the diagonal elements of the matrix are non-zero and non-diagonal elements of the matrix are zero.

3.1.2 In case of $\vec{R}_m + \vec{d}_j \neq \vec{R}_n + \vec{d}_i$

If we consider, $\vec{R}_m + \vec{d}_j \neq \vec{R}_n + \vec{d}_i$ then $a_j \neq a_i$, $\delta_{\vec{R}_m, \vec{R}_n} = 0$ and $\delta_{j,i} = 0$, then Eq. (3.12) becomes

$$H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} = \frac{1}{2}\sum_{l\neq j}\int \psi_\eta^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^\dagger V_{a_l}\left(\vec{r}-\vec{R}_m-\vec{d}_l\right)\psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$
$$+\frac{1}{2}\sum_{l\neq i}\int \psi_\eta^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^\dagger V_{a_l}\left(\vec{r}-\vec{R}_n-\vec{d}_l\right)\psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$
$$+\frac{1}{2}\sum_{k\neq m}\sum_l\int \psi_\eta^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^\dagger V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$
$$+\frac{1}{2}\sum_{k\neq n}\sum_l\int \psi_\eta^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^\dagger V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \quad (3.16)$$

In Eq. (3.16), it is noticeable that in 1st term, $l \neq$j and in 2nd term, $l \neq$ i are present, so three centers are involved. So, the numerical values of these two integrals are small comparing two centers or one center. So, we can neglect these two terms. But, in 3rd term $l \neq$j or $l \neq$ i are not present and k$\neq m$: $\vec{R}_k \neq \vec{R}_m$ but $\vec{R}_k = \vec{R}_n$. The 4th term $l \neq$ i or $l \neq$j is not present and k$\neq$ n, $\vec{R}_k \neq \vec{R}_n$ but $\vec{R}_k = \vec{R}_m$. So, there are very possible to form both two centers and three centers. We can get matrix elements for the two centers in the following fashion. Therefore, Eq. (3.16) becomes

$$H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} = \frac{1}{2}\sum_{k\neq m}\sum_l\int \psi_\eta^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^\dagger V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$
$$+\frac{1}{2}\sum_{k\neq n}\sum_l\int \psi_\eta^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^\dagger V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$
$$=\frac{1}{2}\int \psi_\eta^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^\dagger V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i\right)\psi_\xi^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$

$$+\frac{1}{2}\sum_{k\neq m}\sum_{n}\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}V_{a_i}\left(\vec{r}-\vec{R}_k-\vec{d}_i\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$

$$+\frac{1}{2}\sum_{k\neq m}\sum_{l\neq i}\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$

$$+\frac{1}{2}\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}V_{a_j}\left(\vec{r}-\vec{R}_m-\vec{d}_j\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$

$$+\frac{1}{2}\sum_{k\neq n}\sum_{m}\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}V_{a_j}\left(\vec{r}-\vec{R}_k-\vec{d}_j\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$

$$+\frac{1}{2}\sum_{k\neq n}\sum_{l\neq j}\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}V_{a_l}\left(\vec{r}-\vec{R}_k-\vec{d}_l\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \tag{3.17}$$

In Eq. (3.17) the 2nd, 3rd, 5th and 6th terms are three centers. Therefore, we can neglect these integrals. Then, Eq. (3.17) becomes

$$H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} = \frac{1}{2}\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$

$$+\frac{1}{2}\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}V_{a_j}\left(\vec{r}-\vec{R}_m-\vec{d}_j\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r$$

$$=\frac{1}{2}\int[\,\psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i\right)+V_{a_j}\left(\vec{r}-\vec{R}_m-\vec{d}_j\right)\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})]d^3r$$

$$=\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}\frac{V_{a_j}\left(\vec{r}-\vec{R}_m-\vec{d}_j\right)+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i\right)}{2}\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \tag{3.18}$$

Finally, we can get the matrix elements from Eq. (3.12) by using Eqs. (3.14) and (3.18)

$$H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} = (\,\varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}+\Delta\varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i})\delta_{j,i}\delta_{\eta,\xi}\,\delta_{\vec{R}_m,\vec{R}_n}+(1-\delta_{j,i}\delta_{\vec{R}_m,\vec{R}_n})\times$$

$$\int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}\frac{V_{a_j}\left(\vec{r}-\vec{R}_m-\vec{d}_j\right)+V_{a_i}\left(\vec{r}-\vec{R}_n-\vec{d}_i\right)}{2}\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \tag{3.19}$$

For the simplicity, let us consider that an electron moves in a uniform magnetic field and periodic potential which is caused by the nucleus of an atom, where the atom is located at origin. The Dirac equation for this electron is given by

$$c\vec{\alpha}.\{\vec{p}+e\vec{A}(\vec{r})\}+\beta mc^2+V_{a_i}(\vec{r})]\,\psi_{\xi}^{a_i,0}(\vec{r})=\varepsilon_{\xi}^{a_i,0}\;\psi_{\xi}^{a_i,0}(\vec{r}) \tag{3.20}$$

In Eq. (3.20), the eigenfunction, $\psi_{\xi}^{a_i,0}(\vec{r})$ and eigenvalue, $\varepsilon_{\xi}^{a_i,0}$ are the relativistic atomic orbital and atomic spectra of an atom, a_i in the presence of a magnetic field respectively. For our convenience, the vector, $\vec{r}$ can be changed by the vector $(\vec{r}-\vec{R}_n-\vec{d}_i)$. Then, Eq. (3.20) becomes

$$[c\vec{\alpha}.\{\vec{p}+e\vec{A}(\vec{r}-\vec{R}_n-\vec{d}_i)\}+\beta mc^2+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i)]\,\psi_{\xi}^{a_i,0}(\vec{r}-\vec{R}_n-\vec{d}_i)$$
$$=\varepsilon_{\xi}^{a_i,0}\;\psi_{\xi}^{a_i,0}(\vec{r}-\vec{R}_n-\vec{d}_i) \tag{3.21}$$

In Eq. (3.21), $\vec{A}(\vec{r}-\vec{R}_n-\vec{d}_i)$ is the vector potential in uniform magnetic field. The vector potentials $\vec{A}(\vec{r})$ and $\vec{A}(\vec{r}-\vec{R}_n-\vec{d}_i)$ are related by the following gauge transformation.

$$\vec{A}(\vec{r}-\vec{R}_n-\vec{d}_i)=\vec{A}(\vec{r})+\nabla\chi(\vec{r},\,\vec{R}_n+\vec{d}_i) \tag{3.22}$$

Using Eqs. (3.3) and (3.22), we have

$$\chi(\vec{r},\,\vec{R}_n+\vec{d}_i)=B(R_{nx}+d_{ix})y \tag{3.23}$$

In Eq. (3.23), R_{nx} and d_{ix} are the x component of the vector $\vec{R}_n$ and $\vec{d}_i$ respectively. By the choice of the gauge transformation, the eigenfunction and eigenvalue are related in the following equations

$$\psi_{\xi}^{a_i,0}(\vec{r}-\vec{R}_n-\vec{d}_i)=e^{-i\frac{e}{\hbar}\chi(\vec{r},\;\vec{R}_n+\vec{d}_i)}\,\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r}) \tag{3.24}$$

and

$$\varepsilon_{\xi}^{a_i,\,0} = \varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i} \tag{3.25}$$

respectively.
Eq. (3.25) leads the following equation

$$\Delta\varepsilon_{\xi}^{a_i,\vec{d}_i} = \Delta\varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i} \tag{3.26}$$

Using Eqs. (3.24), (3.25) and (3.26), the matrix element becomes

$$\begin{aligned} H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi} &= (\,\varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i} + \Delta\varepsilon_{\xi}^{a_i,\vec{R}_n+\vec{d}_i})\delta_{j,i}\delta_{\eta,\xi}\,\delta_{\vec{R}_m,\vec{R}_n} + (1-\delta_{j,i}\delta_{\vec{R}_m,\vec{R}_n})\times \\ &\qquad \int \psi_{\eta}^{a_j,\vec{R}_m+\vec{d}_j}(\vec{r})^{\dagger}\,\frac{V_{a_j}(\vec{r}-\vec{R}_m-\vec{d}_j)+V_{a_i}(\vec{r}-\vec{R}_n-\vec{d}_i)}{2}\,\psi_{\xi}^{a_i,\vec{R}_n+\vec{d}_i}(\vec{r})d^3r \\ &= (\varepsilon_{\xi}^{a_i,\,0} + \Delta\varepsilon_{\xi}^{a_i,\vec{d}_i})\delta_{j,i}\delta_{\eta,\xi}\,\delta_{\vec{R}_m,\vec{R}_n} + \left(1-\delta_{j,i}\delta_{\vec{R}_m,\vec{R}_n}\right)e^{-i\frac{eB}{\hbar}(R_{nx}+d_{ix}-R_{mx}-d_{jx})(R_{my}+d_{jy})} \\ &\qquad \times \int \psi_{\eta}^{a_j,0}\,(\vec{r})^{\dagger}\,\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)}{2}\,\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})d^3r \\ &= (\varepsilon_{\xi}^{a_i,\,0} + \Delta\varepsilon_{\xi}^{a_i,\vec{d}_i})\delta_{j,i}\delta_{\eta,\xi}\,\delta_{\vec{R}_m,\vec{R}_n} + \left(1-\delta_{j,i}\delta_{\vec{R}_m,\vec{R}_n}\right)e^{-i\frac{eB}{\hbar}(R_{nx}+d_{ix}-R_{mx}-d_{jx})(R_{my}+d_{jy})} \\ &\qquad \times T_{\eta\,\xi}^{a_j a_i}(\vec{R}_n-\vec{R}_m+\vec{d}_i-\vec{d}_j) \end{aligned} \tag{3.27}$$

With

$$T_{\eta\,\xi}^{a_j a_i}(\vec{R}_n-\vec{R}_m+\vec{d}_i-\vec{d}_j) = \int \psi_{\eta}^{a_j,0}\,(\vec{r})^{\dagger}\,\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)}{2}\,\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})d^3r \tag{3.28}$$

In Eq. (3.27), the hopping integrals, $T_{\eta\,\xi}^{a_j a_i}(\vec{R}_n-\vec{R}_m+\vec{d}_i-\vec{d}_j)$ are known as the magnetic hopping integrals that is defined in Eq. (3.28). In order to calculate the matrix element, $H_{\vec{R}_m j\eta,\vec{R}_n i\xi}$ of the

Dirac Hamiltonian, it is very urgent to calculate the magnetic hopping integrals and overlap integrals. Again, in order to calculate magnetic hopping integrals and overlap integrals, it is need to calculate eigenvalues, $\varepsilon_{\xi}^{a_i,0}$, $\Delta\varepsilon_{\xi}^{a_i,0}$and eigenfunction, $\psi_{\xi}^{a_i 0}(\vec{r})$. Now, I will explain how to calculate these in the following sequence:

3.2 Approximation of eigenvalues, $(\varepsilon_{\xi}^{a_i,\,0} + \Delta\varepsilon_{\xi}^{a_i,\vec{d}_i})$ and eigenfunctions, $\psi_{\xi}^{a_i 0}(\vec{r})$

In this subsection, the estimation of the eigenvalue and eigenfunction using non-perturbative MFRTB method is explained. In order to calculate of $H_{\vec{R}_m j\,\eta,\ \vec{R}_n i\,\xi}$, firstly, we need to estimate of $(\varepsilon_{\xi}^{a_i,\,0} + (\Delta\varepsilon_{\xi}^{a_i,\vec{d}_i} \approx 0))$ and $\psi_{\xi}^{a_i 0}(\vec{r})$ by avoiding some difficulties by using the perturbation theory. Because the perturbation theory becomes invalid for the estimation of the correction terms in the eigenvalue and eigenfunction in high magnetic field case due to the power series of the ratio (x_{nl} is defined Eq. (3.31) later in this Chapter) of the spin Zeeman splitting and spin-orbit splitting [51]. For this difficulty, the Hofstadter butterfly diagram becomes worse in the high magnetic field case [51]. For this reason, the non-perturbative MFRTB is applied in the high magnetic case in order to overcome these difficulties using in the perturbation theory [51]. For this purpose, we consider the Dirac equation for an isolated atom, a_i at origin in the uniform magnetic field.

$$[c\vec{\alpha}.\{\vec{p} + e\vec{A}(\vec{r})\} + \beta mc^2 + V_{a_i}(\vec{r})]\,\psi_{\xi}^{a_i,0}(\vec{r}) = \varepsilon_{\xi}^{a_i,0}\,\psi_{\xi}^{a_i 0}(\vec{r}) \tag{3.29}$$

In Eq. (3.29), the term $ec\vec{\alpha}.\vec{A}(\vec{r})$ appears due to the magnetic field which is known as the perturbation term. In order to evaluate the value of $(\varepsilon_{\xi}^{a_i,\,0} + (\Delta\varepsilon_{\xi}^{a_i,\vec{d}_i} \approx 0))$ and $\psi_{\xi}^{a_i 0}(\vec{r})$, we have to estimate the solution of Eq. (3.29). The solutions of Eq. (3.29) are obtained by the nonperturbative MFRTB method, specifically the variational method [51]. The eigenvalues and eigenfunctions are approximated by

$$\varepsilon_{\xi}^{a_i,\,0} = \left\{ \begin{array}{c} \bar{\varepsilon}_{nlJ}^{\,a_i} \pm \frac{e\hbar B}{2m} \\ \frac{\bar{\varepsilon}_{nlJ}^{\,a_i} + \bar{\varepsilon}_{nlJ-1}^{\,a_i}}{2} + \frac{e\hbar B}{4m} \pm \frac{\bar{\varepsilon}_{nlJ}^{\,a_i} - \bar{\varepsilon}_{nlJ-1}^{\,a_i}}{2}\sqrt{1+\frac{2}{3}x_{nl}+\frac{1+8S_{nl}^2}{9}x_{nl}^2} \\ \frac{\bar{\varepsilon}_{nlJ}^{\,a_i} + \bar{\varepsilon}_{nlJ-1}^{\,a_i}}{2} + \frac{e\hbar B}{4m} - \frac{\bar{\varepsilon}_{nlJ}^{\,a_i} - \bar{\varepsilon}_{nlJ-1}^{\,a_i}}{2}\sqrt{1+\frac{2}{3}x_{nl}+\frac{1+8S_{nl}^2}{9}x_{nl}^2} \\ \frac{\bar{\varepsilon}_{nlJ}^{\,a_i} + \bar{\varepsilon}_{nlJ-1}^{\,a_i}}{2} + \frac{e\hbar B}{4m} + \frac{\bar{\varepsilon}_{nlJ}^{\,a_i} - \bar{\varepsilon}_{nlJ-1}^{\,a_i}}{2}\sqrt{1-\frac{2}{3}x_{nl}+\frac{1+8S_{nl}^2}{9}x_{nl}^2} \\ \frac{\bar{\varepsilon}_{nlJ}^{\,a_i} + \bar{\varepsilon}_{nlJ-1}^{\,a_i}}{2} + \frac{e\hbar B}{4m} - \frac{\bar{\varepsilon}_{nlJ}^{\,a_i} - \bar{\varepsilon}_{nlJ-1}^{\,a_i}}{2}\sqrt{1-\frac{2}{3}x_{nl}+\frac{1+8S_{nl}^2}{9}x_{nl}^2} \\ \bar{\varepsilon}_{nlJ}^{\,a_i} \pm \frac{e\hbar B}{m} \end{array} \right\} \tag{3.30}$$

With

$$x_{nl} = \frac{\frac{e\hbar B}{2m}}{\bar{\varepsilon}_{nlJ}^{\,a_i} - \bar{\varepsilon}_{nlJ-1}^{\,a_i}} \tag{3.31}$$

and

$$\psi_{\xi}^{a_i,0}(\vec{r}) = \left\{ \begin{array}{c} \varphi_{nlJ\pm M}^{a_i}(\vec{r}) \\ \frac{\varphi_{nlJM}^{a_i}(\vec{r}) + \eta_{+}^{a_i}\varphi_{nlJ-1M}^{a_i}(\vec{r})}{\sqrt{1+(\eta_{+}^{a_i})^2}} \\ \frac{-\eta_{+}^{a_i}\varphi_{nlJM}^{a_i}(\vec{r}) + \varphi_{nlJ-1M}^{a_i}(\vec{r})}{\sqrt{1+(\eta_{+}^{a_i})^2}} \\ \frac{\varphi_{nlJ\,-M}^{a_i}(\vec{r}) + \eta_{-}^{a_i}\varphi_{nlJ-1\,-M}^{a_i}(\vec{r})}{\sqrt{1+(\eta_{-}^{a_i})^2}} \\ \frac{-\eta_{-}^{a_i}\varphi_{nlJ\,-M}^{a_i}(\vec{r}) + \varphi_{nlJ-1\,-M}^{a_i}(\vec{r})}{\sqrt{1+(\eta_{-}^{a_i})^2}} \\ \varphi_{nlJ\pm M}^{a_i}(\vec{r}), \end{array} \right\} \tag{3.32}$$

With

$$\eta_{\pm}^{a_i} = \frac{3}{2\sqrt{2}\ S_{nl}\, x_{nl}}\left\{1 \pm \frac{x_{nl}}{3} - \sqrt{1 \pm \frac{2}{3}x_{nl} + \frac{1+8S_{nl}^2}{9}x_{nl}^2}\right\} \tag{3.33}$$

respectively.

In Eq. (3.31), x_{nl} is the ratio of the spin Zeeman splitting energy ($\frac{e\hbar B}{2m}$) and spin-orbit splitting energy ($\bar{\varepsilon}_{nlJ}^{\ a_i} - \bar{\varepsilon}_{nlJ-1}^{a_i}$). In Eq. (3.34), S_{nl} is overlap integral between the radial parts of the atomic orbitals of $\emptyset_{nlJM}^{a_i}(\vec{r})$ and $\emptyset_{nlJ-1M}^{a_i}(\vec{r})$. From Eq. (3.31), in the low magnetic field case, $x_{nl} \ll 1$ because spin Zeeman splitting term is small compare to the spin-orbit splitting. In this case, spin-orbit interaction is the dominant part that is called the anomalous Zeeman effect. In the high magnetic field case, $x_{nl} \gg 1$ because spin Zeeman splitting term is large compare to the spin-orbit splitting. In this case, spin Zeeman splitting term is the dominant part that is called the Paschen–Back effect.

3.3 Approximation of magnetic hopping integrals, $\boldsymbol{T_{\eta\xi}^{a_j a_i}(\vec{R}_n - \vec{R}_m + \vec{d}_i - \vec{d}_j)}$

In this subsection, the approximation of the magnetic hopping integrals is explained briefly. For this purpose, let us consider an electron moves in uniform magnetic field and in a periodic potential in the crystal. Let us consider the atoms, a_j and a_i are located at origin and ($\vec{R}_l + \vec{d}_i - \vec{d}_j$) respectively. The Dirac equation for an atom, a_j is given by

$$\left[c\vec{\alpha}.\left\{\vec{p} + e(\vec{A}(\vec{r}) + \nabla\chi(\vec{r}))\right\} + \beta mc^2 + V(\vec{r})\right]\bar{\psi}_{\eta}^{a_j,0}(\vec{r}) = \varepsilon_{\eta}^{a_j,0}\ \bar{\psi}_{\eta}^{a_j,0}(\vec{r}) \tag{3.34}$$

With

$$\bar{\psi}_{\eta}^{a_j,0}(\vec{r}) = e^{-i\frac{e}{\hbar}\chi(\vec{r})}\psi_{\eta}^{a_j,0}(\vec{r}) \tag{3.35}$$

And the Dirac equation for an atom, a_i is given by

$$\left[c\vec{\alpha}.\left\{\vec{p}+e\left(\vec{A}(\vec{r})+\nabla\chi(\vec{r})\right)\right\}+\beta mc^2+V\left(\vec{r}-\vec{d}_l-\vec{d}_i+\vec{d}_j\right)\right]\bar{\psi}_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})$$
$$=\varepsilon_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}\bar{\psi}_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r}) \quad (3.36)$$

With

$$\bar{\psi}_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})=e^{-i\frac{e}{\hbar}\chi(\vec{r})}\,\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r}) \quad (3.37)$$

Eqs. (3.35) and (3.37) have been written by using Eq. (3.24). It is noted that, in Eqs. (3.35) and (3.37), the transformation of the wave function is called Landau gauge transformation that can be obtained from the symmetric gauge transformation. By using the gauge transformation of a function from the symmetric gauge to the Landau gauge leads the following equation

$$\chi(\vec{r})=\frac{Bxy}{2} \quad (3.38)$$

Using Eq. (3.38), then, the Eqs. (3.35) and (3.37) become

$$\psi_{\eta}^{a_j,0}(\vec{r})=e^{-i\frac{e}{2\hbar}Bxy}\psi_{\eta}^{a_j,0}(\vec{r})_{sym} \quad (3.39)$$

$$\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})=e^{-i\frac{e}{2\hbar}Bxy}\,\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})_{sym} \quad (3.40)$$

Since the eigenfunction of atom, a_j is localized around the origin, so the phase factor, $e^{-i\frac{e}{2\hbar}Bxy}$ is nearly equal to 1. So, the eigenfunction, $\psi_{\eta}^{a_j,0}(\vec{r})_{sym}$ in Eq. (3.39) is approximated by

$$\psi_{\eta}^{a_j,0}(\vec{r})\approx\varphi_{\acute{n}\acute{l}\acute{j}\acute{M}}^{a_j}(\vec{r}) \quad (3.41)$$

By using the gauge transformation of a function of Landau gauge, $\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r})$ that leads the following equation

$$\chi(\vec{r}) = \frac{1}{2}B\{(R_{ly} + d_{iy} - d_{jy})x - (R_{ly} + d_{iy} - d_{jy})y\} \tag{3.42}$$

Using the symmetric gauge the eigenfunction, $\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})_{sym}$ is related by the eigenfunction , $\psi_{\xi}^{a_i,0}\left(\vec{r} - \vec{R}_l - \vec{d}_i + \vec{d}_j\right)_{sym}$. For this gauge transformation in Eq. (3.42), the wave function in Eq. (3.40) becomes

$$\psi_{\xi}^{a_i,0}\left(\vec{r} - \vec{R}_l - \vec{d}_i + \vec{d}_j\right)_{sym} = e^{-i\frac{e}{2\hbar}B\{(R_{ly}+d_{iy}-d_{jy})x-(R_{lx}+d_{ix}-d_{jx})y\}} \times \psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})_{sym} \tag{3.43}$$

Using Eqs. (3.40) and (3.43), we have

$$\begin{aligned}
\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r}) &= e^{-i\frac{e}{2\hbar}Bxy}\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})_{sym} \\
&= e^{-i\frac{e}{2\hbar}Bxy}\psi_{\xi}^{a_i,0}\left(\vec{r} - \vec{R}_l - \vec{d}_i + \vec{d}_j\right)_{sym} \\
&= e^{-i\frac{e}{2\hbar}Bxy}\, e^{i\frac{e}{2\hbar}B\{(R_{ly}+d_{iy}-d_{jy})x-(R_{lx}+d_{ix}-d_{jx})y\}}\, \psi_{\xi}^{a_i,0}\left(\vec{r} - \vec{R}_l - \vec{d}_i + \vec{d}_j\right)_{sym} \\
&= e^{-i\frac{e}{2\hbar}B\{(R_{ly}+d_{iy}-d_{jy})x-(R_{lx}+d_{ix}-d_{jx})y+xy\}}\, \psi_{\xi}^{a_i,0}\left(\vec{r} - \vec{R}_l - \vec{d}_i + \vec{d}_j\right)_{sym} \\
&= e^{-i\frac{e}{2\hbar}B\{(R_{ly}+d_{iy}-d_{jy})x-(R_{lx}+d_{ix}-d_{jx})y+xy\}}\, \psi_{\xi}^{a_i,0}\left(\vec{r} - \vec{R}_l - \vec{d}_i + \vec{d}_j\right)_{sym}
\end{aligned} \tag{3.44}$$

If we consider the wave function, $\psi_{\xi}^{a_i,0}\left(\vec{r} - \vec{R}_l - \vec{d}_i + \vec{d}_j\right)_{sym}$ in Eq. (3.44) is localized at $\vec{r} = \vec{R}_l + \vec{d}_i - \vec{d}_j$, then the wave function approximated by

$$\psi_{\xi}^{a_i,0}\left(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j\right)_{sym}=\varphi_{nlJM}^{a_i}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j) \tag{3.45}$$

If the phase factor $e^{-i\frac{e}{2\hbar}B\{(R_{ly}+d_{iy}-d_{jy})x-(R_{lx}+d_{ix}-d_{jx})y+xy\}}$ is approximated at $\vec{r}=\vec{R}_l+\vec{d}_i-\vec{d}_j$ and the components are approximated at $x=R_{lx}+d_{ix}-d_{jx}$ and $y=R_{ly}+d_{iy}-d_{jy}$, using these components, the phase factor becomes

$$\begin{aligned}
&e^{-i\frac{e}{2\hbar}B\{(R_{ly}+d_{iy}-d_{jy})x-(R_{lx}+d_{ix}-d_{jx})y+xy\}}\\
&=e^{-i\frac{e}{2\hbar}B\{(R_{ly}+d_{iy}-d_{jy})(R_{lx}+d_{ix}-d_{jx})-(R_{lx}+d_{ix}-d_{jx})(R_{ly}+d_{iy}-d_{jy})+(R_{lx}+d_{ix}-d_{jx})(R_{ly}+d_{iy}-d_{jy})\}}\\
&=e^{-i\frac{e}{2\hbar}B\{(R_{ly}+d_{iy}-d_{jy})(R_{lx}+d_{ix}-d_{jx})}\\
&\approx e^{-i\frac{e}{2\hbar}B(R_{ly}+d_{iy}-d_{jy})(R_{lx}+d_{ix}-d_{jx})}
\end{aligned} \tag{3.46}$$

Using Eqs. (3.44) and (3.46), the wave function becomes

$$\begin{aligned}
\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})&=e^{-i\frac{e}{2\hbar}B\{(R_{ly}+d_{iy}-d_{jy})x-(R_{lx}+d_{ix}-d_{jx})y+xy\}}\,\psi_{\xi}^{a_i,0}\left(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j\right)_{sym}\\
\psi_{\xi}^{a_i,\vec{R}_l+\vec{d}_i-\vec{d}_j}(\vec{r})&\approx e^{-i\frac{e}{2\hbar}B(R_{ly}+d_{iy}-d_{jy})(R_{lx}+d_{ix}-d_{jx})}\,\varphi_{nlJM}^{a_i,0}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)
\end{aligned} \tag{3.47}$$

Using Eq. (3.47), the magnetic hopping integrals from Eq. (3.28) become

$$\begin{aligned}
T_{\eta\,\xi}^{a_j a_i}(\vec{R}_l+\vec{d}_i-\vec{d}_j)\;&=\int\varphi_{\acute{n}\acute{l}\acute{J}\acute{M}}^{a_j}(\vec{r})^{\dagger}\,\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)}{2}\\
&\qquad\times e^{-i\frac{e}{2\hbar}B(R_{ly}+d_{iy}-d_{jy})(R_{lx}+d_{ix}-d_{jx})}\varphi_{nlJM}^{a_i}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)d^3r\\
&=\int\varphi_{\acute{n}\acute{l}\acute{J}\acute{M}}^{a_j}(\vec{r})^{\dagger}\,\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)}{2}\;\varphi_{nlJM}^{a_i}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)d^3r\\
&\qquad\times e^{-i\frac{e}{2\hbar}B(R_{ly}+d_{iy}-d_{jy})(R_{lx}+d_{ix}-d_{jx})}\\
&=\int\varphi_{\acute{n}\acute{l}\acute{J}\acute{M}}^{a_j}(\vec{r})\,(\vec{r})^{\dagger}\,\frac{V_{a_j}(\vec{r})+V_{a_i}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)}{2}\;\varphi_{nlJM}^{a_i}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)d^3r
\end{aligned}$$

$$\times e^{-i\frac{e}{2\hbar}B\left(R_{ly}+d_{iy}-d_{jy}\right)\left(R_{lx}+d_{ix}-d_{jx}\right)}$$

$$=e^{-i\frac{e}{2\hbar}B\left(R_{ly}+d_{iy}-d_{jy}\right)\left(R_{lx}+d_{ix}-d_{jx}\right)}t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},\,nlJM}(\vec{R}_l+\vec{d}_i-\vec{d}_j) \qquad (3.48)$$

With

$$t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},\,nlJM}(\vec{R}_l+\vec{d}_i-\vec{d}_j)$$

$$=\int \varphi^{a_j}_{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{r})\,(\vec{r})^{\dagger}\frac{V_{a_j}(\vec{r})+V_{a_i}\left(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j\right)}{2}\,\varphi^{a_i}_{nlJM}(\vec{r}-\vec{R}_l-\vec{d}_i+\vec{d}_j)d^3r \qquad (3.49)$$

In Eq. (3.49), $t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},\,nlJM}(\vec{R}_l+\vec{d}_i-\vec{d}_j)$ is known as the relativistic hopping integral for zero magnetic fields. From Eq. (3.48), it is clear that the magnetic hopping integral is affected by the phase factor, $e^{-i\frac{e}{2\hbar}B\left(R_{ly}+d_{iy}-d_{jy}\right)\left(R_{lx}+d_{ix}-d_{jx}\right)}$ due to the uniform magnetic field. The magnetic hopping integrals are the product of the hopping integrals in the absence of magnetic field and the phase factor (Peiperl's phase factor). The hopping integrals, $t^{a_j a_i}_{\acute{n}\acute{l}\acute{j}\acute{M},\,nlJM}(\vec{R}_l+\vec{d}_i-\vec{d}_j)$ in the absence of magnetic field can be calculated easily which is called the relativistic version of the Slater-Koster table [52]. It is noted that Eq. (3.48) corresponds to the well-known approximation of using the Peierls phase factor [46,62]. Eq. (3.48) is widely used as the approximation of the magnetic hopping integral [62]. The resultant approximated forms of the resultant magnetic atomic orbital and atomic spectrum are given in Refs. [24, 51]. Since the resultant magnetic atomic orbital is expressed in the linear combination of the relativistic atomic orbital, $T^{a_j a_i}_{\eta\,\xi}\left(\vec{R}_l+\vec{d}_i-\vec{d}_j\right)$ can be expressed using the linear combination of relativistic hopping integrals and overlap integrals in the absence of a magnetic field. The resultant approximate forms for $T^{a_j a_i}_{\eta\,\xi}\left(\vec{R}_l+\vec{d}_i-\vec{d}_j\right)$ are given in Table II of Ref [51].

Chapter 4

Derivation of Streda formula for the Hall Conductivity

In this Chapter, the magnetic field dependence Hall Conductivity via Streda formula is described.

Magnetic field dependence Hall conductivity

The quantum Hall effect can be analyzed by the Streda formula [50].The derivation of Streda formula [50] for the magnetic field dependence Hall conductivity, σ_{Hall} is discussed. It is noted that the Hall conductivity σ_{Hall} is quantized immersed in a uniform magnetic field according to experimental results [4,33,41-44], and theoretical predictions [31,32]. According to the Streda formula the Hall conductivity is the derivative of the number of electrons which means the number of states with respect to the magnetic field at the Fermi energy. The numbers of states change with magnetic field at a fixed Fermi energy level. So, the σ_{Hall} is a function of a magnetic field. The 2D electron system has integral values of the Hall conductivity in unit of $\frac{e^2}{h}$ if the Fermi energy lies in a gap between two successive Landau levels in a magnetic field.

Let us consider, a uniform magnetic field is applied in a system along the z-direction, so the Hamiltonian of the system is given by

$$\widehat{H}_0 = \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}(\vec{r})\right)^2 + V(\vec{r}) \tag{4.1}$$

In Eq. (4.1), $\vec{A}(\vec{r})$, $V(\vec{r})$, m, e and c are the vector potential due to the magnetic field, periodic potential that is caused by the nucleus of an atom, rest mass of the electron, charge of the electron and velocity of light respectively.
If we consider the electric field is applied along the y-direction, additional Hamiltonian will be added with Hamiltonian in Eq. (4.1). The additional Hamiltonian is given by

$$\widehat{H} = -eEy \tag{4.2}$$

We can write the following equation for the ket, $|\alpha>$

$$\widehat{H}_0|\alpha> = E_\alpha|\alpha> \tag{4.3}$$

For the total Hamiltonian, we can write the following equation for the ket, $|\phi>$

$$(\widehat{H}_0 + \widehat{\hat{H}})|\phi> = E|\phi> \tag{4.4}$$

The Hall current

$$j_x =< \phi|\hat{j}_x|\phi> \tag{4.5}$$

For the perturbation theory, we can write

$$|\phi> = |\alpha> + \sum_{\alpha,\beta} \frac{<\beta|\widehat{\hat{H}}|\alpha>}{E_\alpha - E_\beta} |\beta> + \cdots \tag{4.6}$$

Using Eq. (4.2), from eqn. (4.6), we have

$$|\phi> = |\alpha> + \sum_{\alpha,\beta} \frac{<\beta|-eEy|\alpha>}{E_\alpha - E_\beta} |\beta> + \cdots \tag{4.7}$$

And

$$< \phi| =< \alpha| + < \beta| \sum_{\alpha,\beta} \frac{<\beta|eEy|\alpha>^*}{E_\alpha - E_\beta} + \cdots \tag{4.8}$$

The charge current density operator is given by

$$\hat{j}_x = + \frac{1}{L^2} e \hat{v}_x \tag{4.9}$$

In Eq. (4.9), L^2 is the area of the system.

Using Eqs. (4.7), (4.8) and (4.9) then, Eq. (4.5) becomes

$$\hat{J}_x = -\frac{1}{L^2} e < \alpha|\hat{v}_x|\alpha > -\frac{1}{L^2} e < \alpha|\hat{v}_x \sum_{\alpha,\beta} \frac{<\beta|eEy|\alpha>}{E_\alpha - E_\beta} |\beta > - \cdots$$

$$-\frac{1}{L^2} e < \beta| \sum_{\alpha,\beta} \frac{<\beta|eEy|\alpha>^*}{E_\alpha - E_\beta} \hat{v}_x|\alpha > - \cdots \quad (4.10$$

The 1st term $< \alpha|\hat{v}_x|\alpha >= 0$, vanishes, then Eq. (4.10) becomes

$$\hat{J}_x = -\frac{e^2}{L^2} \sum_{\alpha,\beta} \frac{<\alpha|\hat{v}_x|\beta><\beta|y|\alpha>+<\beta|y|\alpha>^*<\beta|\hat{v}_x|\alpha>}{E_\alpha - E_\beta} E$$

$$= \sigma_{Hall} E \quad (4.11)$$

With

$$\sigma_{Hall} = -\frac{e^2}{L^2} \sum_{\alpha,\beta} \frac{<\alpha|\hat{v}_x|\beta><\beta|y|\alpha>+<\beta|y|\alpha>^*<\beta|\hat{v}_x|\alpha>}{E_\alpha - E_\beta} \quad (4.12)$$

In Eq. (4.11), σ_{Hall} is the Hall conductivity.

The velocity operator along the y direction

$$\hat{v}_y = \frac{1}{i\hbar}(y\hat{H}_0 - \hat{H}_0 y) \quad (4.13)$$

Using Eq. (4.13), we can write

$$< \beta|\hat{v}_y|\alpha >= \frac{1}{i\hbar} < \beta|y\hat{H}_0 - \hat{H}_0 y\,|\alpha > \quad (4.14)$$

Using Eq. (4.3), then, Eq. (4.14) becomes

$$< \beta|\hat{v}_y|\alpha >= \frac{1}{i\hbar}(E_\alpha - E_\beta) < \beta|y\,|\alpha > \quad (4.15)$$

Eq. (4.15) implies that

$$< \beta|y\ |\alpha > = i\hbar \frac{<\beta|\hat{v}_y|\alpha>}{(E_\alpha - E_\beta)} \tag{4.16}$$

Similarly, the velocity operator for the x direction

$$< \beta|x\ |\alpha > = i\hbar \frac{<\beta|\hat{v}_x|\alpha>}{(E_\alpha - E_\beta)} \tag{4.17}$$

Using Eqs. (4.16) and (4.17), the Hall conductivity from Eq. (51.12) becomes

$$\sigma_{Hall} = -i\hbar \frac{e^2}{L^2} \sum_{\alpha,\beta} \int_{-\infty}^{E_F} \delta(E - E_\alpha) \frac{<\alpha|\hat{v}_x|\beta><\beta|\hat{v}_y|\alpha> - <\alpha|\hat{v}_y|\beta><\beta|\hat{v}_x|\alpha>}{(E_\alpha - E_\beta)^2}\, dE \tag{4.18}$$

Eq. (4.18) is Hall conductivity which is known as the Kubo formula. This expression is also known as the linear response formula for the first-order perturbation because first-order perturbation is linear. A linear response of the current in the perpendicular direction to the applied electric field is Hall conductivity. So, Eqn. (4.18) represents the Hall conductivity.
The total Hall conductivity can be written as:

$$\sigma_{Hall} = -\frac{ie^2\hbar}{L^2}\, Tr[\int_{-\infty}^{\varepsilon_F} d\varepsilon \sum_\beta f(\varepsilon) \frac{v_x|\beta><\beta|v_y - v_y|\beta><\beta|v_x}{(\varepsilon - \varepsilon_\beta)^2}\, \delta(\varepsilon - \widehat{H})] \tag{4.19}$$

In Eq. (4.19), $\delta(\varepsilon - \widehat{H})|\alpha > = \delta(\varepsilon - \varepsilon_\alpha)|\alpha >$ is used.

After simplification, the Hall conductivity in Eq. (4.19) becomes

$$\sigma_{Hall} = +\frac{ie^2\hbar}{L^2} Tr[\int_{-\infty}^{\varepsilon_F} d\varepsilon\, \delta(\varepsilon - \widehat{H}) f(\varepsilon) \{v_x \sum_\beta |\beta > \frac{d}{d\varepsilon}\left(\frac{1}{\varepsilon - \varepsilon_\beta}\right) < \beta|v_y - v_y \sum_\beta |\beta > \frac{d}{d\varepsilon}\left(\frac{1}{\varepsilon - \varepsilon_\beta}\right) < \beta|v_x\}] \tag{4.20}$$

For the better treatment in Eq. (4.20), we need to use the following equation namely Green`s functions, $G^{\pm}(\varepsilon)$:

$$\sum_{\beta} |\beta > \left(\frac{1}{\varepsilon - \varepsilon_{\beta}}\right) < \beta| = \frac{1}{\varepsilon - \hat{H} \pm i\delta} = G^{\pm}(\varepsilon) \tag{4.21}$$

Using Eqs. (4.20) and (4.21), the Hall conductivity becomes

$$\sigma_{Hall} = \frac{ie^2\hbar}{L^2} Tr\left[\int_{-\infty}^{\varepsilon_F} \left\{v_x \frac{d\, G^{+}(\varepsilon)}{d\varepsilon} v_y \delta\left(\varepsilon - \hat{H}\right) - v_x \delta\left(\varepsilon - \hat{H}\right) v_y \frac{d\, G^{-}(\varepsilon)}{d\varepsilon}\right\} d\varepsilon\right] \tag{4.22}$$

For the simplification, we can define the following term from Eq. (4.22) by $A_{Hall}(\varepsilon)$ as:

$$A_{Hall}(\varepsilon) = i\hbar\, Tr\left\{v_x \frac{d\, G^{+}(\varepsilon)}{d\varepsilon} v_y \delta\left(\varepsilon - \hat{H}\right) - v_x \delta\left(\varepsilon - \hat{H}\right) v_y \frac{d\, G^{-}(\varepsilon)}{d\varepsilon}\right\} \tag{4.23}$$

The Hall conductivity from Eq. (4.22) becomes

$$\sigma_{Hall} = \frac{e^2}{L^2} \int_{-\infty}^{\varepsilon_F} A_{Hall}(\varepsilon)\, d\varepsilon \tag{4.24}$$

The Hall conductivity can be split into two parts for convenience and after simplification, Eq. (4.24) becomes

$$\begin{aligned} \sigma_{Hall} = \frac{e^2}{2L^2} \int_{-\infty}^{\varepsilon_F} i\hbar\, \frac{d}{d\varepsilon}\, Tr\{\, v_x\, G^{+}(\varepsilon) v_y \delta\left(\varepsilon - \hat{H}\right) - v_x\, \delta\left(\varepsilon - \hat{H}\right) v_y G^{-}(\varepsilon)\} d\varepsilon \\ - \frac{e^2}{2L^2} \int_{-\infty}^{\varepsilon_F} i\hbar\, Tr\{v_x\, G^{+}(\varepsilon) v_y \frac{d\delta(\varepsilon - \hat{H})}{d\varepsilon} - v_x\, \frac{d\delta(\varepsilon - \hat{H})}{d\varepsilon} v_y G^{-}(\varepsilon)\, \}\, d\varepsilon \\ + \frac{e^2}{2L^2} \int_{-\infty}^{\varepsilon_F} A_{Hall}(\varepsilon)\, d\varepsilon \end{aligned} \tag{4.25}$$

We can define the 1st part from Eq. (4.25) by $B_{Hall}(\varepsilon)$as:

$$B_{Hall}(\varepsilon) = i\hbar\, Tr\left\{v_x\, G^{+}(\varepsilon) v_y \delta\left(\varepsilon - \widehat{H}\right) - v_x\, \delta\left(\varepsilon - \widehat{H}\right) v_y G^{-}(\varepsilon)\right\} \tag{4.26}$$

The Hall conductivity in Eq. (4.25) becomes

$$\begin{aligned}\sigma_{Hall} = \frac{e^2}{2L^2}\int_{-\infty}^{\varepsilon_F} \frac{d}{d\varepsilon} B_{Hall}(\varepsilon) d\varepsilon \\ -\frac{e^2}{2L^2}\int_{-\infty}^{\varepsilon_F} i\hbar\, Tr\{v_x\, G^{+}(\varepsilon) v_y \frac{d\delta(\varepsilon-\hat{H})}{d\varepsilon} - v_x\, \frac{d\delta(\varepsilon-\hat{H})}{d\varepsilon} v_y G^{-}(\varepsilon)\}\, d\varepsilon \\ +\frac{e^2}{2L^2}\int_{-\infty}^{\varepsilon_F} A_{Hall}(\varepsilon)\, d\varepsilon\end{aligned} \tag{4.27}$$

For the better treatment in Eq. (4.27), we can use the following delta function in terms of Green function:

$$\delta\left(\varepsilon - \widehat{H}\right) = \frac{-1}{2\pi i}\{G^{+}(\varepsilon) - G^{-}(\varepsilon)\} \tag{4.28}$$

Eq. (4.28) implies that

$$\frac{d}{d\varepsilon}\delta\left(\varepsilon - \widehat{H}\right) = \frac{-1}{2\pi i}\left\{\frac{d}{d\varepsilon}G^{+}(\varepsilon) - \frac{d}{d\varepsilon}G^{-}(\varepsilon)\right\} \tag{4.29}$$

And

$$\frac{d}{d\varepsilon}G^{\pm}(\varepsilon) = -G^{\pm}(\varepsilon)G^{\pm}(\varepsilon) \tag{4.30}$$

Using Eqs. (4.29) and (4.30), we have

$$\frac{d}{d\varepsilon}\delta\left(\varepsilon - \widehat{H}\right) = \frac{1}{2\pi i}\{G^{+}(\varepsilon)G^{+}(\varepsilon) - G^{-}(\varepsilon)G^{-}(\varepsilon)\} \tag{4.31}$$

After simplification the 2nd part in Eq. (4.27) becomes

$$\begin{aligned} i\hbar\, Tr\left\{v_x\, G^{+}(\varepsilon) v_y \frac{d\delta(\varepsilon-\widehat{H})}{d\varepsilon} - v_x\, \frac{d\delta(\varepsilon-\widehat{H})}{d\varepsilon} v_y G^{-}(\varepsilon)\right\} \\ = \frac{\hbar}{2\pi}\, Tr\, [v_x\, G^{+}(\varepsilon) v_y G^{+}(\varepsilon) G^{+}(\varepsilon) - v_x\, G^{+}(\varepsilon) v_y G^{-}(\varepsilon) G^{-}(\varepsilon)\end{aligned}$$

$$-v_x G^+(\varepsilon)G^+(\varepsilon)v_y G^-(\varepsilon) + v_x G^-(\varepsilon)G^-(\varepsilon)v_y G^-(\varepsilon)] \quad (4.32)$$

In the 3rd part in Eq. (4.27) using Eq. (4.23) we have

$$A_{Hall}(\varepsilon) = i\hbar\, Tr\left\{v_x \frac{d\, G^+(\varepsilon)}{d\varepsilon} v_y \delta\left(\varepsilon - \widehat{H}\right) - v_x \delta\left(\varepsilon - \widehat{H}\right) v_y \frac{d\, G^-(\varepsilon)}{d\varepsilon}\right\} \quad (4.33)$$

Using Eq. (4.30), then, Eq. (4.33) becomes

$$A_{Hall}(\varepsilon) = -i\hbar\, Tr\left\{v_x G^+(\varepsilon)G^+(\varepsilon)v_y\{G^+(\varepsilon) - G^-(\varepsilon)\} - v_x \delta\left(\varepsilon - \widehat{H}\right) v_y G^-(\varepsilon)G^-(\varepsilon)\right\} \quad (4.34)$$

Using Eq. (4.28), then, Eq. (4.33) becomes

$$A_{Hall}(\varepsilon) = \frac{\hbar}{2\pi} Tr[v_x G^+(\varepsilon)G^+(\varepsilon)v_y G^+(\varepsilon) - v_x G^+(\varepsilon)G^+(\varepsilon)v_y G^-(\varepsilon) - v_x G^+(\varepsilon)v_y G^-(\varepsilon)G^-(\varepsilon) + v_x G^-(\varepsilon)v_y G^-(\varepsilon)G^-(\varepsilon)] \quad (4.35)$$

Using Eqs. (4.32), (4.34) and (4.35), after simplification Eq. (4.27) becomes

$$\sigma_{Hall} = \frac{e^2}{2L^2}\int_{-\infty}^{\varepsilon_F} \frac{d}{d\varepsilon} B_{Hall}(\varepsilon)d\varepsilon - \frac{e^2}{2L^2}\left(\frac{\hbar}{2\pi}\right)\int_{-\infty}^{E_F} Tr\,[v_x\, G^+(\varepsilon)v_y G^+(\varepsilon)G^+(\varepsilon) - v_y G^+(\varepsilon)v_x G^+(\varepsilon)G^+(\varepsilon) - v_x G^-(\varepsilon)v_y G^-(\varepsilon)G^-(\varepsilon) + v_y G^-(\varepsilon)v_x G^-(\varepsilon)G^-(\varepsilon)]d\varepsilon \quad (4.36)$$

The velocity operator, $\hat{v}_x$

$$\hat{v}_x = \frac{-1}{i\hbar}[x,\ G^{\pm}(\varepsilon)^{-1}] \quad (4.37)$$

Eq. (4.37), implies that

$$i\hbar\hat{v}_x = G^{\pm}(\varepsilon)^{-1}x - x\,G^{\pm}(\varepsilon)^{-1} \tag{4.38}$$

Multiplying by $G^{\pm}(\varepsilon)^{+1}$ from left on both sides in Eq. (4.38) and after simplification

$$i\hbar G^{\pm}(\varepsilon)\,\hat{v}_x = x - G^{\pm}(\varepsilon)x\,G^{\pm}(\varepsilon)^{-1} \tag{4.39}$$

Multiplying by $G^{\pm}(\varepsilon)^{+1}$ from right on both sides in Eq. (4.39) and after simplification

$$G^{\pm}(\varepsilon)\,\hat{v}_x G^{\pm}(\varepsilon) = \frac{1}{i\hbar}\{xG^{\pm}(\varepsilon) - G^{\pm}(\varepsilon)x\} \tag{4.40}$$

Similarly, for the velocity operator, $\hat{v}_y$

$$G^{\pm}(\varepsilon)\,\hat{v}_y G^{\pm}(\varepsilon) = \frac{1}{i\hbar}\{yG^{\pm}(\varepsilon) - G^{\pm}(\varepsilon)y\} \tag{4.41}$$

After simplification the 2nd part in Eq. (4.36), becomes

$$\begin{aligned} Tr\,[v_x\,G^{+}(\varepsilon)v_yG^{+}(\varepsilon)G^{+}(\varepsilon) - v_yG^{+}(\varepsilon)v_xG^{+}(\varepsilon)G^{+}(\varepsilon) \\ -v_xG^{-}(\varepsilon)v_yG^{-}(\varepsilon)G^{-}(\varepsilon) + v_yG^{-}(\varepsilon)v_xG^{-}(\varepsilon)G^{-}(\varepsilon)] \\ = \sum_{\xi=\pm}\xi\;Tr\,\{G^{\xi}(\varepsilon)v_x\,G^{\xi}(\varepsilon)v_yG^{\xi}(\varepsilon) - G^{\xi}(\varepsilon)v_yG^{\xi}(\varepsilon)v_xG^{\xi}(\varepsilon) \end{aligned} \tag{4.42}$$

Using Eqs. (4.40) and (4.41) into (4.41) and after simplification Eq. (4.42) becomes

$$\begin{aligned} Tr\,[v_x\,G^{+}(\varepsilon)v_yG^{+}(\varepsilon)G^{+}(\varepsilon) - v_yG^{+}(\varepsilon)v_xG^{+}(\varepsilon)G^{+}(\varepsilon) \\ -v_xG^{-}(\varepsilon)v_yG^{-}(\varepsilon)G^{-}(\varepsilon) + v_yG^{-}(\varepsilon)v_xG^{-}(\varepsilon)G^{-}(\varepsilon)] \\ = -\frac{2\pi}{\hbar}\;Tr\,\left\{\left(xv_y - yv_x\right)\frac{d}{d\varepsilon}\delta\left(\varepsilon - \hat{H}\right)\right\} \end{aligned} \tag{4.43}$$

The Hall conductivity from Eq. (4.36) becomes

$$\sigma_{Hall} = \frac{e^2}{L^2}\int_{-\infty}^{\varepsilon_F}\left[\frac{1}{2}\frac{d}{d\varepsilon}B_{xy}(\varepsilon) + \frac{1}{2}Tr\ \frac{d}{d\varepsilon}\delta\left(\varepsilon - \widehat{H}\right)\left(xv_y - yv_x\right)\right]d\varepsilon \tag{4.44}$$

We know the following relation [Appendix C],

$$\frac{1}{2}Tr\frac{d}{d\varepsilon}\delta\left(\varepsilon - \widehat{H}\right)\left\{xv_y - yv_x\right\} = \frac{c}{e}\frac{\partial}{\partial B}Tr\delta(\varepsilon - \widehat{H}) \tag{4.45}$$

Using Eq. (4.45) into Eq. (4.44) and after simplification, the Hall conductivity from Eq. (4.44) becomes

$$\sigma_{Hall} = \frac{e^2}{L^2}[i\hbar Tr\left\{\hat{v}_x G^+(\varepsilon_F)\ \hat{v}_y\delta\left(\varepsilon_F - \widehat{H}\right) - \hat{v}_x\delta\left(\varepsilon_F - \widehat{H}\right)\hat{v}_y G^-(\varepsilon_F)\right\}$$
$$+\frac{\mathrm{ec}}{L^2}\frac{\partial}{\partial B}\int_{-\infty}^{\varepsilon_F} Tr\delta\left(\varepsilon - \widehat{H}\right)d\varepsilon \tag{4.46}$$

We have

$$Tr\delta\left(\varepsilon - \widehat{H}\right) = \sum_\alpha < \alpha\left|\delta\left(\varepsilon - \widehat{H}\right)\right|\alpha >$$
$$= \frac{1}{\pi}\sum_\alpha \frac{\delta}{(\varepsilon-\varepsilon_\alpha)^2+\delta^2} \tag{4.47}$$

Using $\underset{\delta \to 0}{Lim}\ \frac{1}{\pi}\frac{\delta}{(\varepsilon-\varepsilon_\alpha)^2+\delta^2} = \delta(\varepsilon - \varepsilon_\alpha)$ into Eq. (4.44)

$$Tr\delta\left(\varepsilon - \widehat{H}\right) = \sum_\alpha \delta(\varepsilon - \varepsilon_\alpha)$$
$$= D(\varepsilon) \tag{4.48}$$

$D(\varepsilon)$ is the density of states.

The total number of states below the Fermi energy level

$$\int_{-\infty}^{\varepsilon_F} Tr\delta\left(\varepsilon - \widehat{H}\right)d\varepsilon\ = \int_{-\infty}^{\varepsilon_F} D(\varepsilon)d\varepsilon$$

$$= N(\varepsilon_F) \tag{4.49}$$

$N(E_F)$ is the number of states below Fermi energy.

Using Eq. (4.49) into Eq. (4.46), then the Hall conductivity from Eq. (4.42) becomes

$$\sigma_{Hall} = \frac{e^2}{2\,L^2}\left[i\hbar Tr\left\{\hat{v}_x G^+(\varepsilon_F)\,\hat{v}_y \delta\left(\varepsilon_F - \widehat{H}\right) - \hat{v}_x \delta\left(\varepsilon_F - \widehat{H}\right)\hat{v}_y G^-(\varepsilon_F)\right\} + \frac{\mathrm{ec}}{L^2}\frac{\partial}{\partial B}N(\varepsilon_F)\right.$$

$$= \frac{e^2}{2L^2} B_{Hall}(\varepsilon_F) + \frac{\mathrm{ec}}{L^2}\frac{\partial}{\partial B}N(\varepsilon_F) \tag{4.50}$$

In Eq. (4.50), σ_{Hall} is the Hall conductivity. It is noticeable that the second term is the magnetic field dependence Hall conductivity below the Fermi energy level. It is more clear that the Hall conductivity is the derivative of the number of states below Fermi energy level with respect to the magnetic field.

Chapter 5

Application of the nonperturbative MFRTB method in graphene immersed in the uniform magnetic field

In this Chapter, the application procedure of the nonperturbative MFRTB method in graphene is described in the following sequence:

5.1 Applied rational magnetic field

5.2 Magnetic Brillouin zone

5.3 Matrix Elements of the Dirac Hamiltonian

5.4 Approximated forms of Eigenvalues, $\varepsilon_{\xi}^{C_A,\,0}$

5.5 Approximated forms of Eigenfunctions, $\psi_{\xi}^{C_A,0}(\vec{r})$

5.6 Magnetic hopping integrals, $T^{C_A C_{Bi}}_{(\acute{n}\acute{l}\acute{j}\acute{M}),(nlJM)}\left(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A}\right)$

5.7 Simultaneous equation for graphene

5.1 Applied rational magnetic field

A rational magnetic field [51] which is defined by the following Eq. (5.1) is described for the calculation of the Hall conductivity in graphene using the nonperturbative MFRTB method based on the obtained magnetic energy band structure. The magnetic field is applied perpendicular to the plane of graphene.

$$B = \frac{8\pi\hbar}{\sqrt{3}ea^2}\ \frac{p}{q}, \tag{5.1}$$

In Eq. (5.1), a is the lattice constant of graphene, its value is $24.6\ nm$, and p and q are relatively prime integers [51]. The values p/q determine the strength of the applied magnetic field. The magnitude of the magnetic field is proportional to the rational number p/q, for this reason, the magnetic field is called rational the magnetic field [46, 63,64]. In the present calculations, the magnetic hopping integrals between the outer shells (2s- and 2p-orbitals) of the nearest-neighbor carbon atoms were considered. Their values were calculated using a table of the nonperturbative magnetic hopping integrals (Table I of Ref. [51]) and the relativistic version of the Slater–Koster table [52]. In this work, it is adopted a set of relativistic tight-binding parameters for graphene that is given in the previous paper [51].

5.2 Magnetic Brillouin zone

Figure 1 shows the magnetic Brillouin zone (MBZ) of graphene immersed in a uniform magnetic field. The area of the magnetic unit cell is q times larger than that of a conventional unit cell of graphene. The magnetic energy band structure of graphene is calculated for the wave vectors lying in the MBZ [52]. The MBZ of graphene immersed in the magnetic field of Eq. (5.1) is illustrated

in Figure. 1. The total number of k points in the MBZ represents the degree of degeneracy for the magnetic energy spectrum.

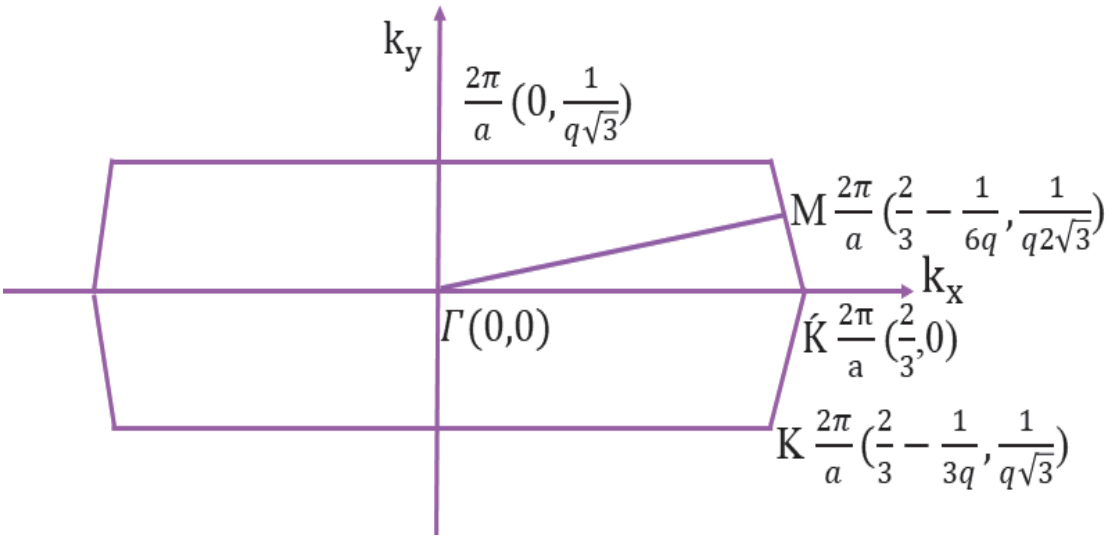


Figure. 1: Magnetic first Brillouin zone (MBZ) of graphene immersed in a magnetic field [45].

5.3 Matrix Elements of the Dirac Hamiltonian

In this subsection, the nonperturbative MFRTB method [27] considering the magnetic hopping and overlap integrals is explained for the description of the electronic band structure of graphene immersed in a uniform magnetic field. Let us consider an electron of the carbon atom that moves in both a uniform magnetic field and the periodic potential of the graphene. In this case, the total Hamiltonian becomes [59],

$$H = c\vec{\alpha}.\{\vec{p} + e\vec{A}(\vec{r})\} + \beta mc^2 + \sum_{\vec{R}_n}\sum_A V_{C_A}(\vec{r} - \vec{R}_n - \vec{d}_A) \tag{5.2}$$

The Dirac equation in this system is given by [59]

$$H\Phi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\Phi_{\vec{k}}(\vec{r}) \tag{5.3}$$

In Eq. (5.2), $\vec{p}$ is the momentum of the moving Bloch electron in the system, $\vec{A}(\vec{r})$ and $V_{C_A}(\vec{r}-\vec{R}_n-\vec{d}_A)$ are the vector potential for an applied uniform magnetic field along the z axis and scalar potential caused by the nucleus of an atom C_A located at $\vec{R}_n+\vec{d}_A$ respectively. It is noted that the vector potential $\vec{A}(\vec{r})$ follows the gauge transformation. The vectors $\vec{R}_n$ and $\vec{d}_A$ are the translational vector of the lattice and the vector determine the position of an atom C_A respectively. The letters c, e, and m represent the velocity of light, a charge of the Bloch electron, and rest mass of the Bloch electron respectively. The quantities $\vec{\alpha}$ $(=\alpha_x,\alpha_y,\alpha_z)$, and β denote the usual 4×4 matrices, and also the Hermitian operators [59]. The eigenfunction $\Phi_{\vec{k}}(\vec{r})$ is the four-component eigenfunction that can be expanded by the following Eq. (5.4). The subscript, $\vec{k}$ in the eigenfunction, $\Phi_{\vec{k}}(\vec{r})$ is the wave vector and also denotes the crystal momentum that belongs to the magnetic first Brillouin zone [25].
The expanded wave function is given by

$$\Phi_{\vec{k}}(\vec{r})=\sum_{\vec{R}_n}\sum_A\sum_\xi C_{\vec{k}}^{\xi}(\vec{R}_n+\vec{d}_A)\ \psi_\xi^{C_A,\vec{R}_n+\vec{d}_A}(\vec{r}) \tag{5.4}$$

In Eq. (5.4), $C_{\vec{k}}^{\xi}(\vec{R}_n+\vec{d}_A)$ is the expansion coefficient and the eigenfunction, $\psi_\xi^{C_A,\vec{R}_n+\vec{d}_A}(\vec{r})$ is the relativistic atomic orbitals for an atom $C_A$located at $\vec{R}_n+\vec{d}_A$ that is immersed in a uniform magnetic field. The generalized eigenvalue problem for the expansion coefficient, $C_{\vec{k}}^{\xi}(\vec{R}_n+\vec{d}_A)$ that can be solved by the following equation Eq. (5.5). The Eq. (5.5) can be obtained by the similar treatment which is used in Eq. (2.13) in Chapter 2 and Eq. (3.10) in Chapter 3.

$$\sum_{\vec{R}_n}\sum_A\sum_\xi H_{\vec{R}_{mB}\,\eta,\ \vec{R}_{nA}\,\xi}\,C_{\vec{k}}^{\xi}(\vec{R}_n+\vec{d}_A) = E_k\sum_{\vec{R}_n}\sum_A\sum_\xi S_{\vec{R}_{mB}\,\eta,\ \vec{R}_{nA}\,\xi}\,C_{\vec{k}}^{\xi}(\vec{R}_n+\vec{d}_A) \tag{5.5}$$

In Eq. (5.5), $H_{\vec{R}_{mB}\,\eta,\ \vec{R}_{nA}\,\xi}$ and $S_{\vec{R}_{mB}\,\eta,\ \vec{R}_{nA}\,\xi}$ are the matrix elements of the Hamiltonian and overlap integral between the two relativistic atomic orbitals; $\psi_{\eta}^{C_B,\vec{R}_m+\vec{d}_B}(\vec{r})$ and $\psi_{\xi}^{C_A,\vec{R}_n+\vec{d}_A}(\vec{r})$, respectively.

The matrix elements of the Hamiltonian by using the similar treatment which is used in Eq. (3.27) in chapter 3 by neglecting both integrals involving three different centers.

$$H_{\vec{R}_{mB}\,\eta,\ \vec{R}_{nA}\,\xi} = (\varepsilon_{\xi}^{C_A,\,0} + \Delta\varepsilon_{\xi}^{C_A,\vec{d}_A})\delta_{B,A}\delta_{\eta,\xi}\ \delta_{\vec{R}_m,\vec{R}_n} + \left(1 - \delta_{B,A}\delta_{\vec{R}_m,\vec{R}_n}\right) \times e^{-i\frac{eB}{\hbar}(R_{nx}+d_{Ax}-R_{mx}-d_{Bx})(R_{my}+d_{By})}\ \tilde{T}_{\eta\,\xi}^{C_BC_A}(\vec{R}_n - \vec{R}_m + \vec{d}_A - \vec{d}_B) \tag{5.6}$$

With

$$T_{\eta\,\xi}^{C_BC_A}\left(\vec{R}_l + \vec{d}_A - \vec{d}_B\right) = \int \psi_{\eta}^{C_B,0}(\vec{r})^{\dagger}\,\frac{V_{C_B}(\vec{r})+V_{C_A}\left(\vec{r}-\vec{R}_l-\vec{d}_A+\vec{d}_B\right)}{2}\,\psi_{\xi}^{C_A,\vec{R}_l+\vec{d}_A-\vec{d}_B}(\vec{r})d^3r \tag{5.7}$$

The overlap integrals between the two relativistic atomic orbitals; $\psi_{\eta}^{C_B,\vec{R}_m+\vec{d}_B}(\vec{r})$ and $\psi_{\xi}^{C_A,\vec{R}_n+\vec{d}_A}(\vec{r})$ is given by

$$S_{\eta\,\xi}^{C_BC_A}\left(\vec{R}_l + \vec{d}_A - \vec{d}_B\right) = \int \psi_{\eta}^{C_B,0}(\vec{r})^{\dagger}\,\psi_{\xi}^{C_A,\vec{R}_l+\vec{d}_A-\vec{d}_B}(\vec{r})d^3r \tag{5.8}$$

In Eq. (5.6), the eigenvalues, $\varepsilon_{\xi}^{C_A,\,0}$ and $\Delta\varepsilon_{\xi}^{C_A,\vec{d}_A}$, $T_{\eta\,\xi}^{C_BC_A}\left(\vec{R}_l + \vec{d}_A - \vec{d}_B\right)$ are the atomic spectrum, energy of the crystal field in the presence of a magnetic field, magnetic hopping integral [51] respectively. This magnetic hopping integral is affected by a phase factor due to the uniform magnetic field (similar to the Eq. (3.48) in Chapter 3). This magnetic hopping integral is the product of the hopping integral in the absence of a magnetic field and a phase factor which is known as Peiperl's phase factor. The hopping integral in the absence of a magnetic field can be calculated easily which is called the relativistic version of the Slater-Koster table [52].

Using Eq. (5.6), it is very easy to calculate the matrix elements of the Dirac Hamiltonian. For this reason, firstly, we have to calculate the $T_{\eta\,\xi}^{C_BC_A}\left(\vec{R}_l + \vec{d}_A - \vec{d}_B\right)$ and in order to calculate

$T_{\eta\xi}^{C_B C_A}\left(\vec{R}_l + \vec{d}_A - \vec{d}_B\right)$, we have to calculate $\varepsilon_\xi^{C_A,0}$, $\Delta\varepsilon_\xi^{C_A,\vec{d}_A}$ and $\psi_\xi^{C_A,0}(\vec{r})$. For this purpose, let us consider an electron in an isolated atom that is immersed in a uniform magnetic field.
The Dirac equation is given by

$$\left[c\vec{\alpha}.\left\{\vec{p} + e\vec{A}(\vec{r})\right\} + \beta mc^2 + V_{C_A}(\vec{r})\right]\psi_\xi^{C_A,0}(\vec{r}) = \varepsilon_\xi^{C_A,0}\,\psi_\xi^{C_A,0}(\vec{r}) \tag{5.9}$$

The solutions of the eigenfunctions, $\psi_\xi^{C_A,0}(\vec{r})$ and eigenvalues, $\varepsilon_\xi^{C_A,0}$ in Eq. (5.9) are approximately estimated by the nonperturbative MFRTB method specifically the variational method [51]. For these calculations, the matrix elements of the Hamiltonian are considered of Eq. (5.9) by using a finite number of the relativistic atomic orbitals $\left\{\varphi_{nljM}^{C_A}(\vec{r})\right\}$ as a basis functions [27,51], where $\varphi_{nljM}^{C_A}(\vec{r})$ is the relativistic atomic orbital for the atom C_A in the zero magnetic field case. The subscripts $n, l, J \ and \ M$ in the $\varphi_{nljM}^{C_A}(\vec{r})$, are the principal, azimuthal, total angular momentum, and magnetic quantum numbers, respectively.

In order to calculate the matrix elements of the Hamiltonian under this approximation by taking only the outermost, $(2s, 2p_x, 2p_y \text{ and } 2p_z)$ atomic orbitals, $\varphi_{nljM}^{C_A}(\vec{r})$ by neglecting inner atomic orbitals. The atomic orbitals, $\varphi_{nljM}^{C_A}(\vec{r})$ have two components same as Eq. (2.6) in Chapter 2. The small component is approximated by the relation $G_{nljM}^{C_A}(\vec{r}) = \frac{\sigma.\vec{p}}{2mc}F_{nljM}^{C_A}(\vec{r})$, where σ, $F_{nljM}^{C_A}(\vec{r})$ and $G_{nljM}^{C_A}(\vec{r})$ are the Pauli matrix, the large and small components of the radial part of the relativistic atomic orbital $\varphi_{nljM}^{C_A}(\vec{r})$ respectively [27]. By diagonalizing the resultant matrix, the approximated forms of the eigenvalues, $\varepsilon_\xi^{C_A,0}$ and the eigen function, $\psi_\xi^{C_A,0}(\vec{r})$ are given [27].

5.4 Approximated forms of Eigenvalues, $\boldsymbol{\varepsilon_\xi^{C_A,0}}$

In this subsection, similar to Eq. (3.30) in Chapter 3, the approximated forms of the eigenvalues, $\varepsilon_\xi^{C_A,0}$ for the case of s-orbitals $(l = 0)$ and p-orbitals $(l = 1)$ is given by [24]:

$$\varepsilon_{\xi}^{C_A,\,0} = \left\{ \begin{array}{c} \bar{\varepsilon}_{nlJ}^{\,C_A} \pm \frac{e\hbar B}{2m} \\ \frac{\bar{\varepsilon}_{nlJ}^{\,C_A} + \bar{\varepsilon}_{nlJ-1}^{\,C_A}}{2} + \frac{e\hbar B}{4m} \pm \frac{\bar{\varepsilon}_{nlJ}^{\,C_A} - \bar{\varepsilon}_{nlJ-1}^{\,C_A}}{2}\sqrt{1+\frac{2}{3}x_{nl}+\frac{1+8S_{nl}^2}{9}x_{nl}^2} \\ \frac{\bar{\varepsilon}_{nlJ}^{\,C_A} + \bar{\varepsilon}_{nlJ-1}^{\,C_A}}{2} + \frac{e\hbar B}{4m} - \frac{\bar{\varepsilon}_{nlJ}^{\,C_A} - \bar{\varepsilon}_{nlJ-1}^{\,C_A}}{2}\sqrt{1+\frac{2}{3}x_{nl}+\frac{1+8S_{nl}^2}{9}x_{nl}^2} \\ \frac{\bar{\varepsilon}_{nlJ}^{\,C_A} + \bar{\varepsilon}_{nlJ-1}^{\,C_A}}{2} + \frac{e\hbar B}{4m} + \frac{\bar{\varepsilon}_{nlJ}^{\,C_A} - \bar{\varepsilon}_{nlJ-1}^{\,C_A}}{2}\sqrt{1-\frac{2}{3}x_{nl}+\frac{1+8S_{nl}^2}{9}x_{nl}^2} \\ \frac{\bar{\varepsilon}_{nlJ}^{\,C_A} + \bar{\varepsilon}_{nlJ-1}^{\,C_A}}{2} + \frac{e\hbar B}{4m} - \frac{\bar{\varepsilon}_{nlJ}^{\,C_A} - \bar{\varepsilon}_{nlJ-1}^{\,C_A}}{2}\sqrt{1-\frac{2}{3}x_{nl}+\frac{1+8S_{nl}^2}{9}x_{nl}^2} \\ \bar{\varepsilon}_{nlJ}^{\,C_A} \pm \frac{e\hbar B}{m} \end{array} \right\} \tag{5.10}$$

With

$$x_{nl} = \frac{\frac{e\hbar B}{2m}}{\bar{\varepsilon}_{nlJ}^{\,a_i} - \bar{\varepsilon}_{nlJ-1}^{\,a_i}} \tag{5.11}$$

In Eq. (5.10), S_{nlJ} is the overlap integral between the radial parts of the atomic orbitals of $\emptyset_{nljM}^{a_i}(\vec{r})$ and $\emptyset_{nlJ-1M}^{a_i}(\vec{r})$ and x_{nl} is the ratio of the spin Zeeman splitting, $\frac{e\hbar B}{2m}$ and spin-orbit splitting, $\bar{\varepsilon}_{nlJ}^{\,a_i} - \bar{\varepsilon}_{nlJ-1}^{\,a_i}$ that is expressed in Eq. (5.11). It is noticeable from Eq. (5.11), in the low magnetic field case, $x_{nl} \ll 1$ because the spin Zeeman splitting term is small compared to the spin-orbit splitting. In this case, spin-orbit interaction is the dominant part which is known as the anomalous Zeeman effect in graphene. In the high magnetic field case, $x_{nl} \gg 1$ because spin Zeeman splitting term is large compared to the spin-orbit splitting. In this case, the spin Zeeman splitting term is the dominant part which is known as the Paschen–Back effect graphene.

5.5 Approximated forms of Eigenfunctions, $\psi_{\xi}^{C_A,0}(\vec{r})$

In this subsection, similar to Eq. (3.32) in Chapter 3, the approximated forms of the eigen function, $\psi_{\xi}^{C_A,0}(\vec{r})$ for the case of s-orbitals ($l = 0$) and the case of p-orbitals ($l = 1$)is given by [24]

$$\psi_{\xi}^{C_A,0}(\vec{r}) = \left\{ \begin{array}{c} \varphi_{nlJ\pm M}^{C_A}(\vec{r}) \\ \frac{\varphi_{nlJM}^{C_A}(\vec{r}) + \eta_{+}^{C_A}\varphi_{nlJ-1M}^{C_A}(\vec{r})}{\sqrt{1+(\eta_{+}^{C_A})^2}} \\ \frac{-\eta_{+}^{C_A}\varphi_{nlJM}^{C_A}(\vec{r}) + \varphi_{nlJ-1M}^{C_A}(\vec{r})}{\sqrt{1+(\eta_{+}^{C_A})^2}} \\ \frac{\varphi_{nlJ-M}^{C_A}(\vec{r}) + \eta_{-}^{C_A}\varphi_{nlJ-M}^{C_A}(\vec{r})}{\sqrt{1+(\eta_{-}^{C_A})^2}} \\ \frac{-\eta_{-}^{C_A}\varphi_{nlJ-M}^{C_A}(\vec{r}) + \varphi_{nlJ-M}^{C_A}(\vec{r})}{\sqrt{1+(\eta_{-}^{C_A})^2}} \\ \varphi_{nlJ\pm M}^{C_A}(\vec{r}), \end{array} \right\} \tag{5.12}$$

With

$$\eta_{\pm}^{C_A} = \frac{3}{2\sqrt{2}\, S_{nl}\, x_{nl}} \left\{ 1 \pm \frac{x_{nl}}{3} - \sqrt{1 \pm \frac{2}{3}x_{nl} + \frac{1+8S_{nl}^2}{9}x_{nl}^2} \right\} \tag{5.13}$$

In Eq. (5.12), S_{nl} is overlap integral between the radial parts of the atomic orbitals of $\emptyset_{nlJM}^{a_i}(\vec{r})$ and $\emptyset_{nlJ-1M}^{a_i}(\vec{r})$.

5.6 Magnetic hopping integrals, $T_{(\acute{n}\acute{l}\acute{j}\acute{M}),(nlJM)}^{C_A C_{Bi}}\left(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A}\right)$

In order to calculate the matrix element from Eq. (5.6), we need to calculate the magnetic hopping integral from Eq. (5.7). Similar to Eq. (3.49) in subsection 3.3 in Chapter 3, we can calculate the magnetic hopping integrals via Eq. (5.7) which are the product of relativistic hopping integral for zero magnetic field and the Peiperl's phase factor. Using Eq. (5.12) into Eq. (5.7), we can get the resultant approximated magnetic hopping integrals, $T_{\eta\,\xi}^{C_B C_A}\left(\vec{R}_l + \vec{d}_A - \vec{d}_B\right)$ [51]. The resultant approximated magnetic hopping integrals, $T_{\eta\,\xi}^{C_B C_A}\left(\vec{R}_l + \vec{d}_A - \vec{d}_B\right)$ are reported in **Table-2**.

Table 2: Magnetic hopping integrals for graphene. In this table, $\eta_{\alpha}^{C_A}$ and $\eta_{\beta}^{C_A}$ defined by $\eta_{\alpha}^{C_A} = \eta_{2lJ-1M}^{C_A} = -\eta_{2lJM}^{C_A}$ and $\eta_{\beta}^{C_A} = \eta_{2lJ-1-M}^{C_A} = -\eta_{2lJ-M}^{C_A}$, respectively. C_{Bi} $(i = 1,2,3)$ indicate the 1st nn B carbon atoms of A atom.

$(\acute{n}\acute{l}\acute{J}\acute{M})$	$(nlJM)$	Magnetic hopping integrals, $T^{C_AC_{Bi}}_{(\acute{n}\acute{l}\acute{J}\acute{M}),(nlJM)}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})$
$(20\frac{1}{2}\frac{1}{2})$	$(20\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(20\frac{11}{22}),(20\frac{11}{22})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})$
$(20\frac{1}{2}\frac{1}{2})$	$(20\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(20\frac{11}{22}),(20\frac{1}{2}-\frac{1}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})$
$(20\frac{1}{2}\frac{1}{2})$	$(21\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{31}{22})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A}) - \eta_{\alpha}^{C_A}t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{11}{22})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})]/\sqrt{1+(\eta_{\alpha}^{C_A})^2}$
$(20\frac{1}{2}\frac{1}{2})$	$(21\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A}) - \eta_{\beta}^{C_A}t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})]/\sqrt{1+(\eta_{\beta}^{C_A})^2}$
$(20\frac{1}{2}\frac{1}{2})$	$(21\frac{3}{2}\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{3}{2}\frac{3}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})$
$(20\frac{1}{2}\frac{1}{2})$	$(21\frac{3}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A}) + \eta_{\alpha}^{C_A}t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})]/\sqrt{1+(\eta_{\alpha}^{C_A})^2}$
$(20\frac{1}{2}\frac{1}{2})$	$(21\frac{3}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A}) + \eta_{\beta}^{C_A}t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})]/\sqrt{1+(\eta_{\beta}^{C_A})^2}$
$(20\frac{1}{2}\frac{1}{2})$	$(21\frac{3}{2}-\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(20\frac{11}{22}),(21\frac{3}{2}-\frac{3}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})$
$20\frac{1}{2}-\frac{1}{2})$	$(20\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(20\frac{11}{22})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})$
$20\frac{1}{2}-\frac{1}{2})$	$(20\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(20\frac{1}{2}-\frac{1}{2})}(\vec{R}_n + \vec{d}_{C_B} - \vec{d}_{C_A})$

$20\frac{1}{2}-\frac{1}{2})$	$(21\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{31}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{11}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})]/\ \sqrt{1+(\eta_\alpha^{C_A})^2}$
$20\frac{1}{2}-\frac{1}{2})$	$(21\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})]/\sqrt{1+(\eta_\beta^{C_A})^2}$
$20\frac{1}{2}-\frac{1}{2})$	$(21\frac{3}{2}\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{3}{2}\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$
$20\frac{1}{2}-\frac{1}{2})$	$(21\frac{3}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}\ [t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\alpha^{C_A})^2}$
$20\frac{1}{2}-\frac{1}{2})$	$(21\frac{3}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}\ [t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\beta^{C_A})^2}$
$20\frac{1}{2}-\frac{1}{2})$	$(21\frac{3}{2}-\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(20\frac{1}{2}-\frac{1}{2}),(21\frac{3}{2}-\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$
$(21\frac{1}{2}\frac{1}{2})$	$(20\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{31}{22}),(20\frac{11}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{11}{22}),(20\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\alpha^{C_A})^2}$
$(21\frac{1}{2}\frac{1}{2})$	$(20\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{31}{22}),(20\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{11}{22}),(20\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\alpha^{C_A})^2}$
$(21\frac{1}{2}\frac{1}{2})$	$(21\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{31}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{11}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{31}{22})}(\vec{R}_n+$ $\vec{d}_{C_B}-\vec{d}_{C_A})+(\eta_\alpha^{C_A})^2t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{11}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\ ]\ /\ 1+$ $(\eta_\alpha^{C_A})^2$

$(21\frac{1}{2}\frac{1}{2})$	$(21\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n+$ $\vec{d}_{C_B}-\vec{d}_{C_A})+(\eta_\alpha^{C_A})(\eta_\beta^{C_A})t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\ ]/$ $\sqrt{1+(\eta_\alpha^{C_A})^2}\sqrt{1+(\eta_\beta^{C_A})^2}$
$(21\frac{1}{2}\frac{1}{2})$	$(21\frac{3}{2}\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{33}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{3}{2}\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\alpha^{C_A})^2}$
$(21\frac{1}{2}\frac{1}{2})$	$(21\frac{3}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{31}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{31}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{11}{22})}(\vec{R}_n+$ $\vec{d}_{C_B}-\vec{d}_{C_A})-(\eta_\alpha^{C_A})^2t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{11}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\ ]/1+$ $(\eta_\alpha^{C_A})^2$
$(21\frac{1}{2}\frac{1}{2})$	$(21\frac{3}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+$ $\vec{d}_{C_B}-\vec{d}_{C_A})-(\eta_\alpha^{C_A})(\eta_\beta^{C_A})t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\ ]/$ $\sqrt{1+(\eta_\alpha^{C_A})^2}\sqrt{1+(\eta_\beta^{C_A})^2}$
$(21\frac{1}{2}\frac{1}{2})$	$(21\frac{3}{2}-\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{11}{22}),(21\frac{3}{2}-\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{31}{22}),(21\frac{3}{2}-\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\alpha^{C_A})^2}$
$(21\frac{1}{2}-\frac{1}{2})$	$(20\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(20\frac{11}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}-\frac{1}{2}),(20\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\beta^{C_A})^2}$

$(21\frac{1}{2}-\frac{1}{2})$	$(20\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(20\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}-\frac{1}{2}),(20\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\,]/\sqrt{1+(\eta_\beta^{C_A})^2}$
$(21\frac{1}{2}-\frac{1}{2})$	$(21\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(21\frac{11}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}-\frac{1}{2}),(21\frac{11}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(21\frac{31}{22})}(\vec{R}_n+$ $\vec{d}_{C_B}-\vec{d}_{C_A})+(\eta_\alpha^{C_A})(\eta_\beta^{C_A})t^{C_AC_{Bi}}_{(21\frac{3}{2}-\frac{1}{2}),(21\frac{31}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\,]\,/$ $\sqrt{1+(\eta_\alpha^{C_A})^2}\sqrt{1+(\eta_\beta^{C_A})^2}$
$(21\frac{1}{2}-\frac{1}{2})$	$(21\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}-\frac{1}{2}),(21\frac{1}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n+$ $\vec{d}_{C_B}-\vec{d}_{C_A})+(\eta_\beta^{C_A})^2\,t^{C_AC_{Bi}}_{(21\frac{3}{2}-\frac{1}{2}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\,]\,/(1+$ $(\eta_\beta^{C_A})^2\ )$
$(21\frac{1}{2}-\frac{1}{2})$	$(21\frac{3}{2}\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(21\frac{3}{2}\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}-\frac{1}{2}),(21\frac{3}{2}\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\,]/\sqrt{1+(\eta_\beta^{C_A})^2}$
$(21\frac{1}{2}-\frac{1}{2})$	$(21\frac{3}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(21\frac{31}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}-\frac{1}{2}),(21\frac{31}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(21\frac{11}{22})}(\vec{R}_n+$ $\vec{d}_{C_B}-\vec{d}_{C_A})-(\eta_\alpha^{C_A})(\eta_\beta^{C_A})t^{C_AC_{Bi}}_{(21\frac{3}{2}-\frac{1}{2}),(21\frac{11}{22})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\,]\,/$ $\sqrt{1+(\eta_\alpha^{C_A})^2}\sqrt{1+(\eta_\beta^{C_A})^2}$
$(21\frac{1}{2}-\frac{1}{2})$	$(21\frac{3}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{1}{2}-\frac{1}{2}),(21\frac{3}{2}-\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$

		$\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)+\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{1}{2}\frac{-1}{2}\right),\left(21\frac{1}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)-(\eta_{\beta}^{C_A})^2 t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-1}{2}\right),\left(21\frac{1}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)/\ ]\ /\ \sqrt{1+\left(\eta_{\alpha}^{C_A}\right)^2}\sqrt{1+(\eta_{\beta}^{C_A})^2}$
$(21\frac{1}{2}-\frac{1}{2})$	$(21\frac{3}{2}-\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_x R_y}[t^{C_A C_{Bi}}_{\left(21\frac{1-1}{2\ 2}\right),\left(21\frac{3}{2}\frac{-3}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)-\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{3-1}{2\ 2}\right),\left(21\frac{3}{2}\frac{-3}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)]/\ \sqrt{1+(\eta_{\beta}^{C_A})^2}$
$(21\frac{3}{2}\frac{3}{2})$	$(20\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_x R_y} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(20\frac{1}{2}\ \frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$
$(21\frac{3}{2}\frac{3}{2})$	$(20\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_x R_y} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(20\frac{1}{2}\ \frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$
$(21\frac{3}{2}\frac{3}{2})$	$(21\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_x R_y}[t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\frac{1}{2}\ \frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)-\eta_{\alpha}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\frac{3}{2}\ \frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)]/\ \sqrt{1+(\eta_{\alpha}^{C_A})^2}$
$(21\frac{3}{2}\frac{3}{2})$	$(21\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_x R_y}[t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\frac{1}{2}\ \frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)-\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\frac{3}{2}\ \frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)]/\ \sqrt{1+(\eta_{\beta}^{C_A})^2}$
$(21\frac{3}{2}\frac{3}{2})$	$(21\frac{3}{2}\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_x R_y} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\frac{3}{2}\ \frac{3}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$
$(21\frac{3}{2}\frac{3}{2})$	$(21\frac{3}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_x R_y}[t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\frac{3}{2}\ \frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)+\eta_{\alpha}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\frac{1}{2}\ \frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)]/\ \sqrt{1+(\eta_{\alpha}^{C_A})^2}$
$(21\frac{3}{2}\frac{3}{2})$	$(21\frac{3}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_x R_y}[t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\frac{3}{2}\ \frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)+\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\frac{1}{2}\ \frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)]/\ \sqrt{1+(\eta_{\beta}^{C_A})^2}$
$(21\frac{3}{2}\frac{3}{2})$	$(21\frac{3}{2}-\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_x R_y} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{3}{2}\right),\left(21\ \frac{3}{2}\ \frac{-3}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$

$(21\frac{3}{2}\frac{1}{2})$	$(20\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(20\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(20\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\,]/\sqrt{1+(\eta_\alpha^{C_A})^2}$
$(21\frac{3}{2}\frac{1}{2})$	$(20\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(20\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(20\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\,]/\sqrt{1+(\eta_\alpha^{C_A})^2}$
$(21\frac{3}{2}\frac{1}{2})$	$(21\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n+$ $\vec{d}_{C_B}-\vec{d}_{C_A})-(\eta_\alpha^{C_A})^2t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\,]/(1+$ $(\eta_\alpha^{C_A})^2\,)$
$(21\frac{3}{2}\frac{1}{2})$	$(21\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$ $-\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{3}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$ $-\eta_\alpha^{C_A}\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{3}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\,]$ $/\sqrt{1+(\eta_\alpha^{C_A})^2}\sqrt{1+(\eta_\beta^{C_A})^2}$
$(21\frac{3}{2}\frac{1}{2})$	$(21\frac{3}{2}\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{3}{2}\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{3}{2}\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\,]/\sqrt{1+(\eta_\alpha^{C_A})^2}$
$(21\frac{3}{2}\frac{1}{2})$	$(21\frac{3}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n+$ $\vec{d}_{C_B}-\vec{d}_{C_A})+(\eta_\alpha^{C_A})^2t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\,]/(1+$ $(\eta_\alpha^{C_A})^2\,)$

$(21\frac{3}{2}\frac{1}{2})$	$(21\frac{3}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{3}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{3}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$ $+\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$ $+\eta_\alpha^{C_A}\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\ ]$ $/(\sqrt{1+(\eta_\alpha^{C_A})^2}\sqrt{1+(\eta_\beta^{C_A})^2})$
$(21\frac{3}{2}\frac{1}{2})$	$(21\frac{3}{2}-\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{1}{2}),(21\frac{3}{2}\frac{-3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{1}{2}),(21\frac{3}{2}\frac{-3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\alpha^{C_A})^2}$
$(21\frac{3}{2}-\frac{1}{2})$	$(20\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-1}{2}),(20\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{-1}{2}),(20\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\beta^{C_A})^2}$
$(21\frac{3}{2}-\frac{1}{2})$	$(20\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-1}{2}),(20\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{-1}{2}),(20\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})\ ]/\ \sqrt{1+(\eta_\beta^{C_A})^2}$
$(21\frac{3}{2}-\frac{1}{2})$	$(21\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-1}{2}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{-1}{2}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$ $-\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-1}{2}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$ $-\eta_\alpha^{C_A}\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{1}{2}\frac{-1}{2}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})/\ ]$ $/(\sqrt{1+(\eta_\alpha^{C_A})^2}\sqrt{1+(\eta_\beta^{C_A})^2})$
$(21\frac{3}{2}-\frac{1}{2})$	$(21\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-1}{2}),(21\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$

		$\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{1}{2}\frac{-1}{2}\right),\left(21\frac{1}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$ $-\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$ $-\left(\eta_{\beta}^{C_A}\right)^2 t^{C_A C_{Bi}}_{\left(21\frac{1}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)/\ ]$ $/(1+\left(\eta_{\beta}^{C_A}\right)^2)$
$(21\frac{3}{2}-\frac{1}{2})$	$(21\frac{3}{2}\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{3}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)+$ $\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{1}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{3}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)]/\ \sqrt{1+(\eta_{\beta}^{C_A})^2}$
$(21\frac{3}{2}-\frac{1}{2})$	$(21\frac{3}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)+$ $\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{1}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$ $+\eta_{\alpha}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-1}{2}\right),\left(21\frac{1}{2}\frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$ $+\eta_{\alpha}^{C_A}\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{1}{2}\frac{-1}{2}\right),\left(21\frac{1}{2}\frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)/\ ]$ $/(\sqrt{1+\left(\eta_{\alpha}^{C_A}\right)^2}\sqrt{1+\left(\eta_{\beta}^{C_A}\right)^2})$
$(21\frac{3}{2}-\frac{1}{2})$	$(21\frac{3}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)+$ $\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{1}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$ $+\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-1}{2}\right),\left(21\frac{1}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$ $+\left(\eta_{\beta}^{C_A}\right)^2 t^{C_A C_{Bi}}_{\left(21\frac{1}{2}\frac{-1}{2}\right),\left(21\frac{1}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)/\ ]$ $/(1+\left(\eta_{\beta}^{C_A}\right)^2)$
$(21\frac{3}{2}-\frac{1}{2})$	$(21\frac{3}{2}-\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{-3}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)+$ $\eta_{\beta}^{C_A} t^{C_A C_{Bi}}_{\left(21\frac{1}{2}\frac{-1}{2}\right),\left(21\frac{3}{2}\frac{-3}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)]/\ \sqrt{1+(\eta_{\beta}^{C_A})^2}$
$21\frac{3}{2}-\frac{3}{2}$	$(20\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-3}{2}\right),\left(20\frac{1}{2}\frac{1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$
$21\frac{3}{2}-\frac{3}{2}$	$(20\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y} t^{C_A C_{Bi}}_{\left(21\frac{3}{2}\frac{-3}{2}\right),\left(20\frac{1}{2}\frac{-1}{2}\right)}\left(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A}\right)$

$21\frac{3}{2}-\frac{3}{2}$	$(21\frac{1}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})]/\sqrt{1+(\eta_\alpha^{C_A})^2}$
$21\frac{3}{2}-\frac{3}{2}$	$(21\frac{1}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})-$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{3}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})]/\sqrt{1+(\eta_\beta^{C_A})^2}$
$21\frac{3}{2}-\frac{3}{2}$	$(21\frac{3}{2}\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{3}{2}\frac{3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$
$21\frac{3}{2}-\frac{3}{2}$	$(21\frac{3}{2}\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{3}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\alpha^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{1}{2}\frac{1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})]/\sqrt{1+(\eta_\alpha^{C_A})^2}$
$21\frac{3}{2}-\frac{3}{2}$	$(21\frac{3}{2}-\frac{1}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}[t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{3}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})+$ $\eta_\beta^{C_A}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{1}{2}\frac{-1}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})]/\sqrt{1+(\eta_\beta^{C_A})^2}$
$21\frac{3}{2}-\frac{3}{2}$	$(21\frac{3}{2}-\frac{3}{2})$	$e^{-i\frac{eB}{2\hbar}R_xR_y}t^{C_AC_{Bi}}_{(21\frac{3}{2}\frac{-3}{2}),(21\frac{3}{2}\frac{-3}{2})}(\vec{R}_n+\vec{d}_{C_B}-\vec{d}_{C_A})$

5.7 Simultaneous equation for graphene

In this subsection, the simultaneous equations with a finite number of coefficients in graphene are explained. The lattice vector of the honeycomb lattice is given by

$$\vec{R}=n_1\vec{a}_1+n_2\vec{a}_2 \tag{5.14}$$

In Eq. (5.14), n_1 and n_2 are integers and the vectors $\vec{a}_1$ and $\vec{a}_2$ are the primitive vectors of the honeycomb lattice that are defined by Eqs. (5.15) and (5.16) respectively.

$$\vec{a}_1 = \frac{1}{2}a\vec{x} + \frac{\sqrt{3}}{2}a\vec{y} \tag{5.15}$$

$$\vec{a}_2 = -\frac{1}{2}a\vec{x} + \frac{\sqrt{3}}{2}a\vec{y} \tag{5.16}$$

In Eqs. (5.15) and (5.16), a is the lattice constant of graphene, and its value is $24.6\,nm$. In order to define the magnetic first Brillouin zone, we should consider a special set of magnetic translation operators that commute to each other [24]. The magnetic translation operator, $U(\vec{R}_n)$ can be defined as:

$$U(\vec{R}_n) = e^{i\frac{e}{\hbar}BR_{nx}y}T(\vec{R}_n) \tag{5.17}$$

In Eq. (5.17), the operator, $T(\vec{R}_n)$ $(= e^{-i\vec{R}_n\cdot\vec{P}/\hbar})$ is the usual translation operator. It is easily shown that the magnetic translation operator, $U(\vec{R}_n)$ commutes with the Hamiltonian.

$$[H, U(\vec{R}_n)] = 0 \tag{5.18}$$

The multiplication of two magnetic translation operators, $U(\vec{R}_n)$ and $U(\vec{R}_m)$ leads [24]

$$\begin{aligned} U(\vec{R}_n)U(\vec{R}_m) &= e^{i\frac{e}{\hbar}B(R_{mx}R_{ny}-R_{nx}R_{my})}U(\vec{R}_m)U(\vec{R}_n) \\ &= e^{2\pi i\frac{p}{q}(m_1n_2-n_1m_2)}U(\vec{R}_m)U(\vec{R}_n) \end{aligned} \tag{5.19}$$

The special set of the magnetic translation operators is given by

$$\{U(\vec{t}_n)|\vec{t}_n = n_1\vec{a}_1 + n_2q\vec{a}_2\} \tag{5.20}$$

With

$$\vec{t}_n = n_1\vec{a}_1 + n_2q\vec{a}_2 \tag{5.21}$$

In Eq. (5.21), $\vec{a}_1$, $\vec{a}_2$ are the primitive lattice vectors and n_1, n_2 are integers. The set in Eq. (5.20) forms an abelian group. We have

$$U(\vec{t}_n)U(\vec{t}_m) = U(\vec{t}_m)U(\vec{t}_n) \tag{5.22}$$

The eigenfunctions of the Hamiltonian form basis functions of the irreducible representation (IRs) of the symmetry group of the Hamiltonian. Therefore, eigenfunctions $\Phi_k(\vec{r})$ are the basis functions of IRs of the Abelian group Eq. (5.20). We have

$$U(\vec{t}_n)\Phi_k(\vec{r}) = C(\vec{t}_n)\,\Phi_k(\vec{r}) \tag{5.23}$$

In Eq. (5.23), $C(\vec{t}_n)$ is the IR of the Abelian group. A set of translation vectors, $\{\vec{t}_n\}$ which are the subsets of translation vectors $\{\vec{R}_n\}$ and also satisfy the following relations by using Eq (5.18).

$$\mathrm{U}(\vec{t}_n)\mathrm{U}(\vec{t}_{\acute{n}}) = \mathrm{U}(\vec{t}_{\acute{n}})\mathrm{U}(\vec{t}_n) \tag{5.24}$$

Therefore, $\mathrm{U}(\vec{t}_n)$ and $\mathrm{U}(\vec{t}_{\acute{n}})$ commute with each other.

$$\left[\mathrm{U}(\vec{t}_n)\mathrm{U}(\vec{t}_{\acute{n}})\right] = 0 \tag{5.25}$$

Using Eqs. (5.18) and (5.24), it is easily shown that H, $\mathrm{U}(\vec{t}_n), \mathrm{U}(\vec{t}_{n'})$, $\mathrm{U}(\vec{t}_{n''})$, ….. are commutes with each other. This information leads that H, $\mathrm{U}(\vec{t}_n), \mathrm{U}(\vec{t}_{n'})$, $\mathrm{U}(\vec{t}_{n''})$, ….. have the simultaneous eigen function. Let, the simultaneous eigen function, $\Phi(\vec{r})$, then we have

$$H\Phi(\vec{r}) = E\,\Phi(\vec{r} \tag{5.26}$$

$$\mathrm{U}(\vec{t}_n)\,\Phi(\vec{r}) = \mathrm{C}(\vec{t}_n)\,\Phi(\vec{r}) \tag{5.27}$$

Multiplying by $\mathrm{U}(\vec{t}_n)$ from left on both sides in Eq. (5.26), after simplifying

$$\mathrm{H}\left\{\mathrm{U}(\vec{t}_n)\Phi(\vec{r})\right\} = E\left\{\mathrm{U}(\vec{t}_n)\,\Phi(\vec{r})\right\} \tag{5.28}$$

Using Eqs. (5.27) and Eq. (5.28), it is confirmed that the function,$\left\{\mathrm{U}(\vec{t}_n)\Phi(\vec{r})\right\}$ is also eigen function of the Hamiltonian, H. These two eigen functions, $\Phi(\vec{r})$ and $\left\{\mathrm{U}(\vec{t}_n)\Phi(\vec{r})\right\}$ are related to each other by a gauge transformation.

Since, normalization condition, $(\left|\mathrm{C}(\vec{t}_n)\right|^2 = 1)$, we can also write from Eq. (5.27)

$$\mathrm{U}(\vec{t}_n)\,\Phi(\vec{r}) = e^{2\pi i(n_1k_1+qn_2k_2)}\;\Phi(\vec{r}) \tag{5.29}$$

The wave vector, $\vec{k}$

$$\vec{k} = k_1\vec{b}_1 + k_2\vec{b}_2 \tag{5.30}$$

In Eq. (5.30), $\vec{b}_1$, $\vec{b}_2$ are magnetic reciprocal lattice vectors.

Using Eqs. (5.21) and (5.30), we have

$$\vec{k}.\vec{t}_n = 2\pi(k_1n_1 + qk_2n_2) \tag{5.31}$$

Using Eq. (5.29) and (5.31) we have

$$\mathrm{U}(\vec{t}_n)\,\Phi(\vec{r}) = e^{i\vec{k}.\vec{t}_n}\;\Phi(\vec{r}) \tag{5.32}$$

The wave functions, $\left\{\mathrm{U}(\vec{t}_n)\right.$ and $\left.\Phi(\vec{r})\right\}$ are related with each other by a gauge transformation. We can write from Eq. (5.32) in the following fashion by using a gauge transformation.

$$\mathrm{U}(\vec{t}_n)\,\Phi(\vec{r}) = e^{i\frac{e}{\hbar}\chi(\vec{r},\vec{t}_n)}T(\vec{t}_n)\Phi(\vec{r})$$

$$\mathrm{U}(\vec{t}_n)\,\Phi(\vec{r}) = e^{i\frac{e}{\hbar}\chi(\vec{r},\vec{t}_n)}\Phi(\vec{r}-\vec{t}_n)$$

$$\Phi(\vec{r}-\vec{t}_n) = e^{-i\frac{e}{\hbar}\chi(\vec{r},\vec{t}_n)}\mathrm{U}(\vec{t}_n)\,\Phi(\vec{r})$$

$$\Phi(\vec{r}-\vec{t}_n) = e^{-i\frac{e}{\hbar}\chi(\vec{r},\vec{t}_n)}\; e^{i\vec{k}.\vec{t}_n}\;\Phi(\vec{r})$$

$$\Phi(\vec{r}-\vec{t}_n) = e^{i\frac{e}{\hbar}Bt_{nx}y}\; e^{i\vec{k}.\vec{t}_n}\;\Phi(\vec{r}) \qquad (5.33)$$

Eq. (5.33) is regarded as the extension of the Bloch theorem for electrons that are moving in the uniform magnetic field and a periodic potential of the crystal. Eq. (5.33) is known as the magnetic Bloch theorem.

All lattice vectors $\vec{R}_n$ in the crystal can be expressed in terms of special lattice vectors $\vec{t}_n$ as:

$$\vec{R}_n = \vec{t}_n + Ia\hat{e}_y \qquad (5.34)$$

In Eq. (5.34), $I = 0,\ 1,2,\ \ldots\ldots\ q-1$ integers.
Using Eqs. (5.4) and (5.34) we have

$$\Phi_{\vec{K}}(\vec{r}) = \sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1} C_{\vec{K}}^{\xi}\;(\vec{t}_n + Ia\hat{e}_y)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}) \qquad (5.35)$$

Similarly,

$$\Phi_{\vec{K}}(\vec{r}-\vec{t}_m) = \sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1} C_{\vec{K}}^{\xi}\;(\vec{t}_n + Ia\hat{e}_y)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}-\vec{t}_m) \qquad (5.36)$$

Using Eqs. (5.33), (5.35) and (5.36) we have

$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1} C_{\vec{K}}^{\xi}\ (\vec{t}_n + Ia\hat{e}_y)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}-\vec{t}_m) = e^{-i\frac{e}{\hbar}\chi(\vec{r},\vec{t}_n)}\ e^{i\vec{k}.\vec{t}_m}\ \times$$
$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1} C_{\vec{K}}^{\xi}\ (\vec{t}_n + Ia\hat{e}_y)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}) \qquad (5.37)$$

In order to calculate the coefficients, $C_{\vec{k}}^{\xi}(\vec{t}_n + Ia\hat{e}_y)$ from Eq. (5.37), we need to find out the relationship between $\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}-\vec{t}_m)$ and $\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r})$. The wave function, $\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r})$ obeys the Dirac equation.

$$\left[c\vec{\alpha}.\left\{\vec{p}+e\vec{A}(\vec{r})\right\}+\beta mc^2+V_{a_i}(\vec{r}-\vec{t}_n-Ia\hat{e}_y)\right]\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}) =$$
$$= E_{\xi}^{\vec{t}_n+Ia\hat{e}_y}\ \psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}) \qquad (5.38)$$

By changing the variable, $\vec{\acute{r}} = \vec{r} + \vec{t}_m$ and $\vec{p} \to \vec{\acute{p}}$, Eq. (5.38) becomes

$$\left[c\vec{\alpha}.\left\{\vec{\acute{p}}+e\vec{A}(\vec{\acute{r}}-\vec{t}_m)\right\}+\beta mc^2+V_{a_i}(\vec{\acute{r}}-\vec{t}_m-\vec{t}_n-Ia\hat{e}_y)\right]\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{\acute{r}}-\vec{t}_m)$$
$$= E_{\xi}^{\vec{t}_n+Ia\hat{e}_y}\ \psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{\acute{r}}-\vec{t}_m) \qquad (5.39)$$

By using, $\vec{A}(\vec{\acute{r}}-\vec{t}_m) = \vec{A}(\vec{\acute{r}}) + \nabla\chi(\vec{\acute{r}},\vec{t}_m)$ this gauge transformation and changing the variable $\vec{\acute{r}}\ to\ \vec{r}$ and $\vec{\acute{p}}\ to\ \vec{p}$, then Eq. (5.39) becomes

$$\left[c\vec{\alpha}.\left\{\vec{p}+e\vec{A}(\vec{r})+e\nabla\chi(\vec{\acute{r}},\vec{t}_m)\right\}+\beta mc^2+V_{a_i}(\vec{r}-\vec{t}_n-Ia\hat{e}_y-\vec{t}_m)\right]$$
$$\times\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}-\vec{t}_m) = E_{\xi}^{\vec{t}_n+Ia\hat{e}_y}\ \psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}-\vec{t}_m) \qquad (5.40)$$

Now, considering the wave function $\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y+\vec{t}_m}(\vec{r})$ obeys the Dirac equation.

$$\left[c\vec{\alpha}.\left\{\vec{p}+e\vec{A}(\vec{r})\right\}+\beta mc^2+V_{a_i}\left(\vec{r}-\vec{t}_n-Ia\hat{e}_y-\vec{t}_m\right)\right]\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y+\vec{t}_m}(\vec{r})$$
$$=E_{\xi}^{\vec{t}_n+Ia\hat{e}_y+\vec{t}_m}\,\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y+\vec{t}_m}(\vec{r}) \tag{5.41}$$

By comparing Eqs. (5.38) and (5.39), $\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}-\vec{t}_m)$ and $\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y+\vec{t}_m}(\vec{r})$ are related with each other by a gauge transformation.

$$\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}\left(\vec{r}-\vec{t}_m\right)=e^{-i\frac{e}{\hbar}\chi(\vec{r},\vec{t}_m)}\,\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y+\vec{t}_m}(\vec{r}) \tag{5.42}$$

Substituting Eq. (5.42) into Eq. (5.3) we have

$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1}C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)e^{-i\frac{e}{\hbar}\chi(\vec{r},\vec{t}_m)}\,\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y+\vec{t}_m}(\vec{r})=e^{-i\frac{e}{\hbar}\chi(\vec{r},\vec{t}_n)}\,e^{i\vec{k}.\vec{t}_m}\times$$
$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1}C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}) \tag{5.43}$$

Canceling this term $e^{-i\frac{e}{\hbar}\chi(\vec{r},\vec{t}_m)}$ from both sides in Eq. (5.43), then we have

$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1}C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y+\vec{t}_m}(\vec{r})=e^{i\vec{k}.\vec{t}_m}\times$$
$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1}C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}) \tag{5.44}$$

By changing the variable, $\vec{t}_n+\vec{t}_m=\vec{t}_l$ in Eq. (5.44), we have

$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1}C_{\vec{K}}^{\xi}\left(\vec{t}_l-\vec{t}_m+Ia\hat{e}_y\right)\psi_{\xi}^{a_{i,}\,\vec{t}_l+Ia\hat{e}_y}(\vec{r})=e^{i\vec{k}.\vec{t}_m}\times$$
$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1}C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}) \tag{5.45}$$

Again, by changing the variable, $\vec{t}_l\ to\ \vec{t}_n$ in Eq. (5.44), we have

$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1} C_{\vec{K}}^{\xi}\left(\vec{t}_n-\vec{t}_m+Ia\hat{e}_y\right)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r}) = e^{i\vec{k}.\vec{t}_m}\times$$

$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1} C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r})$$

$$\sum_{\vec{t}_n}\sum_{\xi}\sum_{I=0}^{q-1}\{C_{\vec{K}}^{\xi}\left(\vec{t}_n-\vec{t}_m+Ia\hat{e}_y\right)-C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)e^{i\vec{k}.\vec{t}_m}\}\psi_{\xi}^{a_{i,}\,\vec{t}_n+Ia\hat{e}_y}(\vec{r})=0 \tag{5.46}$$

Multiplying by $\psi_{\xi}^{a_{i,}\,\vec{t}_k+Ia\hat{e}_y}(\vec{r})$ on the both side in Eq. (5.46) and integrating, we have

$$C_{\vec{K}}^{\xi}\left(\vec{t}_n-\vec{t}_m+Ia\hat{e}_y\right)=C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)e^{i\vec{k}.\vec{t}_m} \tag{5.47}$$

Now replacing by $\vec{t}_n-\vec{t}_m=\vec{t}_l$ in Eq. (5.47), then we have

$$C_{\vec{K}}^{\xi}\left(\vec{t}_l+Ia\hat{e}_y\right)=C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)e^{i\vec{k}.(\vec{t}_n-\vec{t}_l)} \tag{5.48}$$

If $\vec{t}_n=0$ in Eq. (5.48), then we have

$$C_{\vec{K}}^{\xi}\left(\vec{t}_l+Ia\hat{e}_y\right)=C_{\vec{K}}^{\xi}\left(Ia\hat{e}_y\right)e^{-i\vec{k}.\vec{t}_l} \tag{5.49}$$

Finally, by changing the variable, $\vec{t}_l\ to\ \vec{t}_n$ in Eq. (5.45), then we get

$$C_{\vec{K}}^{\xi}\left(\vec{t}_n+Ia\hat{e}_y\right)=C_{\vec{K}}^{\xi}\left(Ia\hat{e}_y\right)e^{-i\vec{k}.\vec{t}_n} \tag{5.50}$$

$$C_{\vec{K}}^{\xi}\left(\vec{t}_n+I\vec{a}_2\right)=e^{-i\vec{k}.\vec{t}_n}C_{\vec{K}}^{\xi}\left(I\vec{a}_2\right) \tag{5.51}$$

From Eq. (5.51), it is noticeable that all lattice vectors, $\vec{R}_n$ can be also expressed as:

$$\vec{t}_n + I\vec{a}_2 = (n_1 q + I)a\hat{e}_x + n_2 a\hat{e}_y \tag{5.52}$$

In Eq. (5.52), means that all coefficients $C_{\vec{K}}^{\xi}\left(\vec{t}_n + I\vec{a}_2\right)$ can be obtained by using Eq. (5.51), then we can get q coefficients $\left\{C_{\vec{K}}^{\xi}(I\vec{a}_2)\middle| I = 0,1,2, \quad \ldots\ldots\ldots\ q-1\right\}$.

By replacing $\vec{R}_m$ with $\vec{t}_m + \acute{I}\vec{a}_2$ ($\acute{I} = 0,1,2, \quad \ldots\ldots\ldots\ q-1$).

$$C_{\vec{K}}^{\xi}\left(\vec{t}_m + \acute{I}\vec{a}_2\right) = e^{-i\vec{k}.\vec{t}_m} C_{\vec{K}}^{\xi}\left(\acute{I}\vec{a}_2\right) \tag{5.53}$$

We know,

$$\begin{aligned}\{\bar{\varepsilon}_{\acute{n}\acute{l}\acute{j}}^{a_j} + \Delta\bar{\varepsilon}_{\acute{n}\acute{l}\acute{j}\acute{M}}^{a_j,\vec{d}_j} + \frac{eB}{2m}\left(\frac{2\acute{j}+1}{2\acute{l}+1}\right)\hbar\acute{M}\} C_{\vec{k}}^{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{R}_m + \vec{d}_j) + \ \sum_{nlJM}\sum_w \times \\ e^{-i\frac{eB}{2\hbar}(R_{nx}+d_{ix}-R_{mx}-d_{jx})(R_{ny}+d_{iy}+R_{my}+d_{jy})} t_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}^{a_j a_i}(\vec{T}_w(\vec{d}_j)) \\ \times C_{\vec{k}}^{nlJM}(\vec{T}_w(\vec{d}_j) + \vec{R}_m + \vec{d}_j) = E_{\vec{k}} C_{\vec{k}}^{\acute{n}\acute{l}\acute{j}\acute{M}}(\vec{R}_m + \vec{d}_j)\end{aligned} \tag{5.54}$$

Using Eq. (5.53) and Eq. (5.54), we have

$$\begin{aligned}\bar{\varepsilon}_{\acute{n}\acute{l}\acute{j}} + \nabla\bar{\varepsilon}_{\acute{n}\acute{l}\acute{j}\acute{M}} + \frac{eB}{2m}\left(\frac{2\acute{j}+1}{2\acute{l}+1}\right)\hbar\acute{M}\} C_{\vec{k}}^{\acute{n}\acute{l}\acute{j}\acute{M}}(\acute{I}\vec{a}_2) + \ \sum_{nlJM}\sum_w e^{-i\frac{eB}{2\hbar}\vec{T}_{wx}(\vec{d}_j)(\vec{T}_{wy}+2\acute{I}\vec{a}_2)} \\ \times t_{\acute{n}\acute{l}\acute{j}\acute{M},nlJM}(\vec{T}_w) C_{\vec{k}}^{nlJM}(\vec{T}_w + \acute{I}\vec{a}_2) = E_{\vec{k}} C_{\vec{k}}^{\acute{n}\acute{l}\acute{j}\acute{M}}\left(\acute{I}\vec{a}_2\right)\end{aligned} \tag{5.55}$$

Since the vector $\vec{T}_w + \acute{I}\vec{a}_2$ is generally rewritten in the form of $\vec{t}_{n``} + I``\vec{a}_2$, the coefficients, $C_{\vec{k}}^{nlJM}(\vec{T}_w + \acute{I}\vec{a}_2)$ of the LHS in Eq. (5.52) can be rewritten as

$$C_{\vec{k}}^{nlJM}\left(\vec{T}_w + \acute{I}\vec{a}_2\right) = e^{-i\vec{k}.\vec{t}_{n``}} C_{\vec{k}}^{nlJM}\ (I``\vec{a}_2) \tag{5.56}$$

Eq. (5.55) is the simultaneous equations with a finite number of coefficients $C_{\vec{k}}^{nlJM}\left(\acute{I}\vec{a}_2\right)\middle|\acute{I} = 0,1,2, \ \ldots..q-1\ \big)$.

Chapter 6

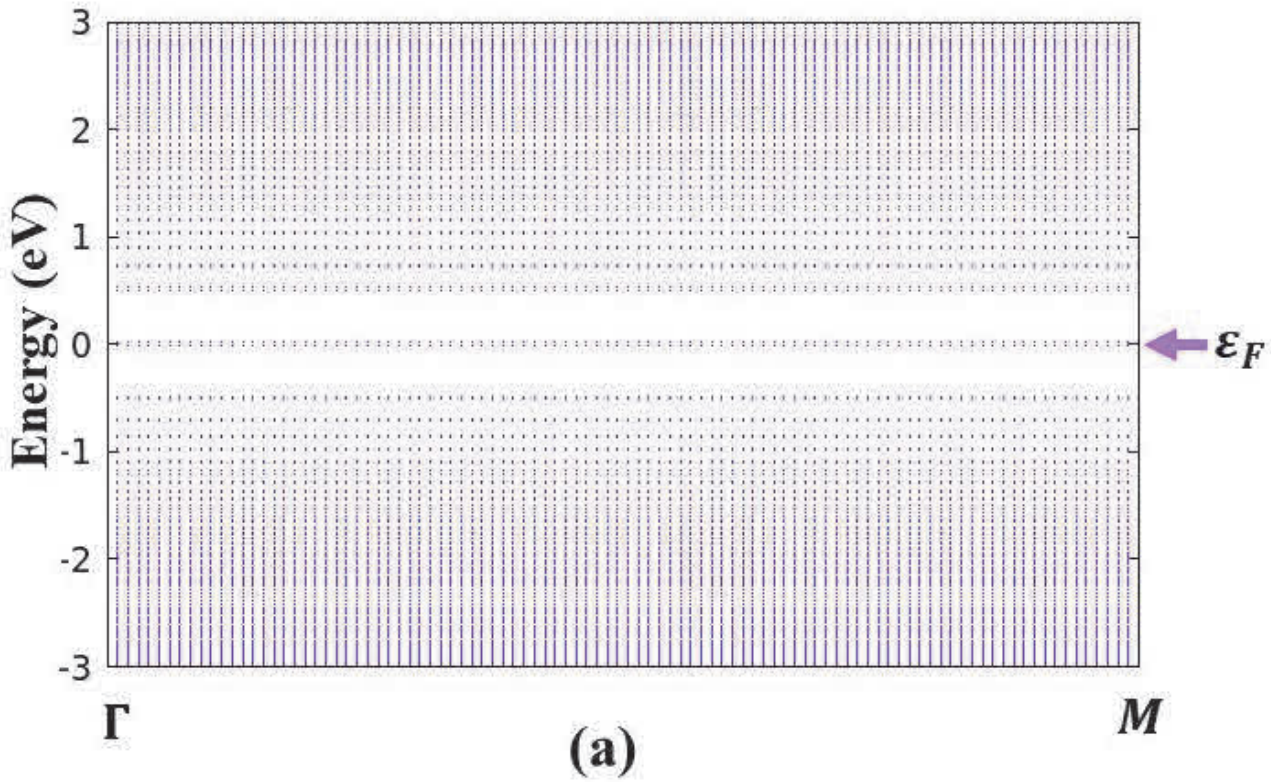
Results and Discussions

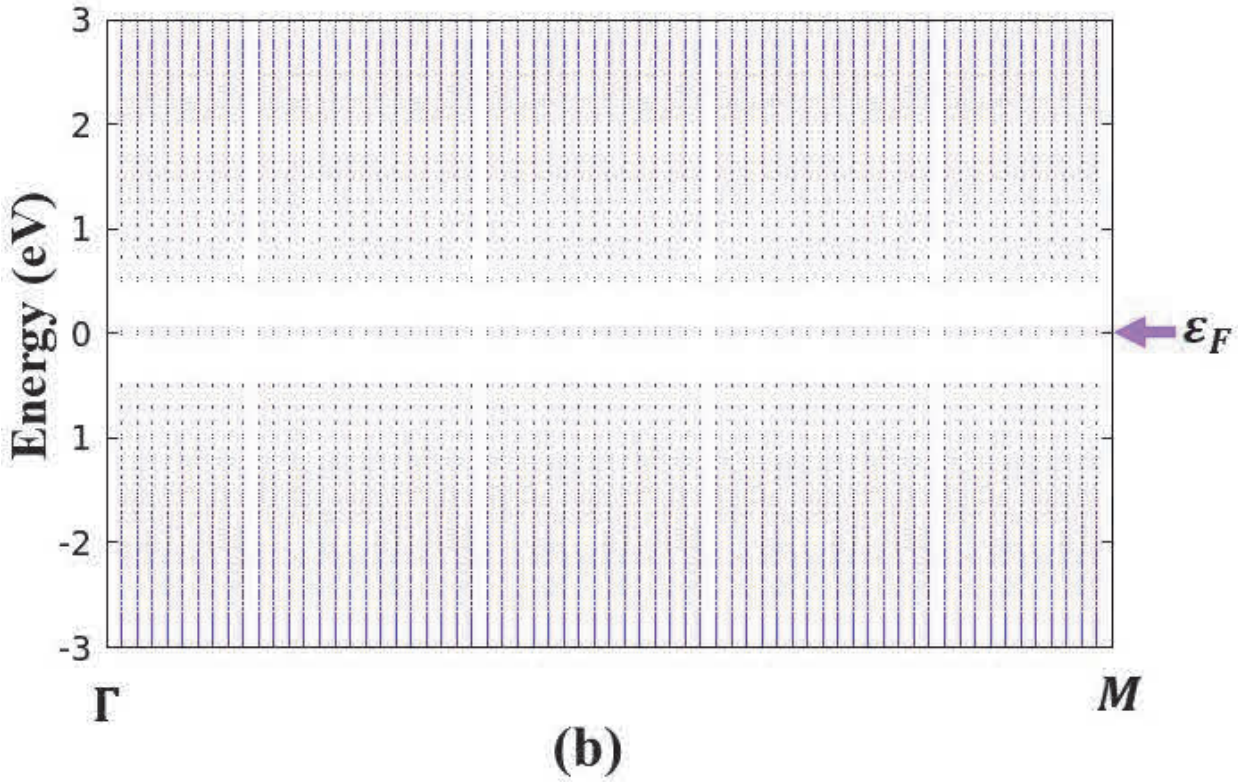
In this Chapter, the results and discussions using the Nonperturbative MFRTB method are described in the following sequence:

6.1 Magnetic energy band structure of graphene
6.2 Magnetic-field dependence of energy levels
6.3 Quantized Hall conductivity using nonperturbative MFRTB method
6.4 Fermi energy dependence of widths of WPs plateaus
6.5 Magnetic field dependence of widths of NPs plateaus
6.6 Description of the quantized Hall conductivity based on the magnetic energy band structure

6.1 Magnetic energy band structure of graphene

In this subsection, the magnetic Bloch band structure of graphene in the presence of a magnetic field that is calculated using the nonperturbative MFRTB method is discussed briefly. Figures 2(a) and 2(b) show the magnetic Bloch energy band structure of B =200.5 (T), where p/q takes the value 1/787 and $B^{'}$=200.9 (T), where p/q takes the value 2/1571 respectively. The main reason for considering of these two close magnetic fields for the investigation of the degeneracy of a magnetic energy band structure of graphene immersed in the respective magnetic field (Eq. (5.1) in Chapter 5). In Figure 2, the horizontal axis represents the wave vector lying in the Magnetic Brillouin Zone (MBZ) shown in Figure.1, and the vertical axis represents the energy in electron volts (eV). From the numerical calculation using the nonperturbative MFRTB method, it is clear that the magnetic energy band structure of graphene immersed in the magnetic field is almost independent of k_x and k_y in the MBZ.





Figures. 2: Magnetic Bloch flat energy bands for **(a)** B=200.5 (T) and **(b)** $B^{'}$=200.9 (T) in the MBZ. The arrow indicates the position of ε_F level for the intrinsic graphene [45].

The discussion of the magnetic energy band structure of graphene immersed in a magnetic field which is presented in Figures 2 in order to investigate the quantized σ_{Hall} based on the magnetic energy band structure. The cluster of the nearly flat magnetic energy bands of graphene immersed in a magnetic field is discussed [56] that are corresponding to the Landau levels due to the energy level splitting in the magnetic field. These Landau levels are attributed due to Onsager's area quantization rule of the orbit of an electron in a magnetic field. The calculation using the nonperturbative MFRTB method is more realistic because the nonperturbative MFRTB method is based on the Dirac equation for the Dirac fermions or electrons (Dirac particles), where these Dirac particles are moving in both a uniform magnetic field and the periodic potential of the crystal. So, the spin-orbit interaction and spin Zeeman effect are inherently included in this calculation using

the nonperturbative MFRTB method. For this reason, each almost flat magnetic energy band splits into two energy bands due to the spin-orbit interaction and the spin Zeeman effect.

In this work, in order to explain the magnetic energy band structure, the degeneracy of the magnetic energy band is discussed briefly by two approximations in the following.

Firstly, for the explanation of the magnetic energy band, a nearly flat band is a completely flat approximation is considered that are shown in Figures 2. It is noted that each eigenvalue corresponding eigenfunction at Γ point is $N_{\vec{k}}$-fold degenerate in the magnetic energy band, where $N_{\vec{k}}$ denotes the number of $\vec{k}$ points in the MBZ of graphene. If the area of the usual unit cell in the absence of a magnetic field is denoted by A_{unit} and if the total number of unit cells contained in the system is denoted by *N*, then the total area of the system is given by $A = A_{unit}\ N$. Because the area of the magnetic unit cell is q-times larger than the area of the usual unit cell in the absence of a magnetic field [24, 51,52], then the total number of magnetic unit cells in the system is given by N/q. The total number of the $\vec{k}$-points in the MBZ, $N_{\vec{k}}$ is equal to the total number of magnetic unit cells [52]. Consequently, under the completely flat approximation, each eigenvalue corresponding eigenfunction at Γ point is N/q-fold degenerate.

Secondly, the magnetic energy band structure for the two close magnetic fields, B and B', are considered (Eq. (5.1) in Chapter 5) for the explanation of the magnetic energy band. Let us consider, that the two magnetic fields B and B' are proportional to values of p/q and $1/q'$, respectively, where q' is also a prime integer. The relationship of $B \approx B'$ for the two close magnetic fields, this implies that q is nearly equal to pq'. According to this relationship, $q \approx pq'$, the period in the real space for the case of B is p times larger than that for the case of B'. If the difference of the Hamiltonian for these two magnetic fields cases is treated as the perturbation potential, and if the Hamiltonian for the case of B' corresponds to the nonperturbative Hamiltonian, then the perturbation potential would be small owing to the relationship $B \approx B'$. This small perturbation potential for these two close magnetic fields makes the periodicity p times longer than that for the nonperturbative system because of this relationship $q \approx pq'$. For the change of the periodicity without considering the small shift in energy due to the small perturbation potential,

the magnetic energy bands for the case of B can be obtained by p-times folding of the magnetic energy bands for the case of B' within the MBZ of the nonperturbative system. Therefore, these two close magnetic fields approximation leads only the change in periodicity without considering the small shift in energy caused by the small perturbation potential. Considering these two close magnetic fields approximation, this the flatness of the magnetic energy bands means the p-times folding in an energy band with p-fold degeneracy. This p-fold degeneracy was confirmed by actual calculations using the nonperturbative MFRTB method that are shown in Figures 2(a) and 2(b) for the case of $B \approx B'$ respectively. From these Figures, it is confirmed that the degeneracy of the magnetic energy band for B' field where p/q takes value of 2/1571 is twice that of the magnetic energy band for B field where 1/q takes value of 1/787. So, the eigenvalue around 0 (eV) at Γ point is 4-fold degeneracy for $1/q' = 1/787$ which is shown in Figure. 2(a), and 8-fold degeneracy for $p/q = 2/1571$ which is shown in Figure. 2(b). According to the above discussion, it is confirmed that the degeneracy of the magnetic energy band is Np/q-fold degenerate.

It is noted that another degeneracy was found except for the above-mentioned degeneracy from the calculated magnetic energy band using the nonperturbative MFRTB method. This degeneracy of the magnetic energy band is a multiple of four. In these calculations, this degeneracy appears due to the two reasons. First, each unit cell of graphene in a honeycomb structure consists of two carbon atoms. For this reason, the number, twice is utilized of bases to expand the magnetic Bloch function [24, 51,52]. This number leads to two-fold degeneracy in the magnetic energy band. Second, Dirac points exist at two inequivalent points, namely the K and K' points, in the BZ. These inequivalent two points lead to another 2-fold degeneracy. Consequently, the degeneracy of the magnetic energy band of graphene becomes a multiple of four. Finally, the degeneracy of the magnetic energy band, $g(B)$, for graphene is given by

$$g(B) = \frac{4Np}{q} \tag{6.1}$$

Since the area of the system is denoted by A, then the number of unit cell in the system is given by $N = A/A_{unit}$. Therefore, we have the degeneracy of the magnetic energy band

$$g(B) = 4\,\frac{A}{A_{unit}}\frac{p}{q} \tag{6.2}$$

Using Eq. (5.1) in chapter 5, Eq. (6.2) can be rewritten as follows:

$$g(B) = \frac{2eA\,B}{h} \tag{6.3}$$

Eq. (6.3) corresponds to the conventional degeneracy of the Landau level given in the literature [54]. From Eq. (6.3), the important point is that $g(B)$ is proportional to the magnetic field. This relation provides the magnetic field dependence Bloch energy band structure in graphene.

6.2 Magnetic-field dependence of energy levels

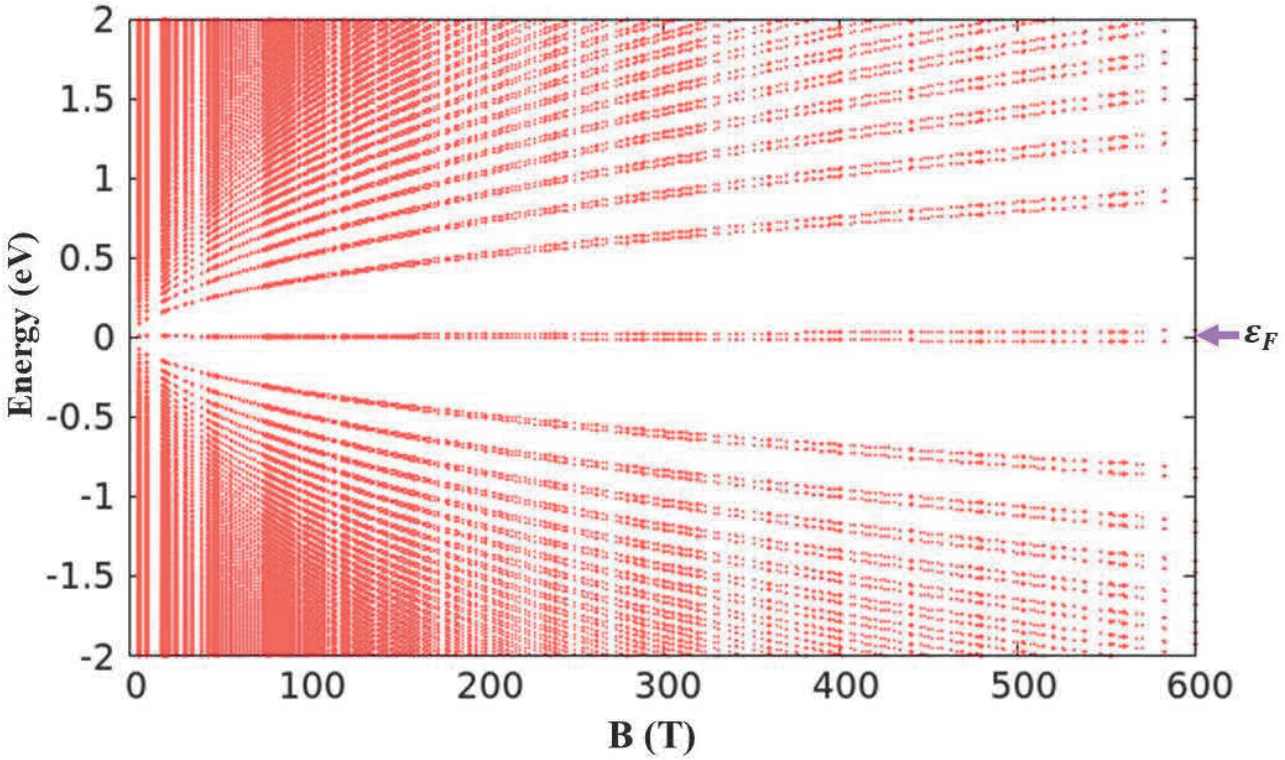


Figure. 3: Magnetic field vs energy of the magnetic energy spectrum of the Bloch electrons (Hofstadter butterfly diagram) at Γ point in the MBZ calculated by using the nonperturbative MFRTB method [45].

Figure 3 shows the magnetic energy spectrum of electrons in graphene with a magnetic-field at the Γ point using the nonperturbative MFRTB method. This magnetic field dependence energy

spectrum is well known as the Hofstadter butterfly diagram [46]. It is noted that the Figure 4 shows a magnified view of Figure. 3. In Figures. 3 and 4, the horizontal axis denotes the magnetic field (B) in Tesla (T) and the vertical axis denotes the energy in eV. It is well discussed in the literature that the magnetic energy spectrum of graphene is proportional to the square root of the magnitude of the magnetic field at low magnetic fields regions [11,12].

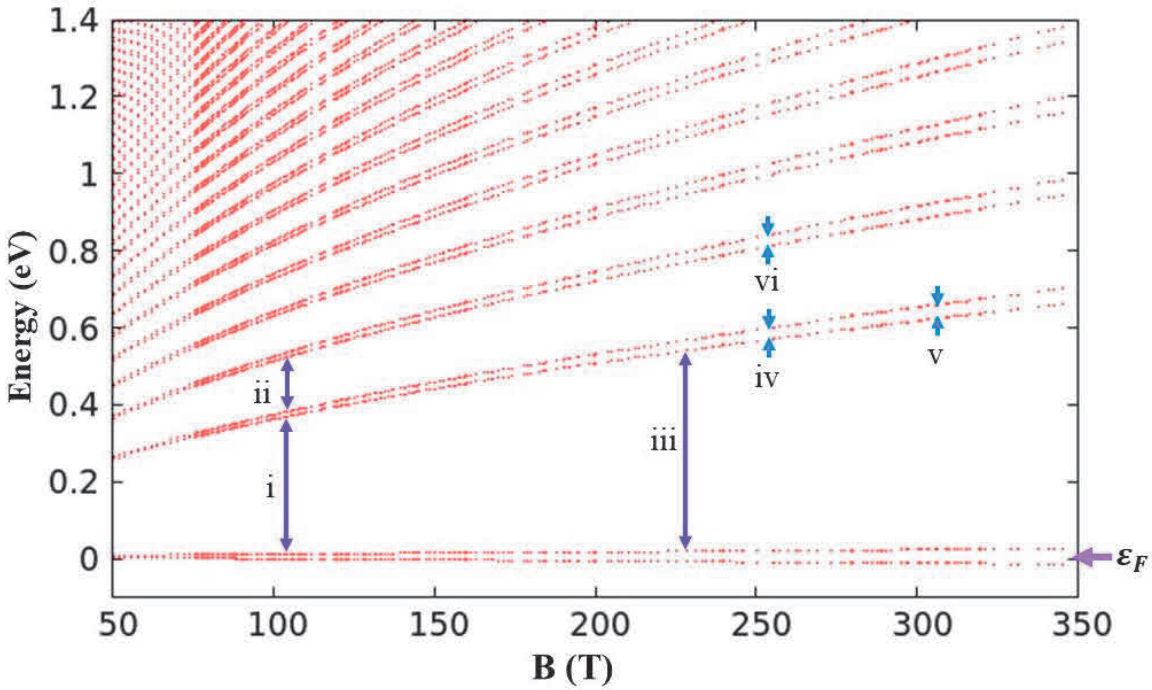


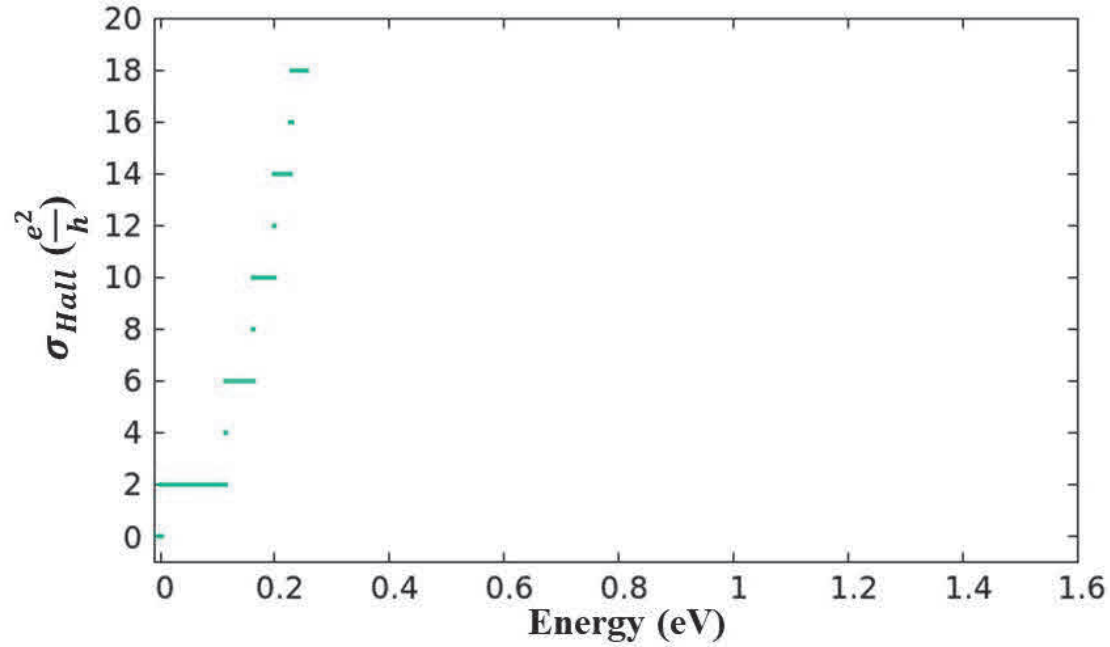
Figure. 4: Magnified view of Fig. 3 for the magnetic energy spectrum of the Bloch electrons [45].

According to the Onsager's area quantization rule, the behavior of the square root of the magnetic field was first predicted by McClure [11,12] The nonperturbative MFRTB method for the calculation of magnetic field dependence energy spectrum can revisit the square-root behavior [24] that is shown in Figure. 3. According to Figure. 4, each quantized energy level of graphene is immersed in a uniform magnetic field split into two energy levels due to the relativistic effects, including the spin-Zeeman effect and spin-orbit interaction. For this reason, there are two types of energy level splitting in the magnetic-field-dependence energy spectrum in graphene. The first type splitting a relatively large gap in the energy spectrum which is related to the Onsager's area quantization rule of the electron orbit that are indicated by (i), (ii), and (iii) in Figure. 4. The other type of splitting energy level relatively narrow gap in the energy spectrum which is related to the

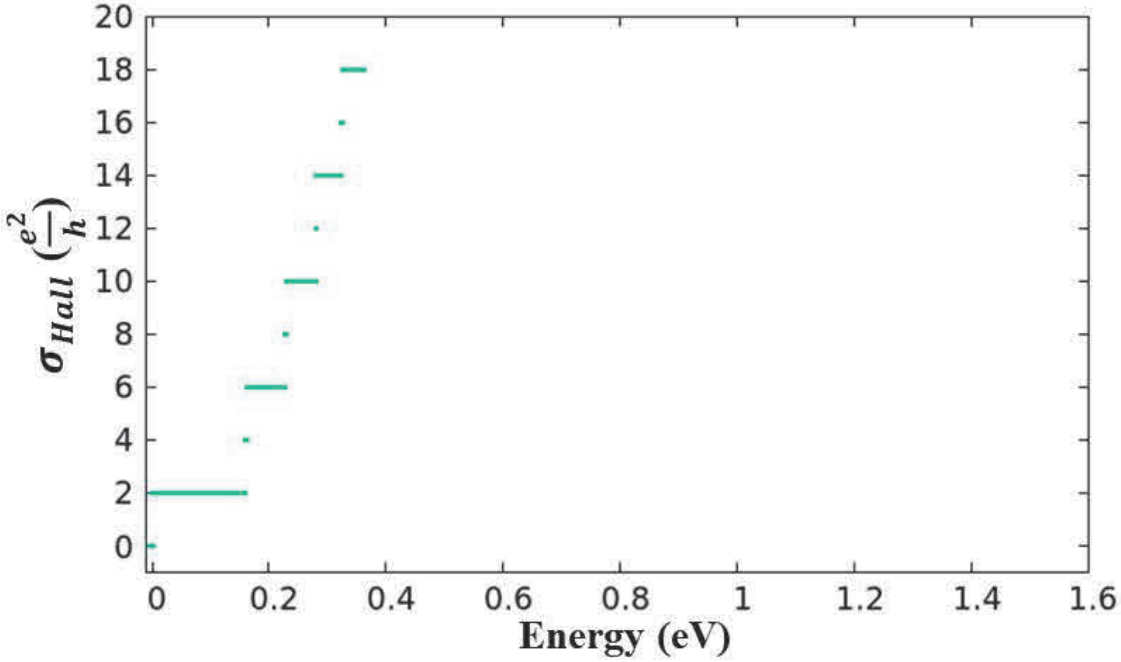
relativistic effects that mean the spin-Zeeman effect and spin-orbit interaction that are indicated by (iv), (v), and (vi) in Figure. 4. The first type energy level splitting gap decreases with the Fermi energy level for a constant magnetic field that are shown at (i) and (ii) and increases with the magnetic field that are shown at (i) and (iii) in Figure. 4. The other type of energy level splitting gap decreases with the Fermi energy level for a constant magnetic field that are shown at (iv) and (vi) and increases with the magnetic field that are shown at (iv) and (v) in Figure. 4. These two types of energy level splitting are the origins of corresponding observed plateaus that means the wide and narrow plateaus attributed for the large energy gap and small energy gap respectively that lead the Fermi energy dependence of the quantized σ_{Hall} in graphene immersed in a uniform magnetic field.

6.3 Quantized Hall conductivity using nonperturbative MFRTB method

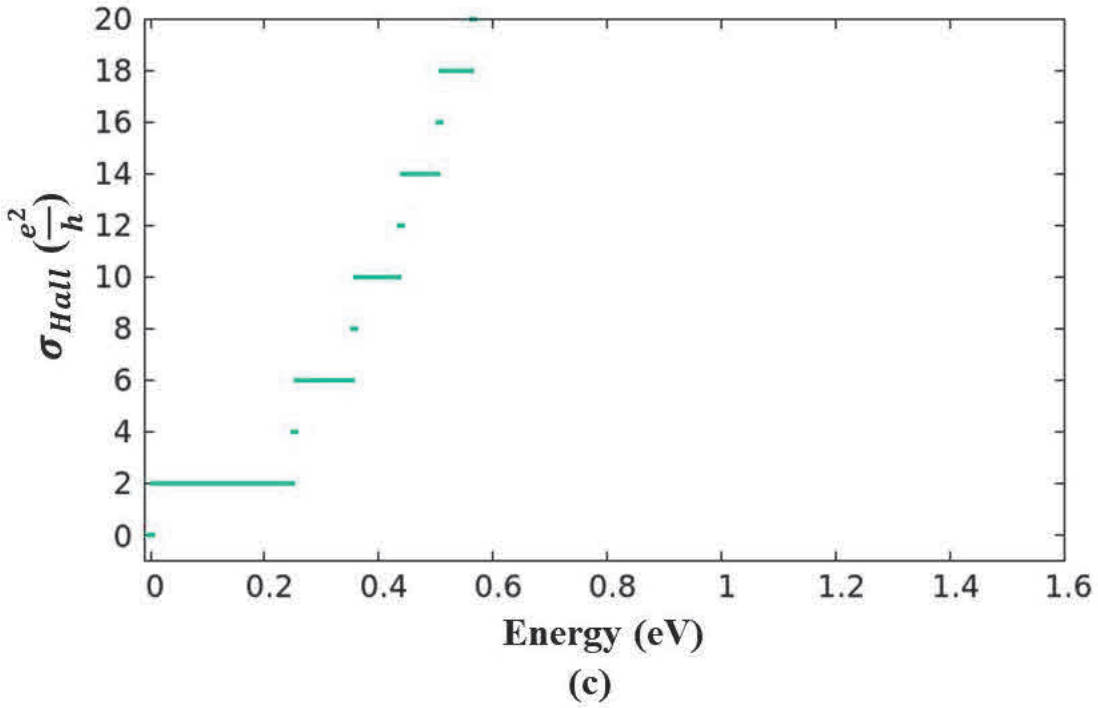
Figures 5(a)–5(f) show the Fermi energy dependence of σ_{Hall} in graphene for (a) $B = 10.00$ (T), (b) $B = 20.02$ (T), (c) $B = 48.50$ (T), (d) $B = 101.50$(T), (e) $B = 239.50$ (T), and (f) $B = 600.50$ (T), respectively. The quantized σ_{Hall} in graphene immersed in a uniform magnetized field based on the magnetic energy band spectrum is calculated using the Streda formula that is discussed in Chapter 4 [50]. According to these Figures 5(a)–5(f), there are two types of plateaus are observed due to the respective energy splitting gap. It is noted that the widths of the attributed plateaus shown in Figures 5(a)–5(f) are consistent with the energy splitting that are shown in Figure. 4. It is clearly shown in Figures 5(a)–5(f) that one set of these plateaus has a comparatively wide width, with FFs of $2, 6, 10, 14$ etc. due to the large energy splitting gap in the magnetic energy band structure. The other set of these plateaus is also shown in figures 5(a)–5(f) has a comparatively narrow width, with FFs of $0, 4, 8, 12$ etc due to the small energy splitting gap. According to the Figures. 5(a)–5(f), the WPs that are corresponded to the energy splitting for the Onsager's area-quantization rule and the NPs that are corresponded to the energy splitting caused by relativistic effects including Zeeman spin effect and spin-orbit interaction. For this reason, the magnetic energy band structure can effectively explain the quantized σ_{Hall} in graphene immersed in a uniform magnetic field.


20
18
16
14
12
10
8
6
4
2
0
$\sigma_{Hall}\left(\frac{e^2}{h}\right)$
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Energy (eV)

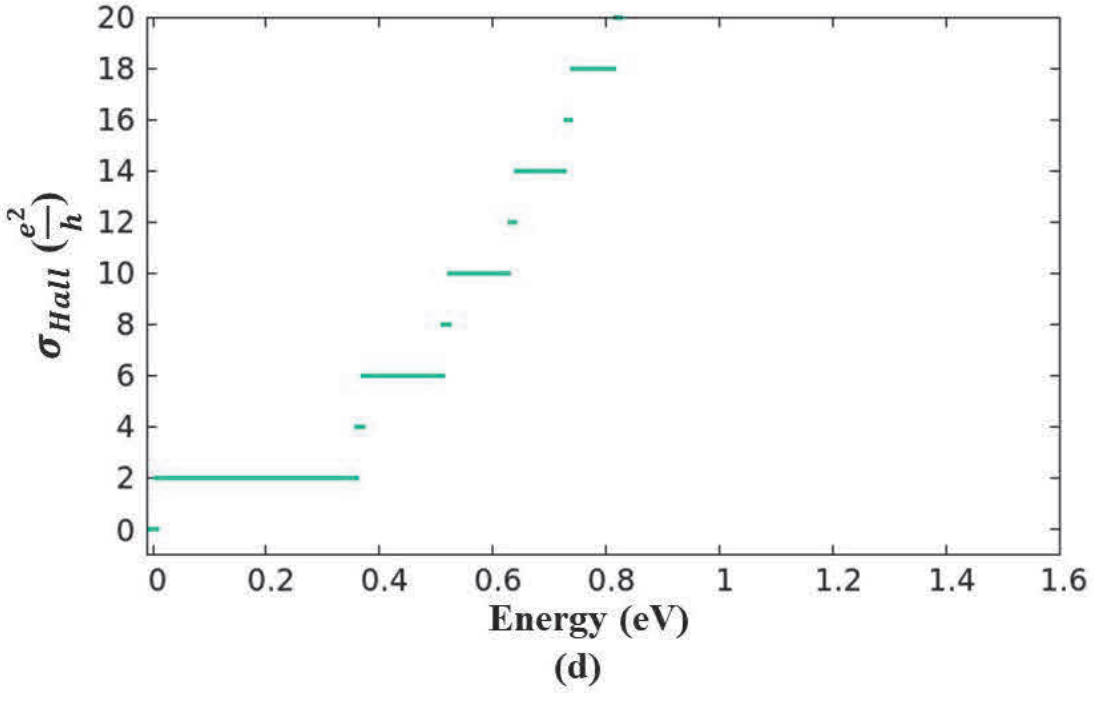
(a)


20
18
16
14
12
10
8
6
4
2
0
$\sigma_{Hall}\left(\frac{e^2}{h}\right)$
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Energy (eV)

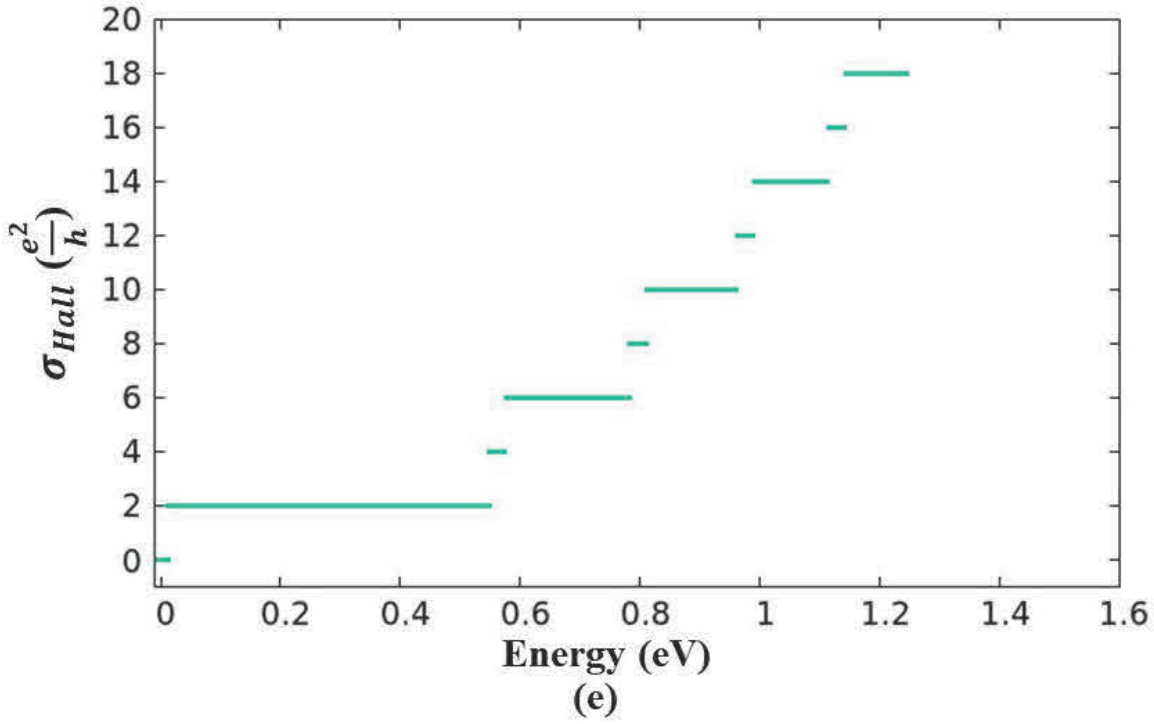
(b)


20
18
16
14
12
10
8
6
4
2
0
$\sigma_{Hall}\left(\frac{e^2}{h}\right)$
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Energy (eV)

(c)


20
18
16
14
12
10
8
6
4
2
0
$\sigma_{Hall}\left(\frac{e^2}{h}\right)$
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Energy (eV)

(d)



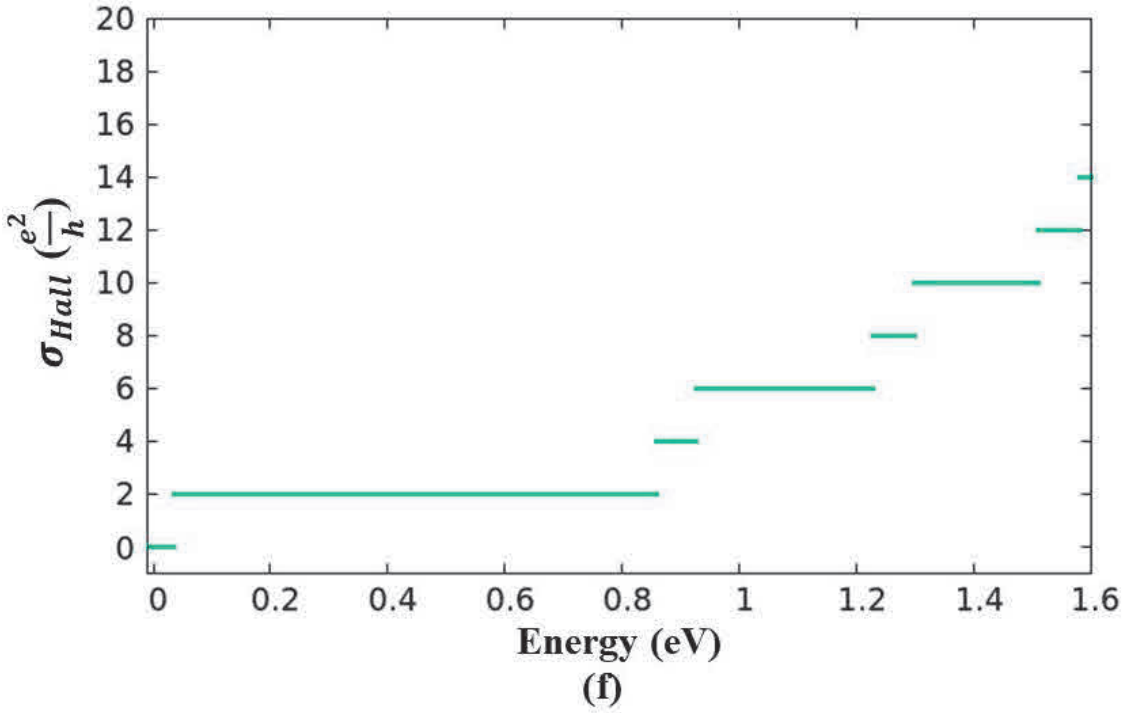


Figure. 5: Fermi energy dependence of the normalized Hall conductivity ($\sigma_{Hall}(e^2/h)$) (a) for 10.00 (T), (b) for 20.02 (T), (c) for 48.50 (T) (d) for 101.50 (T), (e) for 239.50 (T) and (f) for 600.50 (T) [45].

6.4 Fermi energy dependence of widths of WPs plateaus

In this subsection, the Fermi energy dependence of the widths of the observed plateaus using the nonperturbative MFRTB method is discussed. The WPs are attributed due to the energy level splitting that is related to the Onsager's area quantization rule. Figure 6 shows the Fermi energy dependence of the width of WPs. In Figure. 6, the horizontal axis denotes the FFs which means on the position Fermi energy level and the vertical axis denotes the widths of the WPs in eV. According to Figure. 6, the width of WPs decreases with increasing FFs that means with increasing Fermi energy. It is noted that in the conventional 2DEG system, the energy separation of two successive quantized energy levels caused by Onsager's area quantization rule is the same for all energy levels (for the whole energy region) but in graphene, the energy separation of two successive quantized energy levels caused by Onsager's area quantization rule is not the same for all energy levels (for the whole energy region). For this aim, the energy separation of two successive quantized energy levels using Onsager's area quantization rule is calculated in order to justify the above two statements. According to the area quantization rule, the quantized energy level for a magnetic field is given by $E_n = \sqrt{2ev_F^2\hbar|n|B}$, where n denotes the Landau level index, and v_F $(= 1.0 \times 10^6\ m/s)$ is the Fermi velocity of graphene [11,12]. The energy difference between two successive energy levels is given by

$$\Delta E_n = \sqrt{2ev_F^2\hbar B}\left(\sqrt{|n|+1} - \sqrt{|n|}\right) \tag{6.4}$$

In Eq. (6.4), ΔE_n represents the width of WPs for the energy gap due to the two successive energy levels. The width of WPs is calculated by using conventional model using Eq. (6.4) and the nonperturbative MFRTB method that are shown in Figure. 6. According to the Figure. 6, the width of WPs which is calculated using Eq. (6.4), has a good agreement with the result of using the nonperturbative MFRTB method in the lower FF region which means the low-energy region. This implies that the conventional model (Eq. (6.4)) is a good approximation in the low-energy region. The conventional model (Eq. (6.4)) is established based on the Onsager's area quantization rule; more clearly for the linear energy–dispersion relationship at zero magnetic field. The linear

energy–dispersion relationship at zero magnetic field in graphene is valid only in the low energy region which means near the Dirac point. This good agreement suggests that these treatments are valid in the low-energy region, that is, in the lower-FF region. On the other hand, a discrepancy appears in the higher-FF region, that is, in the higher-energy region. The linear energy–dispersion relationship at zero magnetic field in graphene is not valid in the high energy region that means far away from the Dirac point. This discrepancy would be expected that the linear energy–dispersion relationship becomes less appropriate as the energy level moves away from the Dirac point which means in the high energy region. Because in the energy band structure in the absence of a magnetic field, the curvature of the energy dispersion becomes negative as the energy level moves away from the Dirac point. For this reason, the density of the quantized energy levels is different compared with low and high-energy region. As a result, the density of the quantized energy levels that satisfy Onsager's area quantization rule increases with increasing energy range or FFs. Therefore, the width of WPs decreases with increasing FF or energy range.

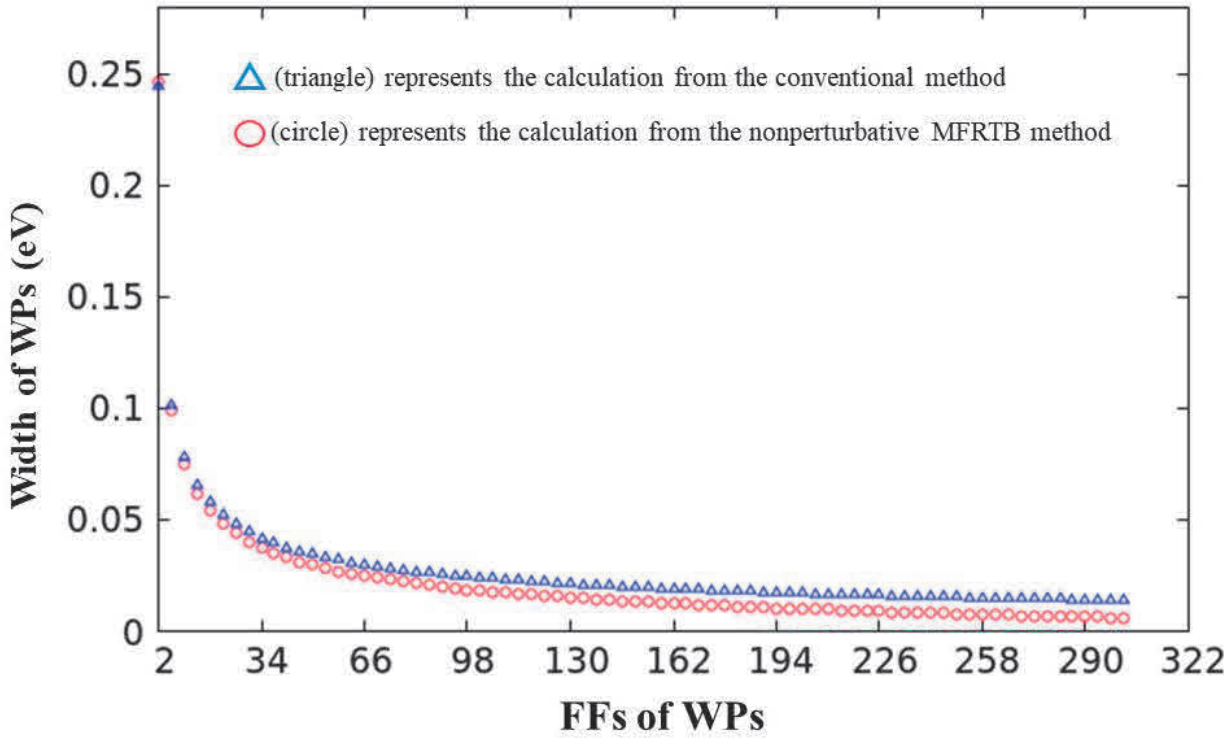


Figure. 6: Filling factor dependence width of WPs for 48.50 (T) [45].

6.5 Magnetic field dependence of widths of NPs plateaus

Figure 7 shows the magnetic-field dependence of the width of NPs for FF=4. In Figure. 7, the horizontal axis denotes the magnetic field in Tesla (T) and the vertical axis denotes the widths of the NPs in eV. The well-known spin-Zeeman energy ($2\mu_B B$) that represents the width of the NP is also indicated in this Figure by a line which is expected. It is noted that this expected width of the NPs is discussed in literature only due to the spin-Zeeman effect (conventional model). On the other hand, it is confirmed that the width of the NPs using the nonperturbative MFRTB method is attributed due to the spin-Zeeman effect and spin-orbit interaction. The difference between the calculation of the conventional model and the nonperturbative MFRTB method is denoted by Δ. This difference, Δ may be regarded by the effect of the spin-orbit interaction. If the spin-orbit interaction is neglected, the NPs are attributed only due to the spin Zeeman effect. So, the width of NPs coincides with the width expected from the spin-Zeeman effect.

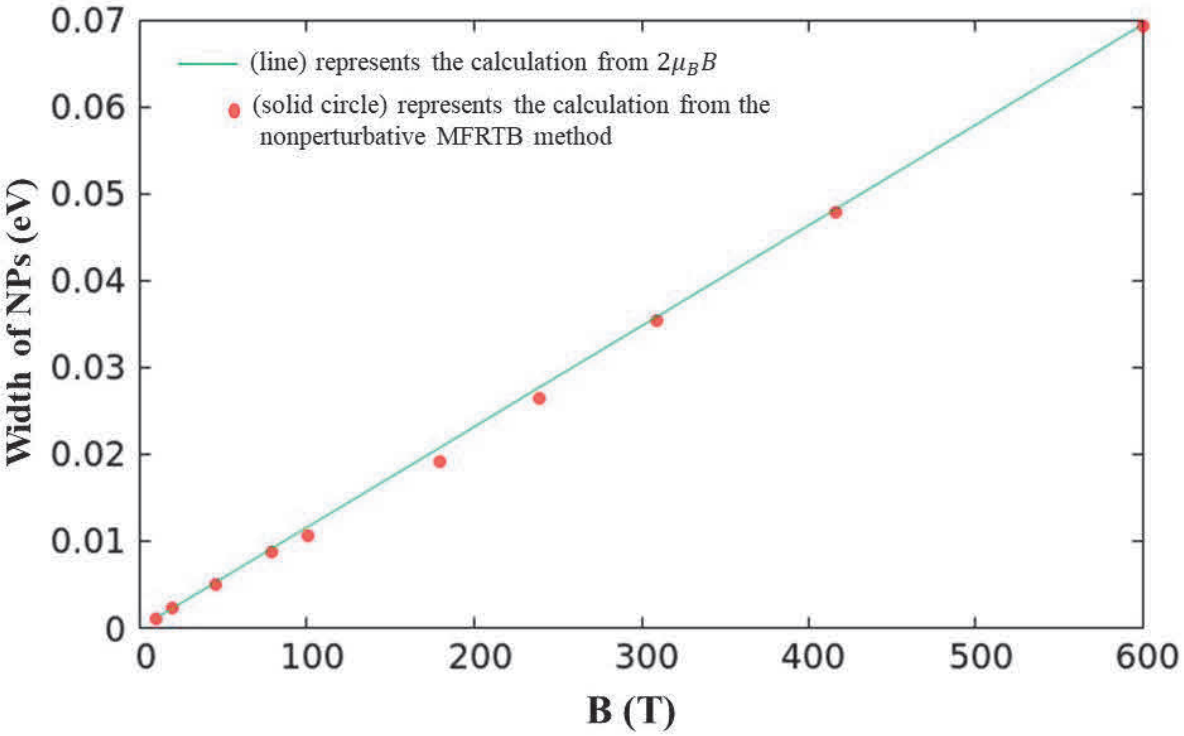


Figure. 7: Magnetic-field dependence width of the NP for the FF=4 [45].

Figure 8 shows the magnetic-field dependence of the difference Δ. In Figure. 8, the horizontal axis denotes the magnetic field in Tesla (T) and the vertical axis denotes the difference, Δ in meV. According to the Figures. 7 and 8, the width of the NP using the nonperturbative MFRTB method coincides with the width expected from a conventional model that is, the spin-Zeeman effect in both the low and high magnetic field regions. Figure. 8, in the high magnetic field region, the difference, Δ is very small. In the high magnetic field region, according to Eq. (5.11) in Chapter 5, the spin-Zeeman effect is more dominant compared to the spin-orbit interaction. For this reason, the calculated width of NPs using the nonperturbative MFRTB method is nearly the same as the calculated width of NPs by the spin-Zeeman effect. So, in this region, the effects of the spin-orbit interaction become negligible compared to the spin-Zeeman effect, which is known as the Paschen–Back effect. Figure. 8, in the low magnetic field region, the difference, Δ is also very small. In the low magnetic field region, according to Eq. (5.11) in Chapter 5, the spin-Zeeman effect is less dominant compared to the spin-orbit interaction. So, the spin-orbit interaction would be expected as a dominant part. The difference, Δ should be large. However, the calculation using the nonperturbative MFRTB method coincides with the result of the conventional model for an FF of four. This agreement is explained in the following as, in this region for this FF of four (4), the agreement indicates that the energy splitting caused by the anomalous Zeeman effect is consistent with that of the spin-Zeeman effect for magnetic Bloch states. This agreement for a particular FF is possible (may be it is not true for all FFs), for example, when the magnetic quantum number of the total angular momentum is given by $\pm 1/2$, the energy splitting caused by the anomalous Zeeman effect is consistent with that caused by the spin-Zeeman effect in a low magnetic field [51]. This agreement in the low magnetic field region implies that the magnetic Bloch states related to FF of four mainly comprise atomic orbitals with the magnetic quantum number of $\pm 1/2$.

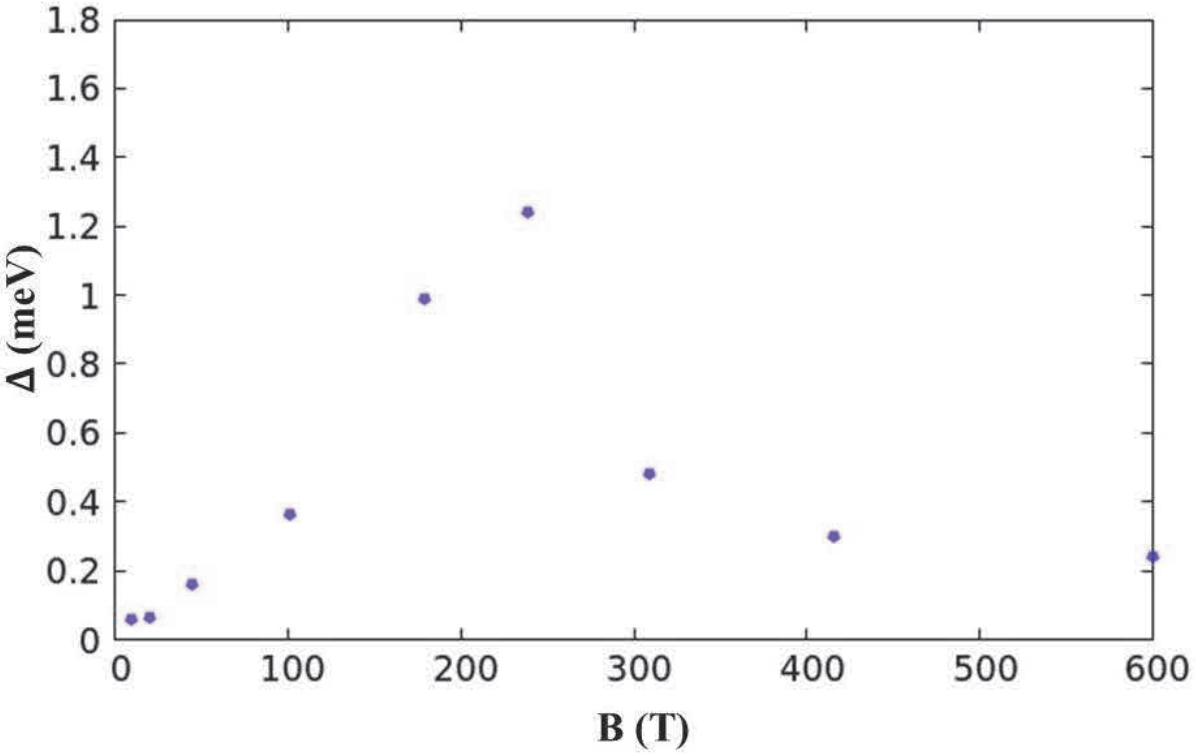


Figure. 8: Magnetic-field vs the difference (Δ) between the width of the NP for the FF=4 and the width expected from the spin-Zeeman effect [45].

On the other hand, in the middle magnetic field region, the difference, Δ is comparatively large. For this reason, the discrepancy is comparatively large in the middle magnetic field region (approximately 200 (T)) that is shown in Figures. 7 and 8. This result suggests that the width of NPs in a magnetic field of approximately 200 (T) can be affected due to the effect of the spin-orbit interaction in graphene. This effect provides very important information in research in graphene around this magnetic field. Although the width of NPs has not necessarily been estimated accurately in experiments [41], it is expected that the effect of the spin-orbit interaction and Paschen–Back effect will be observed in NPs by further experiments, especially in high magnetic fields greater than 100 (T) [65]. The description of the difference, Δ in the middle magnetic field case can be realized for the nonperturbative calculation of the effects of the magnetic field and spin-orbit interaction using the nonperturbative MFRTB method.

6.6 Description of the quantized Hall conductivity based on the magnetic energy band structure

In this subsection, the reason is explained briefly, why the magnetic field dependence σ_{Hall} in graphene can be appeared based on the magnetic energy band structure calculated by using the nonperturbative MFRTB method. It is confirmed that all the magnetic energy bands approximately have a magnetic field dependence degeneracy of $g(B)$, which is proportional to the magnetic field. If the number of completely flat magnetic energy bands below the Fermi energy is $N(\varepsilon_F)$, then the total number of states per unit area below the Fermi energy level is given by

$$\begin{aligned} n(B) &= \frac{N(\varepsilon_F)\, g(B)}{A} \\ &= \frac{2e\, B}{h} N(\varepsilon_F) \end{aligned} \tag{6.5}$$

According to the Streda formula (Eq. (4.50) in Chapter 4), σ_{Hall} is given by [50].

$$\begin{aligned} \sigma_{Hall} &= e \frac{\partial}{\partial B}\, n(B) \\ &= \frac{2e^2}{h} N(\varepsilon_F) \end{aligned} \tag{6.6}$$

The Hall conductivity, σ_{Hall} is proportional to the number of completely flat magnetic energy bands below the Fermi energy level. Since the Fermi energy dependence number, $N(\varepsilon_F)$ is an integer, so the σ_{Hall} from Eq. (6.6) is quantized.

The relationship between the magnetic energy band structure and σ_{Hall} is discussed in more detail in the following. The calculation using nonperturbative MFRTB provides $16q$ eigenvalues for each $\vec{k}$-point in the MBZ in this system. Because the total number of magnetic unit cells is given by N/q, $16N$ states are obtained using the nonperturbative MFRTB method. In the honeycomb lattice structure of graphene, each magnetic unit cell consists $2q$ number of carbon

atoms. Therefore, the magnetic unit cell consists $8q$ number of valence electrons. Therefore, the total number of valence electrons in the system is equal to $8N\ (= 8q \times N/q)$. For intrinsic graphene, half of the $16N$ states, that is, the $8N$ states, are occupied. The completely flat band approximation is described in subsection 6.1, $8q$ of $16q$ magnetic energy bands are fully occupied. As mentioned in subsection 6.1, each cluster of magnetic energy bands consists of $4p$ magnetic energy bands, which leads to an approximate p-fold degeneracy. Considering that the cluster corresponds to the so-called Landau level, the following numbering to the clusters can be assigned: the 0-th cluster can contains $(8q - 4p)$, $(8q - 4p + 1)$,$\cdots$, $(8q - 1)$, $8q$-th magnetic energy bands from the bottom. Similarly, the first cluster contains the $(8q + 1)$, $(8q + 2)$,$\cdots$, $(8q + 4p)$-th magnetic energy bands from the bottom. Herein, the energy level of the nth cluster is denoted by E_n.

For the intrinsic graphene, the Fermi energy level lies between the 0-th and 1st cluster, that is, $E_0 < \varepsilon_F < E_1$. Here, the total number of states below the Fermi energy is $8N$. Therefore, the total number of states per unit area is

$$n(B) = \frac{8N}{A} = \frac{16}{\sqrt{3}a^2} \qquad (\text{for } E_0 < \varepsilon_F < E_1) \tag{6.7}$$

where we used the relation $A/N = A_{unit} = \sqrt{3}a^2/2$. Therefore, $n(B)$ is independent of B when $E_0 < \varepsilon_F < E_1$. This leads the following equation

$$\sigma_{Hall} = 0 \qquad (\text{for } E_0 < \varepsilon_F < E_1). \tag{6.8}$$

Subsequently, in the case of Fermi energy is located between E_1 and E_2, that is, $E_1 < \varepsilon_F < E_2$. Here, the total number of states below the Fermi energy is given as $(8 + 4p/q)N\ (= (8q + 4p) \times N/q)$. Therefore, the total number of states per unit area is

$$n(B) = \frac{\left(8+\frac{4p}{q}\right)N}{A}$$
$$= \frac{16}{\sqrt{3}\,a^2} + \frac{2e}{h}B \qquad (\text{for } E_1 < \varepsilon_F < E_2) \tag{6.9}$$

where we used Eq. (5.1) which is discussed in subsection 5.1 in Chapter 5. Therefore, we have

$$\sigma_{Hall} = \frac{2e^2}{h} \qquad (\text{for } E_1 < \varepsilon_F < E_2) \tag{6.10}$$

Similarly, in the case of Fermi energy lies between the (n-1)th and n-th clusters. That is, $E_{n-1} < \varepsilon_F < E_n$. Here, the total number of states below the Fermi energy level is $(8 + 4np/q)N$ $(= (8q + 4np) \times (N/p))$. Therefore, the total number of states per unit area is

$$n(B) = \frac{\left(8+\frac{4n\,p}{q}\right)N}{A}$$
$$= \frac{16}{\sqrt{3}\,a^2} + \frac{2e}{h}nB \quad (\text{for } E_{n-1} < \varepsilon_F < E_n) \tag{6.11}$$

Therefore, we have

$$\sigma_{Hall} = \frac{e^2}{h}2n \quad (\text{for } E_{n-1} < \varepsilon_F < E_n) \tag{6.12}$$

Finally, the conductivity σ_{Hall} in graphene immersed in a uniform magnetic field which is quantized can be described based on the magnetic energy band structure calculated using the nonperturbative MFRTB method.

Chapter 7

Conclusions

The quantized Hall conductivity, σ_{Hall} in graphene is investigated using the nonperturbative MFRTB method. In these present calculations, it was confirmed that WPs with a set of FFs of 2, 6, 10, 14, etc., and NPs with another set of FFs of 0, 4, 8, 12, etc. were revisited in the Fermi energy dependence of σ_{Hall}. It is noted that the first set of FFs is attributed due to the energy splitting in a magnetic field. This energy splitting corresponds to Onsager's area-quantization rule. The second set of FFs arises due to the energy splitting caused by the spin-Zeeman effect and the spin-orbit interaction in a magnetic field.

It is important to notice that the width of WPs and NPs is dependent on Fermi energy for a constant magnetic field or magnetic field for a fixed Fermi energy level. In this thesis, it is shown that the width of WPs decreases with Fermi energy for a constant magnetic field, which is the same with experimental results. In the lower-energy region, the dependence of the width of WPs is more consistent with the result of the conventional theoretical model [8-11]. This consistency appears in the lower energy region which means near the Dirac point due to the linear energy dispersion relationship approximation for the energy band structure in the absence of a magnetic field. On the other hand, in the higher-energy region, the result of the nonperturbative MFRTB method does not coincide with the conventional theoretical model. In this region, a discrepancy appears when comparing the conventional theoretical model and the nonperturbative MFRTB method. Because the conventional theoretical model is valid only for the linear energy dispersion relationship which appears near the Dirac point or low energy region. On the other hand, the nonperturbative MFRTB method is valid both in the lower and high-energy regions. The nonperturbative MFRTB method provides a practical magnetic energy band structure in both regions. For this reason, the discrepancy appears due to the lack of validity of the linear energy dispersion relationship in the

higher-energy region. Thus, it is confirmed that the description in this thesis of the Fermi energy dependence of the width of WPs is more reliable in both the lower and higher energy regions.

It is possible to observe the effect of the spin-orbit interaction and Pachen–Back effect in graphene by investigating the Fermi energy dependence of the width of NPs at magnetic fields greater than 100 (T). In general, the Pachen–Back effect appears if the ratio of the spin Zeeman splitting to the spin-orbit splitting exceeds one (1) [51]. For graphene, the magnetic field that makes ratio 1 is approximately 144 (T) [51]. This magnetic field appears to be consistent with the results shown in Figures 7 and 8. Thus, the detection of the Paschen–Back effect in NPs is expected to be realized using the recent progress [65] in generating an extremely high magnetic field greater than 1000 (T) and in measuring physical quantities in the extremely high magnetic field [66-68].

In the present calculations, the relationship between the magnetic energy band structure and quantized σ_{Hall} was measured. It is noted that in every case the Fermi energy crosses a cluster of magnetic energy bands, and as a result σ_{Hall} changes by the quantity, $2e^2/h$. This statement coincides with the description of dHvA oscillations based on the magnetic energy band structure [55-57].

The effect of the fine energy band structure of a cluster on σ_{Hall} in graphene is very interesting. Because many properties are affected by the cluster of the band structure. For example, the fine energy band structure in a cluster generates additional oscillation peaks in the magnetic oscillation of the dHvA effect [56] under a high magnetic field. The conventional MFRTB and Hofstadter methods are based on perturbation theory [51]; thus, these methods are not sufficient for describing such phenomena due to some lacking. On the other hand, the nonperturbative MFRTB method is sufficient for describing these phenomena. For this reason, only the nonperturbative MFRTB method may be applied for an accurate result as a first-principles calculation method in a high magnetic field region. The effect of the fine energy band structure due to the splitting of an energy band in the high magnetic field case will be investigated in future studies.

Appendix A

Relation between the large and small components of the relativistic atomic orbitals by using the label by letters $l\ or\ \acute{l}$ takes the value of $0,1,2,\ldots\ldots$ for the atomic orbitals namely $s,p,d,$ .... respectively and the label M is expressed as $\sigma,\pi,\ \delta,$ .... in place of $0,\pm1,\pm2,\ldots\ldots$ respectively.

(1) $$Y_s^*(\theta,\phi)\,Y_s\left(\theta_{ijn},\,\phi_{ijn}\right) = \ (ss\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A1}$$

(2) $$Y_s^*(\theta,\phi)\,Y_x\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_x(sp\sigma)^{L\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A2}$$

(3) $$Y_s^*(\theta,\phi)\,Y_y\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_y(sp\sigma)^{L\ da_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A3}$$

(4) $$Y_s^*(\theta,\phi)\,Y_z\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_z(sp\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A4}$$

(5) $$Y_x^*(\theta,\phi)\,Y_z\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_x g_z(pp\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} - g_x g_z(pp\pi)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A5}$$

(6) $$Y_y^*(\theta,\phi)\,Y_z\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_y g_z(pp\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} - g_y g_z(pp\pi)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A6}$$

(7) $$Y_x^*(\theta,\phi)\,Y_y\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_x g_y(pp\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} - g_x g_y(pp\pi)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A7}$$

(8) $$Y_y^*(\theta,\phi)\,Y_x\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_y g_x(pp\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} - g_y g_x(pp\pi)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A8}$$

(9) $$Y_z^*(\theta,\phi)\,Y_x\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_z g_x(pp\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} - g_z g_x(pp\pi)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A9}$$

(10) $$Y_z^*(\theta,\phi)\,Y_y\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_z g_y(pp\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} - g_z g_y(pp\pi)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A10}$$

(11) $$Y_x^*(\theta,\phi)\,Y_x\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_x^2(pp\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} + (1-g_x^2)(pp\pi)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A11}$$

(12) $$Y_y^*(\theta,\phi)\,Y_y\left(\theta_{ijn},\,\phi_{ijn}\right) = \ g_y^2(pp\sigma)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} + (1-g_y^2)(pp\pi)^{L\ d\ a_j a_i}_{\left(2\,0\,\frac{1}{2},2\,1\,\frac{3}{2}\right)} \tag{A12}$$

(13) $$Y_z^*(\theta,\phi)\,Y_z\left(\theta_{ijn},\,\phi_{ijn}\right) = \; g_z^2(pp\sigma)^{L\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} + (1-g_z^2)(pp\pi)^{L\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A13)

(14) $$Y_z^*(\theta,\phi)Y_{xz}\left(\theta_{ijn},\,\phi_{ijn}\right) = \sqrt{3}\,g_z^2 g_x(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} + (1-2g_z^2)g_x(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A14)

(15) $$Y_z^*(\theta,\phi)Y_{yz}\left(\theta_{ijn},\,\phi_{ijn}\right) = \sqrt{3}\,g_z^2 g_y(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} + (1-2g_z^2)g_y(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A15)

(16) $$Y_y^*(\theta,\phi)Y_{xy}\left(\theta_{ijn},\,\phi_{ijn}\right) = \sqrt{3}\,g_y^2 g_x(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} + (1-2g_y^2)g_x(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A16)

(17) $$Y_y^*(\theta,\phi)Y_{zy}\left(\theta_{ijn},\,\phi_{ijn}\right) = \sqrt{3}\,g_y^2 g_z(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} + (1-2g_y^2)g_z(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A17)

(18) $$Y_x^*(\theta,\phi)Y_{yx}\left(\theta_{ijn},\,\phi_{ijn}\right) = \sqrt{3}\,g_x^2 g_y(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} + (1-2g_x^2)g_y(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A18)

(19) $$Y_x^*(\theta,\phi)Y_{zx}\left(\theta_{ijn},\,\phi_{ijn}\right) = \sqrt{3}\,g_x^2 g_z(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} + (1-2g_x^2)g_z(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A19)

(20) $$Y_x^*(\theta,\phi)Y_{x^2-y^2}\left(\theta_{ijn},\,\phi_{ijn}\right) = \frac{\sqrt{3}}{2}g_x(g_x^2-g_y^2)(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} + g_x(1-g_x^2+g_y^2)(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A20)

(21) $$Y_y^*(\theta,\phi)Y_{x^2-y^2}\left(\theta_{ijn},\,\phi_{ijn}\right) = \frac{\sqrt{3}}{2}g_y(g_x^2-g_y^2)(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} - g_y(1+g_x^2-g_y^2)(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A21)

(22) $$Y_z^*(\theta,\phi)Y_{x^2-y^2}\left(\theta_{ijn},\,\phi_{ijn}\right) = \frac{\sqrt{3}}{2}g_z(g_x^2-g_y^2)(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} - g_z(g_x^2-g_y^2)(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A22)

(23) $$Y_z^*(\theta,\phi)Y_{3z^2-r^2}\left(\theta_{ijn},\,\phi_{ijn}\right) = g_z\{g_z^2-\tfrac{1}{2}\left(g_x^2+g_y^2\right)\}(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A23)

(24) $$Y_x^*(\theta,\phi)Y_{3z^2-r^2}\left(\theta_{ijn},\,\phi_{ijn}\right) = g_x\{g_z^2-\tfrac{1}{2}\left(g_x^2+g_y^2\right)\}(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} - \sqrt{3}\,g_x g_z^2(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A24)

(25) $$Y_y^*(\theta,\phi)Y_{3z^2-r^2}\left(\theta_{ijn},\,\phi_{ijn}\right) = g_y\{g_z^2-\tfrac{1}{2}\left(g_x^2+g_y^2\right)\}(pd\sigma)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)} - \sqrt{3}\,g_y g_z^2(pd\pi)^{s\,d\,a_j a_i}_{\left(2\,0\frac{1}{2},2\,1\frac{3}{2}\right)}$$ (A25)

Appendix B

Definition of the Cubic Harmonics

(1) $C_s(\theta,\emptyset) = Y_{0,0}(\theta,\emptyset)$ (B1)

(2) $C_z(\theta,\emptyset) = Y_{1,0}(\theta,\emptyset)$ (B2)

(3) $C_x(\theta,\emptyset) = \frac{1}{\sqrt{2}}\left[Y_{1,-1}(\theta,\emptyset) - Y_{1,1}(\theta,\emptyset)\right]$ (B3)

(4) $C_y(\theta,\emptyset) = \frac{i}{\sqrt{2}}\left[Y_{1,-1}(\theta,\emptyset) + Y_{1,1}(\theta,\emptyset)\right]$ (B4)

(5) $C_{3z^2-r^2}(\theta,\emptyset) = Y_{2,0}(\theta,\emptyset)$ (B5)

(6) $C_{yz}(\theta,\emptyset) = \frac{i}{\sqrt{2}}\left[Y_{2,-1}(\theta,\emptyset) + Y_{2,1}(\theta,\emptyset)\right]$ (B6)

(7) $C_{xz}(\theta,\emptyset) = \frac{1}{\sqrt{2}}\left[Y_{2,-1}(\theta,\emptyset) - Y_{2,1}(\theta,\emptyset)\right]$ (B7)

(8) $C_{x^2-y^2}(\theta,\emptyset) = \frac{i}{\sqrt{2}}\left[Y_{2,-2}(\theta,\emptyset) + Y_{2,2}(\theta,\emptyset)\right]$ (B8)

(9) $C_{xy}(\theta,\emptyset) = \frac{i}{\sqrt{2}}\left[Y_{2,-2}(\theta,\emptyset) - Y_{2,2}(\theta,\emptyset)\right]$ (B9)

Definition of the spherical Harmonics

(10) $Y_{0,0}(\theta,\emptyset) = C_s(\theta,\emptyset)$ (B10)

(11) $Y_{1,0}(\theta,\emptyset) = C_z(\theta,\emptyset)$ (B11)

(12) $Y_{1,1}(\theta,\emptyset) = -\frac{1}{\sqrt{2}}\left[C_x(\theta,\emptyset) + iC_y(\theta,\emptyset)\right]$ (B12)

(13) $Y_{1,-1}(\theta,\emptyset) = \frac{1}{\sqrt{2}}\left[C_x(\theta,\emptyset) - iC_y(\theta,\emptyset)\right]$ (B13)

(14) $Y_{2,0}(\theta,\emptyset) = C_{3z^2-r^2}(\theta,\emptyset)$ (B14)

(15) $Y_{2,1}(\theta,\emptyset) = -\frac{1}{\sqrt{2}}\left[C_{xz}(\theta,\emptyset) + iC_{yz}(\theta,\emptyset)\right]$ (B15)

(16) $Y_{2,-1}(\theta,\emptyset) = \frac{1}{\sqrt{2}}\left[C_{xz}(\theta,\emptyset) - iC_{yz}(\theta,\emptyset)\right]$ (B16)

(17) $Y_{2,2}(\theta,\emptyset) = \frac{1}{\sqrt{2}}\left[C_{x^2-y^2}(\theta,\emptyset) + iC_{xy}(\theta,\emptyset)\right]$ (B17)

(18) $Y_{2,-2}(\theta,\emptyset) = \frac{1}{\sqrt{2}}\left[C_{x^2-y^2}(\theta,\emptyset) - iC_{xy}(\theta,\emptyset)\right]$ (B18)

Appendix: C

Show that $\frac{c}{e}\frac{\partial}{\partial B}Tr\delta\left(\varepsilon-\hat{H}\right)=\frac{1}{2}Tr\ \frac{d\,\delta\left(\varepsilon-\hat{H}\right)}{d\varepsilon}\left(xv_y-yv_x\right)$

We know the following expressions:

$$\delta\left(\varepsilon-\hat{H}\right)=-\frac{1}{2\pi i}\{G^{+}(\varepsilon)-G^{-}(\varepsilon)\} \tag{C1}$$

and

$$G^{\pm}(\varepsilon)=\ (\varepsilon-\hat{H}\pm i\delta)^{-1}$$
$$G^{\pm}(\varepsilon)(\varepsilon-\hat{H}\pm i\delta)=1 \tag{C2}$$

If we defend $\xi=\pm$, then Eq. (C2) becomes

$$G^{\xi}(\varepsilon)(\varepsilon-\hat{H}+i\xi\ \delta)=1 \tag{C3}$$

Multiplying by $|\alpha>$ on both sides in Eq. (C3)

$$G^{\xi}(\varepsilon)(\varepsilon-\hat{H}+i\xi\delta)|\alpha>=|\alpha>$$
$$G^{\xi}(\varepsilon)(\varepsilon-\varepsilon_\alpha+i\xi\delta)|\alpha>=|\alpha>$$
$$G^{\xi}(\varepsilon)|\alpha>(\varepsilon-\varepsilon_\alpha+i\xi\delta)=|\alpha>$$
$$G^{\pm}(\varepsilon)|\alpha>=\frac{1}{(\varepsilon-\varepsilon_\alpha\pm i\delta)}|\alpha> \tag{C4}$$

Multiplying by $<\alpha|$ on both sides in Eq. (C4)

$$<\alpha|G^{\xi}(\varepsilon)|\alpha>=<\alpha|\frac{1}{(\varepsilon-\varepsilon_\alpha+i\xi\delta)}|\alpha> \tag{C5}$$

Since $\frac{1}{(\varepsilon-\varepsilon_\alpha+i\xi\delta)}$ is a number, Eq. (C5) becomes

$$< \alpha|G^{\pm}(\varepsilon)|\alpha >= \frac{1}{(\varepsilon-\varepsilon_\alpha\pm i\delta)} < \alpha|\alpha >$$
$$< \alpha|G^{\pm}(\varepsilon)|\alpha >= \frac{1}{(\varepsilon-\varepsilon_\alpha\pm i\delta)} \quad \text{(C6)}$$

Again, we know

$$\sum_\alpha < \alpha|\,\delta\big(\varepsilon-\hat{H}\big)|\alpha >= \; Tr\delta\big(\varepsilon-\hat{H}\big) \quad \text{(C7)}$$

By using the above property, we can write

$$\frac{c}{e}\frac{\partial}{\partial B}Tr\delta\big(\varepsilon-\hat{H}\big) = \frac{c}{e}\frac{\partial}{\partial B}\sum_\alpha < \alpha|\,\delta\big(\varepsilon-\hat{H}\big)|\alpha >$$
$$= \frac{c}{e}\frac{\partial}{\partial B}\sum_\alpha < \alpha|-\frac{1}{2\pi i}\{G^{+}(\varepsilon)-G^{-}(\varepsilon)\}|\alpha >$$
$$= -\frac{1}{2\pi i}\frac{c}{e}\frac{\partial}{\partial B}\sum_\alpha < \alpha|\,G^{+}(\varepsilon)|\alpha > +\frac{1}{2\pi i}\frac{c}{e}\frac{\partial}{\partial B}\sum_\alpha < \alpha|\,G^{-}(\varepsilon)|\alpha >$$
$$= -\frac{1}{2\pi i}\frac{c}{e}\frac{\partial}{\partial B}\sum_\alpha \frac{1}{(\varepsilon_i-\varepsilon_\alpha+i\delta)} + \frac{1}{2\pi i}\frac{c}{e}\frac{\partial}{\partial B}\sum_\alpha \frac{1}{(\varepsilon_i-\varepsilon_\alpha-i\delta)} \quad \text{(C8)}$$

If ε_i is number and ε_α is a magnetic field dependent then Eq. (C8) becomes

$$\frac{c}{e}\frac{\partial}{\partial B}Tr\delta\big(\varepsilon-\hat{H}\big) = -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon_i-\varepsilon_\alpha+i\delta)^2}\frac{\partial\varepsilon_\alpha}{\partial B} + \frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon_i-\varepsilon_\alpha-i\delta)^2}\frac{\partial\varepsilon_\alpha}{\partial B}$$
$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon_i-\varepsilon_\alpha+i\delta)^2}\frac{\partial\varepsilon_\alpha}{\partial B} + \frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon_i-\varepsilon_\alpha-i\delta)^2}\frac{\partial\varepsilon_\alpha}{\partial B}$$
$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon_i-\varepsilon_\alpha+i\delta)}\frac{1}{(\varepsilon_i-\varepsilon_\alpha+i\delta)}\frac{\partial\varepsilon_\alpha}{\partial B} + \frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon_i-\varepsilon_\alpha-i\delta)}\frac{1}{(\varepsilon_i-\varepsilon_\alpha-i\delta)}\frac{\partial\varepsilon_\alpha}{\partial B} \quad \text{(C9)}$$

Since $< \alpha|G^{\pm}(\varepsilon)|\alpha >= \frac{1}{(\varepsilon-\varepsilon_\alpha\pm i\delta)}$, Eq. (C9) becomes

$$\frac{c}{e}\frac{\partial}{\partial B}Tr\delta\big(\varepsilon-\hat{H}\big) = -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha < \alpha|G^{+}(\varepsilon)|\alpha >< \alpha|G^{+}(\varepsilon)|\alpha > \frac{\partial\varepsilon_\alpha}{\partial B}$$
$$+\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha < \alpha|G^{-}(\varepsilon)|\alpha >< \alpha|G^{-}(\varepsilon)|\alpha > \frac{\partial\varepsilon_\alpha}{\partial B}$$

$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha < \alpha|G^+(\varepsilon)|\alpha >< \alpha|G^+(\varepsilon)|\alpha > \frac{\partial \varepsilon_\alpha}{\partial B}$$

$$+\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha < \alpha|G^-(\varepsilon)|\alpha >< \alpha|G^-(\varepsilon)|\alpha > \frac{\partial \varepsilon_\alpha}{\partial B}$$

$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \sum_\beta < \alpha|G^+(\varepsilon)|\beta >< \beta|G^+(\varepsilon)|\alpha > \frac{\partial \varepsilon_\alpha}{\partial B}$$

$$+\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \sum_\beta < \alpha|G^-(\varepsilon)|\beta >< \beta|G^-(\varepsilon)|\alpha > \frac{\partial \varepsilon_\alpha}{\partial B}$$

$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \sum_\beta \frac{1}{(\varepsilon-\varepsilon_\beta+i\delta)} < \alpha|\beta >< \beta|\alpha > \frac{1}{(\varepsilon-\varepsilon_\alpha+i\delta)}\frac{\partial \varepsilon_\alpha}{\partial B}$$

$$+\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \sum_\beta \frac{1}{(\varepsilon-\varepsilon_\beta-i\delta)} < \alpha|\beta >< \beta|\alpha > \frac{1}{(\varepsilon-\varepsilon_\alpha-i\delta)}\frac{\partial \varepsilon_\alpha}{\partial B}$$

$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon-\varepsilon_\alpha+i\delta)^2}\frac{\partial \varepsilon_\alpha}{\partial B} + \frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon-\varepsilon_\alpha-i\delta)^2}\frac{\partial \varepsilon_\alpha}{\partial B}$$

$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon-\varepsilon_\alpha+i\delta)^2} < \alpha|\alpha > \frac{\partial \varepsilon_\alpha}{\partial B} + \frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon-\varepsilon_\alpha-i\delta)^2} < \alpha|\alpha > \frac{\partial \varepsilon_\alpha}{\partial B}$$

$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon-\varepsilon_\alpha+i\delta)^2} < \alpha|\frac{\partial \hat{H}}{\partial B}|\alpha > + \frac{1}{2\pi i}\frac{c}{e}\sum_\alpha \frac{1}{(\varepsilon-\varepsilon_\alpha-i\delta)^2} < \alpha|\frac{\partial \hat{H}}{\partial B}|\alpha >$$

$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha < \alpha|\frac{\partial \hat{H}}{\partial B}\frac{1}{(\varepsilon-\varepsilon_\alpha+i\delta)^2}|\alpha > + \frac{1}{2\pi i}\frac{c}{e}\sum_\alpha < \alpha|\frac{\partial \hat{H}}{\partial B}\frac{1}{(\varepsilon-\varepsilon_\alpha-i\delta)^2}|\alpha >$$

$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha < \alpha|\frac{\partial \hat{H}}{\partial B}G^+(\varepsilon)G^+(\varepsilon)|\alpha > + \frac{1}{2\pi i}\frac{c}{e}\sum_\alpha < \alpha|\frac{\partial \hat{H}}{\partial B}G^-(\varepsilon)G^-(\varepsilon)|\alpha >$$

$$= -\frac{1}{2\pi i}\frac{c}{e}\sum_\alpha < \alpha\left|\frac{\partial \hat{H}}{\partial B}\{G^+(\varepsilon)G^+(\varepsilon) - G^-(\varepsilon)G^-(\varepsilon)\}\right|\alpha > \quad \text{(C10)}$$

Since $\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon} = \frac{1}{2\pi i}\{G^+(\varepsilon)G^+(\varepsilon) - G^-(\varepsilon)G^-(\varepsilon)\}$, Eq. (C10) becomes

$$\frac{c}{e}\frac{\partial}{\partial B}Tr\delta\left(\varepsilon - \hat{H}\right) = -\frac{c}{e}\sum_\alpha < \alpha|\frac{\partial \hat{H}}{\partial B}\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}|\alpha > \quad \text{(C11)}$$

Since $Tr\left(\frac{\partial \hat{H}}{\partial B}\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\right) = \sum_\alpha < \alpha|\frac{\partial \hat{H}}{\partial B}\left\{\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\right\}|\alpha >$, Eq. (C11) becomes

$$\frac{c}{e}\frac{\partial}{\partial B}Tr\delta\left(\varepsilon - \hat{H}\right) = -\frac{c}{e}\sum_\alpha < \alpha|\frac{\partial \hat{H}}{\partial B}\left\{\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\right\}|\alpha >$$

$$= -\frac{c}{e}Tr\left(\frac{\partial \hat{H}}{\partial B}\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\right) \quad \text{(C12)}$$

We know the expression for the Hamiltonian, $\widehat{H} = \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}(\vec{r})\right)^2 + V(\vec{r})$, the derivative of the Hamiltonian, $\widehat{H}$ with respect to magnetic field, B

$$\frac{\partial \hat{H}}{\partial B} = \frac{\partial}{\partial B}\left\{\frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}(\vec{r})\right)^2 + V(\vec{r})\right\}$$

$$= \frac{\partial}{\partial B}\left\{\frac{1}{2m}\left((p_x + p_y + p_z) - \frac{e}{c}\left(A_x + A_y + A_z\right)\right)^2 + V(\vec{r})\right\}$$

$$= \frac{\partial}{\partial B}\left\{\frac{1}{2m}\left(\left(p_x - \frac{e}{c}A_x\right)^2 + \left(p_y - \frac{e}{c}A_y\right)^2 + \left(p_z - \frac{e}{c}A_z\right)^2\right) + V(\vec{r})\right\}$$

$$= \frac{\partial}{\partial B}\left\{\frac{1}{2m}\left(p_x^2 + 2\,p_x\frac{e}{c}\frac{1}{2}By + \left(\frac{e}{c}\frac{1}{2}By\right)^2 + p_y^2 - 2\,p_y\frac{e}{c}\frac{1}{2}Bx + \left(\frac{e}{c}\frac{1}{2}Bx\right)^2 + p_z^2\right) + V(\vec{r})\right\}$$

$$= \frac{\partial}{\partial B}\left\{\frac{1}{2m}\left(p_x^2 + \frac{e}{c}p_xBy + \frac{1}{4}\frac{e}{c^2}^2 B^2y^2 + p_y^2 - \frac{e}{c}p_yBx + \frac{1}{4}\frac{e}{c^2}^2 B^2x^2 + p_z^2\right) + V(\vec{r})\right\}$$

$$= \frac{\partial}{\partial B}\left\{\frac{1}{2m}\left(p_x^2 + \frac{e}{c}p_xBy + \frac{1}{4}\frac{e}{c^2}^2 B^2y^2 + p_y^2 - \frac{e}{c}p_yBx + \frac{1}{4}\frac{e}{c^2}^2 B^2x^2 + p_z^2\right) + V(\vec{r})\right\}$$

$$= \frac{\partial}{\partial B}\left\{\frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2 + \frac{e}{c}p_xBy - \frac{e}{c}p_yBx + \frac{1}{4}\frac{e}{c^2}^2 B^2y^2 + \frac{1}{4}\frac{e}{c^2}^2 B^2x^2\right) + V(\vec{r})\right\}$$

$$= \frac{\partial}{\partial B}\left\{\frac{1}{2m}\left(p^2 + \frac{e}{c}B\left(p_xy - p_yx\right) + \frac{1}{4}\frac{e}{c^2}^2 B^2(y^2 + x^2)\right) + V(\vec{r})\right\}$$

$$= \frac{\partial}{\partial B}\left\{\frac{1}{2m}\left(p^2 + \frac{e}{c}B\left(p_xy - p_yx\right) + \frac{1}{4}\frac{e}{c^2}^2 B^2(y^2 + x^2)\right) + V(\vec{r})\right\}$$

$$= \frac{\partial}{\partial B}\frac{1}{2m}B\left(\frac{e}{c}\left(p_xy - p_yx\right) + \frac{\partial}{\partial B}\left(p^2 + \frac{1}{2}\frac{e}{c^2}^2 B^2(y^2 + x^2)\right) + \frac{\partial}{\partial B}V(\vec{r})\right.$$

$$= \frac{1}{2m}\frac{e}{c}\left(p_xy - p_yx\right) + \frac{\partial}{\partial B}\left\{\left(\frac{1}{2m}\left(p^2 + \frac{1}{2}\frac{e}{c^2}^2 B^2(y^2 + x^2)\right) + V(\vec{r})\right\}\right.$$

$$= \frac{1}{2m}\frac{e}{c}\left(p_xy - p_yx\right) + \left(\frac{1}{2m}\frac{e}{c^2}^2 B(y^2 + x^2)\right)$$

$$= -\frac{1}{2m}\frac{e}{c}\left(p_yx - p_xy\right) + \left(\frac{1}{2m}\frac{e}{c^2}^2 B(y^2 + x^2)\right)$$

$$= \frac{1}{2m}\frac{e}{c}\left\{\frac{e}{c}B(y^2 + x^2) - \left(p_yx - p_xy\right)\right\}$$

$$= \frac{1}{2m}\frac{e}{c}\left\{\frac{e}{c}(Byy + Bxx) - p_yx + p_xy\right\}$$

$$= \frac{1}{2m}\frac{e}{c}\left\{\frac{e}{c}Byy + \frac{e}{c}Bxx - p_yx + p_xy\right\}$$

$$= \frac{1}{m}\frac{e}{c}\left\{y\left(p_x + \frac{e}{2c}By\right) - x\left(p_y - \frac{e}{2c}Bx\right)\right\}$$

$$= \frac{1}{m}\frac{e}{c}\left\{y\left(p_x - \frac{e}{c}A_x\right) - x\left(p_y - \frac{e}{c}A_x\right)\right\}$$
$$= \frac{e}{c}\left\{y\,\frac{1}{m}\left(p_x - \frac{e}{c}A_x\right) - x\frac{1}{m}\left(p_y - \frac{e}{c}A_x\right)\right\}$$
$$= \frac{e}{c}\{y\,v_x - xv_y\}$$
$$= \frac{e}{c}\{y\,v_x - xv_y\} \qquad \text{(C13)}$$

Using Eq. (C12) and (C13), we have

$$\frac{c}{e}\frac{\partial}{\partial B}Tr\delta\left(\varepsilon - \hat{H}\right) = -\frac{c}{e}Tr\left(\frac{\partial\hat{H}}{\partial B}\,\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\right)$$
$$= -\frac{c}{e}Tr\left(\frac{e}{2c}\left(v_x y - v_y x\right)\,\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\right)$$
$$= \frac{1}{2}Tr\left(\left(v_y x - v_x y\right)\,\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\right)$$
$$= \frac{1}{2}Tr\,\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\left(xv_y - yv_x\right)$$
$$= \frac{1}{2}Tr\,\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\left(xv_y - yv_x\right)$$
$$= \frac{1}{2}Tr\,\frac{d\,\delta(\varepsilon-\hat{H})}{d\varepsilon}\left(xv_y - yv_x\right) \qquad \text{(C14)}$$

References

[1] K. v. Klitzing, G. Dorda, and M. Pepper, Phys. Rev. Lett. **45**, 494(1980).

[2] R. B. Laughlin, Phys. Rev. B **23**, 5632 (1981).

[3] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Sci. **306**, 666 (2004).

[4] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nat. **438**,197 (2005).

[5] A. K. Geim and K. S. Novoselov, Nature Mat. **6**, 183 (2007).

[6] P. Avouris, T. F. Heinz, and T. Low, *2D Materials: Properties and Devices* (Cambridge University Press, Cambridge, 2017)

[7] K. Higuchi, M. Kudo, M. Mori, and T. Mishima, IEDM Tech. Dig. 891 (1994).

[8] M. Balkanski, *Devices Based on Low-Dimensional Semiconductor Structures* (Kluwer Academic Publishers, Dordrecht, 1996)

[9] K. Higuchi, H. Matsumoto, T. Mishima, and T. Nakamura, IEEE Trans. Elec. Dev. **46**, 1312 (1999).

[10] G. Hellings and K. De Myer, *High Mobility and Quantum Well Transistors* (Springer, New York, 2013)

[11] J. W. McClure, Phys. Rev. **104**, 666 (1956).

[12] J. W. McClure, Phys. Rev. **119**, 606 (1960).

[13] S. A. Safran and F. J. DiSalvo, Phys. Rev. B **20**, 4889 (1979).

[14] S. A. Safran, Phys. Rev. B **30**, 421 (1984).

[15] R. Saito and H. Kamimura, Phys. Rev. B **33**, 7218 (1986).

[16] H. Fukuyama, J. Phys. Soc. Jpn. **76**, 043711 (2007).

[17] M. Koshino and T. Ando, Phys. Rev. B **75**, 235333 (2007).

[18] M. Koshino, Y. Arimura, and T. Ando, Phys. Rev. Lett. **102**, 177203 (2009).

[19] M. Sepioni, R. R. Nair, S. Rablen, J. Narayanan, F. Tuna, R. Winpenny, A. K. Geim, and I. V. Grigorieva, Phys. Rev. Lett. **105**, 207205 (2010).

[20] G. Gómez-Santos and T. Stauber, Phys. Rev. Lett. **106**, 045504 (2011).

[21] A. Raoux, F. Píechon, J. -N. Fuchs, and G. Montambaux, Phys. Rev. B **91**, 085120 (2015).

[22] Y. Gao, S. A. Yang, and Q. Niu, Phys. Rev. B **91**, 214405 (2015).

[23] M. Ogata and H. Fukuyama, J. Phys. Soc. Jpn. **84**, 124708 (2015).

[24] M. Higuchi, D. B. Hamal, A. Shrestha, and K. Higuchi, J. Phys. Soc. Jpn. **88**, 094707 (2019).

[25] R. G. Mani, J. Hankinson, C. Berger, and W. A. de Heer, Nat. Commun. **3,** 996 (2012).

[26] T. J. Lyon, J. Sichau, A. Dorn, A. Centeno, A. Pesquera, A. Zurutuza, and R. H. Blick, Phys. Rev. Lett. **119**, 066802 (2017).

[27] A. Shrestha, K. Higuchi, S. Yoshida, and M. Higuchi, J. Appl. Phys. **130**, 124303 (2021)

[28] S. G. Sharapov, V. P. Gusynin, and H. Beck, Phys. Rev. B **69**, 075104 (2004).

[29] K. Kishigi and Y. Hasegawa, Phys. Rev. B **90**, 085427 (2014).

[30] F. Escuderoa, J. S. Ardenghi, L. Sourrouille, and P. Jasen, J. Mag. Mag. Mater. **429**, 294 (2017).

[31] F. D. M. Haldane, Phys. Rev. Lett. **61**, 2015 (1988).

[32] Y. Zheng and T. Ando, Phys. Rev. B **65**, 245420 (2002).

[33] Y. Zhang, Y.-W. Tan, H. L. Störmer, and P. Kim, Nat. (London) **438**, 201 (2005).

[34] V. P. Gusynin and S. G. Sharapov, Phys. Rev. Lett. **95**, 146801 (2005).

[35] V. P. Gusynin and S. G. Sharapov, Phys. Rev. B **73**, 245411 (2006).

[36] N. M. R. Peres, F. Guinea, and A. H. Castro Neto, Phys. Rev. B **73**, 125411 (2006).

[37] D. N. Sheng, L. Sheng, and Z. Y. Weng, Phys. Rev. B **73**, 233406 (2006).

[38] Y. Hasegawa and M. Kohmoto, Phys. Rev. B **74**, 155415 (2006).

[39] V. P. Gusynin, V. A. Miransky, S. G. Sharapov, and I. A. Shovkovy, Phys. Rev. B **74**, 195429 (2006).

[40] Y. Hatsugai, T. Fukui, and H. Aoki, Phys. Rev. B **74**, 205414 (2006).

[41] Y. Zhang, Z. Jiang, J. P. Small, M. S. Purewal, Y.-W. Tan, M. Fazlollahi, J. D. Chudow, J. A. Jaszczak, H. L. Stormer, and P. Kim, Phys. Rev. Lett. **96**, 136806 (2006).

[42] Z. Jiang, Y. Zhang, Y.-W. Tan, J. A. Jaszczak, H. L. Stormer, and P. Kim, Int. J. Mod. Phys. B **21**, 1123 (2007).

[43] K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim, and A. K. Geim, Sci. **315,** 1379 (2007).

[44] X. Wu, Y. Hu, M. Ruan, N. K. Madiomanana, J. Hankinson, M. Sprinkle, C. Berger, and W. A. de Heer, Appl. Phys. Lett. **95**, 223108 (2009).

[45] M. A. Rashid, M. Higuchi and K. Higuchi, Phys. Rev. B 108, 125132 (2023)

[46] D. Hofstadter, Phys. Rev. B **14**, 2239 (1976).

[47] D. J. Thouless, M. Kohmoto, M. P. Nightingale, and M. denNijs, Phys. Rev. Lett. **49**, 405 (1982).

[48] M. Kohmoto, Ann. Phys. **160**, 343 (1985).

[49] A. H. MacDonald, Phys. Rev. B **28**, 6713 (1983).

[50] P. Streda, J. Phys. C **15**, L1299 (1982).

[51] K. Higuchi, D. B. Hamal, and M. Higuchi, Phys. Rev. B **97**, 195135 (2018).

[52] K. Higuchi, D. B. Hamal, and M. Higuchi, Phys. Rev. B **91**, 075122 (2015).

[53] W. J. de Haas and P. M. van Alphen, Proc. Netherland R. Acad. Sci. 33, 680 (1930).

[54] D. Shoenberg, *Magnetic Oscillation in Metals* (Cambridge University Press, Cambridge, 1984).

[55] D. B. Hamal, M. Higuchi, and K. Higuchi, Phys. Rev. B **91**, 245101 (2015).

[56] M. Higuchi, D. Bahadur Hamal, and K. Higuchi, Phys. Rev. B **95**, 195153 (2017).

[57] K. Higuchi, D. B. Hamal, and M. Higuchi, Phys. Rev. B **96**, 235125 (2017).

[58] K. Higuchi, D. B. Hamal, and M. Higuchi, New J. Phys. **24** 103028 (2022).

[59] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1966), Chap. 20.

[60] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954)

[61] R. M. Martin, *Electronic Structure* (Cambridge University Press, Cambridge, 2004), Chap.14.

[62] M. P. Marder, Condensed Matter Physics (Wiley, New York, 2000), Chap. 25

[63] E. Brown, Phys. Rev. **133**, A1038 (1964).

[64] J. Zak, Phys. Rev. **134**, A1602 (1964).

[65] D. Nakamura, A. Ikeda, H. Sawabe, Y. H. Matsuda, and S. Takeyama, Rev. Sci. Instrum. **89**, 095106 (2018).

[66] Y. H. Matsuda, D. Nakamura, A. Ikeda, S. Takeyama, Y. Suga, H. Nakahara, and Y. Muraoka, Nat. Commun. **11**, 3591 (2020).

[67] D. Nakamura, H. Saito, H. Hibino, K. Asano, and S. Takeyama, Phys. Rev. B **101**, 115420 (2020).

[68] A. Ikeda, Y. H. Matsuda, K. Sato, Y. Ishii, H. Sawabe, D. Nakamura, S. Takeyama and J. Nasu, Nat. Commun. **14**, 1744 (2023)